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Edited by J. E. McIntyre

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Historical background

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1.1 Introduction

This chapter reviews the early development of synthetic fibres, which are defined[1] by the International Organization for Standardization (ISO) as fibres manufactured from polymers built up from chemical elements or compounds, in contrast to fibres made from naturally occurring fibre-forming polymers. The definition excludes fibres made from regenerated cellulose, such as viscose rayon and cuprammonium rayon, and from cellulose esters, such as secondary cellulose acetate and cellulose triacetate. These fibres manufactured from cellulose became established commercially many years before the first synthetic fibres were discovered and developed. There was therefore quite a considerable amount of information already available to the developers of fibres from new polymeric materials about the production of fibres from solutions of high polymers by extrusion into non-solvents, i.e. by wet-spinning, and into evaporative atmospheres, i.e. by dry-spinning, and also about filament orientation by stretching and about subsequent downstream handling. There was, however, only a very limited understanding of the nature of polymers and of their macromolecular structure and synthesis.

A major step forward in developing this understanding was taken in the 1920s, when it was convincingly demonstrated, notably by Hermann Staudinger at the Technische Hochschule in Zürich, that polymers were not colloidal assemblies of molecules of low molecular weight, as many believed, but consisted of molecules of high molecular weight. Staudinger was awarded the Nobel Prize for chemistry in 1953 for his work on this subject. A major factor in convincing the chemical community was work on polymer synthesis directed by W. H. Carothers in the early 1930s at the Experimental Station of the DuPont company in Wilmington, Delaware.

The terms *addition polymerisation* and *condensation polymerisation* were introduced by Carothers.[2] Addition polymerisation was defined as the chemical union of many similar molecules without the elimination of simpler molecules, and condensation polymerisation as the chemical union of many similar molecules with the elimination of simpler molecules. Carothers recognised and stated that some polymer structures could be made by either polyaddition or polycondensation processes. Consequently the terms *addition polymer* and *condensation polymer* should strictly be applied only to samples of known polymerisation history.

An alternative method of classification that depends on the nature of the mechanism of growth of the polymer divides polymerisation reactions into those exhibiting either chain-growth or step-growth mechanisms. Most chain-growth polymerisations are addition polymerisations, and most step-growth polymerisations are condensation polymerisations, but not all. For example, stepwise polymerisations without elimination of a simple molecule, such as the formation of a polyurethane, $(\text{–OROOCNHR}'\text{NHCO–})_n$, from a diol, HOROH, and a di-isocyanate, OCNR′NCO, cannot be classed as condensation polymerisations. In the ensuing discussion of the early historical development of synthetic fibre-forming polymers, polymers normally formed by chain-growth polymerisation will be considered before those formed by step-growth polymerisation.

1.2 Fibres from chain-growth polymers

1.2.1 Chlorofibres

1.2.1.1 European development[3]

Research in Germany during the period 1911–1913 by Klatte at Chemische Fabrik Griesheim Elektron led to the definition of conditions for reacting acetylene with acids to form vinyl compounds, particularly vinyl chloride and vinyl acetate. Klatte's work on the polymerisation of these products formed the basis of an application on 4 July 1913 for a patent[4] covering the formation of fibres from poly(vinyl chloride) (PVC). Subsequent workers, such as Rein,[5] describe Klatte's work and the filing of this patent as the beginning of the story of synthetic fibres. The polymer is shown to be soluble in hot chlorobenzene, and useful (*künstliche*) fibres are said to be obtained directly by extrusion of the solution into a precipitating bath.[4] A US patent,[6] filed just under a year later and evidently a considerably amplified equivalent of the patent originally filed in Germany, claims the production of polymers from vinyl acetate, vinyl chloroacetate or vinyl chloride. The formation of fibres from solutions of poly(vinyl chloride) by spinning a solution in hot chlorobenzene into a precipitating bath is described, and the spinning of fibres from poly(vinyl chloroacetate) and poly(vinyl acetate) from solvents such as acetone is also included. Despite the examples, there are no specific claims to fibre formation, and no industrial development of fibres ensued.

According to Bode,[7] the first synthetic fibre was produced by Hubert at the laboratories of IG Farben at Wolfen, north of Leipzig, from PVC. Work on this topic had begun in the rayon laboratories at Wolfen in about 1928, and all the high polymers made within IG Farben, other than cross-linked products such as phenol–formaldehyde and urea–formaldehyde resins, were tested. In 1931 Hubert, Pabst and Hecht filed a patent[8] in which they described the production of fibres by wet-spinning PVC, dissolved in cyclohexanone at room temperature, into 30 % acetic acid. The claims are directed specifically towards a multistage drawing process at a draw ratio of 3 : 1 or above. Tenacities up to 2.5 grams per denier (gpd) are obtained in examples.

So far no product suitable for commercial use had emerged, but it was then found that post-chlorination of PVC to the point where it contained about 1.5 chlorine atoms per vinyl residue in the chain gave a polymer that was readily soluble in acetone. Although, according to Bode,[7] the suggestion for post-chlorination may have originated with Hubert, the patent covering this process was filed in 1932 with Schönburg named as the sole inventor.[9]

This post-chlorinated PVC fibre had a softening point 25–30 °C higher than the unmodified PVC, but fabrics still had to be washed at a temperature no higher than 40 °C in order to avoid shrinkage. Solutions in acetone could easily be spun into water, and commercial production of the resulting perchlorovinyl fibre, named *PeCe*, began on a small scale at Wolfen in 1934. A larger plant commenced production in 1938.[7] The areas of use were, and remained, principally technical textiles such as filter fabrics, rot-free fishing nets, and acid-resistant industrial clothing. After World War II, this plant lay in East Germany (DDR) and production there continued under the name *Piviacid*. A similar product was manufactured in the USSR under the tradename *Chlorin*.[10]

In France, it was found by Rhône-Poulenc that mixed solvents (acetone plus carbon disulphide or acetone plus perchloroethylene[11]) would dissolve PVC. A dry-spinning process based on such mixed solvents was introduced in1949, the product being sold under various trade names such as *Rhovyl*. In Japan, a mixture of acetone and benzene (40 : 60) was used in a similar way by Teijin to produce *Teviron*.[12]

1.2.1.2 US development

Development of chlorofibres in the USA occurred later than in Germany. In September 1937, Rugeley, Feild and Conlon of Carbide and Carbon Chemicals filed a patent application[13] that described the formation of synthetic fibres from copolymers of vinyl halides with vinyl esters of aliphatic acids, the average molecular weight being at least about 15 000. Typically the polymer was a 90 : 10 molar copolymer of vinyl chloride with vinyl acetate. It was dry-spun into air at 80 ºC from a solution in acetone containing 23 % of the polymer. The filaments were stretched in two stages by about 140 % and set at constant length by immersion in water at 65 °C for 2 to 3 hours, to give a yarn with a wet tenacity of 2.75 gpd, an elongation to break of 15 %, and elasticity ‘similar to silk’.

This was the basic patent covering *Vinyon*, one of the first synthetic fibres made commercially available in the USA. Production and sale of *Vinyon* by the American Viscose Corporation began in 1938, using *Vinylite* copolymer supplied by Carbide and Carbon.[14] An elastomeric version of this product, Vinyon E, was introduced in 1943. It contained a plasticiser that permitted the production of yarns with reversible elongation approaching 400 %. Its use was confined to products for military purposes, and its production ceased after the end of World War II. Neoprene (polychloroprene), which had been discovered by Collins, a member of Carothers's research group, in April 1930 and commercialised as an elastomeric polymer by DuPont, was also used to make elastic threads during the war.[15]

1.2.2 Modacrylic fibres

The prospects for fibres manufactured from copolymers of vinyl chloride with vinyl acetate were limited by their low softening points and poor dyeing properties. Carbide and Carbon Chemicals therefore went on to develop a fibre based upon a copolymer of about 60 % vinyl chloride and 40 % acrylonitrile, which was dry-spun from acetone.[16] Despite containing over 50 % of vinyl chloride, this type of product is now classed generically as a modacrylic fibre because it contains more than 35 % (but less than 85 %) by mass of groups derived from acrylonitrile.

An early patent for this type of product, filed in May 1943,[17] describes a process for making a VC/VN, i.e. vinyl chloride/acrylonitrile, VC/AN (VN, or vinyl nitrile, is an old name for acrylonitrile) copolymer containing typically about 60 % of vinyl chloride by weight, which is soluble in acetone and resists deformation at temperatures above 100 ºC. It is made by operating an emulsion copolymerisation at high VC/AN ratio with maintenance of that ratio by adding AN at intervals. Neither homopolymer is soluble in acetone.

A continuous-filament yarn, *Vinyon N*, based on this polymer was introduced in 1948, but the main commercial potential of the product was in staple fibre.[18,19] *Dynel* staple fibre was introduced in 1949; and the continuous-filament product was withdrawn in 1954. Several other modacrylic fibres were commercialised, notably *Verel* (1956, Tennessee Eastman) and *Teklan* (1962, Courtaulds), both AN/VDC copolymers.[20]

The inherently flame-retardant nature of modacrylic fibres has been the chief property leading to their use, which has been largely in furnishing fabrics and in pile fabrics. Subjecting them to very high temperatures, however, can lead to the evolution of toxic gases.

1.2.3 Poly(vinylidene chloride) (*Saran*) (PVDC)

The most widely recognised tradename for poly(vinylidene chloride), *Saran*, was introduced by the Dow Chemical Company. Patents covering the production of PVDC fibres were filed by Dow, initially in 1937.[21] Commercial production began in 1940. The Firestone company employed Dow's *Saran* polymer to manufacture monofilaments, using the tradename *Velon*, and several other extruding companies also entered the monofilament market using Dow's polymer and their *Saran* tradename. PVDC, unlike PVC, is crystallisable – a consequence of the symmetric nature of the $–CH_2–CCl_2–$ repeating unit – with a melting temperature of about 220 ºC. The molten homopolymer is not sufficiently stable for sustained melt spinning, so in practice small amounts of other monomers, usually vinyl chloride or acrylonitrile, are copolymerised into the PVDC to lower the melting temperature. Fabrics made from the monofilaments, which are tough, readily cleaned and resistant to combustion, have been widely used in, for example, deck chairs.

PVDC fibres are classed as chlorofibres in the list of generic terms for fibres approved by the ISO, which does not recognise Saran as a generic term. In the USA, however, *Saran* is approved by the Federal Trade Commission as a generic name for fibres made from PVDC containing more than 80 % by weight of units derived from vinylidene chloride (VDC).

1.2.4 Poly(vinyl alcohol)

A patent filed in Germany in March 1931 by Herrmann and Haehnel, from the laboratories of the Association for Electrochemical Industry in Munich, and succeeding patents in other countries, including the USA, claim the use of poly(vinyl alcohol) fibres as surgical sutures.[22–24] These products made for use as sutures were probably the first commercial synthetic fibres, but fibres made from unmodified poly(vinyl alcohol) were not suitable for normal textile use because of their sensitivity to water.

An early patent, first filed in France by Belloc in April 1932 and assigned to Société Nobel,[25] describes the manufacture of an artificial textile fibre spun from a condensation product of polyvinyl alcohol and an aldehyde, such as formaldehyde or acetaldehyde. It includes formation of fibres by hydrolysing poly(vinyl acetate) in hydrochloric acid, reacting the product with trioxymethylene (a source of formaldehyde), and wet-spinning this reaction product from the aqueous acidic solution in which it is formed into dilute aqueous sodium carbonate. The polymer can alternatively be isolated and dry-spun from solutions in various volatile solvents, for example a mixture of methyl acetate and ethanol. This process was not commercialised.

In the USA, early research on poly(vinyl alcohol) fibres at DuPont led to two patents, USP 2 169 250[26] and 2 236 061,[27] both applied for in May 1937 and issued respectively in 1939 and 1941. The patent with the later issue date describes the formation of films and fibres from poly(vinyl alcohol) by extruding an aqueous solution of the polymer, typically 16.7 % concentration, into a concentrated solution of an inorganic salt, such as 18 % ammonium sulphate. The fibres made in this way were of course still soluble in water. The other patent overcomes this deficiency by including a polymerisable material such as methacrylic acid (plus a polymerisation catalyst) or dimethylolurea in the solution. The product is then heated at a temperature sufficient to cause this second component to polymerise and also to react with the poly(vinyl alcohol), which is thus insolubilised. This product and process were not developed further by DuPont.

Sakurada and his co-workers found that poly(vinyl alcohol) wet-spun into concentrated aqueous sodium sulphate could be made insoluble in water by heat treatment at temperatures in the order of 210 °C followed by reaction with formaldehyde.[28] This procedure, reported and patented in Japan in 1939, became the most commonly used basis for production of the class of fibres known generically as Vinylal fibres (but in the USA as Vinal fibres). Although a pilot plant was built in Kyoto in 1942, commercial production of *Kuralon* by Kurashiki Rayon (Kuraray) did not begin until 1950. Production of poly(vinyl alcohol) fibres is still mainly located in Japan, where most of the further process development has taken place, and in other Far Eastern countries such as China and North Korea.

1.2.5 Acrylic fibres

The earliest descriptions of potentially useful solvents for spinning polyacrylonitrile are in two patents due to Rein, of I G Farbenindustrie, that were originally filed in Germany in 1934. In the first,[29] the solvents are low-melting quaternary ammonium compounds, such as benzylpyridinium chloride. In the second,[30] they are concentrated solutions of metal salts in water, such as 67 % lithium bromide, 80 % zinc chloride and 77 % sodium thiocyanate. Although Rein later reported[31] that these early German procedures had proved impractical, concentrated aqueous sodium thiocyanate was to become one of the most important solvents for wet-spinning acrylic fibres (e.g. *Courtelle* from Courtaulds, *Creslan* from American Cyanamid) and concentrated aqueous zinc chloride has also been used by at least two producers (*Beslon* from Toho, *Zefran* from Dow-Badische).[32] A patent filed by American Cyanamid in the USA in April 1940 covers polymerisation of acrylonitrile in concentrated aqueous zinc chloride and formation of fibres by wet-spinning the resulting solutions,[33] although Cyanamid's commercial product, *Creslan*, was ultimately wet-spun from aqueous sodium thiocyanate. Concentrated metal salt solutions were also shown by Rein to dissolve some other vinyl polymers, such as the reaction product of poly(vinyl alcohol) with formaldehyde.

In a paper published in 1950, R. C. Houtz of DuPont described the results of a research programme carried out in that company's laboratories aimed at identifying suitable organic solvents for spinning polyacrylonitrile fibres.[34] The programme, stimulated by the fundamental work of C. S. Marvel on the solvation of polymers, led to the filing by DuPont of 15 patent applications, in the names of six different inventors. They were issued as US patents 2 404 713 to 2 404 727 on one day, 23 July 1946, but generated from applications some of which dated back to June 1942. Of these, the most significant for DuPont's development of *Orlon* was due to Latham.[35] It included spinning from dimethyl formamide (DMF), the solvent chosen for commercial production of *Orlon*, and is cited in other patents in the series as representing ‘the first successful dissolution of polyacrylonitrile in a solvent suitable for solvent spinning’.

Although DuPont supplied experimental acrylic fibres for military applications as early as 1942,[18] it did not announce plans for commercial production of *Orlon* until 1949. Production of *Orlon* continuous-filament yarn began in 1950, and of staple fibre in 1952. Production of *Acrilan* staple fibre by Chemstrand also began in 1952, and staple fibre was to prove much the more important product for acrylic fibre producers in general.

1.2.6 Polyethylene (PE)

Fibre-forming polyethylene is reported to have been discovered by ICI early in 1933,[36] although the basic patent was not filed until 1936.[37] A further ICI patent,[38] also filed in 1936, describes its melt-spinning and orientational drawing to form fibres with tensile strength as high as 25 kg mm^{-2}. Despite its low cost, its low melting point, lack of dye sites and relatively poor tensile recovery made it unsuitable for major development in textile end-uses.

Polyethylene monofilaments were produced commercially on a small scale by conventional melt extrusion and drawing of polymers made by the high-pressure type of polymerisation process, starting during World War II. A typical product of this type was *Courlene*, first produced in 1950 by Courtaulds and used, for example, in fusible interlinings. Solution spinning processes were patented at an early stage by both ICI and DuPont, particularly for making fine filaments, but did not prove commercially viable. More recently, processes for manufacturing polyethylene with a very low degree of branching and very high molecular weight have been discovered and developed. Polyethylene fibres with outstandingly high tensile strength and modulus have been produced from such polymers by novel processes, notably by gel-spinning[39] and by solid-state extrusion.[40]

1.2.7 Polypropylene (PP)

Polypropylene was the last of the four major synthetic fibres of the title to be commercialised. As discussed above, ethylene, the lower homologue of propylene, can be converted into a useful crystallisable polymer that consists of slightly branched polyethylene by free radical polymerisation under very high pressure. Propylene, however, only forms non-crystallisable gums of low molecular weight under analogous conditions. In 1953 Karl Ziegler, director of the Max Planck Institute for Coal Research at Mülheim in Germany, discovered inorganic co-ordination catalyst systems based on complexes of aluminium alkyls and titanium chloride that permitted polymerisation of ethylene to give a product of high molecular weight with little or no chain branching, using pressures typically of 1 to 10 bar. Ziegler licensed this process to the Italian firm Montecatini, for whom Giulio Natta was a consultant.[41]

Early in 1954 Natta and his co-workers at Milan Polytechnic began to study the application to other olefins of catalysts of the type discovered by Ziegler and found that their use for polymerisation of propylene led to crystalline polymers of high molecular weight. Natta's first patent on this subject was filed in Italy on 8 June, 1954. This date was incorrectly given in the corresponding US patents[42,43] as 1955, and the error was not corrected until 14 months after the grant and publication of the patents in the USA. The assignment of the corresponding British patent[44] to Montecatini and Karl Ziegler is interesting in that it seems to give Ziegler, who was not an inventor, a beneficial interest in the invention.

Since their introduction, production of polypropylene fibres has steadily grown in volume to become second among synthetic fibres only to polyester, in spite of their manifest limitations. They melt at a temperature (about 165 °C) that was deemed too low for commercial development during DuPont's early choice of a nylon structure for commercial exploitation. Using the catalyst systems of the original Natta type, the polymer has a very wide molecular weight distribution, which leads to rheological problems during extrusion, such as melt fracture. The fibres are virtually undyeable using established classes of dyestuff, so coloration depends almost entirely on melt pigmentation using master-batch techniques. On the other hand, the monomer and polymer are among the cheapest available, and are the basis of a very large plastics industry, of which polypropylene for fibres forms a relatively minor part. There are many large-scale producers of the polymer, which is widely available on a commodity basis. Although this has sometimes led to a situation where the price and availability of the polymer have been controlled by the current needs of the plastics outlets, it has also encouraged a situation where there are very many relatively small-scale fibre-producing units, often concentrating upon particular sectors of the fibre market. This contrasts sharply with the structure of the market for the other major synthetic fibres, where production of the polymer and the fibre are commonly linked within a single company. It is easy, for example, for small-scale producers to spin polypropylene fibres competitively using the 'short-spin' or 'compact' process, which employs a slow extrusion rate and a take-up speed of only 200–500 m min^{-1} and thus allows the filaments to solidify in the threadline very soon after extrusion. Such processes require much less space than processes operating at higher speeds, and consequently incur significantly lower capital cost.

The present position of polypropylene fibres is dealt with in Chapter 5.

1.3 Fibres from step-growth polymers

1.3.1 Nylon; polyamide

The word *nylon* was coined by the American chemical company E I duPont de Nemours (DuPont) as a name for its aliphatic polyamide fibre, which was launched commercially in 1938. It was deliberately not registered as a trademark, and *nylon fibre* became an internationally accepted generic name for fibres based upon linear polyamides. The generic name *polyamide fibre* has the same meaning as nylon fibre, but *nylon fibre* is used principally in countries that derive their fibre technology directly or indirectly from the USA, and *polyamide fibre* in countries that derive their fibre technology from Germany. These two generic names continued to retain identical meanings when they were jointly redefined by ISO in 1977 as 'having in the chain recurring amide groups at least 85 % of which are attached to aliphatic or cyclo-aliphatic groups'. This change was made in order to exclude the new aromatic polyamide (aramid) fibres such as *Nomex* and *Kevlar* that had very different properties and uses. Nomenclature in this field, and in some other fields of synthetic fibre production such as polyester, remains rather confusing since the definitions of the generic names often exclude products that would be included when using the same term for standard chemical nomenclature.

In February 1928, Wallace H. Carothers joined DuPont from a position as an Instructor in organic chemistry at Harvard University, and set up a major research programme to elucidate the nature of polymers. In 1930, Carothers and Berchet[45] studied the thermal polymerisation of ε-aminocaproic acid and found that it produced a mixture of a polyamide and the cyclic monomer ε-caprolactam. Fibres were not obtained from the polymer, probably because it was of too low a molecular weight. Moreover, the authors stated that the lactam does not polymerise under the conditions of formation of the polyamide either in the presence or in the absence of catalysts. This statement was later used by Schlack to justify the novelty of his invention of fibres from polymerised caprolactam.

In a review[46] written early in 1931, Carothers reported that a number of polyamides had been prepared by J. E. Kirby in Carothers's laboratory at DuPont by the action of aliphatic dibasic acids on aliphatic diamines. These materials were all much less soluble than the analogous polyesters, which had already been synthesised in the same laboratory. The polyamides also had much higher melting temperatures than the corresponding polyesters. No indication of their molecular weight or of any fibre formation was provided.

The first polyamide fibre was not prepared until 24 May 1934,[47] when D. D. Coffman, a member of the Carothers team, made fibres by melt-spinning nylon 9 that had been synthesised by polymerising ethyl 9-aminononanoate, $H_2N(CH_2)_8COOC_2H_5$. Fibre-forming polyamides of this nylon *x* type were claimed in a DuPont patent[48] filed in the USA on 2 January 1935. The examples included formation of fibres not only from nylon 9 but also from nylon 6 made by polymerisation from both 6-aminocaproic acid and ethyl 6-aminocaproate, but not from caprolactam, which the Carothers team seems still to have regarded as unpolymerisable.

The success with nylon 9 was rapidly followed by the synthesis of fibre-forming polyamides of the nylon *x,y* type from a wide range of diamines and dicarboxylic acids. Initially, the favoured candidate for commercial development was nylon

5,10, made from 1,5-diaminopentane and sebacic acid, but it was displaced on grounds of its low melting temperature (about 190 ºC) and higher cost by nylon 6,6, which was first made by G. J. Berchet on 28 February 1935.[47] A decision in favour of commercial exploitation of 6,6 was taken by E. K. Bolton in July 1935.[47] A patent[49] claiming fibres from polymers of this nylon *x*,*y* type was filed on 9 April 1937, just 20 days before Carothers died. The first large-scale production plant was constructed at Seaford, Delaware, and started operation early in 1940.[50]

In January 1938, Paul Schlack found that, contrary to statements by Carothers, caprolactam could be polymerised and the polymer could be melt-spun and drawn to form strong fibres.[7] In June of that year I G Farbenindustrie filed a patent[51] based on Schlack's work that claimed a process of polymerising a monomeric lactam containing no fewer than five aliphatic carbon atoms in the ring other than the carbonyl group at a temperature above the melting point of the lactam to a stage where the resulting product can be continuously spun from the melt into continuous threads, without removal of volatile products. One of the 31 examples in Schlack's patent describes the polymerisation of ε-caprolactam using the corresponding amino acid hydrochloride as a catalyst, followed by melt-spinning and orientational drawing of the product to form acid-dyeable fibres with a tenacity of 6 gpd. Polymerisation of the amino acids, particularly 6-aminohexanoic acid, had previously[49] been shown by DuPont to lead to melt-spinnable products, but further progress along that route was inhibited by lack of availability of the amino acids and by the difficulty of purifying them, neither of which was a problem with caprolactam.

I G Farbenindustrie immediately began to develop an industrial process for caprolactam production, polymerisation and melt-spinning. The polymerisation unit, developed by Ludewig,[52] was based upon a continuous process using a tubular polymerisation unit called a VK tube (*Vereinfacht Kontinuerlich* = simplified continuous). In spring 1938, DuPont offered I G Farben a licence to produce nylon 6,6. The Americans were surprised when I G Farben told them of their own development and offered them a licence for nylon 6. The following year, DuPont's nylon 6,6 melt-spinning technology, based on a grid-melting process rather than rod spinning as used initially by the Germans, was made available to I G Farben, and thereafter production of nylon 6 fibres in Germany was implemented using melt-spinning units imported from the USA. The first industrial production unit for the lactam, based on phenol and using the Beckmann rearrangement process for converting cyclohexanone oxime to caprolactam, started up in 1940. A larger plant at Ludwigshafen the following year was devoted mainly to nylon 6 moulding plastic, but a plant dedicated to production of the fibre, by now known as *Perlon*, started up at Landsberg in April 1943.

It is interesting to note that further patents filed by Schlack in this field that were issued in the USA after its entry into World War II were at first[53] granted 'by mesne assignments' to DuPont and later[54] to the Alien Property Custodian. The present position of nylon fibres is dealt with in Chapter 2.

1.3.2 Polyesters

Among the earliest commercial synthetic polyesters were the alkyd resins or glyptals, based typically upon reaction of glycerol and phthalic anhydride to form a highly branched and ultimately cross-linked polymer and used, for example, in paints and varnishes. In 1928 a patent[55] was filed, initially by Allgemeine Elektrizitäts-Gesellschaft in Germany, that claimed processes for making fibres by melt extrusion of incompletely cross-linked polymers of this type and then baking them at a temperature sufficient to cause further cross-linking. Solution spinning from solvents such as acetone was also claimed. These fibres did not become commercial products.

At about the same time, in February 1928, Carothers joined DuPont and set up a major research programme to elucidate the nature of polymers. He chose as one of his main topics the reaction between diols and dicarboxylic acids, which could confidently be expected to produce polyesters in a structurally unequivocal way. By using a 5 % excess of the diols over that theoretically required, Carothers and Arvin[56] obtained polyesters with molecular weights up to about 4000. These products were not fibre-forming, but J. W. Hill[57] devised a polymerisation unit in which a mercury diffusion pump was used to reduce the pressure to 10^{-5} mm of mercury. Hill reacted octadecandioic acid with an excess of propane-1,3-diol and used his molecular still to reduce the amount of propanediol present in the vapour space. He thus obtained a product with a molecular weight of about 12 000. On 30 April 1930, he found that he could pull fibres from the molten polymer, and that when these fibres were subjected to an extensional force they extended irreversibly at a neck to form an oriented fibre of greatly increased tensile strength and modulus.[58,59] Carothers's research team went on to make many such fibre-forming polyesters, but they were nearly all made from aliphatic reactants and melted at temperatures that were too low to permit their use in textiles. Internal DuPont documents show[60] that the possibility of forming a polyester from ethylene glycol and dimethyl terephthalate was examined in October 1934 by a member of the team, E. W. Spanagel, but the conditions used did not lead to a useful product.

An aliphatic polyester with a relatively high melting temperature (223 °C) which had much earlier been made by polymerisation of glycolide, which is the cyclic dimer of hydroxyacetic acid,[61] was known to Carothers but not further evaluated. It is in fact too readily hydrolysed to be commercialised for general fibre use. This very simple polyester was nevertheless used some 30 years later by American Cyanamid[62] to make absorbable surgical sutures (*Dexon*), whose efficacy depended upon their gradual hydrolysis within the body.

The publications of Carothers were read with keen interest by J. R. Whinfield, who had previously worked with C. F. Cross, one of the inventors of viscose rayon. Whinfield initiated a programme of research in his laboratory at the Calico Printers Association (CPA) in Accrington, UK, and early in 1941 his junior colleague, J. T. Dickson, synthesised a high-melting, fibre-forming polyester from ethylene glycol and terephthalic acid.[63] A patent application was filed on 29 July 1941.[64] Its potential importance led the UK Ministry of Supply, applying war-time regulations, to place an embargo on its publication. The patent, which was not published until 1946, covers poly(alkylene terephthalate)s in general. In addition to poly(ethylene terephthalate) it exemplifies other members of the series, notably poly(trimethylene terephthalate), which has more recently also become of commercial importance due to the development of improved syntheses of propane-1,3-diol, as discussed in Chapter 3.

An initial evaluation was carried out in UK government laboratories.[65] The results were very encouraging, and in December 1943 ICI was told about the discovery. ICI then took over further development. In July 1944 ICI told DuPont about the new polyester fibre under the terms of an existing long-term agreement to exchange research results and DuPont began its own evaluation and development. DuPont acquired the US patent rights directly from CPA. The US patent[66] was not filed until September 1945 and was completed by and assigned to DuPont. ICI acquired the rights for the rest of the world, built production plants in the UK and Canada, and licensed producers elsewhere, initially seven companies in five other countries. ICI and its subsidiary companies used the name *Terylene*, which had been given to the fibre by Whinfield. DuPont initially gave it the temporary name *Fiber V*, and in early 1951 named the product *Dacron*.

Polyester fibre production grew rapidly. Polyester displaced nylon as the leading class of synthetic fibre in 1972. The present position of polyester fibres is dealt with in Chapter 3.

1.4 Elastomeric fibres

The generic name 'elastane fibre', approved by the ISO, defines 'a manufactured fibre composed of synthetic linear macromolecules having in the chain at least 85 % (by mass) of segmented polyurethane groups that rapidly reverts substantially to its unstretched length after extension to three times that length'. This definition is unusual among the ISO generic descriptions of fibres in containing a physical property as well as specifying a chemical structure. In the USA another generic name, 'spandex', is approved by the Federal Trade Commission (FTC) and generally used. It differs from the ISO definition in omitting the physical property, and also in omitting the restriction to linear polymers. The development of elastomeric fibres of this type has largely been based on the concept of using polymers containing alternating hard segments and soft segments. The former provide long-term stability of the initial unstressed dimensions of the fibre through association between polymer chains, and the latter provide recoverable stretchability through their relatively low polymer chain modulus, coupled with relatively athermal extension and recovery behaviour.

In 1942, DuPont began work designed to identify a synthetic replacement for cotton-wrapped rubber, based at first on the rubber-like properties of *N*-substituted polyamides.[67] This and the products from other early approaches to elastomeric fibres, such as block copolyesters formed from reaction of poly(ethylene terephthalate) with poly(ethylene sebacate), or more reproducibly with poly(ethylene glycol) [(polyoxyethylene diol); $HO(CH_2CH_2O)_nCH_2CH_2OH$; (PEG)],[68] although possessing good immediate recovery from stretching, suffered from stress decay. This meant that if they were held in the extended form for a period of time, their immediate recovery on releasing the extensional force was very seriously impaired.

The chemical basis for successful elastomeric fibres was provided by Otto Bayer and his coworkers, initially within I G Farbenindustrie, and after the post-war division of I G within one of its successor companies, Farbenfabriken Bayer.[69] They developed the use of aromatic diisocyanates to end-cap and couple flexible polymer units, at first using flexible polyesters of modest molecular weight with hydroxyl end groups. The capping reaction provided urethane linking groups (–NHCOO–) and isocyanate end-groups (–NCO). The isocyanate groups were then coupled using water or difunctional compounds such as diamines. The capping and coupling reactions, using water as the coupling agent, are typically

$$\begin{array}{r} \mathrm{OCNR_2NCO + HOR_1OH + OCNR_2NCO \rightarrow OCNR_2NHCOOR_1OOCNHR_2NCO} \\ \mathrm{+\,H_2O} \;\downarrow\; \mathrm{-\,CO_2} \quad \\ \mathrm{–[R_1OOCNHR_2NHCONHR_2NHCOO]_n–} \end{array}$$

where R_1 = soft segment and R_2 = arylene group.

This technology was used commercially in Farbenfabriken Bayer's *Vulcollan* series of elastomeric polymers. The company investigated the production of fibres from these segmented polyurethanes. It filed a patent application in 1949 that described, rather sketchily, the formation of fibres by extruding flexible polyesters, such as that formed from diethylene glycol and adipic acid, capped with isocyanate end groups, into aqueous solutions of chain-coupling agents such as piperazine (reaction spinning).[70] In 1951 a further patent was filed that described the formation of fibres by wet-spinning a solution of the preformed polyurethane in a solvent such as dimethyl formamide or dimethyl acetamide.[71] This work, however, did not lead immediately to commercial fibre development by Bayer.

Meanwhile DuPont developed and commercialised a segmented polyurethane based upon a polyether soft segment.[72,73] They had produced a new polyurethane elastomer, later named *Adiprene.* Polyoxytetramethylene with hydroxyl end groups, $HO(CH_2CH_2CH_2CH_2O)_nH$, was end-capped with diphenylmethane-4,4′-diisocyanate ($OCN\varphi CH_2\varphi NCO$ where φ = 1,4-phenylene) (MDI), and the isocyanate end groups so formed were coupled by reaction with hydrazine, N_2H_4, to form a poly(ether–urea–urethane), with hard segments consisting typically of groups such as

$$–OCNH\varphi CH_2\varphi NHCONHNHCONH\varphi CH_2\varphi NHCO–$$

This polymer could be synthesised and spun into fibres using solvents of the type already used by DuPont to make the acrylic fibre *Orlon*, and its commercial production was based on the same solvent, dimethyl formamide. The product was supplied initially (from 1959) as *Fiber K* and then (from 1962) from a full-scale production plant as *Lycra*.

When DuPont announced its intention of producing an elastomeric fibre based on this type of chemistry, the Bayer company rapidly revived its interest in a similar product. By 1964 it had commercialised a fibre named *Dorlastan*, the initial form of which was based on aliphatic polyester soft segments connected by hard segments. These hard segments were produced by first end-capping the soft segments with MDI and then reacting the product, dissolved in dimethyl formamide, with carbodihydrazide, $H_2N.NH.CO.NH.NH_2$.[74]

A new method of producing elastomeric fibres, reaction spinning, was developed by the US Rubber Company. A copolyester soft segment was capped by an aromatic diisocyanate, and the product was extruded through a spinnerette into a bath containing a diamine dissolved in water. The filaments produced in this way had a skin of segmented polyurethane but an incompletely reacted core, and were then reacted with further diamine or water to chain-extend or cross-link the polymer precursors inside them.[75] A commercial product, *Vyrene*, was introduced in about 1958, but discontinued after a few years.

Another reaction spinning process, which is described in patents filed in 1962[76] and 1964[77] by Globe Manufacturing Co, was based on extrusion of liquid, slightly branched aliphatic polyesters or polyethers, capped with diisocyanates, into a solution of a polyamine such as ethylenediamine in an inert organic solvent such as toluene. Globe's product was named *Glospan*. Wet-spinning was used in a process developed by Peters[78] and even melt-spinning has been used commercially for elastane thread production.

A feature of elastomeric fibre development and production is the large number of different chemical and fibre extrusion processes that have been described and practised industrially.[73] There has been continuous evolution of improved products, aimed largely at overcoming problems of oxidative and thermal instability, particularly of the products based on polyether soft segments, and hydrolytic instability, particularly of the polyester-based products. The market is, however, now dominated by the dry-spun fibres, and particularly by *Lycra*.

1.5 Brief overview

The foregoing discussion of the early evolution of synthetic fibres deals largely with the dates, locations and key individuals involved in the inventive steps leading to the various classes of synthetic fibre. The earliest published description of formation of synthetic fibres is generally acknowledged to be that in a patent filed in Germany by Klatte in 1913, describing the spinning of chlorofibres from solutions of poly(vinylchloride). The earliest commercial production of a synthetic fibre seems to have been due to Herrmann and Haehnel, based on patents filed in Germany in 1931–33. This product, however, was a poly(vinyl alcohol) surgical suture, unsuitable for conventional textile applications. The earliest commercial development of fibres for textile use was that of partially chlorinated PVC fibres (*Pe-Ce*) by I G Farbenindustrie in Germany, based on a patent filed in 1932. Small-scale commercial production began in 1934.

Polyamides were the earliest class of fibre to become established as major commercial products. The first fibre of this class to be made on a laboratory scale, nylon 9, was synthesised by Coffman, a member of the research team at DuPont headed by Carothers, in May 1934. Nylon 6,6 fibres were first made in a laboratory in January 1935, and the first major production unit began operation in December 1939. A patent-free route to nylon 6, based on polymerisation of caprolactam, was discovered in January 1938 by Paul Schlack of I G Farbenindustrie. A plant for commercial production of this fibre (*Perlon*) began production in Germany in January 1943.

Acrylic fibres and polyester fibres were the next two major classes of synthetic fibre to be commercialised. The early development of both took place in the 1940s. In the case of the acrylics, identification of suitable solvents for spinning fibres led many companies to enter the market, the first two being DuPont (1950) and Chemstrand (1952), both in the USA. In the case of polyester, the crucial invention was due to Whinfield of Calico Printers Association in the UK, and the product was developed into commercial production by ICI in the UK and DuPont in the USA. The fourth major fibre, polypropylene, was discovered in 1954 as a result of academic research into catalysts for polymerising olefins by Ziegler in Germany and Natta in Italy. The polymer rapidly became available to a wide range of fibre producers, large and small, so that the market rapidly became highly competitive.

These four major fibre classes, nylon, acrylic, polyester and polypropylene, are the subject of the following four chapters.

1.6 References

Note: The dates given here for patents are those of grant and/or publication. Dates of filing, which may be several years earlier, are given in the text where they are of particular significance.

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2

Nylon fibres

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2.1 Introduction

Nylon was the first synthetic fibre to go into full-scale production and the only one to do so prior to World War II. The development arose from the work of Wallace Carothers for DuPont at Wilmington in the USA starting in 1928.[1] By 1935 the first nylon 6,6 polymers had been prepared and pilot plant production started in 1938. The following year, the first plant for nylon fibres went into production and the first stockings went on sale in October 1939.[2] The first production in the UK was under licence from DuPont by British Nylon Spinners, a company jointly formed by Courtaulds and ICI, and started in 1941.[3] Most production during World War II was devoted to military uses, particularly for parachute fabrics. Only in 1946 did the fibre start to be available for domestic uses. A parallel development occurred in Germany starting in 1931, leading to nylon 6 rather than 6,6. Some coarse monofilaments were produced in 1939 with small-scale production of continuous filament in 1940 and larger-scale production a year later. Subsequent to the war, full-scale production in Germany did not resume until 1950.[4–7]

The extent of these developments in the USA and Germany can best be appreciated when it is realised that they were undertaken without the benefit of modern ideas of polymer characterisation and that many of the monomers evaluated were not commercially available. Carothers synthesised diamines with from 2 to 18 carbon atoms in order to react them with various aliphatic carboxylic diacids to evaluate the polyamides as fibres.[7–10]

In 1950 the total world production of synthetic fibres was only 69 000 tonnes, and almost all of this was nylon. Over the next 20 years production of polyester, acrylic and polypropylene fibres started, and the volume produced increased to 4.8×10^6 tonnes. Nylon remained the most important synthetic fibre in volume terms. In 1970 nylon accounted for 40 % of the total synthetic fibre production with just under 2×10^6 tonnes.[11] The applications also expanded from the initial hosiery market to reinforcement of rubber in tyres and belts, and to carpets, often in blends with wool. The easy-care properties of the fibre were exploited in its use in underwear, bedsheets, shirts and other apparel. However, in many of these textile applications, flat yarns with relatively coarse filaments were used in tightly woven or knitted fabrics. These fabrics had a limp and rather plastic handle, poor ability to wick moisture away from the body, and a strong tendency to build up static charges, leading to clinging and sparking. The fabrics were frequently shiny.

In the 1970s the newly developed polyester/cotton blends offered superior user comfort in many of these apparel and domestic applications, and nylon was displaced from these end-uses. In the fashion industry the word ‘nylon’ became almost pejorative. By 1975, polyester had become the most important synthetic fibre in terms of volume of production; nylon had ceased to be a speciality product and had become a commodity that was bought and sold on price. Many producers experienced falling returns on their capital investment.

Polyester has remained the most used synthetic fibre and accounted for over 60 % of the 28×10^6 tonnes of synthetic fibres produced in the world in 1999. The world production of nylon has continued to increase slowly and now exceeds 4×10^6 tonnes per annum. Producers have marketed the fibre for applications in which its properties are best utilised. These include carpets, tights and stockings, tyres and belts. For apparel, producers engineer their products to meet the needs of particular uses – filaments have become finer and frequently non-circular in cross-section; textured yarns are often used. These products, together with changes in fashion, led in the late 1990s to a revival of interest in nylon for outerwear. Inclusive brand names for nylon such as *Bri-Nylon* are no longer used and specific brand names for particular applications, e.g. *Antron*, *Tactel* and *Tactesse*, are used. The words ‘nylon’ or ‘polyamide’ often do not appear prominently in marketing literature. The emphasis is on the properties of the particular fibre and its suitability for applications. Sometimes it is not clear if it is based on polyester or polyamide, even in manufacturers’ promotional literature.

2.2 Chemical structures

Nylon fibres are made up of linear macromolecules whose structural units are linked by the –NH–CO– group. Consequently the term polyamide is frequently used. However, in nylons the structural units are essentially aliphatic and, by definition, less than 85 % of the amide linkages may be attached to two aromatic rings. In practice, in almost all examples of nylons none of the amide links are attached to two aromatic rings. If 85 % or more of the amide linkages are attached to two aromatic rings, then the fibres are still polyamides but fall into a different generic group. These fibres are the aramids and their production processes and properties differ markedly from those of the nylons. They will not be discussed further in this chapter.

Nylon polymers can be formed in many ways. The four most important for industrial polymers are:

1. the condensation of diamines with diacids;
2. the self-condensation of amino acids;

3. the hydrolytic polymerisation of lactams, which involves partial hydrolysis of the lactam to an amino acid; and
4. the anhydrous addition polymerisation of lactams.

Methods 1 and 3 are of major importance in the manufacture of fibres; method 2 is used for certain speciality nylons; and method 4 is used for reaction moulding, but not for fibre manufacture. The process developed by Carothers involved method 1, the condensation of two difunctional monomers, an amine and a carboxylic acid. Polyamides derived from diacids and diamines are generally referred to as the AABB type. They are identified as nylon *x,y*, where *x* and *y* are the numbers of carbon atoms in the diamine and the diacid respectively. Although this route can form potentially many different polymers, the one that is of major commercial importance is nylon 6,6. The alternative process involves the condensation of an ω-amino acid with the amine and the carboxylic acid groups on opposite ends of the molecule. Nylons derived from amino acids are termed the AB type. They are identified as Nylon *x* where *x* is the number of carbon atoms in the monomer. Nylon 6 is the member of this group which is of greatest commercial importance.

Nylon 6,6 is produced from the polycondensation of 1,6-diaminohexane, the traditional name of which is hexamethylenediamine, and hexandioic acid, which is often called adipic acid. The formation of nylon 6,6 may be represented by eq. 2.1.

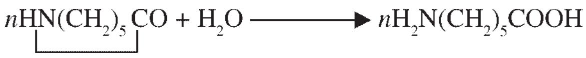
$$n\mathrm{H_2N{-}(CH_2)_6{-}NH_2} + n\mathrm{HOOC{-}(CH_2)_4{-}COOH} \longrightarrow$$

$$\mathrm{H{+}HN{-}(CH_2)_6{-}NH{-}CO{-}(CH_2)_4{-}CO{+}}_n\mathrm{{-}OH} + (2n{-}1)\mathrm{H_2O} \qquad [2.1]$$

In the case of nylon 6, the normal monomer is caprolactam, which is formed when 6-aminohexanoic acid (ε-amino-caproic acid) loses water internally to form a lactam, as represented in eq. 2.2:

$$\mathrm{H_2N(CH_2)_5COOH} \longrightarrow \mathrm{HN(CH_2)_5CO} + \mathrm{H_2O} \qquad [2.2]$$

Caprolactam does not polymerise readily when it is dry. It may be converted to nylon 6 under anhydrous conditions by an anionic polymerisation using alkali or alkaline earth hydroxides, hydrides or alcoholates as catalysts. However, a hydrolytic polymerisation is normally used for fibres. A small quantity of water, aminocaproic acid or another monobasic carboxylic acid needs to be added to catalyse the reaction. An addition of 5–10 % of water is often used in industry. The reaction involves a water-initiated ring opening of the caprolactam (eq.2.3), which is a reversal of the reaction in eq. 2.2, followed by a condensation polymerisation (eq. 2.4) of the aminocaproic acid. Mechanistic studies indicate that a direct addition polymerisation of caprolactam also takes place in the reaction[12] (eq. 2.5).



$$n\mathrm{HN(CH_2)_5CO} + \mathrm{H_2O} \longrightarrow n\mathrm{H_2N(CH_2)_5COOH} \qquad [2.3]$$

$$nH_2N(CH_2)_5COOH \longrightarrow H\!\left[HN(CH_2)_5CO\right]_n\!\!-\!OH + nH_20 \qquad [2.4]$$

$$n\underbrace{HN(CH_2)_5CO} \longrightarrow \left[HN(CH_2)_5CO\right]_n \qquad [2.5]$$

Some other nylons have been used commercially. Nylon 11 of the AB type is produced on a small scale as fibres under the trade name of *Rilsan.* It is still widely used as a plastic. The formula of the repeat unit is given in eq. 2.6:

$$\left[HN(CH_2)_{10}CO\right]_n \qquad [2.6]$$

A further nylon was introduced in 1968 by DuPont under the brand name of '*Qiana*®'. It was claimed to give a more silk-like handle and lustre in fabrics as well as dimensional stability and wrinkle resistance similar to polyester. However, the complex diamine was more expensive, and a carrier was required for dyeing, making coloration more difficult than for nylon 6,6 and 6. It was later withdrawn from the market. The polymer, of the AABB type, was formed from the condensation of bis(4-aminocyclohexyl)methane and dodecandioic acid. The diamine exists as *cis* and *trans* isomers, and the monomer used in *Qiana*® was 20 % *cis–trans* and 80 % *trans–trans*. The repeat unit is shown in eq. [2.7], where C_6H_{10} is a 1,4-disubstituted cyclohexylene ring:[13]

$$\left[HNC_6H_{10}CH_2C_6H_{10}NHOC(CH_2)_{10}CO\right]_n \qquad [2.7]$$

Nylon 4,6 is produced as *Stanyl* by the DSM (Dutch State Mines) Group and is polymerised from 1,4-diaminobutane and adipic acid. It was first produced on a pilot plant scale in 1984 and marketed in 1989. The polymer has a higher melting temperature, 295 ºC, than nylon 6,6 or 6. While this makes extrusion more difficult, the yarn has benefits, especially at elevated temperatures in terms of dimensional stability, heat capacity, creep and shrinkage behaviour. It is used for V- and timing belts, tyre cord, hoses and abrasion-resistant fabrics.[14] The formula of the repeat unit is given in eq. 2.8:

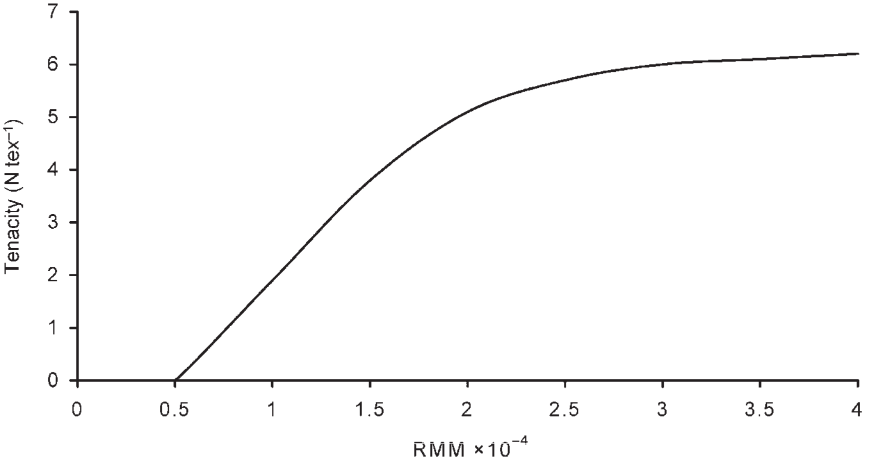
$$\left[HN(CH_2)_4NHOC(CH_2)_4CO\right]_n \qquad [2.8]$$

Two other nylons are used commercially to a small extent, nylons 6,10 and 6,12. The former is produced for press felts for paper-making (Rhodia, France) and is also used with nylon 6,6 in self-crimping bicomponent fibres.[15] Nylon 6,12 is produced as a monofilament under the brand name *Tynex* (DuPont, USA), for use in floor care, paint, tooth and cosmetic brushes. The reduced proportion of amide groups gives lower moisture absorption as well as enhanced chemical resistance.[16]

2.3 Polymerisation

2.3.1 Extent of polymerisation

In the preparation of any polyamide, the relative molecular mass, often called the molecular weight, of the polymer and its control are of vital importance. The



2.1 Schematic graph of the effect of the polymer relative molecular mass (RMM) on the nylon fibre tenacity.

molecular mass and its distribution as described in Section 2.3.2 are important in a polymer for a number of reasons. A high molecular mass leads to a high viscosity in the molten polymer during extrusion. The polymer around the walls of the extrusion head will be slow moving and the molecules will tend to degrade, cross-link and solidify. Particles of the solid polymer can then break off and block the spinneret holes or cause discoloration of the extruded polymer. In a much later process, acid and reactive dyes, which are commonly used for nylon, are attracted to the amine end groups in the polymer. The higher the molecular mass, the lower the number of amine end groups and hence the lower the affinity to these dyes. If the polymer molecular mass is low, then the fibres extruded will have only a low tenacity. Figure 2.1 is a schematic representation of the effect of polymer molecular mass on the fibre tenacity.[17] The influence of the molecular mass on the extension at break and the work of rupture of the fibres is similar. It can be seen that increases in molecular mass beyond a certain point have little further effect, and normally for nylon production the molecular mass is in this region where the graph levels.

Initially the number of end groups in a condensation polymerisation is twice the number of monomer molecules. The polymerisation proceeds until the concentration of end groups has been reduced to a low level. It is possible to define a quantity, the extent of polymerisation, p, which is the fraction of the original end groups that have reacted. Therefore $1 - p$ is the fraction that has not reacted.

The number average degree of polymerisation, P_n, gives the mean number of repeat units in a polymer molecule.

$$P_n = 1/(1 - p) \qquad [2.9]$$

The number average molecular mass is then P_n times the molecular mass of the repeating unit, W. For AABB polymers such as nylon 6,6 prepared from equivalent concentrations of each monomer, p is the same for each type of functional group. Conventionally, following Carothers, W is taken as the mean molecular mass of the diacid and the diamine portions of the polymer, rather than the molecular mass of the whole repeat unit as given in eq. 2.1. In the preparation of nylon 6,6, if $p = 0.99$, meaning that 99 % of the original end groups have reacted, then the number average degree of polymerisation will be 100 and the number average molecular mass of the polymer will be 11 300. Commercial nylon 6,6 fibres for apparel have a molecular mass in the range 12 000–15 000, corresponding to an extent of polymerisation in the range 0.991–0.993. Polymer with a higher molecular mass is used for high-tenacity yarns. If an AABB polymer is prepared with an excess of one of the reagents, then an average value of p can be used to calculate the degree of polymerisation.

2.3.2 Molecular mass distribution

Although a figure can be given for the degree of polymerisation of a polymer sample, it would be very surprising if every molecule had the same length. There is normally a broad distribution of chain lengths, called the most probable distribution. This can be calculated by equations first put forward by Flory[18] and later confirmed by experiment.[19]

The number fraction, n_x, of x-mers of the polymer chains containing x repeat units, where p is the extent of the polymerisation as defined above, is given by

$$n_x = p^{x-1}(1 - p) \tag{2.10}$$

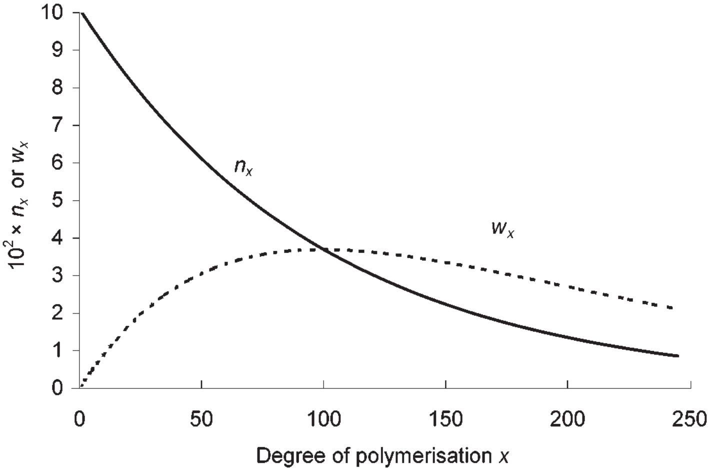
However, the number fraction is of limited usefulness. There are many molecules where x is low, but fewer where it is higher. The larger molecules form a more significant proportion of the polymer by weight and also make a more positive contribution to the properties of the polymer and of the fibres. An analogy may be drawn between fibres in a yarn and molecules in a fibre. The short fibres in a yarn contribute little to the tensile properties and may migrate to the surface, causing pilling. The weight fraction distribution, w_x is given by eq. 2.11:

$$w_x = xp^{x-1}(1 - p)^2 \tag{2.11}$$

The distribution curves calculated from these equations are given in Fig. 2.2. They relate to the case where $p = 0.99$. The weight average degree of polymerisation, P_w, is given by eq. 2.12:

$$P_w = \frac{(1 + p)}{(1 - p)} \tag{2.12}$$

The ratio of the weight average to the number average degree of polymerisation, P_w/P_n, is termed the polydispersity of the polymer and tends to 2 at high extents of



2.2 Most probable molecular mass distribution for nylon showing variation of mole and weight fraction for $p = 0.99$.

reaction. The polydispersity is an important characteristic of a nylon polymer, owing to its effects on the rheological properties of the polymer and on the final characteristics of the fibres. Nylon with an extent of reaction, p, of 0.992 will have a number average molecular mass of 14 100 and a weight average molecular mass of 28 100. The polydispersity is therefore 1.992, very close to the maximum of 2.

2.3.3 Polymerisation equilibrium

The polymerisation of nylons, shown in equations 2.1–2.5, reaches an equilibrium. This may be represented by the equation:

$$\text{–NH}_2 + \text{HOOC–} \rightleftharpoons \text{–NHOC–} + \text{H}_2\text{O} \qquad [2.13]$$

The equilibrium constant for the reaction is therefore:

$$K = \frac{[\text{–NHOC–}][\text{H}_2\text{O}]}{[\text{–COOH}][\text{–NH}_2]} = B \exp\{-\Delta H_a/RT\} \qquad [2.14]$$

where B is the temperature-independent part of the equilibrium constant and ΔH_a is the enthalpy change for the polymerisation reaction. Published estimates of ΔH_a vary, but the reaction is exothermic and values in the range –25 to –29 kJ mol^{-1} appear to be reasonable.[20,21] The exothermic nature of the reaction means that a decrease in temperature favours a polymer of a higher molecular mass if the water concentration is constant. However, the scope for variation in the temperature of the reaction is limited. For nylon 6,6 the polymer melts at approximately 260 °C and decomposition of the polymer is excessive above 290 °C, leading to discoloration of the fibres. In addition, at lower temperatures the rate of the reaction is lower, leading to increased times in the reaction vessels.

The effect of the equilibrium is that as the polymerisation proceeds, water is evolved. Eventually the reaction will reach a stage where it will not continue to give higher molecular mass polymer. At this point it is necessary to remove water as it is formed to displace the equilibrium towards the formation of polyamide. A limitation is that the polymerisation is often carried out under a steam blanket at 1 atmosphere. Even at 280 ºC there will be residual water content within the polymer. For nylon 6,6 at equilibrium at 280 ºC this has been reported to be 0.16 %.[22]

2.3.4 End group imbalance

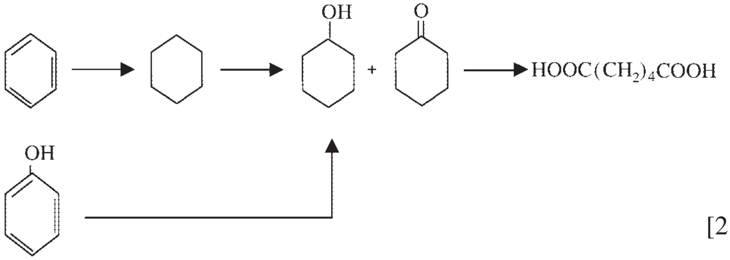
Normally for the polymerisation reactions in eqs 2.1–2.3 the concentrations of the amine and carboxylic acid end groups should be equal. However, there are a number of reasons why an imbalance can occur. In an AB-type polymer, a monobasic acid may be added to the mixture to react with amine end groups to block further polymerisation and stabilise the polymer molecular mass; some amine end groups may be oxidised during processing. In an AABB-type polymer, an imbalance can result from non-equivalence in the concentrations in the monomers; this can be caused by adding monobasic acids to stabilise the polymer or it may be inadvertent. The performance of the polymer during extrusion is also important. Favourable effects on the spinning performance of nylon 6 have been reported using dicarboxylic acids as chain stabilisers, but this leads to a poor dye affinity and low fastness when colouring with acid dyes.[23] Amines are therefore added to improve the dyeing performance and balance the polymer properties. Some nylon 6,6 fibres, are produced with an affinity for cationic (basic) dyes. The polymers have almost all of the amine end groups blocked and compounds containing groups that will attract basic dyes are added (Section 2.7).

2.3.5 Monomer synthesis

The domination of the nylon market by nylon 6,6 and 6 reflects not only that the resulting fibres have convenient melting temperatures, but also the availability of benzene and phenol as convenient starting materials containing six carbon atoms per molecule. All of the relevant monomers were produced originally from these aromatic compounds. Alternative routes have been developed from unsaturated aliphatic compounds. In this section, the processes to produce the monomers for nylon 6,6, adipic acid and hexamethylenediamine, and for nylon 6, caprolactam, are discussed.

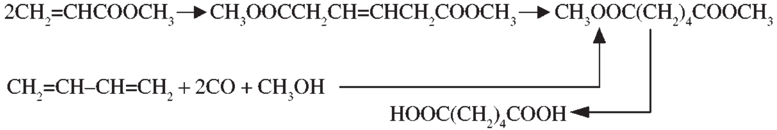
2.3.5.1 Adipic acid

The original approaches for the synthesis of adipic acid used benzene or phenol as the raw material. The first stage of the production of adipic acid from benzene is hydrogenation to yield cyclohexane, which undergoes an air oxidation to a mixture of cyclohexanol and cyclohexanone, called KA or 'ketone alcohol'. For adipic acid, cyclohexanol is the preferred compound and a high proportion of the alcohol is obtained by using a boric acid catalyst at 170–180 °C.[24, 25] For caprolactam, cyclohexanone is the preferred product (Section 2.3.5.3). If phenol is the starting product, then hydrogenation gives the ketone alcohol mixture. The conversion to adipic acid involves a further oxidation with 50–60 % nitric acid containing a copper/vanadium catalyst.[26] The reactions are summarised in eq. 2.15:



[2.15]

An alternative route to adipic acid involves the dimerisation of methyl acrylate (methyl propenoate) to form dimethyl hexenoate. This is carried out either electrolytically or by coupling using a transition metal catalyst; the latter process was patented by ICI.[27] Hydrogenation and hydrolysis of dimethyl hexendioate yields adipic acid. A process patented by BASF involves a two-stage carbonylation of butadiene with carbon monoxide and methanol to yield dimethyl hexanoate, which requires hydrolysis to give adipic acid.[28] An outline of these reactions is given in eq. 2.16:



$$\mathrm{2CH_2{=}CHCOOCH_3 \rightarrow CH_3OOCCH_2CH{=}CHCH_2COOCH_3 \rightarrow CH_3OOC(CH_2)_4COOCH_3}$$
$$\mathrm{CH_2{=}CH{-}CH{=}CH_2 + 2CO + CH_3OH \rightarrow CH_3OOC(CH_2)_4COOCH_3 \rightarrow HOOC(CH_2)_4COOH}$$

[2.16]

2.3.5.2 *Hexamethylene diamine*

The commercial processes for the production of hexamethylene diamine all involve the reduction of adiponitrile (1,4-dicyanobutane) with hydrogen. This reaction is carried out in the liquid phase using a Raney nickel catalyst at 75 °C at a moderate pressure and in alkaline conditions (eq. 2.18).[29] The processes differ in the route to produce the adiponitrile. The original method uses adipic acid as the starting material. It is converted to the amide by a direct reaction with ammonia in the gas phase and then dehydrated using suitable catalysts such as phosphorus and boron oxides (eq. 2.17):

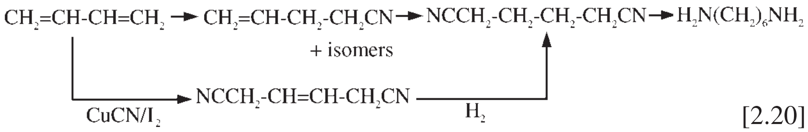
$$\mathrm{HOOC(CH_2)_4COOH \rightarrow H_2NOC(CH_2)_4CONH_2 \rightarrow NC(CH_2)_4CN} \qquad [2.17]$$

$$NC(CH_2)_4CN \longrightarrow H_2N(CH_2)_6NH_2 \qquad [2.18]$$

The first process to produce hexamethylene diamine from other starting materials was developed by Monsanto (now Solutia) and introduced in 1965. This involved the electrolytic dimerisation of acrylonitrile (cyanoethene). The reductive dimerisation occurs at the cathode at 25–35 °C and gives a high yield of adiponitrile (eq. 2.19):[30]

$$2CH_2{=}CHCN + 2H_2O + 2e^- \longrightarrow NC(CH_2)_4CN + 2OH^- \qquad [2.19]$$

Later processes for hexamethylene diamine have used butadiene as the major feedstock. Two separate catalytic processes were developed by DuPont and Exxon for this conversion. In the DuPont route, the initial addition of one molecule of HCN gives a mixture of isomeric cyanobutenes. The second addition of HCN is accompanied by a catalytic isomerisation to form adiponitrile.[31] In the Exxon process the butadiene reacts with copper(I) cyanide in the presence of iodine to give 1,4-dicyanobut-2-ene, which is then hydrogenated to form adiponitrile. This is reduced with hydrogen to hexamethylenediamine.[32] These changes are summarised in eq. 2.20:



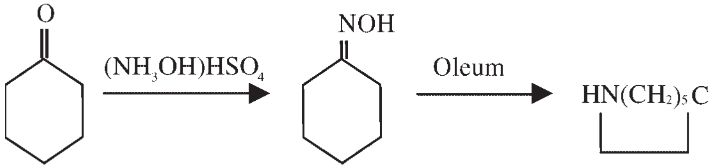
$$CH_2{=}CH\text{-}CH{=}CH_2 \rightarrow \underset{+\text{ isomers}}{CH_2{=}CH\text{-}CH_2\text{-}CH_2CN} \rightarrow NCCH_2\text{-}CH_2\text{-}CH_2\text{-}CH_2CN \rightarrow H_2N(CH_2)_6NH_2$$

$$CH_2{=}CH\text{-}CH{=}CH_2 \xrightarrow{CuCN/I_2} NCCH_2\text{-}CH{=}CH\text{-}CH_2CN \xrightarrow{H_2} NCCH_2\text{-}CH_2\text{-}CH_2\text{-}CH_2CN$$

[2.20]

2.3.5.3 *Caprolactam*

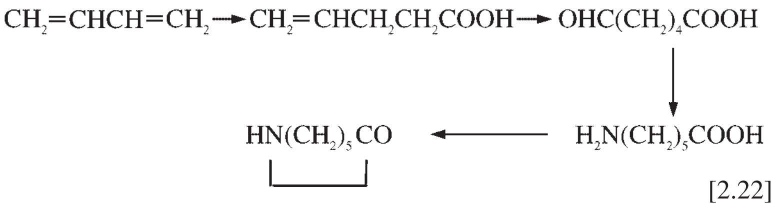
The first stages in the synthesis of caprolactam are similar to those for adipic acid. Benzene is hydrogenated to cyclohexane, which then undergoes a catalytic air oxidation to a cyclohexanone/cyclohexanol mixture (ketone alcohol). Cyclohexanone is the preferred starting material for the production of caprolactam and the yield is increased by dehydrogenation of the cyclohexanol by passing it over a copper catalyst. Alternatively, phenol can be hydrogenated with a palladium catalyst to cyclohexanone. The cyclohexanone is converted to the oxime by a carbonyl addition reaction with hydroxylamine (NH_2OH). A Beckman rearrangement in oleum (highly concentrated sulphuric acid) then gives caprolactam. Much development work has centred on methods of generating and using the hydroxylamine. Some processes have the disadvantage economically that large quantities of ammonium sulphate, a low-price by-product, are formed. In the Allied-Signal (now Honeywell) process, hydroxylamine sulphate is prepared by absorbing nitrogen oxides in ammonium carbonate solution, then reducing the ammonium nitrite formed with sulphur dioxide to hydroxylamine disulphonate. This is hydrolysed to hydroxylamine sulphate, $(NH_3OH)HSO_4$, which is reacted with the cyclohexanone to form the hydroxylamine sulphate oxime (HSO). Hence this route to caprolactam is termed the HSO process (eq. 2.21):



[2.21]

DSM has developed a hydroxylamine phosphate oxime process (HPO). An aqueous mixture of nitric and phosphoric acids is reduced with hydrogen using a palladium catalyst to form the hydroxylamine phosphate, which is then reacted with the cyclohexanone dissolved in toluene.[33] The oxime is formed in the toluene layer, enabling the aqueous phase containing the nitric and phosphoric acids to be recycled. The Beckman rearrangement is still necessary but the formation of ammonium sulphate is minimised.[34]

The Altam process developed by the DSM Group and Shell uses butadiene (C_4H_6), carbon monoxide, ammonia and hydrogen as the feedstocks. All are easily available and relatively inexpensive materials. They can be converted to caprolactam in four stages; in the first, carbonylation of the butadiene with carbon monoxide using a palladium catalyst gives pentenoic acid. This undergoes hydroformylation to generate formylvaleric acid and then a reductive amination using a ruthenium catalyst to aminocaproic acid and hence caprolactam. The process is claimed to offer considerable cost and energy savings, to produce no major by-products and to be more environmentally friendly.[35] These changes are outlined in eq. 2.22:



$$\begin{tikzcd} CH_2{=}CHCH{=}CH_2 \arrow[r] & CH_2{=}CHCH_2CH_2COOH \arrow[r] & OHC(CH_2)_4COOH \arrow[d] \\ & \underbrace{HN(CH_2)_5CO} & H_2N(CH_2)_5COOH \arrow[l] \end{tikzcd}$$

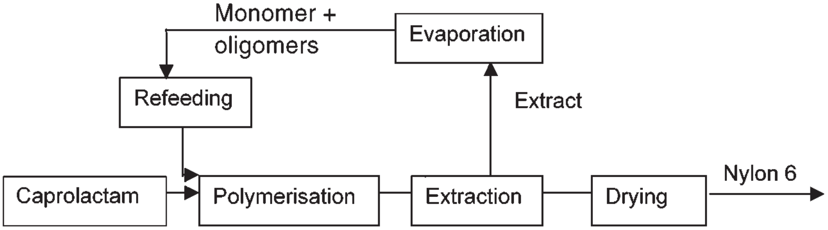
[2.22]

2.3.6 Practical aspects of polymerisation

Polymerisation for either nylon 6,6 or 6 may be a batch, semi-continuous or continuous process. Although batch polymerisation was used in the early production of nylon, continuous processes where the polymerisation is integrated with the fibre production have been increasingly favoured. They give a more consistent, higher-quality product and are cheaper to operate. Both fibre production and polymerisation benefit from long periods of uninterrupted production. However, fully integrated systems of this type lack flexibility. A stoppage for any reason in fibre production means that the polymerisation has to stop as well. Molten polymer cannot be held in the reaction vessels for any length of time as it will degrade; a fault in one section of the plant therefore leads to a shut-down in the other. For this reason some producers still prefer to separate the processes by converting the newly formed polymer into chips which can be stored until required.

The equipment for the preparation of nylon polymers is usually divided into three sections. The first is monomer preparation, which is designed to provide a carefully controlled monomer composition. Then, additives such as delustrants, pigments, antistatic agents and stabilisers against heat and light degradation are added where large quantities of polymer of a particular specification are required. Additives can also be added to the polymer shortly before extrusion; this is used when short production runs with certain additives are needed. The monomers are then fed into the polymerisation reactor where the conversion to polyamide takes place under precisely controlled conditions of pressure, temperature and residence time in the reactor. High-quality nylon suitable for high-speed extrusion requires very homogeneous and consistent polymer properties such as melt viscosity and end group concentrations. After polymerisation the nylon can be passed directly to the extrusion process for conversion into fibre. Alternatively the nylon polymer can be extruded as coarse monofilaments, quenched in water and cut into chips, which have to be remelted before extrusion.

In the polymerisation of nylon 6,6 the adipic acid and the hexamethylenediamine react together in equimolar quantities at room temperature to form ‘nylon salt’. The salt is prepared by mixing a dispersion of the diacid in water with a solution of the diamine to give a 50–60 % solution of the salt in water. Alternatively, alcoholic solutions of the two components can be mixed, the pure salt precipitates and is dissolved to a solution in water. The salt is transferred to an evaporator and is concentrated to 80–85 %. The concentrated solution is passed under a blanket of nitrogen to an autoclave and heated under 1.8 MPa pressure to 275 °C. Polymerisation begins and a prepolymer with a molecular mass of approximately 4000 is formed. The pressure is released by allowing the water from the reaction to escape while maintaining the temperature, until the polymer equilibrates to a relative molecular mass of around 12 000, which is a satisfactory nylon for apparel. The molecular mass of the product is limited by the polymer–steam equilibrium at atmospheric pressure; higher values of the molecular mass are of interest for high-tenacity industrial yarns. They are achieved by conducting the final stages of the melt polymerisation under reduced pressure or by the addition of chain coupling agents, such as diphenyl esters of dicarboxylic acids, to the melt to react with the amine end groups. In nylon 6,6 the polymerisation reaction goes almost to completion. The formation of cyclic oligomers is less probable than for nylon 6 since the smallest possible ring is large, with 14 members for nylon 6,6, and the end groups are, consequently, less likely to approach each other and react. Concentrations as low as 1–2 % have been reported; this level is acceptable in fibres and consequently no removal of the oligomers takes place.[36]



2.3 Block flow diagram of a continuous nylon 6 polymerisation process.

In the production of nylon 6 polymers there is a further stage, monomer recovery, in addition to monomer preparation, polymerisation and extruding into chips or fibres. This is necessary because the conversion to polymer is not complete for nylon 6 and an equilibrium is reached. Following polymerisation at 270 °C, as much as 10 % of the polymer can consist of cyclic oligomers; most of this material is the monomer caprolactam, although some low molecular mass material with degrees of polymerisation in the range 2–10 is also present. The unreacted monomer needs to be separated from the polymer and recycled back to the monomer preparation system. If it is not removed before extrusion, the unreacted monomers and oligomer migrate out of the fibres during high-temperature processing, such as texturing, heat setting or dyeing, and this leads to difficulties with deposits on machines. The stages in the polymerisation of nylon 6 are summarised in Fig. 2.3.

In the polymerisation the caprolactam is heated to 250–280 °C for 12–24 hours at atmospheric pressure. Water, acids or bases can initiate the reaction, but usually in industry, water is used. Reimschuessel has identified that for a minimum residence time of the reaction mixture in the reactor, the process can be considered to fall into two parts. In the first part a high water content is desirable while in the second part a low water content is to be preferred. The transition therefore involves the removal of free water. The relative molecular mass is controlled for fibre formation by adding small quantities of monobasic carboxylic acids to react with the amine end groups in nylon 6 and the molecular mass is controlled at 18–30 000.[37]

Continuous processes for nylon 6 have been in use since the 1940s and use a reaction vessel called a VK tube (from the German expression *Vereinfacht Kontinuierlich* or ‘simplified continuous’ in English). Bergmann of Inventa-Fischer AG of Switzerland has described recent developments of the process. Good mixing of the reaction mixture during polymerisation can result in some monomer being passed out of the vessel before it has the chance to react and hence the conversion to polymer will be incomplete. The VK tube is a tall and narrow reaction vessel where the monomers are fed in at the top. In the upper part of the tube, the reaction mass is heated and thoroughly mixed; in the lower part there is plug flow. The newly formed polymer at the lower end of the tube is cooled gently, increasing the viscosity, preventing back-mixing of the polymer and ensuring plug flow. The cooling also gives a high conversion of caprolactam to polymer. Two VK tubes may be used in series, one for pre-polymerisation and the other to complete the process. With one tube capacities of up to 130 tonnes/day are possible; this can be doubled with two reaction vessels using one for prepolymerisation.[38]

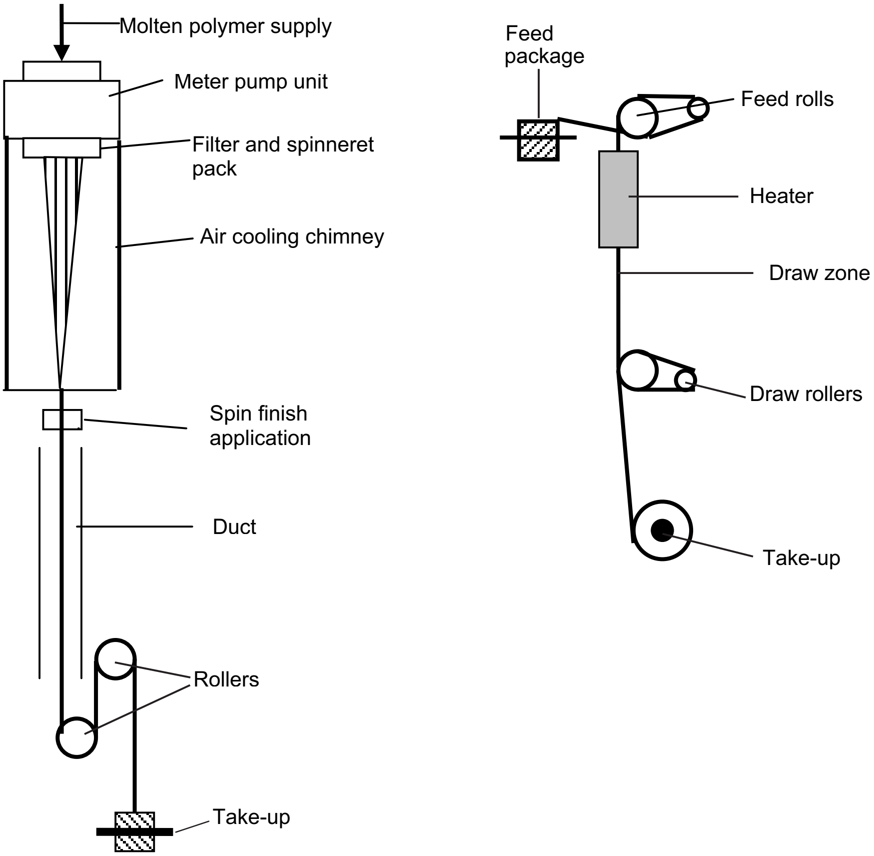
The concentration of oligomers in the polymer for nylon 6 can be as high as 10 %. Most of this is unreacted caprolactam but some cyclic dimer and higher oligomers are present. The oligomers may be removed by hot aqueous or vacuum extraction. The aqueous extraction can be used only if the polymer emerging from the VK tube is extruded into strands and cut into chips. It involves a counter current washing with water at 112–120 °C and reduces the monomer content to less than 0.3 %. The nylon 6 chips are dried under nitrogen and must be remelted during extrusion into fibres. The wash water is concentrated and recycled to the top of the polymerisation reaction vessel. Both the extraction and drying are steps that involve long residence times since the diffusion rates of the monomers or water in solid nylon are low.[39] Vacuum extraction of the monomers does allow the molten polymer to be passed directly to extrusion without the need to solidify the nylon, cut it into chips and then remelt. In vacuum extraction the molten nylon polymer is passed as a thin film through a vacuum. Most of the caprolactam and part of the oligomers are distilled from the melt and the nylon polymer can then either be converted to chips or passed immediately to extrusion. Vacuum extraction is, however, less efficient at removing the monomers and oligomer, and concentrations in the range 2.8–3.8 % are characteristic of the process. This is too high for some industrial applications and consequently washing, drying and remelting of chips continue to be used.

2.4 Fibre production

The initial stage of fibre production is often referred to as ‘spinning’. Inevitably there is some confusion with the process of assembling staple fibres into yarns. In this chapter the term ‘extrusion’ will be used for the initial process. For most nylon fibres extrusion is followed by drawing, and frequently by texturing. These processes will be described separately but are interlinked. One of the most important parameters of the final yarn from the point of view of the textile processor and the consumer is the linear density. This is determined by the rate at which polymer is pumped through the spinneret during extrusion, the wind-up speed and the draw ratio.

2.4.1 Fibre extrusion

All of the aliphatic nylon fibres are produced by melt extrusion, as it is the most



2.4 Schematic diagram of nylon extrusion and drawing.

economical process of fibre formation. Melt extrusion requires a polymer that is stable in the molten condition, and no solvents are involved. The speeds at which the yarn is wound on to the package are comparatively high, normally above 1 000 m min^{-1}. This means that the production rates from each spinneret are adequate for low linear density continuous filament yarn. Originally, almost all nylon was of this type, although as the overall production volume has increased, industrial yarns and fibre for carpets have become more important. These are normally medium to high linear density continuous filament yarns. A schematic diagram of an extrusion and drawing line is shown in Fig. 2.4.

In melt extrusion, the polymer chips are melted by a heated grid, or by an extruder where an Archimedean screw forces the chips along a heated tube. Alternatively, the polymer may be supplied directly from continuous polymerisation. The molten polymer is fed to an accurately controlled metering pump, which is of vital importance in controlling the linear density of the final product. This is the tex, or the mass in grams of 1000 m of the yarn. The pump must maintain an exact volume of molten nylon polymer per unit time to the spinneret at a temperature of 280–300 ºC and against a pressure as high as 50–70 MPa. The molten polymer is then filtered by passing it through a bed of fine sand supported on a metal mesh or through a series of sintered metal screens. The filters remove from the polymer melt any particulate matter or gels that could block the spinneret holes. The filter material also subjects the molten polymer to a high shear that affects the rheological behaviour by inducing some molecular orientation. Extrusion, particularly for nylon 6,6, takes place close to the temperatures at which the polymers rapidly thermally degrade. Consequently, the pack designs must avoid stagnant areas where the polymer may be trapped and thermally degrade, and air must be rigorously excluded. The extrusion heads consisting of the filter and the spinneret are changed when holes become blocked or the pressures become excessive. The new packs are pre-heated before installation to prevent the molten polymer solidifying as it flows into the head.

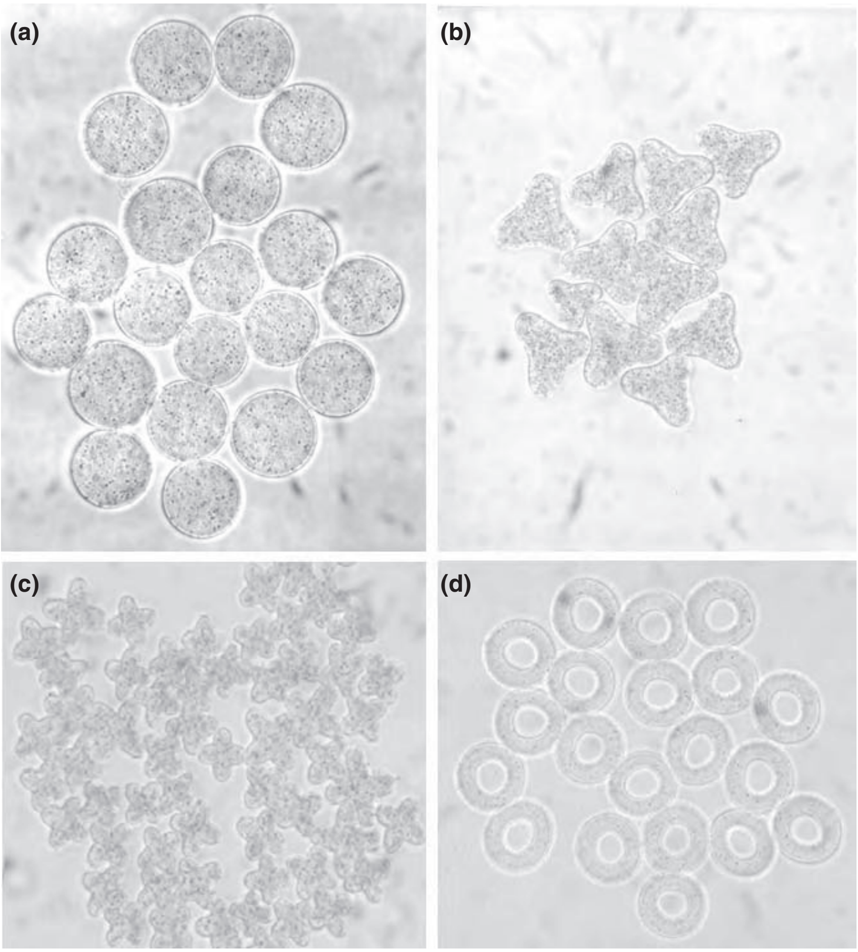
The molten polymer then passes through the spinneret, which has a number of small holes, typically 100–400 μm in diameter, corresponding to the number of filaments required in the final yarn. The spinneret is a stainless steel plate 5 mm or more in thickness. Normally the holes in the spinneret are circular, yielding fibres with a circular cross-section. Each hole is made up of a counter-bore, a conical transition zone, and the capillary. The capillaries must be consistent not only in their diameter but also in length; L/D ratios of 2–5 are typical. If there are variations in diameter and length between holes then some filaments in the yarn produced will be coarser or finer than others, with a risk of breakage and a reduction in the yarn quality. Tolerances for standard spinnerets of ±2 μm for the hole diameter and ±20 μm for the length are quoted with ±1 μm and ±5 μm tolerances respectively in spinnerets for critical applications. In addition, the inner surfaces of the orifices must be smooth and the holes distributed over the face of the spinneret so that the quenching air reaches the fibres optimally, preventing stickiness of the fibres, cross-section deformation or crystallisation differences as the filaments are formed.[40] The number of holes in the spinneret corresponds to the number of filaments required in the final product, although for fine yarns the holes may be grouped so that several threads are wound up from the same extrusion head. For nylon staple the number of holes may be many thousands.

Some orientation is induced in the polymer by the shear as it passes through the filter and the capillary. The nylon polymer emerges from the spinneret holes into air; immediately the orientation imparted in the filaments by the flow of the molten nylon polymer through the spinneret holes tends to relax and a post-extrusion swelling is observed. The heated pack body often extends a few centimetres below the spinneret to provide a heated zone around the newly formed fibres. This reduces any air turbulence around the face of the spinneret and minimises the cooling of the surfaces of the newly formed fibres when they undergo the post-extrusion swelling as the molecular alignment arising from the shear in the capillary relaxes. Following this post-extrusion swelling, the polymer stream is drawn down by the take-up reel and undergoes a considerable acceleration. It also enters the quenching air stream, which can come from the side of the filaments or from a perforated chimney at the centre of the fibres; in the latter case the spinneret is annular rather than circular. The accelerated filaments solidify in the cool air at a temperature of 18–20 °C and a relative humidity of 55–65 %; at this stage there is some orientation of the molecules along the fibre axis and some crystallisation. The yarn is pulled through cool air in an enclosed protective cabinet for as much as 5 m to complete the solidification.

The filaments converge at a guide and at this stage a spin finish is applied by allowing the yarn to contact a roller rotating in a small bath. The yarn is then wound onto a package termed a 'cheese' if it is for continuous filament. Often a standard length of yarn is required on each package to facilitate subsequent processing, and systems are in place to wind the yarn on to a new package as soon as that length is reached. If tow is required then the output from a number of spinning heads is combined and coiled into a can before drawing as a separate process. The purpose of the spin finish is principally to lubricate the fibres to protect them from abrasion and to dissipate static electricity. The spin finish may include lubricants, emulsifiers, antistatic agents, bactericides and antioxidants. The concentration of the active parts of the finish on the yarn is usually in the range 0.2–1.0 %. A further function of the spin finish is to saturate the fibres with the equilibrium water concentration for the relative humidity prevailing during the subsequent finishing operations. Nylon fibres become slightly longer as they take up moisture from the air and there is a danger that if they are wound on to a package in the dry state they will become slack as they absorb moisture. This would make it difficult to wind the yarn off the package for drawing.

There is some evidence that the quench stage is critical in determining the properties of the final fibres. If the cool airstream into which the newly formed filaments emerge comes from the side, then the filaments on the windward or cooler side have a higher diameter, lower molecular orientation and lower tenacity than those on the other side.[41] Quenching by an outflow of cool air from the centre of the filament gives more even cooling and hence more uniform filaments within the yarn. One producer, Rhodia, uses a water quench for the newly formed fibres of *Noval Opal* staple carpet fibres and claims that the strength and the elasticity are improved.[42]

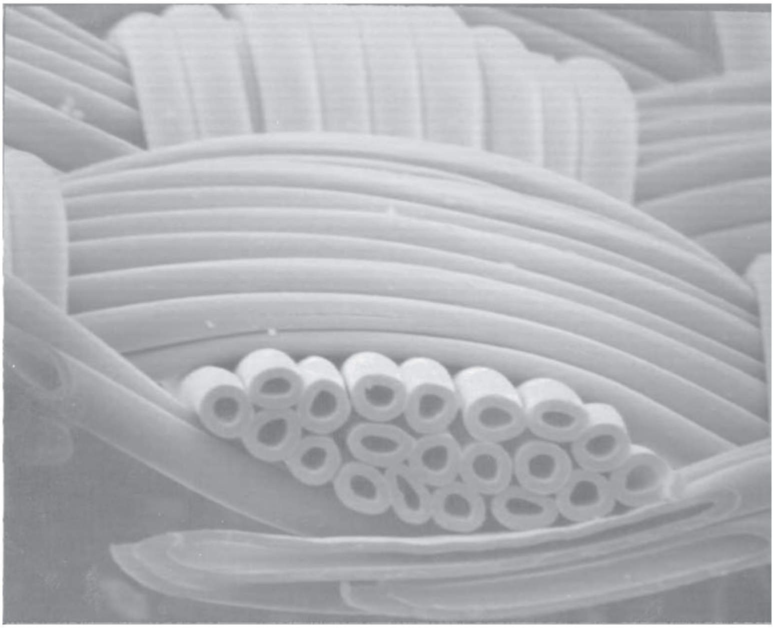
Nylon fibres are extruded with a variety of cross-sectional shapes. Most common is the conventional round cross-section from a circular spinneret hole shape. This is preferred for strength in industrial applications and for apparel where the lustre may be modified by the addition of titanium dioxide to the polymer before extrusion. However, the cross-sectional shape of the fibres is an important parameter in engineering fibres for particular applications and modern machining techniques such as electron beam milling or electro discharge machining, enable fine spinneret orifices to be shaped to produce non-circular fibres. Fibre shapes do not correspond exactly to the spinneret orifice shapes, however; the



2.5 Nylstar *Meryl*® nylon fibres with (a) round cross-section; (b) trilobal; (c) tetralobal; and (d) hollow cross-section (by courtesy of Nylstar; *Meryl* is a registered trade mark of Nylstar).

polymer emerges from the spinneret as a liquid and the effect of surface tension is to attempt to return the molten stream of polymer to a circular shape. Solidification takes place before this is completed and fibres with modified cross-sections are wound up. In extruding different fibre cross-sections, it is essential that the spinneret orifices be made to close tolerances and that changes in the polymer melt viscosity, extrusion temperature and quenching conditions be controlled to give the required fibre shape with adequate yarn quality.

The first non-circular fibres were trilobal and were extruded through Y-shaped spinneret holes. A number of multilobal shapes are now available. The cross-sections are used to enhance bulk and for bright lustre, in bulked continuous



2.6 Nylstar *Meryl*® *Nexten* hollow fibres in a woven fabric (by courtesy of Nylstar; *Meryl* is a registered trade mark of Nylstar).

filament (BCF) and spun staple yarns for carpets and upholstery.[43] They also have the effect of hiding soiling as compared with conventional round fibres. The lustre can vary from a bright sheen to a glitter depending on how the fibre is designed to converge and transmit internally reflected light. In apparel, multilobal shapes improve moisture transport by wicking water away from the skin by capillary action. Flat ribbon-like cross-sections provide better cover in apparel applications. Figure 2.5 shows circular, tri- and quadri-lobal fibres as well as hollow fibres.[44]

Hollow fibres provide greater bulk and as a result air entrapment and heat retention properties in fabrics are improved. Most hollow fibres are extruded from polyester; however, some, including Kanebo® *Lightron*[45] and Nylstar *Meryl*® *Nexten*, are nylon. The spinneret holes are C-shaped; the ends of the C are sufficiently close for the polymer streams to coalesce after extrusion to close the fibre cross-section. The lower density of nylon as compared with polyester is an advantage here and the void in the centre of the fibre reduces the average density of the fibre giving greater bulk for a particular fabric area density and hence improved thermal insulation properties. Figure 2.6 shows hollow Nylstar *Meryl*® *Nexten* fibres woven into a fabric.[46]

For their *Antron*® commercial carpet fibre, DuPont (US) use a square cross-section fibre with four internal holes. The spinneret orifice shape is of two ‘I’ shapes superimposed at right angles and with extended bars at the top and bottom.

2.7 DuPont *Antron*® carpet fibres in transverse cross-section (by courtesy of DuPont Commercial Flooring).

The ends of the bars are close enough together for the emerging polymer streams to coalesce leaving four voids within the fibres. The cross-sectional form of a DuPont *Antron*® carpet fibre is shown in Fig. 2.7.[47] The smooth fibre exterior surface has no crevices to trap soil and the holes are claimed to refract and diffuse light to hide any soiling. The fibre, which is extruded from nylon 6,6, is said to have superior resilience properties, which may be enhanced by the voids in the cross-section and the greater bulk arising from it.

2.4.2 Fibre drawing

Following the extrusion process the polymer is in a fibrous form, but lacks adequate tensile properties. The extension at break is very high and most importantly the initial modulus is low; in use the product would have poor dimensional stability and would stretch by a factor of up to six times. Extrusion at around 1 000 m min^{-1} does not greatly orientate the polymer molecules in the direction of the fibre axis and the crystallinity of the fibres is also low. The objective of the drawing process is to yield a yarn with acceptable fibre properties. The yarn is wound off the package from extrusion and passes around a set of feed rollers. It then progresses to the draw rollers, which run faster than the feed rollers. For apparel and carpet end-uses the nylon yarns are drawn cold, while for high-tenacity industrial applications the yarns are heated before drawing. After drawing, the yarn is again wound on to a package: this may be with twist using a ring and traveller, or without twist onto a cheese. If the yarn is wound without twist, it must be coherent during subsequent processes. This is most frequently achieved by interlacing the individual filaments of the yarn by passing it through an air or steam jet shortly before wind-up. A diagrammatic representation of the drawing process is shown in Fig. 2.4.

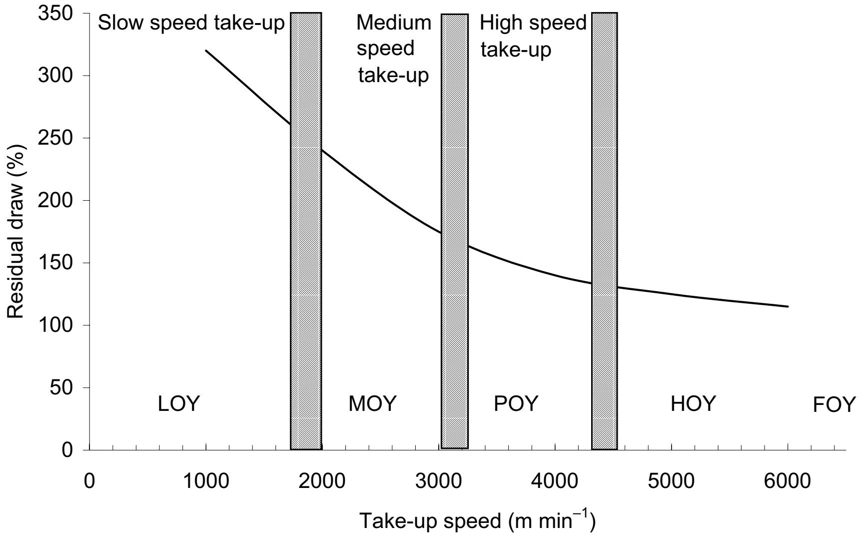
The machine draw ratio, which is defined as in eq. 2.23, is chosen to give a final product with a reasonable extension at break (30 % or less) and initial modulus. The yarn collected after the extrusion stage is of a higher linear density to allow for the attenuation that occurs during drawing. If the final product is to have a linear density of 100 tex after being drawn at a ratio of 4 : 1, then the extruded yarn will have a linear density of 400 tex. Thus at a wind-up speed of 1000 m min^{-1} the metering pump will need to deliver 400 g min^{-1} of nylon polymer to the spinneret.

$$\text{Draw ratio} = \frac{\text{Surface speed of the draw rollers}}{\text{Surface speed of the feed rollers}} \qquad [2.23]$$

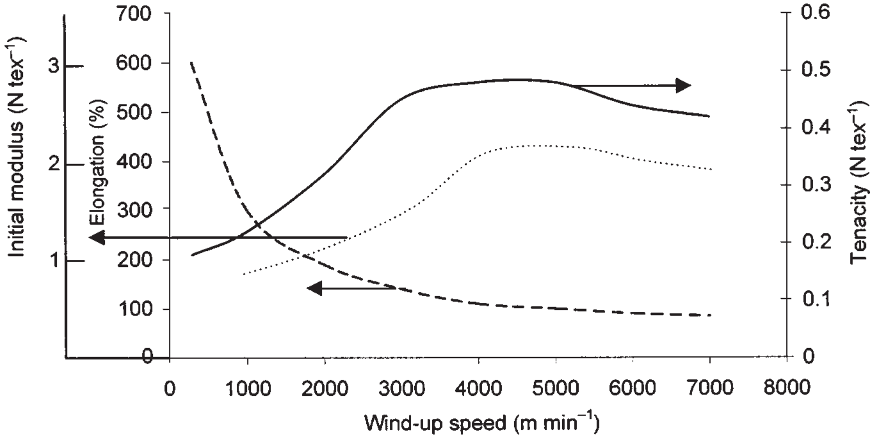
Drawing is normally carried out as a separate process to extrusion. Yarn quality is highest if the extrusion machinery runs continuously, whereas drawing can be interrupted to change packages when necessary. A combined extrusion–drawing process would, if the yarn were collected after extrusion at 1000 m min^{-1}, involve winding after drawing at more than 4000 m min^{-1}. Although equipment to wind at these speeds is now available, most producers find it more convenient to separate the processes. Frequently it is necessary to insert twist into the drawn yarn and this is done using a standard ring and traveller mechanism. This type of twist insertion cannot be operated at high speeds.

2.4.3 Developments in fibre extrusion and drawing

Fibre producers have made a continual effort to reduce manufacturing costs, increase the production rate and improve quality. This has led to an increased understanding of the effects of the extrusion and drawing process on the structure of nylon fibres and yarns. Most of the effort has centred on the use of increased wind-up rates at the extrusion stage. It might be expected that if the wind-up speed of the newly extruded nylon yarn was increased from 1000 to 3000 m min^{-1}, the mass of polymer pumped through the spinneret to give yarn of a constant linear density would increase by a factor of 3. However, this is not the case; the polymer throughput is calculated allowing for the attenuation during drawing. At high wind-up speeds, the aerodynamic drag on the filaments after extrusion and the effect of the shear as the newly formed fibres are drawn down becomes significant



2.8 Dependence of the residual draw ratio of nylon on the take-up speed.



2.9 Effect of take-up speed on the tenacity (——), extension at break (– – –) and initial modulus (······) of nylon 6 fibres.

and the result is a high degree of orientation in the fibre molecules, prior to solidification and crystallisation.[48] The more orientation is put into the fibre during extrusion, the less drawing is possible. The polymer molecules become oriented along the fibre axis and hence crystallise rapidly and substantially. As a consequence, the orientation in the non-crystalline regions of the fibre is low.

If the extruded yarn is wound up at less than 1800 m min^{-1}, then it will have a high residual draw factor, low crystallinity and a limited shelf-life as the crystallinity of the yarn develops slowly at room temperatures and makes the eventual drawing of the yarn more difficult. These yarns are termed low-oriented yarns (LOY) and are normally processed through a draw-twisting process. Medium-oriented yarns (MOY) produced at 1800–2500 m min^{-1} are slightly more crystalline but still have a limited shelf-life. Partially oriented yarns (POY) are wound up after extrusion at 3000–4000 m min^{-1}. They require some residual drawing and still have a low crystallinity. Highly oriented yarns (HOY), wound up at 4000–6000 m min^{-1}, are not fully drawn and have an elongation of 50–60 %. At wind-up speeds of 6000 m min^{-1} and above, nylon yarns are fully oriented (FOY) and have an elongation of 20–30 %. The effect of wind-up speed on the residual drawing ability of the extruded yarn is illustrated in Fig. 2.8[49] and on the tensile properties in Fig. 2.9.[50]

The benefits of the higher extrusion speeds for nylon production were first appreciated in the 1970s when increased false twist texturing speeds became available. Before that time many apparel yarns required three separate processes: extrusion, drawing and texturing. The use of POY enabled the residual drawing to be combined with texturing as draw texturing. Consequently, the three separate processes were reduced to two, with considerable economies in production costs. The objectives and methods of texturing will be dealt with in Section 2.4.5.

2.4.4 Staple fibre

The production of staple fibre consists of extrusion, drawing, crimping, cutting and baling. As the fibre is going to be cut into short lengths and baled, there is no need to keep the output from each spinneret separate and it is common practice to combine the yarns from a number of extrusion heads. Spinnerets having a large number of holes are also used; the only limitation is the need for each filament to cool and solidify before passing over the take-up rollers. It is often the practice to crimp the combined tows and allow them to fall into a can prior to drawing. In this case, the crimp has the function of holding the tow together and ensuring that it can easily be wound out of the can again for drawing, cutting and baling.

The length of the staple will depend on the application of the fibre. If it is to be processed into yarn on the cotton system then the tow is cut to fibres of 40 mm or less. Staple for carpets or knitwear, where nylon is commonly blended with wool, is cut to staple in the range 60–150 mm. The Lummus radial blade cutter winds the tow onto a drum with outward facing blades. The spacing of the blades corresponds to the staple length required. As the tow builds up on the drum, it is forced onto the blades by the tension and cut. The staple fibre is withdrawn by suction from the centre of the drum and blown to the baler. This type of cutter can deal with tow of up to 550 000 tex at 450 m min^{-1}.[51] The radial blade cutters manufactured in the USA by DM&E operate on a similar principle but use a presser wheel to force the tow on to the blades.[52]

2.4.5 Texturing

Texturing is the conversion of flat (straight) to crimped fibres. The objective is to simulate the properties of natural staple yarns of increased bulk with the benefits of thermal insulation, cover, softness and fullness, and moisture transport. Stretch properties can be imparted to nylon yarns; using the textured nylon in combination with elastane yarns can enhance these. A number of stages can be identified in any texturing process. The yarn is heated and the filaments are deformed longitudinally by twisting or passing through a turbulent air or fluid jet to insert the crimp; this may also deform the cross-sectional shape of the fibres; the yarn is then cooled to set the crimp. A further on-line process may then heat set the yarn. There are a number of processes that are used to insert the crimp in the yarn; the actual process used depends on the linear density of the yarn as well as the requirements of the final product. If the yarn is below 22 tex, then false twist texturing is used. Yarns at the lower end of this range, 3.3 tex and below, are used for hosiery, 4–22 tex for apparel. Coarser yarns in the range 50–400 tex, which are used mainly for carpets as well as for upholstery and the robust fabrics used in soft sided luggage, are mostly textured by entanglement.

In false twist texturing, the feed yarn is heated close to its melting point – typical temperatures are 220 and 185 ºC for nylon 6,6 and nylon 6 respectively – and twisted. The yarn is cooled and then untwisted. Originally the twist was inserted by looping it around a pin at the centre of a small tube. The tube was rotated and each rotation inserted one twist in the yarn. This was termed the pin twist process. The twist required to be inserted was high at approximately 3200 turns m^{-1} for 7.8 tex yarn. In later developments of the pin-twist process the tubes were rotating at 800 000 rev min^{-1}, but still only had a throughput of less than 300 m min^{-1} of yarn. To improve the productivity of the process, faster twist insertion was needed.

This faster twist insertion came with friction twisting. The twist is inserted by running the yarn over the edge of rotating discs; often a stack of nine discs rotating on three centres in an equilateral triangle. The yarn runs through the centre of the triangle and over the edge of each disc. Each disc has a ceramic or polyurethane surface to minimise yarn slippage; polyurethane discs impart a soft handle and give high-bulk yarn, but have a short life in use. Ceramic discs are more often used for nylon yarns. Another benefit of the stack of discs is that it will positively advance the thread, allowing drawing to be combined with texturing. If the yarn had to be pulled through the triple stack of discs then the tension would be unacceptably high. The forwarding action of the triple stack of discs on three centres enables drawing to be combined with twist insertion and removal and the process is termed ‘simultaneous draw texturing’. The combined draw and false twist does have an effect on the cross-section of the filaments. It changes from a circular to an almost triangular cross-section. This is likely to be due to the high temperature breakdown of the intermolecular bonds allowing the compression forces during twisting and drawing to distort the fibre cross-section. In practical terms, the yarn can have a glittery appearance, which may not always be desirable. False twist gives good bulk but the product is used mainly for its stretch properties.[53]

A number of processes are used for texturing the coarser yarns. Wilson and Kollu have reviewed the production of textured yarns by other than the false twist process.[54] In air jet texturing, the yarn passes into a Venturi tube where turbulence from an air jet causes the filaments to entangle and form surface loops. The air jets can be axial, e.g. above and below the thread line or radial. Radial jets are preferred for finer yarns; the weft yarns for stretch skiwear, which are around 190 dtex, are textured at above 300 m min^{-1}. The product has good bulk but no stretch. Air jet texturing is used for at least one of the *Tactel*® range of nylon 6,6 continuous filament yarns.[55]

BCF yarns for carpets are textured with an air or fluid jet. After drawing, the yarns are heated by passing them over rollers in a hot chest and then through a hot air or steam jet under controlled conditions. The texturing may be achieved by forcing the yarn at speed onto a baffle plate, screen or the walls of a specially designed chamber. BCF yarns have a random three-dimensional crimp form, which gives bulk but only moderate stretch. Texturing for these yarns is frequently integrated with drawing. Colour effects can be achieved by feeding differently pigmented (solution dyed) yarns simultaneously to the texturing head so that the filaments intermingle.

Edge crimping involves drawing the yarn over a knife-edge after heating. The side closest to the edge is compressed and the other side stretched. When the stresses are relaxed, then the yarn crimps and coils, giving a stretch yarn. In gear crimping the yarn is again heated and passed between the teeth of intermeshing gear wheels. The shape of the crimp is determined by the profile of the gear teeth. For nylon staple fibre, stuffer box crimping is used. The tow of fibre is fed into the constricted stuffer box by the feed rollers. The tow is also heated either by rollers or by injecting steam into the box. At the far end of the box is a hinged and weighted gate. When the pressure of the fibre forced into the box is greater than the pressure on the gate, the gate rises to allow the tow to escape. As it does so, a crimp is imparted to the fibre.

2.5 Fibre properties

The inherent properties of nylon and those characteristics that can be engineered into the fibre and ultimately into the final textile product determine the many end-uses of nylon. No fibre can be perfect for every use, but it must offer a reasonable balance of performance, market value, economics and processability. The properties of a textile fibre may be considered under three different categories: geometric, physical and chemical. These characteristics are measurable and quantifiable.

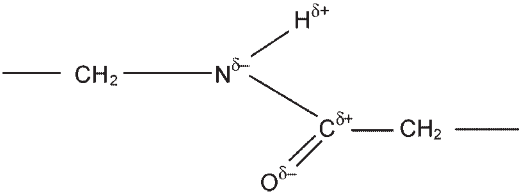
Other textile characteristics such as feel, appearance and comfort are less measurable, and come not only from the fibre properties but also from the yarn and fabric construction and from the finishing processes. They are no less important in determining the marketability of the final product.

2.5.1 Fibre structure

All nylon fibres consist of linear polymers with molecules that are oriented along the fibre axis to a greater or lesser extent. The properties of the fibre are determined by the molecular structure and the molecular organisation. The fibre structure may be viewed at three different levels. The chemical structure is determined by the polymer extruded to form the fibre and it influences characteristics such as the chemical reactivity, the moisture absorption, dyeability and swelling properties. The fine structure of a fibre is concerned with the way in which the polymer molecules are arranged within the fibre and determines the physical properties and some of the chemical characteristics. The gross morphology of a fibre is concerned with its appearance under a normal optical microscope: thus only features on the fibre surface and larger than approximately 0.3 μm are considered in the gross morphology. The appearance under an optical microscope of the majority of nylon fibres is rather featureless. If the fibre is extruded through circular spinneret holes then the fibre will be cylindrical in longitudinal view. Often small black dots are visible in the fibre. These are titanium dioxide added to reduce the natural lustre and transparency of the fibre; the application of this additive is discussed in Section 2.6.1. Ridges in the fibre surface identify non-circular cross-sections; the production of these fibres is described in Section 2.4.1. Internal voids can be seen as black lines along the fibre length. The shape of the cross-section in the transverse microscopic view demonstrates these features more clearly. The type of texturing employed also influences the cross-sectional shape.

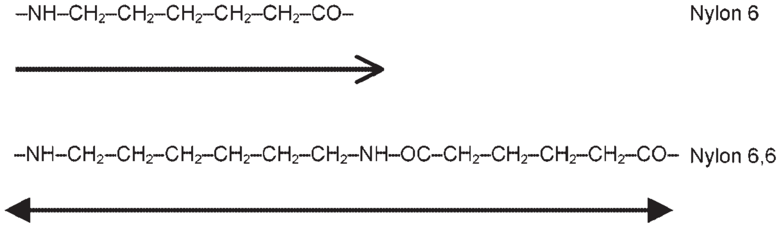
Most fibres consist of semicrystalline solids. In synthetic fibres the development of the crystal structures is restricted by the rapid changes in temperature that take place during extrusion and processing. The fibre is formed by the extrusion of the molten polymer. Once the fibre is cooled below its melting point then crystallisation can start, but with rapid cooling the growth of the crystals is inhibited. Some skin–core differentiation may occur due to the more rapid cooling at the surface of the fibre. Later processes, which involve heating the fibre and also drawing, will allow some further rearrangement of the molecules and increased crystallinity. Information about the structures can only be obtained by indirect methods, mainly by X-ray diffraction on the fibres, but other techniques such as infrared spectroscopy and differential thermal analysis can also supply information about the structure.

The character of the fibre-forming polymer has an important role to play in the development of crystallinity in the fibre. Although all fibres are made up of polymers, not all polymers are fibre-forming. There are certain requirements if a polymer is to be fibre-forming. The polymer must be linear and regular with no bulky side groups on the polymer chain. Nylon 6 and 6,6 both have regular repeat units joined end to end and consequently meet this criterion. There must be intermolecular attractions between the polymer molecules and ideally there should be some inflexibility in the molecular chain. Both these requirements arise from the need for the polymer to partially crystallise in the fibre. In nylon, the amide groups in adjacent polymer chains are able to form hydrogen bonds with each other, which allows the molecules to cohere. In addition, the amide groups also provide inflexibility in the structure. This arises from the polarity of the carbon–oxygen and the nitrogen–hydrogen bonds in the groups.

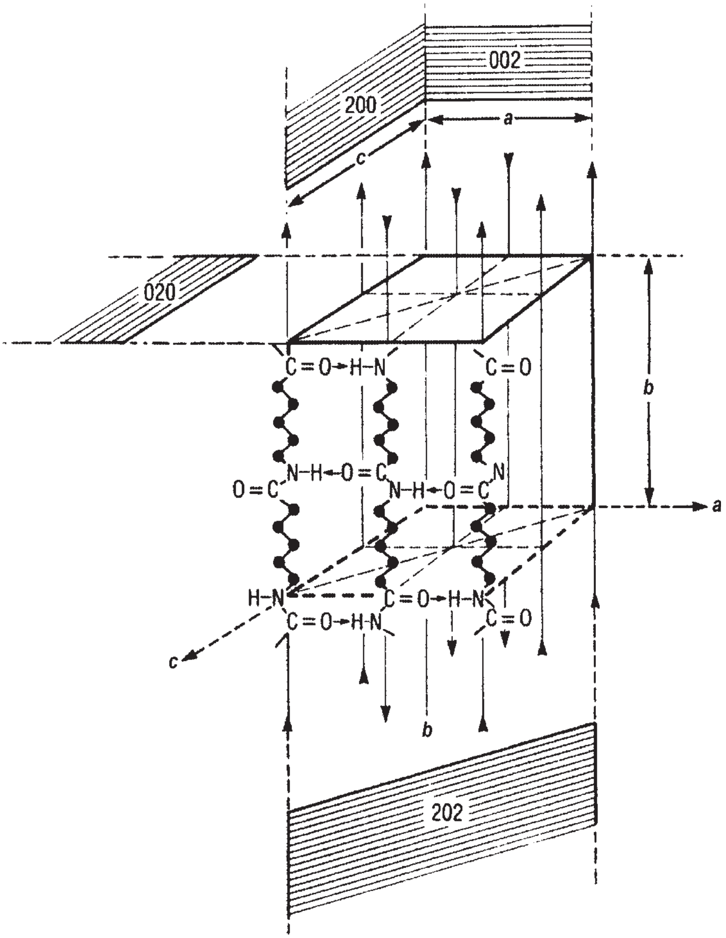


The polarity enables the carbonyl oxygen from an amide group in one molecule to attract and hydrogen bond with an amide hydrogen in another molecule. It also leads to an appreciable double bond character in the carbon–nitrogen bond and inflexibility in the group. Puffr explained this effect in terms of the *sp*^{2} hybridisation of the carbonyl oxygen atoms.[56] In all nylons the –CH_2– sequences will be flexible at room temperature with only weak van der Waals attractions for their neighbours.

There are some regions of the fibre where the molecules are packed regularly together and others where the packing is more random. Nylon 6 and 6,6 contain the same groups in the same proportions along the chain. In nylon 6 the molecules are directional with all of the amide links in a particular direction, e.g. –NH–CO–, while in nylon 6,6 there is a reversal in the order of alternate amide linkages.

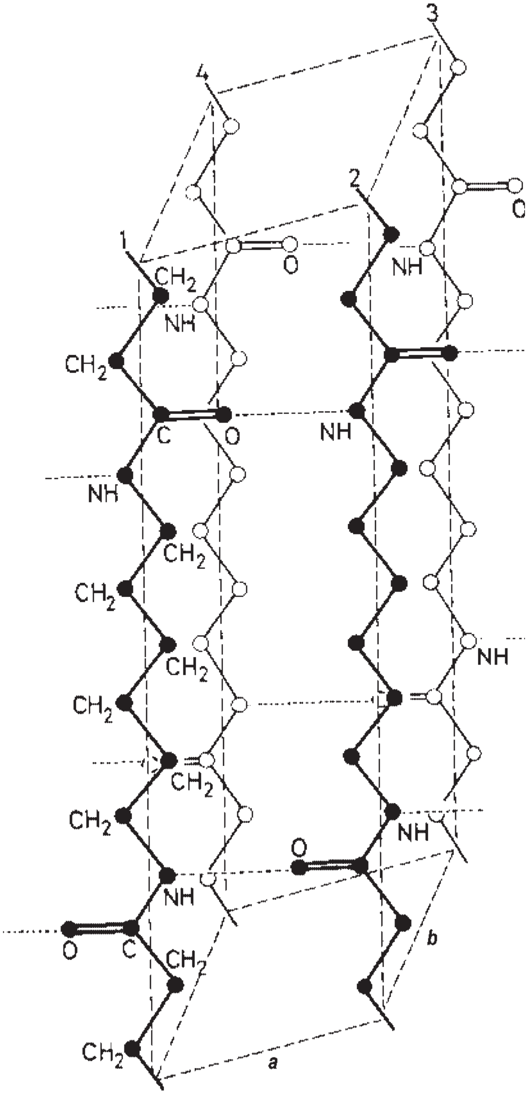


The repeat unit in nylon 6 is only half the length of that in nylon 6,6. The repeat unit in nylon 6,6 has 38 atoms overall and 14 linked in the chain with a length of 1.7nm. Hearle and Morton[57] suggested that this means that a mismatch in crystal packing can result in a significant region of disorder; however, Reimschuessel[58] has postulated that the lack of directionality may allow any disorder to correct itself more readily.



2.10 Unit cell of the α-form of nylon 6.

The hydrogen bonding between the >C=O in one chain and the >N−H in an adjacent chain leads to nylon polymers crystallising with the lattices shown in Figures 2.10[59] and 2.11[60]. In nylon 6 and 6,6 the structure is composed of stacks of sheets of planar hydrogen bonded extended chain segments. In nylon 6,6 there is parallel alignment of the adjacent molecules. They are spaced with a perpendicular chain-to-chain distance of 0.42 nm and adjacent molecules are displaced in the chain direction by a distance corresponding to one chain atom. The stacking gives a sheet-to-sheet distance of 0.36 nm with a displacement of the successive sheets of 0.5 nm in the chain direction. This leads to the feature in nylon 6,6 that the cross-face of the unit cell marked as 1234 in Fig. 2.11 makes an angle of 48 ° with the molecular axis. The overall structure for nylon 6,6 is triclinic. Nylon 4,6 is similar to nylon 6,6 in that the chains are not directional. However, the concentration of



2.11 Unit cell of nylon 6,6.

amide linkages in the molecular chain is greater, and the distance between the amide linkages in nylon 4,6 is the same in the diamine and the diacid unit. This greater chain regularity is the reason for a higher melting point and crystallinity compared with other nylons.

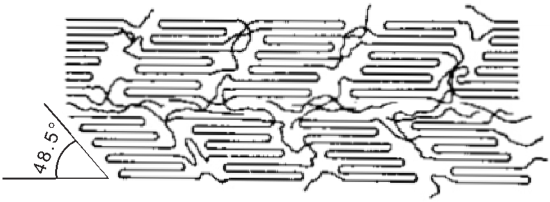
The crystal structure is monoclinic for nylon 6 with the molecules also in an extended configuration. The hydrogen bonds in nylon 6 connect the molecules in antiparallel chains. The opposite directionality of the successive amide groups allows formation of unstrained hydrogen bonds. The unit cell as shown in Fig. 2.10

contains two chemical repeat units in the chain direction and four extended chain segments; it contains therefore eight chemical repeat units. The distance between the planar sheets of hydrogen bonded molecules is 0.37 nm, similar to that in nylon 6,6.

The crystal structures shown in Figures 2.10 and 2.11 are the α-forms, which are favoured on thermodynamic grounds. Heuvel and Huisman suggested that the stresses on the fibre during high-speed winding of nylon 6 at above 3000 m min^{-1}, lead to an alternative γ-crystalline form. The crystallisation is induced by the orientation and the kinetics appear to favour this form. This has a similar arrangement of molecules to the α-form, but the hydrogen bonds connect parallel molecules. To form the bonds the chains need to twist slightly about the amide unit and as a result the height of the unit cell is slightly less. Fibres produced at low speeds were found to contain equal amounts of the α- and γ- forms, while the γ-form predominates at take up speeds above 3000 m min^{-1}. Annealing of nylon 6 fibres at 100 °C in the presence of moisture or at 150 °C dry, results in moderate increases in both forms with the α-form slightly favoured. At higher temperatures conversion of the γ-form to the α-form occurs. Drawing also influences the amount of each structure present. At low temperatures there is still a mixture of both forms after drawing. If the yarn is heated during drawing then the proportion of the γ-form is sharply reduced.[61]

Nylon fibres are often considered to be approximately 50 % crystalline. Different values can be obtained from such techniques as infrared spectroscopy, wide angle X-ray diffraction and iodine absorption, although the above estimate is generally accepted. The use of the term crystalline implies that there are discrete crystalline and amorphous regions and that the fibres exist with a two-phase structure with definite boundaries between the phases. The terms crystalline and amorphous are convenient when considering fibre structure, but it seems unlikely that the morphological structure of nylons consist entirely of a simple two-phase model in which perfectly ordered crystallites exist in equilibrium with totally amorphous regions. This is really one of two limiting cases. The other is that the fibres consist of a paracrystalline form in which all deviations from the ideal crystal structure are attributed to defects and distortions of the lattice. This suggests that all regions of the fibres are in an intermediate state of order. This led Hearle and Greer to propose the modified fringed fibril structure with molecular folding for the fibre shown in Fig. 2.12. In this, the molecules fold back on themselves; the areas between the folded regions are amorphous with comparatively few tie molecules linking the folded structures.[62]

Many observations of possible structures in fibres arise from work on the thin layers of polymers solidifying from the molten phase. Microscopic observations of nylon polymers using polarised light show the formation of lamellae with a thickness of 6–10 nm. The macromolecules are at right angles to the lamellae and are folded backwards and forwards on themselves. A single molecule may take part in several lamellae. When nylon is allowed to crystallise from the melt the



2.12 Modified fringed fibril structure with molecular folding for nylon.

lamellae can be incorporated into spherical aggregates called spherulites. These can be recognised in the polarising light microscope as circular birefringent (see Section 2.5.5) areas, giving a Maltese cross pattern. When spherulites are formed in nylon 6, the spherulite radius is parallel to the major crystal axis and they are positively birefringent. The growth of a spherulite in a nylon polymer can be initiated either spontaneously or by the presence of a foreign particle. Reimschuessel has suggested that as a sample cools from the melt the rate of spherulite growth increases to a maximum at 140–150 ºC and then decreases on further cooling as molecular mobility decreases.[63]

When nylon fibres are drawn, the polymer molecules and the crystalline aggregates will be oriented in the direction of draw. If the specimen is already crystalline then drawing will not alter the degree of crystallinity greatly. In amorphous or partly crystalline material, however, the crystallinity is likely to develop further. The extent of orientation will depend on the rate of drawing and the temperature. During drawing the spherulites are likely to be highly distorted. Reimschuessel and Prevorsek have suggested that while the information on the morphological structure of drawn fibres is inconclusive, it can be explained using a two-phase model involving oriented amorphous and crystalline regions, the latter having both folded structures and fibrillar aggregates. The aggregates have extended tie molecules that result from chain unfolding during the drawing process and that connect crystalline blocks.[64] The number of tie molecules affects the modulus and the tenacity of the nylon fibres.

2.5.2 Tensile properties

The tensile properties of nylon and other fibres are the most studied and also the most important characteristics of textile fibres. They depend on the polymer relative molecular mass, the extrusion speed, the draw ratio and the thermal history of the fibre. The tensile properties indicate the responses of the fibre to forces and deformations. They are vital in determining the suitability of a fibre for a particular application, and in comparing it with other fibre types.

It must not be thought that the properties of a textile structure depend only on the fibre; they also depend on the way in which the fibres are assembled into a yarn or fabric. Thus an understanding of the fibre properties is useful in appreciating the characteristics of a yarn or fabric, but in itself it is not sufficient. Some properties may be modified by the presence of other fibres or depend on the particular structure. The fibre properties do, however, give a limit to what is possible in a yarn or fabric; the strength of a yarn cannot be greater than that of the component fibres.

The mechanical properties of a nylon fibre cover a large number of attributes, all of which combine to determine the characteristics of the fibre. The most quoted attributes are the breaking stress and strain. Although these are important, in practice they do not give a realistic assessment of the performance of the textile material in use. Normally textiles are not stressed to the breaking point in use. The response of the fibre to low levels of stress or to repeated stress or to prolonged stress can also be important. In choosing a fibre for a particular application, the fibre whose attributes best fit the needs of the application needs to be determined. The effect on the fibre of small amounts of stress or strain and the extent to which any elongation is recovered are often of more interest than the breaking stress and strain.

When a load is applied to a nylon fibre it will become elongated. The extent of the elongation will depend on the linear density of the fibre or yarn. A coarse fibre will be more resistant to elongation than a fine one. To standardise, the tensile stress on the fibre is expressed in terms of a 1 tex fibre as the load per unit linear density, with units of N tex^{-1}. The tensile strain is the elongation as a proportion of the original length of the fibre. As the fibre initially comes under load, then there will be a region of the stress–strain curve where the tensile strain is proportional to the tensile stress. The slope of the graph in this region is the initial modulus of the fibre. This is the figure that indicates the response of the fibre to small stresses. It is important in that, as will be described later, it is related to the handle of a yarn and can, in addition, indicate which fibres are suitable for blending. The yield point marks the end of the region of the stress–strain curve where the stress and strain are proportional. If the fibre is stressed beyond this point, then a permanent elongation will occur.[65]

The work of rupture is the energy needed to break a fibre or yarn. Normally this is standardised as the specific work of rupture; the energy needed to break a 1 m length of a 1 tex fibre. It may be measured as the area under the stress-strain curve. The units are N tex^{-1}. The work of rupture gives an indication of the probable abrasion resistance of a fabric in that fibres with a relatively high work of rupture are likely to have the best resistance to wear. It is also important in applications such as climbing ropes and car seat belts. Nylon is used in both of these applications. The work of rupture of the rope or belt must be greater than the kinetic energy of a falling climber or the car driver. The elongation at break of the fibres or yarns has to be considered here. A high elongation will allow the car driver to impact with the car steering wheel; a low elongation will subject the driver or the climber to a very drastic deceleration. Not all of the elongation is due to the fibre; the construction of the rope or belt has a part to play.

The major tensile properties of nylon 6,6 and nylon 6 are summarised in Table 2.1. The corresponding figures for polyester are included for comparison as the

Table 2.1 Tensile properties of nylon fibres

	Nylon 6,6	Nylon 6	Polyester
Tenacity (N tex^{-1})			
Normal	0.4–0.6	0.4–0.6	0.4–0.6
High tenacity	0.6–0.9	0.6–0.9	0.8–1.0
Breaking extension (%)			
Normal	20–30	20–40	10–20
High tenacity	15–20	15–20	5–10
Initial modulus (N tex^{-1})			
Normal	2.0–3.5	1.5–3.5	8–10
High tenacity	4.0–5.0	4.0–5.0	10–13
Work of rupture (mN tex^{-1})			
Normal	60–70	70–80	50–60
High tenacity	50–60	60–70	20–30

fibres are interchangeable in at least some applications. Ranges of values for the properties are given. The exact value for a sample will depend on the degree of polymerisation of the nylon, the extrusion and drawing conditions, and the thermal history of the yarn; a variation is likely among the individual filaments within a yarn. There is, therefore, little benefit to be gained from quoting a set of exact values. The figures show that there are few differences in the tenacities, breaking extensions and moduli of nylon 6,6 and 6. Polyester does have a considerably lower extension at break than the nylons, resulting in a higher initial modulus. This has practical implications for fabric handle. The force needed to bend a fibre is proportional to the initial modulus of the fibre. Consequently, a nylon filament will bend more easily than a polyester one, and all other factors being equal a nylon fabric will have a softer handle than one made from polyester.

The other practical implication of the lower modulus of nylon is in blending fibres into staple yarns. Fibres are more compatible if they have similar responses to low levels of stress, i.e. similar initial moduli. Most varieties of cotton have higher initial moduli but considerably lower tenacity and extension at break than nylon. As a result in a cotton/nylon blended yarn, as it comes under load, the cotton will resist the load while the nylon will extend easily. Eventually the cotton will reach its breaking extension and the nylon will then take the load. Even though nylon is a much higher-tenacity fibre than cotton, the strength of a 50/50 cotton/nylon blended yarn, for example, is likely to be less than that of a 100 % cotton yarn. Polyester has a higher initial modulus than cotton and is more compatible. For this reason cotton/nylon blends are rare while cotton/polyester blends are ubiquitous. Some nylon staple fibre is produced for blending with cotton. It has compatible linear density and length to cotton, and the extrusion and drawing conditions are modified to give it a similar stress at around the breaking strain of cotton.

Table 2.2 Typical values for the yield strain and elastic recovery of various fibres

Material	Yield strain (%)	Elastic recovery % from		
		1 % extension	5 % extension	10 % extension
Nylon	16	90	89	89
Polyester	3	98	65	51
Cotton	1	91	52	
Viscose	2	67	32	23

Wool has a low initial modulus and wool/nylon blends are used in carpets and in socks. In both of these examples the nylon is added to improve the abrasion resistance of a 100 % wool product. It may be argued that if similar initial moduli are a prerequisite for an effective fibre blend then wool/polyester blends should not exist. They are found, however, in suiting and trouser fabrics. It is possible to adjust the production conditions for polyester to give a lower initial modulus and hence make it more compatible with wool in blends.

Two other mechanical properties have to be considered in assessing the suitability of nylon fibres for particular applications. These are elastic recovery and creep. Elasticity is the ability of a material to recover its size and shape after a deformation. If a yarn is stressed to a particular extension, then when the stress is removed only part of the extension will be recovered. The elasticity is expressed by the recovered extension as a proportion of the total extension. Complete recovery will correspond to 100 % elasticity, partial recovery will be a proportionately lower percentage and no recovery at all will be zero. Table 2.2 shows the yield strain and the percentage recovery of nylon and some other fibres from various elongations.[66]

These figures have important practical implications. Nylon is used for stockings and tights because it has a good elastic recovery. These garments are subjected to continual stretching at the knees and ankles as the wearer moves her legs. Without a good elastic recovery they would rapidly become wrinkled; this would be unsightly as well as uncomfortable. Similarly the reinforcement for the rubber in a tyre is subjected to repeated stresses and strains as it rolls along the road. It is important that any elongation is rapidly recovered, otherwise the tyre will quickly become distorted.

Creep is the time-dependent elongation of a material while it is subject to a stress. Some elongation occurs instantly and this is shown on the stress–strain curve. If, however, the load is applied over a long period, then a further elongation occurs. This is termed creep; when the load is removed there is an instant contraction followed by a long, slow recovery. In nylon, at both low and high loads the total recovery will be complete, but at high stresses the instantaneous contraction will be less than the instantaneous extension. A low level of creep is important in textile products as the dimensional stability of a garment or other product depends on it. Achieving a high crystallinity in the nylon yarn by heat setting at constant length reduces creep in use.

Repeated application of a small load will also produce an extension in a yarn. Meredith and Pierce imposed repeated 2 % extension followed by relaxation cycles on samples of various fibres and measured the permanent extension of the fibres after a number of cycles.[67] Nylon was found to have a low level of permanent extension after a number of cycles. This type of test reproduces the condition a yarn is likely to meet in use. Where nylon is used in rubber reinforcement for tyres and belts then it is likely to be subjected to repeat stresses and it is particularly important that the overall distortion of the yarns should be low. However, in applications of this type the nylon yarn is not subjected to repeated stresses alone. The action of stressing the yarns will have the effect of increasing the temperature; this factor will also have a significant effect.

2.5.3 Thermal properties

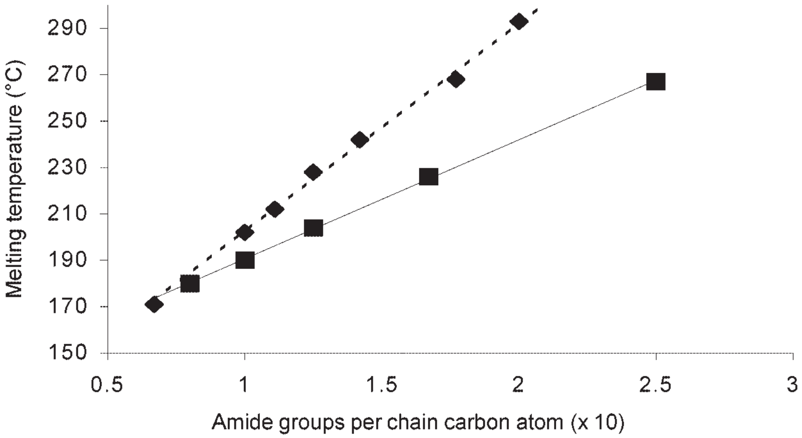
2.5.3.1 Melting temperature

The thermal behaviour of nylon polymer and fibre is of fundamental importance in determining the conditions of manufacture and conversion into fabric, and in use. Frequently the influence of water cannot be isolated from that of heat. The role of water is to act as a powerful plasticiser, increasing the mobility of the molecules in the amorphous regions of the fibre. In processing and use water will always be present and will influence the rate of crystallisation after extrusion, the tensile strength, the modulus of the fibre in use and the coloration behaviour.

The presence of the amide linkages in the molecular chains has a considerable effect on the thermal properties. Without the amide links the polymer would be identical chemically to polythene (poly-ethene). The molecules would have only weak van der Waals intermolecular attractions to each other and the polymer a melting point of 120 °C. This is too low for most textile applications. The presence of the amide groups raises the melting point and the relationship between the number of amide links and the melting point is shown in Fig. 2.13.

It can be seen that as the proportion of amide linkages increases and the numbers of carbon atoms between each amide group reduces, the melting point increases for both the AABB and the AB polymers. In the AABB series the polymers with odd numbers of carbon atoms in the repeat units tend to be less crystalline and have lower melting points. The even–even polymers, as shown in Fig. 2.13, allow greater interaction between the amide groups giving a crystalline structure and consequently have higher melting points. Nylon 4,6 has a melting point of 290 °C and this is close to the maximum melting point for which conventional melt extrusion can be used. In the nylon AB series the polymers with odd numbers of carbon atoms in the repeat units have higher melting points than those with even numbers. Of these, only nylon 11 has been produced on a large scale as a fibre. Table 2.3 summarises the thermal properties of nylon 6 and 6,6.[68]

As may be expected from the thermal properties listed above, temperature has

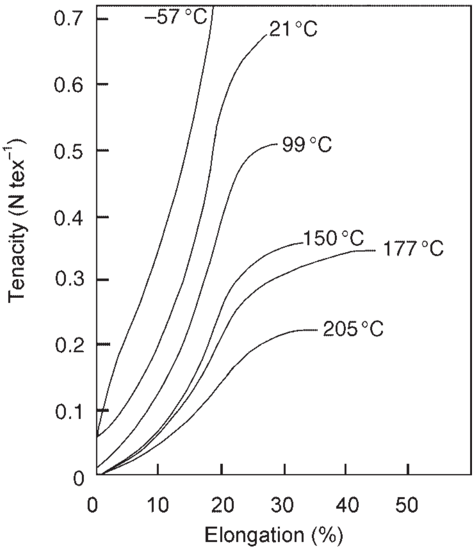


2.13 Effect of the frequency of amide groups on the melting point of AB nylons (——) and AABB nylons (– – –).

Table 2.3 Thermal properties of nylon 6 and 6,6 at zero relative humidity

	Temperature, °C	
Property	Nylon 6	Nylon 6,6
Melting point	215–220	255–260
Zero strength	220	240
Maximum setting temperature	190	225
Softening point	170	235
Starts to become plastic	160	210
Maximum ironing temperature	150	180
Optimum setting temp. (steam)	128	130
Glass transition temp. (T_g) (at low frequency of measurement)	40–50	40–50

a profound effect on the tensile properties of nylon 6 and 6,6 yarns. Stress–strain curves at various temperatures for nylon 6,6 are shown in Fig. 2.14.[69] It can be seen that as the temperature is increased, the tenacity of the nylon 6,6 yarn is reduced and the extension at break is increased. The initial modulus is also decreased. There is a drastic reduction in both tenacity and extension at break at 205 °C compared with the test at 177 °C; the higher temperature is close to that at which softening occurs in nylon 6,6. There are thermal properties of nylon that occur below the melting points, but that underlie the alterations in the tensile properties as the temperature is raised. These properties are due to the increasing mobility of the molecular chains in both the crystalline and amorphous regions of the fibre between 70 and 180 °C. If a nylon 6,6 fibre is heated in a dry, relaxed state from 25 to 70 °C, it begins to shrink. At around 70 °C some further crystallisation occurs



2.14 Effect of temperature on the tensile properties of nylon 6,6.

which reduces the chain mobility. As the heating is continued, any absorbed water is lost and the shrinkage continues. Above 125 °C the crystal structure changes from a triclinic to a hexagonal form. At 170–180 °C the crystals begin to break up and the molecular chains become increasingly mobile; this accounts for the marked alteration in tensile properties shown in Fig. 2.14 between 177 and 205 °C.[70]

2.5.3.2 *Irreversible shrinkage*

Many fibres show an irreversible contraction on heating. Nylon yarns taken after drawing will, when heated dry to 100 °C, shrink by around 5 %. In nylon, water is able to penetrate the structure and has the effect of increasing the mobility of the molecules. As a result the shrinkage of wet yarns is considerably greater; in boiling water the shrinkage is around 10 %. The temperature needs to be about 70 °C higher in a dry atmoshere than in steam to produce the same effect.[71]

There are a number of mechanisms giving rise to this shrinkage. When the fibre is drawn, some of the polymer is left as oriented but non-crystalline. On heating, this can revert to a less oriented state. As the crystalline regions are heated they are annealed and become shorter. Some of the polymer molecules may fold to crystallise better and other molecules move relative to each other to crystallise better. In addition some small crystallites melt, allowing the molecules to shrink to a random coil. Recrystallisation elsewhere in the fibre then stabilises the shortened form.[72]

Previous thermal treatments do have a significant effect on this shrinkage however. If nylon 6,6 yarn is heated to 200 °C under zero tension, then no shrinkage is subsequently found when it is boiled in water. Some shrinkage, although reduced, will be found if the heating is carried out under tension. The greater the applied tension at high temperature, the larger the shrinkage during a subsequent treatment in boiling water.

Heat setting is carried out on synthetic fibres at various stages of processing. For nylon, it may immediately follow texturing or it may be used on finished fabrics. As described above, when nylon yarns are heated the mobility of the molecules increases and the fibre structure is able to rearrange. When the filaments are allowed to cool in the new state, it will become set. A permanent set will be achieved when fibres are heated to 180–200 °C for nylon 6,6 and 160–180 °C for nylon 6. The annealing process enables the polymer to form larger crystals, which stabilise it in the deformed fibrous state. Lower temperatures can be used in the presence of steam. Once a set has been imparted to a yarn, it can be overridden in nylon only by more severe treatments at higher temperatures or stresses that further disturb the structure.[73]

2.5.3.3 Glass transition temperature

The glass transition temperature, T_g, is even more important than the melting point in influencing the processing conditions of a fibre. The melting temperature of fibres is well defined and the variation in published values is small. The T_g is the temperature above which there is a degree of mobility in the chain segments in the amorphous regions of the fibre, and it is a function of the chemical structure of the polymer. However, the glass transition temperature is affected considerably by such factors as the water content of the fibre and the methods used to measure it. T_g can be assessed by volume effects using dilatometry or by thermal capacity effects using differential scanning calorimetry (DSC). Both of these give a value for the T_g of nylon 6,6 and 6 in the range 40–55 °C if the fibre has zero water content. An alternative method using pulsed nuclear magnetic resonance gives a higher value in the range 90–100 °C. High-frequency methods give a higher value, as more energy is required in the form of heat to give mobility to a sufficient number of molecular segments. Within this chapter, the term T_g refers to the values measured by low-frequency methods.[74]

Polymers such as nylon with complex repeat units can have two or more glass transitions. In polyamides, mobility occurs in the methylene groups in the repeat unit at temperatures between –50 and –100 °C; these contribute to only weak intermolecular attractions, which are easily broken down as the temperature is raised. This glass transition is of little practical importance since it is well below the temperature at which the fibre is used in most applications.

The more important glass transition for nylon is due to the onset of dissociation of the hydrogen bonds between the amide linkages in the non-crystalline regions. Evidence for the role of the amide linkages in determining the T_g is provided by two observations: (1) the T_g of nylon polymers decreases as the number of amide groups in the repeat unit increases and (2) the T_g also decreases as the water content of the fibres increases; this has been explained by the replacement of the interchain hydrogen bonds by water. Below the T_g, hydrogen bonds hold the amorphous regions together as a three-dimensional cross-linked network. Above the T_g there is a network of molecules with hydrogen bonds continually breaking and forming, in a state of dynamic equilibrium. The transition due to the breaking of the amide hydrogen bonds is very broad because the bonds can break with a considerable degree of independence, since, in the amorphous regions of the fibres, the polymer molecules are largely randomly arranged. As a result, not all of the hydrogen bonds are of the optimum length and their strength varies; different quantities of thermal energy are required to break them.[75] Hearle has linked the T_g to the considerable primary creep in the fibre. If yarns are held under load, the amide hydrogen bonds break intermittently owing to the thermal vibrations in the molecules, and extension is able to occur.[76]

The importance of the glass transition temperature in fibres is that the polymer must be above its T_g to be drawn, textured or dyed. This is not normally a problem with nylon; the widely accepted value for the T_g of the dry fibre is 40–50 °C and it is reduced by the presence of water. At 85 % relative humidity (r.h.), the T_g is reduced to room temperature and is as low as –8 °C for nylon at 100 % r.h. If nylon is cold drawn at ambient temperature and humidity, then the fibre will be above its T_g. If not, then the heat generated by the work done to draw the fibre raises the temperature sufficiently. Likewise, most coloration processes are carried out in water at well above 50 °C; those processes that are carried out in the absence of water, for example transfer printing, require the application of heat.[77]

When nylon is used to reinforce the rubber in tyres, a problem known as flat spotting can occur. While the vehicle is moving, the tyre warms to above the glass transition temperature; but when the vehicle parks, the tyre cools to below the T_g. The tyre becomes set with the flat spot where it is in contact with the road. As the vehicle starts to move again, uneven running occurs until the temperature of the tyre is once again above the T_g. This difficulty is frequently overcome by using several layers of reinforcement, only some of which are nylon. A matrix/fibril bicomponent fibre with nylon 6 and polyester with reduced flat spotting characteristics was produced at one time by Allied Chemicals (now Honeywell), but was later withdrawn from the market.[78]

2.5.4 Moisture properties

Nylon is often thought to be a hydrophobic fibre. In practice, it is significantly hydrophilic and can absorb some water within the structure. Water is able to penetrate the amorphous regions and hydrogen bond to the amide groups. Water is a good plasticiser for nylon and it increases the mobility of the molecular chains, reducing the tenacity and modulus and the T_g, while increasing the extension at break. The effect of the water is not as great as with cellulosic fibres such as viscose, but it is sufficient for its effects to significantly influence tensile tests. In addition, as the fibres take up water, there is a change in dimensions in both the transverse and axial directions. This may alter the size, shape and stiffness of fabrics.[79]

The take-up of water from the air by a fibre is an equilibrium process. Normally the moisture regain is quoted for air at 21 °C with an r.h. of 65 %. Under these conditions nylon 6,6 or 6 contains 3.5–4.5 % of water by weight as a proportion of the mass of dry fibre. If the air is completely dry then the fibres will lose water to the air. If the air is wetter than 65 % r.h., then nylon fibres absorb water, until at 100 % r.h. they contain approximately 10 % moisture. A nylon producer measures the moisture content of newly produced packages and the invoiced weight is adjusted to allow for an agreed moisture content, normally 3.5–4.5 %. The uptake of water by hydrophilic fibres is accompanied by a reversible change in dimensions. When drawn nylon becomes saturated with water, there is a transverse swelling of around 2 %, with an expansion in the longitudinal direction of 2.5–7 %. For all other hydrophilic fibres the transverse is much greater than the longitudinal swelling; by comparison the figures for viscose are 25–35 % in the transverse and 4–5 % in the axial directions. The unusual ratio in nylon has been attributed to the existence of a skin on the fibre that restricts the transverse swelling.[80] It is recognised that if nylon yarn is wound onto a package in the dry state, then it lengthens as it absorbs water from the air; it can, as a result, become slack and fall off the package.

2.5.5 Optical properties

The optical characteristics of nylon fibres, such as the lustre and opacity, contribute to the aesthetic appeal of fabrics and hence to their acceptance by the consumer. Light falling on a nylon fibre can be reflected from the surface, transmitted through the fibre, or scattered or absorbed. The relative magnitude of these processes depends on the cross-sectional shape of the fibre, its crystallinity and whether any additives have been introduced before extrusion. Nylon with a circular cross-section and no additives present has a high lustre and fine fabrics tend to be translucent. The translucency is enhanced when the fabrics are wet. In apparel applications, it is therefore often necessary to introduce an additive, titanium dioxide, to the polymer before extrusion. This has the effect of reducing the inherent lustre of nylon fibres as well as reducing their transparency. The use of this additive is discussed more fully in Section 2.6.1.

The refractive index can also provide information about the fibre structure. Transparent materials such as glass are the same in all directions and are said to be isotropic. Fibres are anisotropic because of the orientation of the molecules in the direction of the fibre axis. The refractive index of the material will vary according

Table 2.4 Birefringence of typical drawn textile nylon and polyester fibres

	Refractive index		Birefringence
	$n_{\parallel}$	$n_{\perp}$	$n_{\parallel}-n_{\perp}$
Nylon	1.582	1.519	0.063
Polyester	1.725	1.539	0.186

to whether the light is polarised in a direction parallel or perpendicular to the fibre axis. The difference in the refractive indices is called the birefringence and can be used to monitor the degree of the molecular orientation in a fibre. Table 2.4 shows the refractive index in each direction and the birefringence for typical drawn nylon and polyester fibres.[81] The actual value of the birefringence increases with the polymer orientation; fibres produced with a high draw ratio and having a relatively high tenacity and initial modulus have a high birefringence. Consequently birefringence is used to monitor the molecular orientation in nylon fibres. The higher value of birefringence for polyester does not imply a higher orientation, only that the polyester molecules with the benzene ring are more effective in retarding light, relative to its velocity *in vacuo*.

2.5.6 Electrical properties

When samples of different materials are brought together and then separated, some movement of electrical charge will take place. If one or both of the materials is an electrical insulator, a build-up of static electricity will occur. This can give rise to a number of undesirable effects in nylon yarns and fibres. Where yarns in processing have similar charges, they will repel each other; filaments in a charged warp will balloon out or fabric coming from a machine will not fold down neatly on itself. In clothing, different layers will take up charges and cling or repel: sparks may be seen and heard when a garment is removed. The sparks have even been known to ignite flammable vapours; this is particularly a problem in hospital operating theatres. A charge is generated in a carpet as a person walks across; again sparking will occur and soiling is accelerated. The electrical fields generated can corrupt data stored magnetically, as in computers. Electrostatic charging of textiles and the various methods used to overcome the problems have been reviewed by Holme *et al.* [82]

Static electricity has been perceived as a particular problem with nylon, which lies at one end of the triboelectric series and is therefore an active electron donor. In comparison to other fibres at this end of the series such as wool, nylon is considerably less hydrophilic and develops a static charge even at high ambient r.h. values. The dissipation of the charge is slow as nylon has a low electrical conductivity and behaves as an insulator. Nylon 6 has a resistivity of $6 \times 10^{14}\ \Omega$ cm at 20 °C when dry, and $2 \times 10^{6}\ \Omega$ cm when conditioned at 100 % r.h.; the figures for nylon 6,6 are similar.[83] An additional factor is that nylon is used in applications where the effects of static are noticeable to the consumer, such as women's underwear, stockings and tights, and in carpets. Techniques have been developed to minimise the problem, and a number of inherently antistatic fibres have been marketed. Antistatic agents can be added to spin finishes to aid fibre processing, but their effect lasts only until the yarn undergoes a wet process. Antistatic agents have also been added to fibres to prevent cling in underwear and conductive fibres are used in low proportions in carpets.

A number of additives are added to fibres to impart inherent antistatic properties. The patent literature suggests that 2–10 % of polyethoxylated compounds such as poly(ethylene glycol) are used. The additive is dispersed in the polymer before extrusion and exists within the fibres as elongated fibrils with diameters in the range 0.1–0.5 μm, but may partially form chemical linkages at the interfaces with the amide groups in the nylon.[84] The polyglycol is water soluble, but the majority of it is trapped inside the fibre structure. A proportion may be extracted from the fibre surface during washing and wet processing. The extraction of some of the polyglycol during washing leaves voids in the fibre structure that can alter the lustre. A polyglycol with a high molecular mass (approximately 20 000) or with end groups that are substantive to nylon is used to minimise the loss.[85] Alternative humectant additives including *N*-alkyl polyamides can also be used. Typical of these additives is the polyamide from *N*,*N′*-diethylhexamethylenedimine and dodecanedioic acid.[86] Increased antistatic activity is also reported from polyethylene glycols containing a zwitterionic structure having quaternary amine and carboxylate or sulphonate groups.[87] All the antistatic agents of this type achieve their effect by absorbing moisture from the atmosphere to increase the electrical conductivity of the fibre. The antistatic effect of humectant additives depends on the presence of moisture in the atmosphere; if the air is dry, the conductivity of the fibres will be low and static build-up will still be possible. For nylon, it is important that any additive should be thermally stable at the extrusion temperature, should not affect the dyeing characteristics of the fibre and should not discolour as it ages.

Another approach to antistatic nylon yarns is the incorporation of a small proportion, typically 0.1–2.0 % of the fibre content, of inherently conductive fibres. The effect of these fibres in a textile material is to increase the electrical conductivity and the effectiveness does not depend on the moisture content. They do not need to provide a continuous electrically conducting path. They can interact with the electrostatic field of the charges, increasing their delocalisation and accelerating dissipation. There are a number of approaches to conductive fibres. The use of fine stainless steel wire, usually of 8 or 12 μm diameter, was developed for textile use in the 1960s; blends with nylon staple are available under the names *Bekitex* (Bekaert, Germany) and *Brunslon* (Brunswick Corp., USA). The modulus of the wire is higher than that of the nylon staple so, to avoid problems during carding the staple, the diameter of the wire is normally much less than that of the fibre.[88] Conductive nylon fibres are produced with a coating of silver. One method involves treating the fibres with a reducing agent that is also a swelling agent, such as catechol, followed by reaction with ammoniacal silver salt solution. These fibres can be blended and additions as low as 0.05 % have been reported to be sufficient for normal antistatic properties.[89] Conductor-based antistatic fibres were reviewed by Nemoz.[90]

Finely divided carbon can be incorporated into nylon fibres either during extrusion or by surface coating. One example of the latter type, *Resistat* (BASF, Germany), involved applying a dispersion of carbon black in dilute formic acid to the fibre. A baking process concentrated the formic acid, softening the surface of the fibre and enabling the carbon to migrate into it.[91] If the carbon is incorporated into the nylon at extrusion, then high levels are required, in the region of 20–40 %. This is sufficient to alter the behaviour of the fibres during drawing and texturing; breaks are more likely when the conductive fibre is combined with normal nylon fibres. This problem may be overcome by extruding the polymer containing carbon as one part of a bicomponent fibre. The first patent for a fibre of this type, granted to DuPont, described a nylon yarn with a core, which is as little as 4 % of the total fibre weight, containing 20–30 % carbon dispersed in polyethylene.[92] Kanebo® *Belltron 931* and *961* are circular bicomponent fibres with a conductive stripe across the diameter; both use carbon but the stripe in the latter variety is grey rather than black.[93] A patent to Monsanto (now Solutia) described a multifilament yarn in which 5 % of each fibre is a stripe loaded with conductive carbon. '*No-shock*' is a nylon 6,6 bicomponent yarn with one to three stripes of nylon 6 containing 34 % carbon. This is blended with normal nylon 6,6 yarn to give only about 0.02 % of conductive nylon 6 in the blend. A variant is a trilobal yarn with the conductive polymer containing 33 % carbon at the tip of one lobe. Only one filament in a multifilament yarn needs to be modified in this way.[94] The varieties and other applications of bicomponent fibres are described in Section 2.6.2.

Metal oxides and salts can also be used to give conductive properties to fibres. BASF has described a technique for binding a mixture of tin and antimony oxides to the fibre surface using a formic acid softening method. A major benefit is that the powders are white and the modified fibres are less visible than if conductive carbon is used.[95] *R.Stat(N)* is a nylon 6,6 yarn produced by R.Stat, formerly part of Rhone-Poulenc, with a 0.2 μm layer containing copper sulphide on the fibre surface, which is applied by a chemical process. The fibres are placed in a hydrogen sulphide atmosphere under pressure; copper sulphate solution is then allowed to diffuse into the fibre. It reacts with the hydrogen sulphide, forming copper sulphide at the surface. The fibres are coloured red but the treatment improves the electrical conductivity by a factor of 10^8.[96] The Kanebo® *Belltron* range includes sheath–core nylon 6 bicomponent fibres where the core contains a white semiconducting metal oxide. *Belltron 632* has a concentric core while *638* has an eccentric elliptical core that comes to the fibre surface at one end.[97]

2.5.7 Chemical properties

The chemical properties of nylon depend mainly on the typical reactions of the amide groups. The methylene groups are chemically inert although the groups adjacent to the amide nitrogen can be sensitised to certain reactions. The chemical properties include the rapid reactions that occur when fibres are exposed to acids, alkalis, solvents, etc. They also include the long-term and slower reactions that go under the title of degradation. Degradation is the term used to describe the reactions that occur in the polymer as a result of the processing and service conditions to which it is exposed. In polyamides, degradation may be caused by sunlight, heat, oxygen, impurities and additives. The degradation may result in bond scission or, alternatively, cross-linking in the polymer chain, leading to embrittlement of the fibre with a decline in tensile properties to ultimate failure. Nylon fibres have a high surface to volume ratio and consequently are readily susceptible to degrading attack. The effects may be isolated experimentally, but in use fibres are commonly exposed to a number of influences. The relative importance of each will depend on the application, but in normal domestic use, these may include the effects of the alkalinity and oxidation of peroxide bleaches in washing powders or liquids, exposure to UV light during line drying and heat at up to 150 °C during pressing. The consumer will see the long-term effects of all these as a yellowing of white fabrics accompanied possibly by a loss of tensile properties and embrittlement; in coloured fabrics there will be a loss of brightness and clarity of the colour. The reduction in tensile properties will increase the normal effects of abrasion during wear on the nylon.

The service life of nylon in an application will depend on the initial properties as well as on the service conditions, which will involve the nylon absorbing radiation, light, or mechanical or thermal energy. In most cases the nylon in use will be surrounded by air and hence degradation almost always involves oxygen. The most realistic assessment of the service life of nylon will come from testing under the actual conditions of use. However, this can often be excessively time consuming. In an extreme example an automotive air bag will spend most of its service life, which may be ten years or more, compressed in a small container in the centre of the steering wheel and exposed to large variations in temperature and humidity. It may then be expected to inflate in 0.01 s. Clearly, accelerated but reliable tests have to be used.

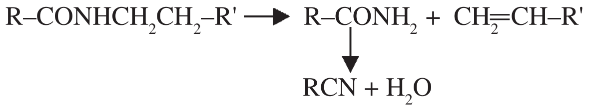
2.5.7.1 Heat

Degradation in the absence of oxygen may occur during extrusion of the polymer as well as in applications such as tyres and belts where the nylon is embedded in rubber and air is excluded. At elevated temperatures, both nylon 6 and 6,6 undergo degradation with the formation of carbon dioxide, ammonia and water. The carbon dioxide and ammonia result from decarboxylation and deamination reactions of the carboxylic and amine end groups respectively (equations 2.24 and 2.25):[98,99]

$$\text{–CH}_2\text{–COOH} + \text{HOOC–CH}_2\text{–} \rightarrow \text{–CH}_2\text{–CO–CH}_2\text{–} + \text{CO}_2 + \text{H}_2\text{O} \qquad [2.24]$$

$$\text{–CH}_2\text{–NH}_2 + \text{H}_2\text{N–CH}_2\text{–} \rightarrow \text{–CH}_2\text{–NH–CH}_2\text{–} + \text{NH}_3 \qquad [2.25]$$

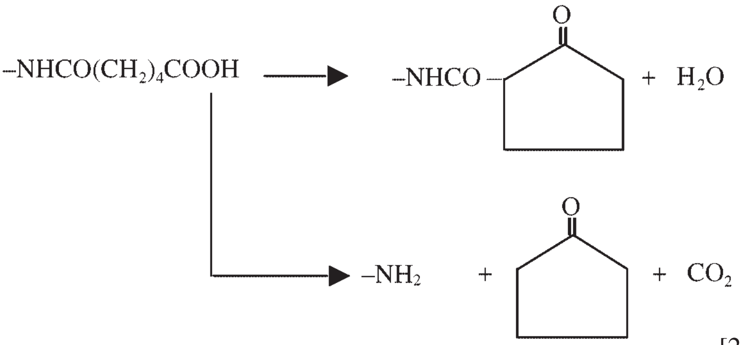
The water may come from condensation and dehydration reactions. In addition, some polymeric amines, acids and nitriles can be formed. A degradation mechanism has been proposed, where under these conditions the dipolar carbonyl group removes a hydrogen atom from the methylene group in the β-position to the amide nitrogen. This leads initially to chain scission to form an amide end group and a double-bonded end group.[100] The amide end group can then eliminate water to form a nitrile (eq. 2.26):



$$\begin{tikzcd} \text{R–CONHCH}_2\text{CH}_2\text{–R}' \arrow[r] & \text{R–CONH}_2 \arrow[d] & + \ \text{CH}_2\text{=CH–R}' \\ & \text{RCN} + \text{H}_2\text{O} & \end{tikzcd}$$

[2.26]

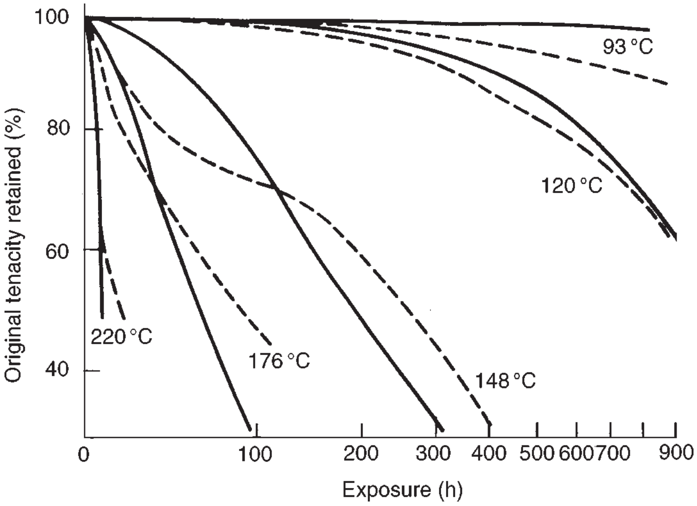
When nylon 6,6 is heated, considerable amounts of cyclopentanone are formed. This is a by-product of heating adipic acid end groups, which tend to cyclise and lose carbon dioxide and water (eq. 2.27). The formation of cyclopentanone is accompanied by an increase in the number of amine end groups owing to the chain scission involved. However, little cyclopentanone is found in the degradation products as it undergoes further condensation reactions to form complex molecules and some substituted cyclopentanone derivatives are found in the decomposition products.[101]



[2.27]

2.5.7.2 *Oxidation*

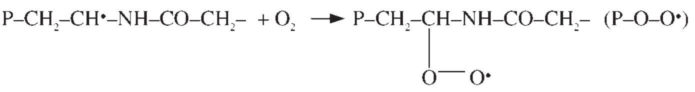
Exposure of nylon 6,6 and 6 to air at temperatures above 100 °C results in a loss of both tenacity and breaking elongation. Figure 2.15 shows the effect of temperature and exposure time in air on the retained tenacity of nylon 6 and 6,6 yarns.[102] The changes are accompanied by discoloration and a reduction in amine end groups. Impurities in the polymer such as metal ions, carbonyl compounds and hydro-



2.15 Effect of temperature and heating time in air on the retained tenacity of nylon 6 (——) and nylon 6,6 (– – –).

peroxides absorb light and produce 'stray' free radicals that can initiate a chain reaction. For nylon, the reaction starts with the methylene group adjacent to the amide nitrogen (the α-carbon). An initial extraction of this hydrogen by a stray free radical leaving a free radical at this carbon is followed by a reaction with oxygen to yield a peroxyl radical. This is then able to extract a further hydrogen atom from the polymer chains to form a hydroperoxide and regenerate another alkyl radical that can, in turn, react with more oxygen in a chain reaction. Decomposition of the hydroperoxide forms alkoxyl and hydroxyl radicals, both of which can participate in new reaction chains (equations 2.28–2.30):

$$\mathrm{P{-}CH_2{-}CH_2{-}NH{-}CO{-}CH_2{-}} + \mathrm{R}\bullet \longrightarrow \mathrm{P{-}CH_2{-}CH}\bullet\mathrm{{-}NH{-}CO{-}CH_2{-}} + \mathrm{RH} \qquad [2.28]$$



$$\mathrm{P{-}CH_2{-}CH}\bullet\mathrm{{-}NH{-}CO{-}CH_2{-}} + \mathrm{O_2} \longrightarrow \mathrm{P{-}CH_2{-}}\underset{\underset{\mathrm{O{-}O}\bullet}{|}}{\mathrm{CH}}\mathrm{{-}NH{-}CO{-}CH_2{-}}\ (\mathrm{P{-}O{-}O}\bullet) \qquad [2.29]$$

$$\begin{array}{lll} \mathrm{P{-}O{-}O}\bullet + \mathrm{P{-}H} & \longrightarrow & \mathrm{P{-}O{-}O{-}H} + \mathrm{P}\bullet \\ \mathrm{P{-}O{-}O{-}H} & \longrightarrow & \mathrm{P{-}O}\bullet + \mathrm{H{-}O}\bullet \end{array} \qquad [2.30]$$

The reaction in eq. 2.29 is controlled by the rate at which oxygen can diffuse into the fibre; this is faster at elevated temperatures. Aldehydes and ketones are formed by decomposition of the hydroperoxides with the consequence of a break of the polymer chain and a progressive loss of tensile strength.[103]

The yellowing of nylon 6 heated at around 160 °C has been attributed to the formation of unsaturated conjugated oligoenimines, which absorb in the ultraviolet and visible range. Azomethine groups are formed in a reaction between the aldehyde and amine end groups and polymerise immediately, resulting in structural units with conjugated double bonds. The degree of conjugation increases with time, shifting the absorption to longer wavelengths. The loss of amine end groups in the fibre can be detected and provides evidence for the formation of oligoenimines, unsaturated conjugated structural units containing nitrogen in the polymer chain (eq. 2.31). The degree of conjugation increases with time and the colour deepens:[104,105]

$$\mathrm{-CH_2-CH_2CHO + H_2N-CH_2-} \longrightarrow \mathrm{-CH_2-CH{=}CH-CH{=}N-CH_2-CH_2- + H_2O} \\ + \text{ by-products} \qquad [2.31]$$

When nylon 6 or 6,6 is exposed to air at temperatures above the melting point, the fibre properties are no longer of interest, but the products of combustion have important implications for the use of nylons in applications (e.g. upholstery in vehicles and aircraft) where combustion in confined places is a possibility. Nylons are considered to have low flammability; the Limiting Oxygen Index (LOI) for nylon is 20 %, above the normal oxygen content of air. Nylon fabrics melt away from a flame and do not continue to burn if ignition occurs at all. However, in melting away from the flame the fabrics cease to provide protection to the user. In apparel, particularly for underwear, the melting away from the source of heat can cause molten polymer to come into contact with the wearer's skin, leading to severe burns. Nylon as an aliphatic polymer produces very little smoke, so vision is not obscured during combustion. The behaviour of the fibre in blends is important. Nylon is not often blended with cotton or viscose where the 'scaffolding' effect of the cellulosic fibres inhibits the shrinking of the synthetic fibre from the flame and increases the ability of a fabric to propagate a flame. Nylon is most frequently blended with wool in carpets and some knitted garments. Wool is normally self-extinguishing and is the majority component in the blends. Consequently, flammability is not normally a problem with these blends.

The toxicity of the products of thermal decomposition and combustion of nylons has been extensively documented. The typical pyrolysis products do not differ greatly between nylons. Apart from some heavy chain fragments as volatile organic compounds, carbon dioxide and water, the major gases detected are CO, NH_3, HCN and nitrogen oxides. At 500 °C nylon 6 generates only 0.04 % of hydrogen cyanide in air. It is has been suggested that during combustion the oxygen oxidises the amide groups and promotes the formation of the small proportion of HCN. The amount of HCN, 0.04 %, is more than an order of magnitude lower than the quantity of HCN produced by polyurethane or polyacrylonitrile fibres.[106]

Considerable efforts have been made to increase the flame resistance of nylon by promotion of char formation and eliminating dripping polymer melt by means of copolymerisation, or the addition of flame retardants. Any additives used must be stable under the usual melt extrusion conditions and must not discolour the fibres. Both soluble additives and co-polymers have the effect of reducing the melting point of the polymer. The flame retardants that have been used are reasonably high molecular mass organic compounds to minimise migration from the fibres, and incorporate halogens, phosphorus or nitrogen. Examples are perbrominated aromatic hydrocarbons, organic derivatives of phosphoric or phosphonic acids and nitrogen-containing melamine and its derivatives. Organic compounds are preferred but inorganic compounds or elements such as red phosphorus or antimony trioxide have been used. These may, however, increase the toxicity of the smoke if the fibre does ignite. With all flame retardants, high levels are required to produce non-dripping and self-extinguishing fibres and these have adverse effects on the melt viscosity and the fibre physical properties.[107] There does not appear to be a commercial nylon with inherent flame-retardant characteristics.

2.5.7.3 Photodegradation

Degradation of nylon fibres does not take place only at high temperatures. Exposure to sunlight and other sources of u.v. radiation also leads to a deterioration in the properties of nylons. The effect is particularly pronounced in fine fibres with a high surface area. The extent of photodegradation depends on the intensity and the spectral distribution of the light. The humidity, the air quality and the presence of substances, on or in the fibre, that may photosensitise it are also factors. Light with a wavelength of less than 300 nm has a higher energy and is particularly effective in promoting degradation. Under nitrogen, light in the 300–400 nm wavelength range has little effect on nylons, but in the presence of air and moisture a rapid deterioration in properties occurs.

The chemical course of degradation, induced by light, is complex. Light at wavelengths of 340 nm or less has sufficient energy to cause direct scission of the amide link in the polymer chain. The major groups formed are amines, aldehydes and carboxylic acids. The aldehydes accumulate in the polymer only to a certain extent as they condense to form structures with conjugated double bonds. At longer wavelengths, additives such as pigments or dyes or impurities within the nylon fibre absorb energy, forming a radical that initiates photo-oxidation. In the initial stage a hydrogen free radical is removed from from the α-carbon to the amide nitrogen as shown in eq. 2.28. This leads, in the absence of molecular oxygen, to the scission of the C—N bond in the amide link, yielding an imide and a carbonyl radical. The latter can then abstract a hydrogen from another polymer chain (P) giving an aldehyde group and another free radical. The aldehyde group is a chromophore that absorbs light at 500 nm. There is therefore an autocatalytic effect, increasing the sensitivity of the fibre to light. Further chemical reactions can occur which result in chain cleavage and/or cross-linking.[108] In the presence of molecular oxygen, the alkyl radicals can form peroxyl radicals and react as shown in equations 2.32–2.34:

$$\text{R–CH}_2\text{CONH–C}^\bullet\text{H–CH}_2\text{–R}' + \text{H}^\bullet \longrightarrow \text{R–CH}_2\text{C}^\bullet\text{O} + \text{HN}=\text{CH–CH}_2\text{R}' \quad [2.32]$$

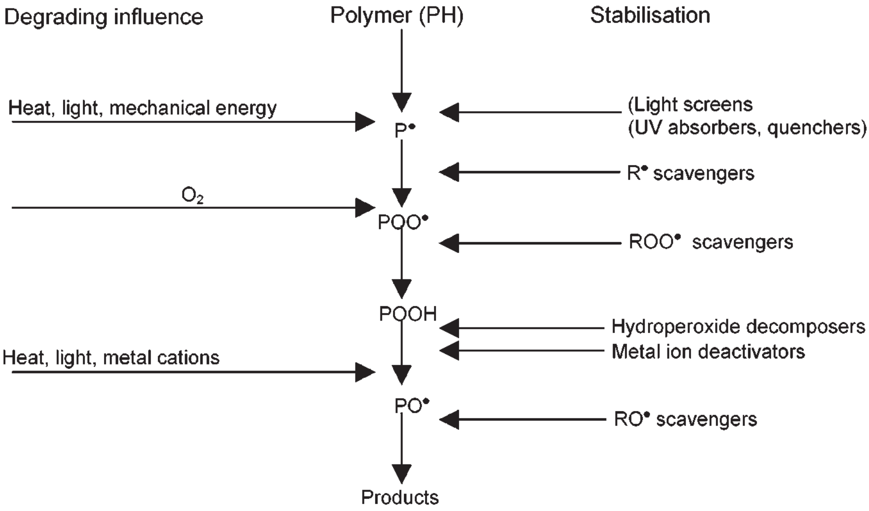
$$\text{R–CH}_2\text{C}^\bullet\text{O} + \text{P–H} \longrightarrow \text{P}^\bullet + \text{RCH}_2\text{CHO (aldehyde)} \quad [2.33]$$

$$2\text{P}^\bullet \longrightarrow \text{P–P} \quad \text{(cross-linking)} \quad [2.34]$$

2.5.7.4 *Stabilisation*

Stabilisation of nylon polymers is possible through the introduction of compounds that increase durability, the so-called stabilisers. These compounds must also have other properties in addition to stabilising effectiveness. They must be of sufficient thermal stability to withstand the extrusion and processing conditions; they must be miscible with the polymer; they must not migrate or be washed out; they should be non-toxic, tasteless and odourless; they should not colour the polymer and ideally they should be cheap. For the polyamides, over 1000 patents exist concerning their stabilisation by the addition of various inorganic and organic compounds, either singly or in mixtures. The function of stabilisers is to interrupt the sequence of reactions leading to the thermal and photolytic degradation of nylons. Manufacturers do not reveal the additives that are used and vary components of the stabilisation system according to the intended applications of the product. The stages of the degradation and the ways in which the polymer can be stabilised are summarised in Fig. 2.16.[109]

The generation of radicals in polymers by the effect of light can be prevented by the addition of compounds that act as light screens, antioxidants, UV absorbers or quenchers of excited states. Light screens are compounds that increase polymer



2.16 Scheme of degradation processes and stabiliser functions for nylon.

photostability by their physical effect; they are opaque substances that increase light reflection from the polymer surface. Titanium dioxide is used to delustre nylons and other fibres but it also acts as a sensitiser in polyamides (Section 2.6.1). Pigments incorporated into the fibre provide opacity but can also have a sensitising effect. Carbon black is an excellent light screen and also a radical scavenger, but the stabilising effect is only for black fibres.

UV absorbers are compounds that preferentially absorb light at the wavelengths that can cause degradation in the fibres and emit it in a form that is harmless to the polymer. The radiation is dissipated as vibrational energy in the hydrogen bond range. Absorbers that absorb the UV radiation at wavelengths that are harmful to nylons are mainly derivatives of 2-hydroxyphenylbenzotriazole, and the recommended concentrations of the additives are in the range 0.1–1.0 %. Other UV absorbers include 2-hydroxybenzophenone and 2-hydroxylphenylsalicylates. At one time UV absorbers were not generally used for increasing the resistance of nylons to photodegradation as they are expensive, tend to colour the fibre and cancel out the effects of amine and phenol type antioxidants. However, a number of producers now market nylon fibres for outdoor applications with superior UV resistance for use in outdoors applications.[110]

Excited state quenchers act as stabilisers by absorbing energy from the light-excited chromophoric groups in the polymer, before the degradation processes start. The quencher dissipates the absorbed energy in the form of heat or by means of another photolytic process. Most quenchers are chelates of metals; one recommended for polyamides is *Cyasorb*® 1084 (Cyanamid), a thio-bis-phenolate complex of nickel. As well as acting as quenchers, these compounds can operate as hydroperoxide decomposers and even UV absorbers.

Antioxidants play an important role in the stabilisation of nylons against both thermal and light-induced degradation. They can be either peroxide decomposers or radical scavengers. The peroxide decomposers for nylon are metal cations where the stabilising effect is based on their ability to react with radicals, $R^\bullet$ and $ROO^\bullet$, and increase the rate of termination of the oxidation chains. The preferred stabilisers are manganese(II), copper(I) or copper(II) salts. These are added to the monomers before polymerisation to give 30–70 ppm of metal ion in the extruded yarn. Manganese(II) improves the light fastness of nylon up to temperatures of 40–50 °C. For technical nylon fibres, copper(I) compounds are used instead to improve the thermal ageing properties. For copper additives, the transition will be between copper(I), Cu^+, and copper(II), Cu^{2+}. The effectiveness of the metal as a stabiliser depends on the copper(I/II) redox potential and the reaction with the radicals formed in the nylon. Alkali metal iodides and bromides have a synergistic effect and stabilise the copper compounds during melt extrusion. They stabilise the copper(I) species, reducing the redox potential, and are added at a 0.1–0.3 % level. One additive, which is said to improve the quality of tyre cord is *Polyad*® 201 (Ciba Speciality Chemicals), which consists of copper iodide.[111] These reactions are shown in equations 2.35 and 2.36:

$$POO^{\bullet} + Cu^{+} \longrightarrow POO^{-} + Cu^{2+} \qquad [2.35]$$

$$P^{\bullet} + Cu^{2+} \longrightarrow P^{+} + Cu^{+} \qquad [2.36]$$

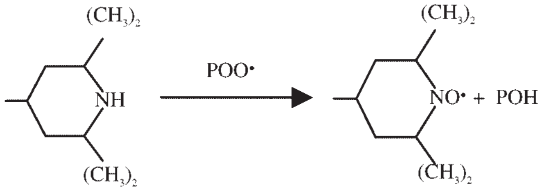
A difficulty with metal stabilisers is that at very low concentrations they may catalyse the oxidation of the nylon. Copper ions at a concentration of 0.01 % have been shown to accelerate the oxidation of nylon considerably. However, there is a critical concentration, above which the stabilising action predominates.

Radical scavenger antioxidants react with the radicals formed in the polymer chain and transform them to stable radicals or to neutral molecules. The antioxidants that are normally used are hydrogen donating and have one or more labile hydrogen atoms in the molecule. These are capable of competing with the propagation reaction of the oxidation process. The reaction of the anti-oxidant (HA) may be represented as in eq. 2.37:

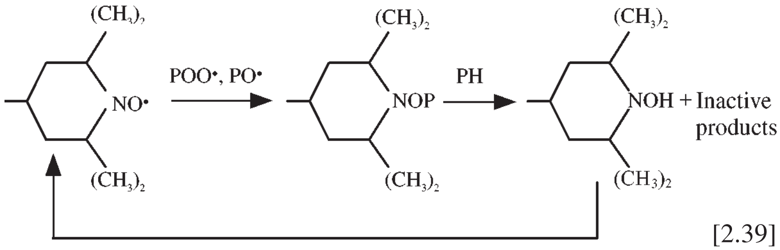
$$POO^{\bullet}\ (\text{or } PO^{\bullet}, P^{\bullet}) + HA \longrightarrow POOH\ (\text{or } POH, PH) + A^{\bullet} \qquad [2.37]$$

The radical scavengers that are used as antioxidants for nylons are of two types: secondary aromatic amines or sterically hindered phenols. The amines are derivatives of 4-phenylenediamine or diphenylamine with the *para* positions substituted with bulky alkyl or aryl groups. A drawback of these compounds is a tendency to colour the polymer and there are suggestions that many may be carcinogens. An example of the hindered phenols is 2,6-di-*t*-butyl-*p*-cresol. The phenol group has the labile proton that can transfer to the radical in the polymer, while the butyl groups tend to stabilise the radical remaining from the antioxidant. Sterically hindered phenols are used for stabilisation in industrial, rather than textile nylon fibres.[112]

An important group of antioxidants is the Hindered Amine Light Stabilisers (HALS). These are derivatives of piperidine, a saturated heterocyclic amine, $C_5H_{10}NH$. The most effective compounds used have fully substituted carbon atoms adjacent to the nitrogen, as in a 2,2,6,6,tetramethylpiperdinyl group. The piperidine derivatives are, however, inactive in polyamide due, it is thought, to hydrogen bonding with the amide groups; consequently they depend on a reaction with peroxyl radicals during processing to form nitroxyl radicals that are effective polymer radical traps (eq. 2.38). Alternatively they may be applied in the form of the nitroxyl radicals. These react in turn with the polymer free radicals to form a polymeric hydroxylamine. If the reaction were to stop at this point it would be difficult to explain why the HALS are so effective. The polymeric hydroxylamine is itself an effective stabiliser and it is likely to react to form the hydroxyl amine equivalent of the hindered amine. This in turn can react with another peroxyl radical to reform the original nitroxyl radical. The regeneration of the nitroxyl radical permits the HALS to be highly effective in preventing the polymer radicals from decomposing in a way that degrades the nylon fibre. The recommended concentration of the HALS in the fibre is in the range 0.1–1.0 %. These changes are summarised in eq. 2.39:



[2.38]



[2.39]

There are a number of HALS recommended to enhance the stability of nylons to UV light. *Tinuvin® C353* is a mixture of a HALS and a UV absorber derived from 2-hydroxylbenzotriazole and is used where a high level of UV resistance is needed. *Tinuvin® 783* is a synergistic mixture of two different HALS (both Ciba Speciality Chemicals). Either can be used, at concentrations in the range 0.1–1.0 %.[113] A nylon 6 with inherent heat and light resistance, *Lumaxx*, is produced by BASF, Germany, by polymerising caprolactam with a 2,2,6,6-tetramethylpiperidine derivative substituted at the 4-position with amide-forming groups. By using two such derivatives, one containing a carboxylic acid group and the other containing a primary amino group, both ends of the polymer chain can be capped with a HALS group. Alternatively, by using hindered piperidines that are difunctional in the polyamide-forming reaction, the HALS units can be incorporated within the nylon 6 chain. The product is available as regular, deep and cationic dyeing carpet yarns.[114,115]

2.5.7.5 Acids, alkalis and solvents

Nylons are only slowly affected by water at the boiling point. With superheated steam at 150 °C and above, hydrolysis of the amide groups occurs. This is the reversal of the polymerisation reaction. Nylon 6,6 is inert to 10 % sodium hydroxide solution at 85 °C over 16 hours. However, nylons are sensitive to acids and rapid degradation occurs with 1 % sulphuric acid at this temperature. The acid hydrolysis rate is faster for nylon 6 than for 6,6; the more random open structure of nylon 6 allows more rapid penetration of aqueous reagents, including acid, alkali and dye solutions.

Nylon 6 and 6,6 are inert to most common organic solvents, but they do dissolve in concentrated formic (methanoic) acid, in phenols such as phenol itself and *m*-cresol (hydroxybenzene and 3-hydroxymethylbenzene), and in alcoholic calcium chloride solution. It would be possible to design a production process for nylon fibres and yarns where the polymer was dissolved in a solvent and the solution converted to fibre by extrusion into water (wet extrusion) or by extrusion into warm air, which would evaporate the solvent, leaving the pure polymer as a fibre (solvent dry extrusion). Some of the available solvents listed above that could be used for these alternative processes are expensive, toxic and unpleasant to handle: alcoholic calcium chloride would need an evaporation process and a washing process to remove the calcium chloride. Effective solvent recovery systems would therefore be needed and would increase the production costs considerably.

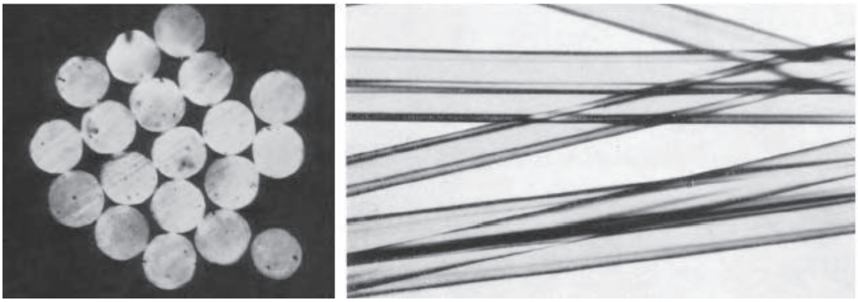
2.6 Fibre modification

This section describes some of the techniques that are available to impart and enhance the desirable properties or to reduce and remove some of the undesirable performance attributes of the fibres and yarns. Both chemical and physical techniques can be used and some have already been mentioned. Indeed the term ‘fibre modification’ implies that some fibres have no modifications at all, being extruded from pure nylon 6 or 6,6 from a circular spinneret with no additives, and not subjected to any form of after treatment. Such fibres are commercially virtually unknown. Almost all fibres have their properties enhanced in some way.

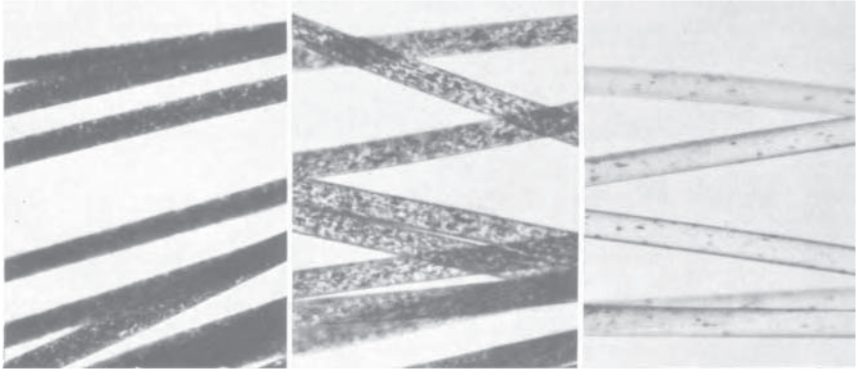
2.6.1 Use of delustrants

The advent of nylon fibres enabled the production of continuous filaments which, when twisted to make yarns, gave sheer, shiny and smooth fabrics. However, the universal shininess of such fabrics led to experiments with delustrants, which were used initially with viscose continuous filament yarns in the 1930s. The need for an effective delustrant became apparent with the production of the first nylons for general apparel applications in the early 1950s. Figure 2.17 shows the transverse cross-sectional view of polyamide fibres demonstrating the featureless morphology that not only reflects incident light but also transmits light. Thus fabrics have a lustre that is only attractive in particular applications and tend to be excessively translucent. The fabrics are even more transparent when wet. The first nylon swimsuits had considerable advantages over the previously used woollen costumes, which could weigh as much as 5 kg when wet. They were strong, light, well fitting and quick drying, but the difficulty was that when wet, they were excessively transparent. The presence of small, highly light-scattering, delustrant particles of titanium dioxide in the fibres not only reduces the surface lustre but increases the fibre opacity and hence the covering power of the derived textile.

Titanium dioxide is consequently added to nylon fibres for two purposes: at low levels to reduce the transparency of the fibres, a typical level for this purpose would



2.17 Transverse and longitudinal cross-sections of bright nylon 6,6 fibres.



2.18 Nylon fibres with three levels of titanium dioxide: left, matt fibre 2% TiO_2; centre, semi-matt fibre, 0.3% TiO_2; right, bright fibre 0.03% TiO_2.

be 0.2 % or less; to roughen the fibre surface to give a matt or semi-matt appearance, typical levels of addition for this purpose would be 0.5% for semi-matt and 1–2 % for matt. The words dull and semi-dull are also used to describe the fibres.[116]

Figure 2.18 shows longitudinal microscopic views of polyamide fibres with three different levels of TiO_2 to give bright, semi-matt and matt fibres.[117] To maximise the light scattering, the particles of delustrant need to be very small, with a diameter in the range 0. 1–1.0 μm. A typical fibre diameter is 15 μm or more, but some modern microfibres have a diameter of only 8 μm. If the TiO_2 is finely divided, blockage of the spinneret holes should not be a problem, although in general it will be necessary to change the spinneret more frequently when producing matt fibre. There has been a tendency for fibres for apparel to become finer, which has meant that finer spinneret holes are used. These will be more susceptible to blockage. Normally, the TiO_2 is added shortly before melt extrusion in the form of a concentrated suspension of the substance in the solid polymer. This

Table 2.5 Residual tensile strength of 40 dtex/8 filament polyamide 6,6 yarn after 150 hours Xenotest exposure

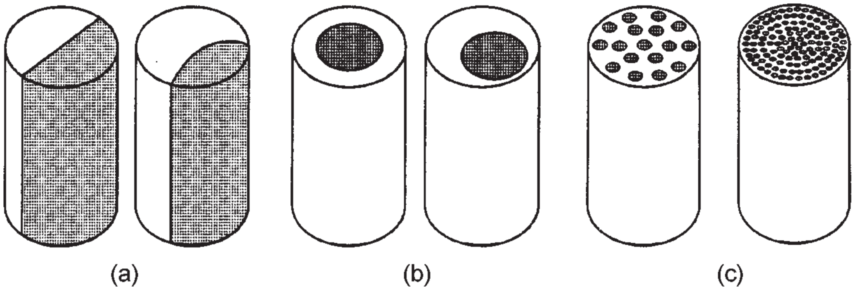
Delustrant	Residual tensile strength (%)
None	80
1 % anatase	39
1 % rutile	62

master batch is metered into the bright polymer to give the required level in the final fibre. Particles within a fibre are a discontinuity in the polymer and there is some loss of tensile properties. This is not critical for most domestic and apparel end-uses.

Although titanium dioxide screens the fibre and prevents light from reaching the interior, it can also initiate photo-oxidation. Polyamides are more susceptible to photo-oxidation when TiO_2 is present. This can lead, eventually, to a complete loss of fibre strength, but is more likely to be seen as a yellowing of the fibre in use with a loss in clarity of pale dyed or printed shades. Table 2.5 shows some data on the photodegradation of nylon yarn containing the two forms of titanium dioxide.[118] The results show that titanium dioxide has a significant effect on the photo-oxidation of polyamide fibres and that the effect is particularly marked for addition of the anatase pigment. The refractive index of anatase is lower than that of the rutile form and consequently it is less effective for scattering light from the fibre surface and interior: in addition, anatase TiO_2 is more expensive than rutile. However, the anatase form of TiO_2 is normally used for nylon; although degradation of the fibres is worse than with the rutile form, the fibre surfaces are less abrasive with anatase TiO_2 and cause less wear on guides during processing. All the figures refer to titanium dioxide that has not been treated to reduce the photocatalytic effect. The sensitising action is avoided by treating the titanium dioxide with manganese compounds or by doping with antimony.[119] However, it has been reported that as much as 70 % of the manganese is removed when dyeing matt fibres under acidic conditions. As a result, not only is the light resistance of the fibres impaired, but the light fastness of dyeings with acid or metal complex dyes is decreased.

2.6.2 Bicomponent fibres

Bicomponent technology has been used to introduce functional and novelty effects, including stretch, to nylon. Bicomponent fibres have two distinct polymer components, usually of the same generic class in the fibre cross-section, e.g. one part of the fibre could be nylon 6,6 and the other nylon 6. They are also described as ‘conjugate fibres’, particularly by some Asian producers. If the components are from different generic classes then the fibre is sometimes said to be biconstituent. In bicomponent and biconstituent fibres, each component is normally fibre-forming. The spinneret and the polymer feed channels can be designed so that the



2.19 Bicomponent fibres: (a) side by side, (b) sheath–core, (c) islands in the sea.

two polymer streams meet just prior to the spinneret hole and emerge side by side or as a sheath and core. Some schematic fibre cross-sections are shown in Fig. 2.19. The fibres then need to be drawn and processed in the usual way. The engineering required to ensure that each hole of a spinneret receives a feed of two polymers at the required rate is complex, but the difficulties have been overcome and there are a large number of bicomponent nylon fibres in commercial production. The ratio of the two polymeric components need not be 50/50 and can be varied according to the application.

The objective of side-by-side bicomponent fibres is to produce an inherent crimp. With nylon and other fibres that are not highly hygroscopic, one of the components needs to shrink more than the other when the fibre is heated. There also needs to be good adhesion between the two components. The inherent crimp can be produced with two nylon 6,6 polymers having a substantial difference in viscosity arising from a difference in relative molecular mass. Alternatively, one of the components can be a copolymer of, for example, nylon 6,6 and 6,10 while the other is nylon 6,6. The crimp developed by this type of fibre is helical and it is especially suitable for stockings and tights. In this and other applications inherent crimp fibres compete economically and technically against yarns produced by conventional extrusion and draw-texturing. The most notable example was *Cantrece*, which was produced for hosiery by DuPont.[120] Yarns are no longer marketed under this brand name, however. Currently, DuPont produce a yarn *Tactel*® T-800, which is a nylon 6,6-based bicomponent, giving self-crimping yarns.[121] The yarns are said to give unique aesthetics and a touch of stretch in garments. Another side-by-side fibre was *Monvelle* produced by Monsanto (now Solutia), also for the stretch hosiery market. This was actually a biconstituent fibre using nylon 6 and a melt-spinnable polyurethane.[122] Currently, a nylon/polyurethane bicomponent, *Sideria*, is produced by Kanebo, which self crimps on the application of heat and which can be used to produce fabrics with moderate stretch.[123]

Sheath–core bicomponent fibres are those where one of the components is completely by surrounded by the second. The configuration may be used in a symmetrical or asymmetrical form to combine the properties of the two components, taking advantage of the particular physical characteristics such as the strength or conductivity of the inner component or the aesthetic textile, adhesive or other properties of the outer component. Some adhesion between the two polymers is necessary, and crimp can be generated from the asymmetrical form. One application of sheath–core bicomponent fibres is in thermally bonded non-woven fabrics. The fibre is extruded with a high melting point (m.p.) core and a lower melting point sheath. An example would be a fibre with a nylon 6,6 (m.p. 260 °C) core surrounded by nylon 6 (m.p. 225 °C). The yarns are laid out in a web which does not need to be made up solely of the bicomponent fibres (some fibres that do not soften can be included) and heated above the softening point of nylon 6. The sheath polymer softens and binds the fabric together. One application of this type of fabric is in the linings of shoes, particularly trainers. The fabrics are dimensionally stable, have good abrasion resistance, and are fully permeable to water vapour. They are marketed by DuPont under the *Cambrelle* brand name.[124] An alternative application is seen in a bicomponent fibre produced by Kanebo, *Masonic N*. One type is heat-accumulating and has a carbonised zirconium compound blended into the molten core polymer. This has the effect of improving the heat retention of garments and is therefore best suited for outerwear. The other type has a core with a ceramic powder, which is an emitter of far-infrared radiation. This makes the wearer of *Masonic N* garments warmer and is recommended for underwear. In both types the sheath is normal nylon.[125]

A third type of bicomponent fibre is matrix–fibril. The polymers are brought together before extrusion, so that one polymer is suspended in droplet form in the melt of the second, usually at a concentration of less than 20 %. After extrusion and drawing the suspended polymer forms fibrils of variable length in the matrix of the other polymer. The fibrils are in fibrous form and are randomly distributed over the cross-section, but do not extend along the full length of the fibres. The presence of polyester fibrils in a nylon 6 matrix has been suggested as a method of increasing the modulus of the high-tenacity fibre and avoiding the problem with flat spotting with nylon tyre cords (see Section 2.5.3.3). Another example of a matrix–fibril bicomponent fibre is *Bodyshell*, a highly opaque nylon produced by Toray. This is said to contain an opaque polymer in nylon filaments with a star-shaped section. Fabrics are sufficiently opaque to be suitable for white swimwear, even when wet.[126]

Other bicomponent fibres are used in the production of microfibres and are described in Section 2.6.3.

2.6.3 Microfibres

The initial objective with microfibres was to produce fabrics with a more silk-like handle than could be achieved with conventional nylon or polyester yarns. There is no formal definition of what constitutes a microfibre but such fabrics will normally be made from yarns containing filaments finer than 1 dtex. By contrast, yarns that were used in fabrics for shirts, underwear and bedsheets in the 1970s contained filaments as coarse as 4–5 dtex. The handle of such fabrics was harsher and considerably less attractive than that of fabrics made up from finer filaments. In addition, the ability of fabrics from the coarser filaments to transmit moisture away from the skin was very limited, making the garments uncomfortable for the wearer. The definition of microfibres is looser for staple fibres and the term can be applied to nylon fibres as coarse as 2 dtex.[127] Nylon staple fibres are generally intended for blending with wool and 2 dtex is therefore much finer than normal. Although finer fibres are attractive to the consumer, they do create problems for the fibre producer and the processor in maintaining product quality.

The feel or handle of a fabric is vital to the consumer. It is one of the major factors that influences a consumer to buy a particular textile product. There are a large number of factors influencing the fabric handle but one of the most important is the flexural rigidity of the individual filaments. The flexural rigidity is defined as the couple needed to bend a filament to unit curvature. The flexural rigidity is an imperfect measure of the handle of a fabric but it does give a useful indication providing that the other variables are the same. The flexural rigidity is defined by eq. 2.40:

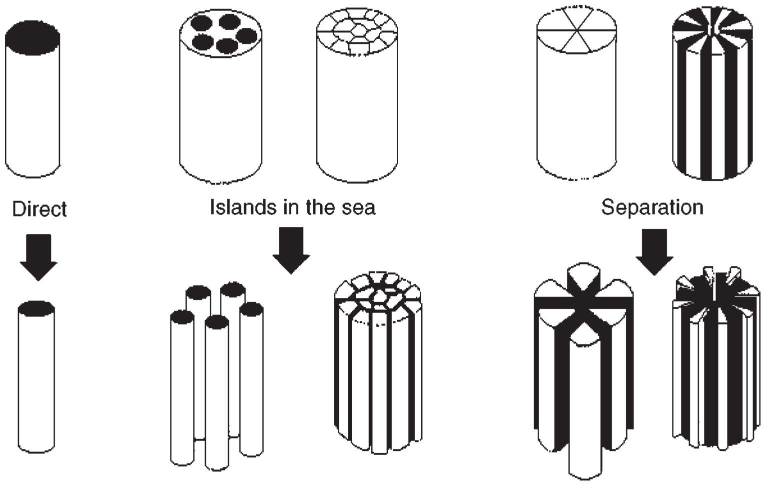
$$\text{Flexural rigidity} = \sigma E T^2/4\pi\rho \tag{2.40}$$

In the equation σ is a shape factor for the fibre and is unity for a solid circular cross-section, E is the initial modulus of the fibre in N tex^{-1}, T is the filament linear density in tex, and ρ is the density of the fibre in g cm^{-3}.[128]

The flexural rigidity of fibres is therefore proportional to the square of the linear density and as the fibres become finer so the handle becomes softer. For a multifilament yarn, the twist will also affect the handle; if the twist is high then the filaments will be bound closely together and the handle will be harsher. If, however, the twist is low, as will normally be the case for a continuous filament yarn, then the flexural rigidity of the yarn will be the sum total of the values for the individual filaments. For filaments of the same linear density, nylon will bend more easily than polyester owing to the lower modulus, and fabrics will be expected to have a softer handle.

As the number of filaments in a yarn of given linear density increases, then the surface area of all the fibres increases and, in a fabric of close construction, the spaces between the fibres become smaller. Liquid water is prevented by surface tension from penetrating the fabric, which will have a degree of water repellency. Water vapour is able to pass through the fabric from the inside to the outside, however, leading to increased comfort in wear. In addition to these advantages, microfibre fabrics will also offer a high degree of wind resistance.

The technique for the production of microfibres depends on the linear density of the filaments. The various methods are summarised in Fig. 2.20.[129] In the linear density range 0.4–1.0 dtex, conventional extrusion can be used, but the production



2.20 Methods of production of microfibres.

of filaments as fine as 7 μm does take melt extrusion technology to its limits. Good filtration of the molten polymer immediately before extrusion is critical. The residence time of the molten polymer in the extrusion head must be minimised to prevent degradation and consequent poor spinnability. Temperature control of the molten polymer is also vital; a 1 °C difference in temperature at 290 °C will alter the melt viscosity by 1.5 % and hence the fineness of some of the filaments within the yarn. Without good temperature control the regularity and quality of the yarns will be affected. In the production of microfibre POY the drag on the filaments is unlikely to alter greatly as the individual filaments become finer. Hence the stress on a fine filament will be greater and the same degree of orientation will be induced in a fine fibre at a lower take-up speed as in coarser fibres. The fine filaments are sensitive to air turbulence in the quenching zone and the yarn guides must be positioned to reduce friction with the yarn and hence breakage. This conventional extrusion process accounts for the bulk of nylon microfibre production and these yarns enhance the properties of normal textile products rather than introducing fibres into totally new products.

The finer microfibres, below 0.4 dtex, extend the applications of textile products into new areas. Conventional extrusion techniques can no longer be used. Extruding a number of fibres together, and allowing them to separate only at a later stage in the production process, protects the fine filaments. There are a number of methods of doing this. In 'islands in the sea', a number of continuous very fine fibres are extruded in a matrix of another polymer. In the spinneret a number of bicomponent sheath–core polymer flows are combined into a single flow and extruded. The 'islands in the sea' fibre is then quenched and drawn in the usual way. After the overall fibre has been processed, the matrix polymer is dissolved away to leave the fine and separate fibres. In one example produced by Fiber

Innovation Technology, 37 fine nylon 6 fibres are extruded in a sea of a polyester copolymer that can be removed by dissolving it in sodium hydroxide after the filaments have been processed into fabric.[130] A further example is Kanebo *Glacem*, which consists of nine segments of nylon separated by a thin layer of a sodium hydroxide soluble polyester in a bicomponent fibre with a circular cross-section. The polyester can be dissolved out after processing, leaving fine nylon filaments. The fibres produced by this method are as fine as 0.18 dtex.[131]

The third method of microfibre production also involves extruding a bicomponent fibre, but in this case two polymers with poor adhesion to each other are used, e.g. nylon and polyester. In one example the cross-sectional configuration is wedge-like and radial, with the V cross-sectional portion the polyester component and the radial portion nylon. The filament is subjected to a chemical treatment in fabric form to swell or expand the nylon component and split the filament. The polyester and nylon components are not causticised. Examples of this type of fibre are Kanebo *Bellima X*, Toray *Ecsaine*, Kuraray *Ranpu* and Teijin *FSY*.[132,133] Applications of these fibres are artificial suedes for clothing and upholstery, wall coverings, automobile trims, golf gloves, etc. A 16-segment fibre of this type is produced by Fibre Innovation Technology from polyester and nylon 6 in two forms: splittable and easy split. The overall shape of the fibre determines the ease of splitting. If the components are in a radial configuration then splitting is more difficult than if one polymer is located at the ends of the lobes in a multilobal shape.[134]

2.6.4 Other modifications

In Sections 2.6.1–2.6.3 a number of ways of modifying nylon fibres have been described and examples of commercial applications given. These have included fibres with non-circular cross-sections, bicomponent fibres, fibres with reduced lustre and transparency and finer fibres. There are some fibres that do not fit into these classifications.

Several producers market antibacterial fibres in which a bacteriostatic agent is incorporated into the polymer prior to extrusion. Examples are Nylstar Meryl *Skinlife*® and Kanebo *Livefresh NEO*®.[135,136] The methods used to achieve the antibacterial effects are a closely guarded commercial secret. However, in the latter example it is stated that the compounds release silver ions throughout the life of the fibre and that the effect is expected to survive 50 washes without yellowing. Commercial antimicrobial additives are available for nylon in a fine particulate form that can be extruded in a nylon polymer. *Irgaguard* B5000® (Ciba Speciality Chemicals) is a silver zeolite that inhibits the growth of bacteria by slow release of silver ions. The suggested addition levels to the fibre are 0.1–1.5 %. Zeolites are crystalline aluminosilicates with a cross-linked framework structure that have good colour retention under sunlight. Another product, *Irgaguard* B7000®, uses fine particles of a silver zinc glass that also releases silver ions slowly. The recommended levels are 0.3–1.5 % on fibre.[137]

Normally in nylon fabrics the priority is to reduce the transparency of garments. There is a small demand for transparent fibre for legwear, underwear and some sportswear. One such fibre is Toray *Miracosmo*®, which is said to be supersheer with exceptional colourability.[138] It has been suggested that the effect can be achieved by adding ethylene bistearamide, ketones containing higher alkyl groups and certain salts such as zinc-*N*-benzoyl-6-aminohexanoate and sodium hypophosphite. Transparency is also enhanced by increases in the polymer molecular mass and any branching of the polymer molecule.[139] The latter effect is likely to be due to a reduction in the crystallinity of the fibres.

The depletion of the ozone layer and increased public awareness of the dangers of skin cancers has led to the marketing of nylon yarns designed to screen the wearer of a garment from the harmful effects of UVA and UVB radiation. Exposure of the skin to UV radiation from sunlight can cause an increase in ageing. In the UK alone there are 40 000 cases of skin cancer each year; some 4500 are malignant melanoma, with 1300 deaths. The fibres giving the greatest protection are extra dull microfibres where the delustrant and the large fibre surface area screen the wearer from the radiation. One example is *Meryl® UV Protection* (Nylstar). A typical fabric of this fibre is said to have a UV protection level (UPF) of 130, meaning that only 0.7 % of incident UV radiation can be transmitted.[140]

There are a number of outdoor fabric applications where a textile material is likely to be continually exposed to sunlight. Examples of these are flags, banners, hot-air balloons, parachutes and life jackets. A major product for these applications is *Solarmax*® (DuPont). The yarns have built-in UV resistance, which suggests that additives are incorporated in the nylon 6,6 polymer. They are available in bright and semi-dull lustres, so possibly the screening effect of titanium dioxide is not essential.[141] Consequently, bright colours are possible. A nylon 6 polymer, *Lumaxx* (BASF), has an inherent stabilising agent, which functions as a radical trap and suppresses essential steps in the autocatalytic degradation scheme, incorporated into the polymer chain. It is available with regular, deep and cationic dye affinities (see Section 2.5.7.4).

2.7 Coloration

Nylon fibres can be coloured either by adding pigments to the polymer before extrusion or by dyeing or printing white fibres in the form of staple fibre, yarn, fabrics or garments and other products. The fibres that are coloured by the addition of pigments prior to extrusion are referred to as mass-dyed, dope-dyed, or solution or producer coloured. The pigments can be inorganic or organic, although inorganic compounds are added more frequently than organic owing to the higher heat stability. Inorganic pigments tend to be used for automotive applications such as upholstery and carpets where a high colour with a good rub and light fastness are fundamental requirements. Organic pigments are limited by the need for stability at the extrusion temperatures. Nylon 6 has a lower melting point than nylon 6,6 and hence more pigments are available for use. Normally the pigments are added in the form of a concentrate dispersed in polymer just before extrusion. The difficulty with the addition of colour at extrusion is that relatively small quantities of a particular colour are often required and there can be considerable wastage because of the production of off-colour material as one shade runs out and the next one comes in. This is minimised by the addition of the colour immediately before extrusion. The most commonly used pigment for nylon is carbon black, which also screens the fibre by preventing light penetration and enhances the resistance to photodegradation.

A number of manufacturers now market yarns for carpets and floor coverings through the bulked continuous filament route as producer or solution dyed. Examples are BASF *Zeftron 2000*®, *Zeftron 2000ZX*® and *Savant*®, and Dupont *Antron*® *Lumena* and *Antron*® *DSDN*. The advantages of producer dyeing are that it is claimed to offer more environmentally friendly coloration and better fastness of the fibres to light. The colour is spread throughout the relatively coarse carpet fibres and is less likely to be changed chemically by sunlight or by cleaning fluids.[142,143]

Colour is normally applied by dyeing or printing late in the sequence of processing operations; this is closest to the end product and has the benefit of giving greatest flexibility. Owing to their chemical and physical structure, nylons have an affinity for every dye class, although the most commonly used are acid, premetallised and disperse dyes. The affinity of acid dyes for nylon depends on the electrostatic attraction between the negatively charged sulphonate groups in the dye and the amine end groups on the fibre that have become positively charged through dyeing under moderately acidic conditions. The relative molecular mass of the polymer is therefore important for the dye affinity of the fibres. The higher the relative molecular mass, the lower the number of amine end groups, but not all of these groups will be accessible to the dye molecules. The amine end groups in the crystalline regions of the fibre are less accessible as acid dye receptor sites. The dye affinity depends therefore on the crystallinity of the fibres and this can be influenced by the rate of cooling of the extruded yarn after extrusion, the draw ratio, exposure to steam, the application of swelling chemicals such as phenol and the texturing conditions. It is critical that packages of continuous filament yarn which are to be made into fabric have a uniform history. Any variation will lead to stripiness in the fabric after dyeing. Drawn nylon 6 has a more open fibre structure than nylon 6,6 and it therefore dyes more rapidly.

The affinity of nylon for acid dyes can also be varied during polymerisation. Adding a monobasic carboxylic acid to the monomers before polymerisation to block some amine end groups gives a light acid dyeable nylon. Equally, deep acid dyeing nylons are produced by incorporating copolymerisable compounds containing tertiary amine groups, such as *N*-(2-aminoethyl) piperazine. This compound is incorporated into the polymer chain by reaction of the primary and secondary amines to form amide groups. These additional basic dye-site groups are not end groups, but are equivalent from the dyeing point of view. It is also possible to increase the acid dyeability by adding a strong monofunctional acid such as phenylphosphinic acid to the polymerisation. The acid, which does not cause degradative reactions, complexes with the amine groups to produce amine salt end groups that do not participate in the amine–carboxyl–amide equilibrium reaction, but are available during dyeing as sites for acid dyes, which displace the strong mono-functional acid from the salt groups.[144] A regular acid-dyeing nylon has 35–45 amine ends expressed as gram-equivalents per 10^6 g of polymer, while the light and deep dyeable varieties have 15–20 and 60–70 amine ends respectively. The use of combinations of nylon yarns having different dyeing properties for dyeing in a single dye bath is of great importance, particularly for carpets, since it offers much greater versatility in colour styling. It is possible to combine yarns with several different levels of acid dye uptake (for example, light normal, deep and ultra-deep) in addition to yarns with cationic dyeability in the same carpet, with obvious savings in processing and stock holding costs.[145]

Acid dyes are divided into three categories depending on their molecular size. Acid levelling dyes have the smallest molecules and are applied under strongly acidic conditions. They have high rates of diffusion and there is little hindrance to the movement of the dye molecules in the fibre structure. The exhaustion rates are high, which can lead to the dye molecules attaching to the most accessible sites and hence poor evenness. In dyeing nylon it is usual to restrict the rate of dyeing initially by using a moderately acidic pH and then lowering the pH as the reaction proceeds. This will then give a level dyeing. Acid levelling dyes give poor washfastness in neutral or alkaline washing; consequently their main use in dyeing nylon is for carpets.

The second category is acid milling dyes, which have a larger molecular size and exhaust onto nylon in the pH range 3.0–5.0. They diffuse into the nylon more slowly and are not as good at covering physical and chemical variations in the fibre, but the washfastness is higher. The usual dyeing technique is to start with the dyebath neutral and then to lower the pH.

The final category is supermilling dyes, which have a high affinity under neutral conditions. These are the acid dyes with the largest molecular size and they are the most sensitive to chemical and physical variations in the fibre. It is most difficult to obtain level dyeing with supermilling dyes on nylons; consequently, anionic auxiliary agents are added to the dyebath to compete with the dye for the active sites on the fibre and aid levelness. These dyes do have excellent fastness and hence it is worth overcoming the difficulties in dye application.

The other class of dye used on nylons are metal complex dyes. These are 1 : 2 complexes between dye molecules and metals such as chromium or cobalt; the metal atom associates with the amine or the carboxyl groups in the nylon. These are large molecules and give excellent wash and light fastness in pale shades. This makes them particularly suitable for coloration of nylon car seat covers. The ability of metal complex dyes to cover affinity differences in the nylon is variable and blocking auxiliaries are normally used during dyeing.

Nylon 6,6 and 6 can be made basic (cationic) dyeable by increasing the level of carboxyl end groups or, more effectively, by incorporating repeating units derived from compounds containing sulphonic acid salt groups. The monosodium and mono-potassium salts of 3,5-dicarboxylbenzenesulphonic acid are particularly useful.[145] A serious problem that is related to the dyeability of nylon is staining, especially of carpets, by strongly coloured materials, natural or artificial, that are present in food and drink such as fruit juices and red wine. These liquids usually contain acid dyes, and are readily absorbed by normal acid-dyeable nylons. In order to minimise stainability, cationic dyeable variants of the type described above can be employed. This variant is particularly useful for mass-pigmented yarns where the coloration process does not require active dye sites. The copolymerised sulphonate units have the further advantage of improving the dispersion of the pigment in the molten nylon, and of making it possible to incorporate photostabiliser systems based on copper compounds without adversely affecting the spinning performance. Some solution dyed (i.e. melt-pigmented) varieties of nylon carpet yarns, such as DuPont *Antron® Lumena Solution Dyed* and *Antron® DSDN*, are cationic and are reported to have better stain resistance than products relying solely on fluorochemical anti staining treatments.

Disperse dyes are insoluble in water and hydrophobic, but readily colour nylon. Their mode of attraction to the fibre is non-ionic and they are relatively insensitive to chemical and physical variations in the nylon and in pH. Small disperse dye molecules with relative molecular mass of around 400 show high rates of diffusion into nylon fibres and have good migration properties. Although disperse dyes are quickly absorbed by nylon at temperatures up to the boil, unfortunately they are also desorbed during washing, leading to poor wash fastness. Washing normally takes place well above the T_g of wet nylon and disperse dyes can migrate freely within the non-crystalline regions of the nylon and desorb into aqueous solutions. Disperse dyes are used on nylon where wash fastness is not critical, for example in the pale shades on stockings and tights. The light fastness of disperse dyes is good and they are therefore used for dyeing nylon carpet yarns.

The dyeing of nylon microfibres differs in some respects from that of fibres of normal linear density. The polymer used in nylon microfibres is usually the same as that employed in conventional fibres and hence the yarns are dyed using similar methods. However, with microfibres there is greater surface reflection arising from the increased surface area. Consequently, dyeings on microfibres will appear visually lighter in shade than identical depth dyeings on conventional linear density fibres. Nylon microfibres may require up to 100 % more dye, depending on the fibre tex and lustre. If dyeings with the same concentration of dye are compared, then the microfibre fabrics will exhibit lower wash fastness because of the greater surface area from which the dye can be desorbed.[146]

2.8 Applications

Nylon 6 and nylon 6,6 are high-cost fibres relative to cotton and polyester. They have, however, been able to resist competition, holding niche markets by exploiting certain characteristics. These are principally their tenacity coupled with suppleness and elasticity.

In the year 2000, approximately 4 million tonnes of nylon were produced in the world; this was approximately 8 % of total fibre production and 13 % of chemical (synthetic and cellulosic) fibre production. In terms of volume of production, nylon ranks third among the major fibres. The total world fibre production in 2000 was 51.6 million tonnes, approximately 8.6 kg of fibres per person of the world's population. Of the world production, 19.2 million tonnes were cotton and 1.3 million tonnes were wool; the remainder was made up of the major synthetic fibres, polyester, acrylic, nylon, and polypropylene and the chemical cellulosic fibres. Over two-thirds of the synthetic fibre produced was polyester. In general, fibre consumption was much higher in the developed countries where the purchasing power of the population is larger and also the need for clothes as a protection against the climatic conditions is greater. World fibre consumption in the long term has tended to grow at a rate of 2.3 % per year, although the rate of growth of production of nylon is rather slower at 1.7 %. If these trends continue, then fibre consumption will reach 63 million tonnes by 2010, while nylon production will be 4.8 million tonnes, approximately 7.5 % of the total. The production of natural fibres was relatively static over the ten-year period 1990–2000 and it seems unlikely that their production can be increased significantly to meet the increased demand. Most of the extra demand will have to be met with synthetic fibres, since the production of cellulosic fibres has been declining and it appears unlikely that this trend will be reversed. Polyester is likely to remain the dominant synthetic fibre in terms of volume of production; if current trends continue, production will reach almost 26 million tonnes by 2010. Associated with the slower growth of nylon, there has been a trend for production to shift from the developed economies of Western Europe, the United States and Japan to the less developed regions. The production of nylon in Western Europe was, at 597 000 tonnes, the same in 1999 as in 1969 in spite of a doubling of world production over the period.

These statistics suggest that the nylon production business is reaching maturity. The expansion of nylon in recent years has been in applications where its intrinsic functional properties are most desirable. Nylon has been quoted as a classic example of how the life-cycle of a maturing business can be extended by using marketing and technical skills to target products for particular sectors of the market and to allow continual growth. A virtually continuous growth pattern in the nylon fibre market since 1938 has been sustained by increasing consumer demand and by the innovative efforts of the fibre producers and their customers, the downstream producers, offering an extensive range of economic technology and products. In the first 25 years of nylon production there were a number of technical, marketing

Table 2.6 Consumption of nylon on major applications (2000)

Application	Consumption ($\times 10^6$ tonnes)	Percentage
Apparel	1.6	39.0
Carpet	1.0	24.4
Industrial	1.0	24.4
Staple	0.5	12.2

and product breakthroughs, which effectively delayed the time of market maturity for nylon. The new end-uses that were introduced in this period included circular knits in 1943; broadwoven fabrics in 1944; tricot warp knits in 1945; carpet staple, automotive upholstery and sheer hosiery in 1947; tyre cord in 1948; textured yarns in 1955, and carpet BCF in 1959. Many of these innovations took a number of years to gain wide acceptance and hence led to steady rather than an explosive growth of nylon production. More recently there has been the development of microfibres, bicomponent fibres and fibres with non-circular cross-sections. A fashion trend for stretch outerwear garments has exploited the characteristics of nylon in combination with elastane fibres such as *Lycra*®, produced by DuPont. These innovations have led to families of fibres marketed for specific end-uses. In the 2000s most of the end-uses for nylon 6 and 6,6, whether filament, tow, staple or flock, fall into three major areas. These are, in descending order of market size, apparel, carpets and industrial. Most manufacturers produce nylon for one or two of these areas; few have the expertise for all of them. The quantities of nylon used worldwide in each of these areas in 2000 are given in Table 2.6.[147]

The available statistics do not reveal the applications for the staple fibre, which for nylon is a small part of the total production. The major uses for the staple are in blends with wool in carpets and in knitwear such as jumpers and socks. The function of the nylon is to improve the resilience and abrasion resistance of the wool in these applications. Some nylon staple is produced for cotton blending, with fibre length and linear density suitable for processing with cotton, and is used in military uniforms, sports and work-wear.

In apparel the basic market for nylon has remained tights, lingerie and swimwear, but changes in fashion and the greater importance of leisure garments have opened new areas for nylon. Combinations of false twist textured nylon with elastane fibres, mainly *Lycra*®, have been used to engineer stretch properties in fabrics. These have in turn also been used in other applications such as leggings, sportswear and skiwear. Manufacturers who previously concentrated on producing fibres of a particular linear density, now have to look seriously at the end products and on the effect the fibre brings to both the fabric and the garment. The aim has been to inspire creativity in design and communicate newness and fashion to consumers. The major technical development of nylon for apparel has come with the use of finer filaments coupled with texturing and non-circular cross-section fibres. The fine filaments of microfibre nylon can be woven or knitted into fabrics with an increased number of small pores that are large enough to allow water vapour out but too small to allow wind and rain in. The ability of nylon fabrics to breathe can be further enhanced by texturing to give yarns more bulk. Variation in the cross-sectional shape of the filaments increases the surface area and allows moisture to pass along the capillaries between them. In its *Tactel®* brand of continuous filament nylon 6,6, DuPont lists no less than 13 sub-brands of fibres for sectors of the apparel market. Some of these exploit developments in fabric rather than fibre technology. For example, *Tactel® Aquator* is a two-sided fabric system designed to move moisture from the skin and allow natural evaporation from the outer layer, which may be of cotton. *Tactel® Diablo*, which has dog-bone shape filaments has been credited with reviving nylon in the lingerie and women's sportswear market by giving fabrics with a softer and silkier handle.[148] Nylstar in its *Meryl®* range has a number of sub-brands, which include *Nateo* for UV protection, *Nexten* with a hollow cross-section, *Satine* with a rectangular section, *Skinlife* which is permanently bacteriostatic and *Souple* which is permanently antistatic.[149]

The carpet application area includes commercial, residential, automotive and rugs. Although some inroads into the market have been made by polypropylene and, at times, polyester, nylon has remained an important fibre owing to its excellent wear resistance, appearance retention and ease of coloration. The other side of the ease of coloration is that it will be more likely to be stained if strongly coloured liquids such as fruit juice or red wine are accidentally spilt on it. One approach, described in Section 2.7, is the production of cationically dyeable yarns. The alternative approach used by a number of manufacturers has been to introduce finishes, usually of a fluorocarbon type, that impart improved soil and stain resistance to nylon carpet fibres. These have been associated with performance guarantees introduced in the mid 1980s for carpets manufactured to agreed specifications. These included DuPont with its *Stainmaster* certification programme, BASF with its *Zeftron* products, and Solutia (formerly Monsanto) has *Stainblocker* with a wear-dated guarantee. These offer guarantees for a designated period for light colourfastness and antistatic resistance as well as against abrasive wear. Nevertheless, polypropylene, with a greater inherent stain resistance and lower cost, has tended to increase market share. In the year 2000 polypropylene had just over 50 % of the market for BCF carpet yarns with nylon 6 and 6,6 supplying most of the rest. Nylon used for the commercial carpet market is now producer dyed, often termed 'solution dyed' although the colour is incorporated into the polymer before extrusion. This gives benefits in terms of stain removal and resistance to cleaning fluids as well as in light fastness. Yarns are available with high, normal and low affinity to acid dyes as well as cationically dyeable. This enables colour effects to be produced in a carpet by dyeing in a single dyebath. In cars, nylon 6,6 is the major fibre used in the carpets. An average new car contains 3.5–4.0 m^2 of carpet weighing, with the backing resin, 5–600 g m^{-2}.

In industrial applications tyre-cord is still the most important single area. Nylon reinforcement cord is used in heavy vehicle and aircraft tyres because of its strength, toughness and excellent adhesion to rubber. The high fatigue resistance, arising from the high elasticity, and the shrinkage force at the rubber-curing temperature and at the operating temperature in a tyre are also important attributes in these end-uses. A related application is the reinforcement of rubber in hoses, drive belts and conveyor belts. Nylon tends not to be used in radial ply automobile tyres owing to flat spotting problems.

It has been a requirement in the USA since 1990 that all new cars must be equipped with automatic crash restraints for the driver and passengers and this led to the adoption of airbags. It has also been a requirement in the European Union since 1994 that new cars are fitted with air bags for drivers. There is now a trend for more airbags to be fitted, giving protection against side impacts as well as head-on crashes. This has created a major development area for nylon industrial fabrics woven from high-tenacity yarns with 35–90 tex and 0.4–0.7 tex/filament in a plain or rip-stop construction. The fabrics need to be heat set and given a neoprene coating to protect them from environmental pollutants and changes in temperature and humidity. The fabrics also need to be flexible enough to fold into a very confined space in the centre of the car steering wheel.

In addition to the automotive uses of tyres, belts and airbags, there are a number of other industrial applications of nylon; these include tough fabrics for soft-sided luggage, coated fabric for truck tarpaulins, webbing, and ropes and twines. High-tenacity nylon is used for climbing ropes because of its relatively high extensibility, which means that a falling climber will be slowed down at an acceptable rate.

The most recent entrant (*c* 1990) to the nylon industrial fibres market is nylon 4,6, which is marketed as *Stanyl*® (DSM). This nylon has a higher melting point than nylon 6,6, at 283 °C, and a higher initial modulus at elevated temperatures. This is said to give it ideal properties for use in the cap ply of tyres and in V-belts.

2.9 Recycling

The recycling of fibres and other textile products to conserve materials and minimise landfill is an important business and technical issue, prompted by increasing concerns about the environment and the use of resources. The materials to be recycled can be divided into pre-consumer and post-consumer waste. The pre-consumer or production nylon waste can normally be recycled by melting and extrusion as reasonable quantities are in one place and are readily identifiable as nylon 6 or 6,6.

Post-consumer textile waste presents more of a problem in that it has to be collected from many different sources and contains a mixture of fibres, often in blends. There are three recycling routes which are feasible for textile waste. These are thermal, mechanical or chemical recycling. Thermal recycling is the combustion of the waste material with recovery of the energy. This is the only feasible route for mixed textile waste, but is also the least satisfactory. It takes the energy from more than 4 tonnes of crude oil to produce a tonne of nylon or polyester. At best, thermal recycling will only recover the energy from 1 tonne of oil. Mechanical recycling involves remelting nylon products into another form, either as fibres or as solid components. It does depend on having a homogeneous material as even a mixture of nylon 6 and 6,6 could give problems.

Much attention in recycling has focused on carpets in that reasonable quantities of nylon fibre are in one place and the old carpet can be collected when a new one is fitted. In a joint venture, DSM and Honeywell (formerly AlliedSignal) have developed a chemical recycling process to produce virgin quality caprolactam from carpet waste. They have set up a production plant that can recycle 90 000 tonnes of carpet waste that would otherwise be destined for landfill. This produces 45 000 tonnes of caprolactam that is equal in quality to virgin material. The facility is claimed to save 700 000 barrels of oil per year and produce the reclaimed monomer at an economic price. A hand-held instrument based on near-infrared spectroscopy rapidly identifies nylon 6 carpets. These carpets are then shredded, the fibres depolymerised by superheated steam and the caprolactam distilled off. The backing and other materials are then incinerated. The recycling of nylon 6 is simpler than for nylon 6,6 as there is only a single monomer to be recovered.[150]

Chemical recycling of nylon 6,6 involving depolymerisation, and isolation of the monomers is possible but is considered to be more expensive and to have less environmental benefit than mechanical recycling because of the additional chemicals and energy needed to reclaim the two monomers. DuPont produces its Antron *Lumena*® solution dyed carpet fibre with a proportion of pre-consumer waste.[151] For post-consumer waste, DuPont has opted to recycle carpets to other products; these include flooring tiles, carpet underlay, soil reinforcement for ‘grass tiles’ (turves) and reinforcing thermoplastic resins in automobile parts.[152] Solutia recycles nylon 6,6 carpets to thermoplastic pellets for moulded automobile parts.

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3

Polyester fibres

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3.1 Introduction

Polyester fibres, and by this we mean largely poly(ethylene terephthalate) (PET) fibres, dominate the world synthetic fibres industry. They constitute, by a considerable margin, the largest volume (≈ 18 million tonnes/yr in 2000) of synthetics and far outweigh nylons, rayon and acrylic fibres.[1] They are inexpensive, easily produced from petrochemical sources, and have a desirable range of physical properties. They are strong, lightweight, easily dyeable and wrinkle-resistant, and have very good wash–wear properties. Their versatility is legendary. Both as continuous filament yarn and staple fibre, they are used in countless varieties, blends and forms of textile apparel fibres, household and furnishing fabrics. They form microfibres for outdoor wear and sportswear. Polyesters are used in carpets, industrial fibres and yarns for tyre cords, car seat belts, filter cloths, tentage fabrics, sailcloth and so on. While the dominant polymer is PET, other polyesters also have their place. Poly(butylene terephthalate) (PBT) and lately poly(trimethylene terephthalate) (PTT) are used in polyester carpet fibre because of their superior fibre resilience. Biodegradable polyesters derived from lactic acid, glycolic acid and other aliphatic hydroxyacids are used in medical appliances (e.g. dissolvable sutures and drug delivery polymer vehicles), as will be seen in due course. The latest innovations are cheap, biodegradable, polylactide fibres made from lactic acid produced by fermentation of cornstarch. This is an essentially ‘green’ chemical process, and the materials are aimed at disposable products that will quickly biodegrade and constitute no threat to the environment.

This chapter cannot hope, in the space available, to cover every aspect of such a large and complex topic. Several excellent publications are recommended at the end of the chapter for general reading and for those who would wish to learn more. The author has taken an historical approach, dealing with the history of the discovery of polyesters and their development as fibrous materials and considering each polymer and its physical properties in chronological order. The chemistries of the production processes for individual polyesters are dealt with in turn. The technology of fibre spinning and subsequent treatments such as dyeing is described in general terms in a separate section. Then follows a discussion of how the chemical properties of the various polyesters affect fibre properties and how these enable each fibre to fit into the appropriate market. Finally, an overview of world fibre demand and the broad economic impact of various polyester fibres and their future is included.

3.2 Brief history of polyesters

Polyesters are, for our purposes, defined as *condensation* (or step-growth) polymers containing in-chain ester units as their essential polymer-forming chain linkage. While it may not be the actual synthetic route followed, polyesters are made, in a formal sense, either by reaction of a dicarboxylic acid with a diol or by the self-condensation of a ω-hydroxy acid. The earliest work on polyesters was done by W. H. Carothers at DuPont in his now-classic studies on condensation polymers in the early 1930s.[2] Nearly all his materials were based upon *aliphatic* constituents. While he succeeded in achieving high molecular weight, crystalline materials, all had low melting points and were easily soluble in chlorinated dry-cleaning solvents. They were thus completely unsuited for textile apparel fibres. For this reason, Carothers turned his attention to the corresponding aliphatic *polyamides*, which were insoluble in such solvents, and this led him to the discovery and commercialisation of *nylon*. In his experimental work, Carothers seems not to have pursued the use of aromatic diacids, apart from *o*-phthalic acid. Other aromatic diacids, such as terephthalic acid, were never examined. One reason may have been that terephthalic acid was, in those days, an obscure chemical entity and its synthesis and purification would not have been trivial. One feasible route available to Carothers would have been the permanganate oxidation of *p*-toluic acid. There is a story, possibly apocryphal, that he had obtained some terephthalic acid of doubtful purity (the free acid is highly insoluble and intractable), but the resulting polyesters were discoloured and of low molecular weight.

It was not until the early days of World War II that J. Rex Whinfield and J. T. Dickson, working at the Calico Printers Association Laboratories in England, synthesised high molecular weight PET from terephthalic acid and its purified dimethyl ester by reaction with ethylene glycol.[3] They showed that the new polymer (shorthand name 2GT) was both melt-stable and colourless and could be melt-spun into fibres having very desirable textile properties. During those difficult days of World War II, circumstances were completely against commercialising a new textile fibre. This development had to wait until peace came in 1945. It was agreed that Imperial Chemical Industries (ICI) in Britain would develop the PET fibre under the trade name *Terylene*®, while in the USA the DuPont Corporation introduced the fibre as *Dacron*®. The two brands of fibre became commercial products in the early 1950s on both sides of the Atlantic and were soon successful. One reason may have been a fortuitous trend in ladies' fashions around that time for accordion-pleated skirts. The excellent pleat-retaining and wash-wear properties of PET staple fibre in blends with wool and cotton were swiftly recognised and exploited. Other manufacturers such as Farbewerke Hoechst in West Germany and Société Rhodiaceta in France took licenses and commercially produced their own PET fibre versions, under their own brand names (*Trevira*® and *Tergal*®). A review of the early development of PET fibres has been published by Brown and Reinhart.[4]

During Whinfield and Dickson's pioneering work, they also synthesised poly(tetramethylene terephthalate) (4GT), poly(trimethylene terephthalate) (3GT) and polyesters derived from 1,2-bis(4-carboxyphenoxy)ethane, known as CPE-acid or 'O-acid'. The first two polymers will be dealt with in due course, but it is worth mentioning that the polyester from O-acid and ethylene glycol (CPE-2G or 'Fibre-O'), while it has never been commercialised, is in many ways an ideal polyester, certainly for industrial fibres. It has many properties superior to those of PET.[5–7] For example, it has twice the tensile modulus of PET, it is easier to melt-polymerise to high molecular weight (since it both polymerises more quickly and has a lower melt viscosity for an equivalent molecular weight), it crystallises faster than PET, and it can be readily melt-spun to fibres whose drawn yarn tenacities are around 11 gm decitex^{-1}. It is more thermally stable and distinctly more hydrolytically stable. As a fibre, it is whiter, more dyeable and more resistant to UV degradation. Its one major weakness is a susceptibility to oxidative degradation at high temperatures, because of ether groups in the acid repeat unit. However, this can be partly overcome by using suitable hindered phenol antioxidants. Many attempts have been made over the years (notably by the Asahi Corporation in Japan) to develop this paragon of polyesters commercially, but none has ever succeeded. The improved properties of 'Fibre O' over PET are simply not commensurate with the high cost of the synthesis of the bis(ether-acid).

Poly(butylene terephthalate) was examined in the early 1950s both in Europe and the USA as a textile fibre. It had many attractive properties compared with PET. It could be melt-spun at lower temperatures; and because it contained a four-carbon diol unit, it did not suffer from vinyl ester end formation on thermal degradation and the subsequent discoloration which results from these ends (see later). Hence it gave inherently whiter fibres than did PET. As a fibre, it was much more elastic and had good resilience and excellent recovery from strain. It dyed very well with disperse dyes at the boil, and did not need to be dyed under pressure, unlike PET. Since it resisted the photo-oxidative yellowing that many polyamides are prone to, it seemed that 4GT might have a bright future. Instead, 4GT never achieved the success of PET in textiles, one reason being the high cost of 1,4-butanediol, which is significantly more expensive than ethylene glycol. Again, PBT did not have the pleat-retaining properties of PET in blends. Where it did succeed was as a polyester carpet fibre,[8] where its resilience and ease of dyeing were assets, although it had to compete against nylon. It also became very successful as an engineering moulding resin (e.g. *Celanex*®) because of its high rate of crystallisation from the melt, an important property in a moulding resin since it allows for short mould-cycle times.

Another of the pioneering polyesters was poly(trimethylene terephthalate), or 3GT. This was recognised very early on as a fibre with outstanding *resilience*. As a newly recruited researcher, fresh out of graduate school, the author recalls his polymer mentor telling him back in the early 1960s that 3GT was in many ways an ideal polymer for textile fibres. It remained ‘on the shelf’ for another 30 years until, since 1990, it has quite suddenly become a commercial product with a bright future, thanks to new and much cheaper routes to the crucial intermediate, 1,3-propanediol. These routes and the chemistry and properties of this novel polyester will be discussed in due course.

In 1958 Eastman Kodak (as it was then) introduced a novel polyester as a staple fibre called *Kodel*. This was the first terephthalate polyester fibre that had not been previously looked at by Whinfield and his collaborators. In order to derive a patent-free composition of matter, a new diol was introduced; a mixture of *cis*- and *trans*-1,4-cyclohexanedimethanol, made by the exhaustive hydrogenation of dimethyl terephthalate.[9] This polyester had a higher T_g than PET and also a higher melting point (which meant it had to be melt-spun at higher temperatures) but it successfully found a market. In recent years, the polyester has been used in polyester carpets and, like PBT, it has been marketed as an engineering thermoplastic moulding resin under the name PCT.[10]

The polyester derived from ethylene glycol and naphthalene-2,6-dicarboxylic acid was first prepared by ICI workers[11] in the late 1940s. It also has a much higher T_g than PET (125 °C) and gives strong fibres with a high modulus, but the inaccessibility of the diacid was an insurmountable problem until comparatively recently. Within the last ten years, firms such as Amoco and Mitsubishi have been able to supply the dimethyl ester of 2,6-NDA on a commercial scale at competitive prices. The diacid is made by the cobalt/manganese-catalysed air-oxidation of 2,6-dimethyl-naphthalene[12] and this is, in turn, synthesised from monocyclic benzene derivatives. A typical dimethylnaphthalene process due to Mitsubishi Gas Chemical Co. reacts toluene with carbon monoxide and 1-butene under strongly acidic conditions, using a hydrogen fluoride/boron trifluoride catalyst, to give *p*-tolyl-*sec*-butyl ketone. This is reduced to the secondary alcohol over copper chromite and the product dehydrated to the corresponding olefin. Finally the olefin is cyclised and dehydrogenated to 2,6-dimethylnaphthalane using proprietary noble metal (Pt, Pd) catalysts.[13–15] Once again, the air oxidation step is complicated by the formation of by-products (such as trimellitic acid and its anhydride) and, exactly as was done in the case of the old dimethyl terephthalate (DMT) process (see Section 3.3.2), it is more convenient to make the dimethyl ester of NDA (DMNDA) and purify this by distillation and recrystallisation.

The polymer with ethylene glycol (PEN) is used increasingly in high-performance polyester films and for high softening-point blow-moulded bottles and containers. It was commercialised in 2002 by Honeywell Performance Fibers (formerly Allied Signal) as a high-performance fibre under the name *Pentex*® for industrial uses such as tyre cord, belting, cordage and high-performance sailcloth; all markets where its high modulus, low stretch and good UV resistance have obvious advantages. The fibre is presently marketed in several gauges from 560 dtex/70 fils to 1670 dtex/210 fils. The quoted tensile properties (tenacity/modulus/elongation) are 8.0 cN dtex^{-1} (9.1 g/den)/220 cN dtex^{-1} (250 g/den)/6%.[16] The UV resistance is due to the naphthalene ring, which absorbs over a wider range of wavelengths than PET. In Japan, stretch blow-moulded PEN containers are used to package vitamins and natural products which would otherwise be adversely affected by UV light.[17] An outstanding copolyester of PEN with 50 moles% of the NDA units replaced with 4,4'-bibenzoic acid (BB) units has been patented by Hoechst Celanese Corporation.[18] This copolymer (PENBB) can be conventionally melt-spun at less than 300 °C to give strong fibres (8.8 cN dtex^{-1}, 10 g/den) with an outstanding modulus (264 cN dtex^{-1}, 300 g/den) without needing a drawing stage, provided that the polymer has a high molecular weight and a high spinning draw-down factor has been used to provide adequate molecular orientation (see Section 3.8.3). In this respect PENBB behaves very much like a thermotropic liquid crystal polymer.[19] It has not yet been commercialised as a high-performance *fibre* but patents on biaxially drawn polyester films of very high stiffness have been published.[20]

Finally we come to biodegradable polyesters. They make up a diverse field but the most well-developed fibre market is in bio-erodible surgical sutures, which slowly dissolve away *in vivo* and do not need subsequent surgical procedures to remove them. Commercial examples were introduced in the early 1970s by firms such as Davis and Geck and the Ethicon Corporation.[21] These sutures are either single-strand monofil fibres or braided multifilaments spun from copolymers of glycolic acid, L-lactic acid (the naturally occurring form) and other synthetic monomers such as caprolactone. Such aliphatic hydroxy acids are completely biocompatible and harmless: in US Food and Drug Administration (FDA) terms, they are materials that are considered to be 'Generally Recognised As Safe' (GRAS). The properties of polyglycolide and stereochemically pure D- or L-polylactide polymers are good. Strong, highly crystalline fibres can be made by melt-spinning. Other biodegradable polyester fibres have been explored. Synthetic lactones such as ε-caprolactone and 2-dioxanone have been copolymerised with glycolide and lactide[22,23]. In the late 1970s, ICI began working on poly(3-hydroxybutyric acid) and later its copolymer with poly(3-hydroxyvaleric acid). Both polyhydroxyacids are stereochemically pure and give crystalline polymers which can be processed into fibres and films. The interesting feature of these polymers is that they are made by a biosynthetic route in very high molecular weight form by bacteria. Suitable strains of bacilli, when starved of nitrogen sources, synthesise large quantities of aliphatic polyesters instead of proteins. ICI (now AstraZeneca) first commercialised *Biopol*®,[24] but its subsequent history has been complex, frustrating and ultimately rather disappointing, as will be seen later. All the polyhydroxyacids are hydrolytically unstable and degrade on exposure to the outdoors or in living systems, but the actual rate of degradation is very much governed by the polymer structure, the ratio of hydrophobic to hydrophilic polymer segments, and the presence of lipases and similar enzymes.

3.3 PET polymer: raw materials, intermediates, polymer synthesis and polymer properties

3.3.1 Terephthalic acid

One of the more extraordinary stories in this study is the way that terephthalic acid (TA) has gone from being an obscure laboratory curiosity in the mid-1930s to one of the largest bulk organic chemicals in the world. We have indeed come a long way from Carothers' day. Since TA is the crucial ingredient in so many polyesters we will discuss its synthesis in some detail. TA is made from the C-8 aromatic distillate fraction isolated in petroleum refining. This fraction consists of ethylbenzene plus the three isomeric xylenes (dimethylbenzenes). The desired product is *p*-xylene, or 1,4-dimethylbenzene.[25] Fortunately, this is the highest melting isomer, and it is possible to isolate it from the mixture by fractional freezing/crystallisation and the residues rich in the unwanted isomers can be re-isomerised by heating with Freidel–Crafts (cationic) catalysts to re-equilibrate the isomer mixture and generate more *p*-xylene. This is the most stable thermodynamic form under such conditions. Another isolation route uses selective adsorption on certain zeolites and a subsequent isomerisation step.[26]

The most important reaction step is the air oxidation of *p*-xylene in an acetic acid solvent, under pressure, with a mixture of transition metal catalysts such as cobalt and manganese acetates, activated by a little bromide anion.[27] The oxidation proceeds smoothly, and the insoluble crude TA can be simply isolated. However, it is still a long way from being a grade suitable for making polymers. The major impurities are *p*-toluic acid (the half-oxidised product) and 4-carboxy-benzaldehyde (4-CBA). The latter is particularly injurious to polymer quality. A simple and elegant process for the removal of both is the 'pure terephthalic acid' or PTA process developed by Amoco. Crude TA (which is highly insoluble in water at atmospheric pressure) is recrystallised from superheated water under high pressure and, at the same time, hydrogenated over a fixed bed noble metal catalyst. All the 4-CBA is hydrogenated to *p*-toluic acid, and this, plus the *p*-toluic acid already present, remains behind in the aqueous liquors since, under such conditions, *p*-toluic acid is much more water-soluble.[28] The resulting PTA, after isolation and drying, is of fibre production quality. It is pure enough to be used directly in the first stage of the polymerisation reaction, in the so-called direct esterification (DE) process. This will be discussed in detail in Section 3.3.4.

3.3.2 Dimethyl terephthalate

Before a satisfactory process for PTA was developed, the basic intermediate for PET was always DMT. In the early days of PET manufacture, *p*-xylene was oxidised with aqueous nitric acid, which gave a product contaminated with many highly undesirable by-products, including nitroaromatic compounds and carbazole derivatives, all of which were harmful to polymer colour and quality. In view of the intractability of TA itself, it was simpler to convert the crude TA into its dimethyl ester by esterification under pressure with methanol and an acid catalyst. DMT is a colourless crystalline solid that can be distilled under high vacuum and recrystallised (under pressure) from methanol. In this manner, very pure DMT could be made and for many years PET was almost universally made via the DMT process. This in turn implied that the polymerisation process was based upon an ester-interchange (EI) reaction between DMT and ethylene glycol. The arrival of PTA at an economic price made the direct reaction of EG and TA possible – and the DE process then took over. DMT is still produced; one reason is the recycling of PET soft-drink bottles, which are made on an enormous scale, particularly in the USA. Some recycling is done via a glycolysis/methanolysis process and DMT is a convenient end-product.[29,30] As we shall see later, DMT is still the preferred starting material for poly(butylene terephthalate).

3.3.3 Ethylene glycol

The other main PET component is ethylene glycol (EG), which was familiar to motorists for many years as antifreeze, although these days EG is being rapidly phased out in favour of the less toxic propylene glycol (PG), following many tragic accidental poisonings of young children (the name ‘glycol’ comes from the Greek *glykos*, meaning ‘sweet’). Ethylene glycol is manufactured on a large scale by a two-stage process from ethylene. The first step is the oxidation of ethylene gas directly with air to ethylene oxide (EO), a process that is operated in many places on an enormous scale. The second step is the ring-opening of EO by reaction with water, thus producing EG.[31] Because of the difficulty of transporting the hazardous chemical ethylene oxide, EG tends to be only one of many EO derivatives, such as glycol ethers and polyethanoxy compounds, all of which are manufactured around one central ethylene oxide facility.

3.3.4 Bishydroxyethyl terephthalate

Bishydroxyethyl terephthalate (BHET) is not a significant article of commerce, yet it is made and consumed on a very large scale as an intermediate in the production of PET. The first stage of any PET polymerisation process can be considered to be the formation of BHET, usually as a complex mixture with various PET oligomers. The second stage of the polymerisation reaction forms PET-high polymer from this BHET–oligomer mixture. (The actual amount of free BHET in the reaction mixture depends greatly on the ratio of ethylene glycol to TA or DMT – for economic reasons this tends to be kept as close to 1 : 1 as possible, thus minimising the level of free BHET.) In a direct esterification process, it is simplest to visualise the process as formally a reaction of PTA with excess EG at elevated temperatures to form BHET, by splitting out water, even though the actual levels of free BHET are low.

$$\begin{aligned}&\mathrm{HOOC{-}C_6H_4{-}COOH + 2HOCH_2CH_2OH} \longrightarrow\\&\mathrm{HOCH_2CH_2OCO{-}C_6H_4{-}COOCH_2CH_2OH + 2H_2O}\end{aligned} \qquad [3.1]$$

Temperature and pH control of this reaction are important because heating EG with acids tends to condense two molecules of EG to give diethylene glycol (DEG), $\mathrm{HOCH_2CH_2{-}O{-}CH_2CH_2OH}$, by dehydrative etherification. This process is analogous to the way diethyl ether can be made from ethanol and sulphuric acid. To minimise this, small amounts of alkali such as sodium hydroxide are added. DEG is formed in other ways and all PET contains unavoidable traces of DEG units in the polymer chain. As BHET forms, so PET oligomers start to form as well and the product mixture (usually misnamed 'monomer') is transferred directly to the polymerisation vessel for the next stage.

In the ester interchange (EI) process, DMT and an excess of glycol are heated together in the presence of various EI catalysts.[32–34]These catalysts are extremely numerous and varied: there are hundreds of patents disclosing new catalyst recipes. Generally speaking they are acetates (or alkoxides) of metallic elements in Groups IIA, IIB, IVA, IVB and VIIB in the Periodic Table. In Pearson's HSAB (Hard and soft acids and bases) terms,[35] they tend to be salts derived from 'hard' bases (e.g. acetate) and 'hard' acids (e.g. $\mathrm{Mn^{2+}}$, $\mathrm{Ti^{4+}}$). The methyl ester groups undergo an exchange reaction with the glycol hydroxyl groups and the much more volatile methanol distils out, via a fractionating column, thus upsetting the equilibrium, and driving the reaction to completion. The product is a mixture of BHET and low molecular weight oligomers. One important process detail concerns the fact that EI catalysts act rather like a two-edged sword.[36] At moderate temperatures (up to 220 °C) they promote ester-bond formation, but in the later stages of polymerisation (up to 290 °C) they can strongly promote thermal ester-bond *breaking* reactions. Thus at the end of the transesterification stage, it is usual to add a sequestering agent such as polyphosphoric acid, triphenyl phosphite or triphenyl phosphate in order to 'kill' the EI catalyst and remove it as insoluble transition metal phosphate salts.[37] The EI process is, in simplified terms:

$$\begin{aligned}&\mathrm{CH_3OCO{-}C_6H_4{-}COOCH_3 + 2HOCH_2CH_2OH} \longrightarrow\\&\mathrm{HOCH_2CH_2OCO{-}C_6H_4{-}COOCH_2CH_2OH\ +\ 2CH_3OH}\uparrow\end{aligned} \qquad [3.2]$$

3.3.5 The melt polymerisation stage

The basic polymerisation reaction, irrespective of how the BHET has been made, is, in reality, another EI process between two molecules of BHET to eliminate one molecule of glycol and to start to build a polyester chain. Short oligomers undergo various EI reactions at their reactive ends to join up into longer chains, and the whole process is a complex equilibrium of forward and backward reactions. As the glycol is removed in high vacuum, the driving force is towards a higher and higher molecular weight. Gradually, the melt grows increasingly viscous; the melt viscosity of fibre-grade PET polymer at 285 °C is of the order of 3000 poise (300 Pa s) under the shear conditions experienced here (roughly 1000 s^{-1}). It is usual to control a batch polymerisation by measuring the power input in watts to the motor driving the agitator paddle. By comparing the rise in differential torque from the starting point against a standardised calibration curve, one may accurately stop the reaction at the desired target molecular weight.

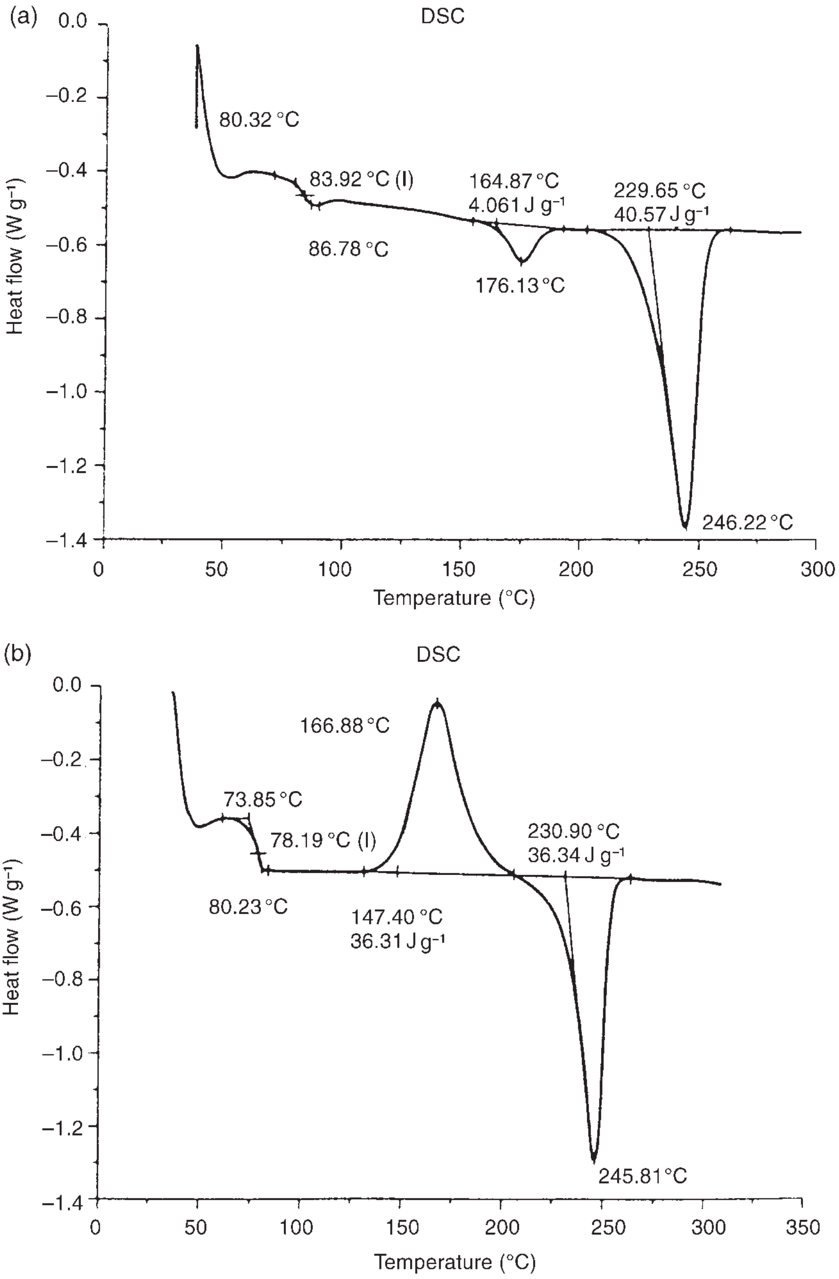
The polymerisation reaction will not work without a catalyst, and the almost universally used PET catalyst hitherto has been antimony trioxide, Sb_2O_3.[38] This functions only at temperatures above 200 °C, so it is conveniently added to the reaction mixture at the esterification stage and remains inactive until the temperature rises during the polymerisation step. The trioxide very probably reacts with the glycol to form various glycoloxides during this process, and it is these compounds that are the true catalysts. Antimony trioxide functions very well but it has one disadvantage: thermal degradation products from the PET act as reducing agents. These in turn reduce the antimony oxides (or glycoloxides) to form metallic antimony in the form of a very fine colloidal suspension in the PET. This causes an unattractive grey discoloration. Since antimony is a toxic heavy metal and large amounts of PET polymer go into bottles for carbonated beverages, some of which are recycled back into fibre, there are worries about the implications of the use of antimony, notably in Germany. (There has never been any evidence of a toxicity problem in normal use.) Alternatives to antimony will not be easy to find for PET: tin and titanium are ruled out because of yellowing. One non-toxic metal that does give a very satisfactory white PET polymer is germanium, in the form of its bis-glycoloxide. However, germanium is an expensive and rare element, and its glycoloxides are volatile. If ever it were to be adopted widely as a catalyst, the world demand for it might easily exceed supply, unless it could be recovered in high yield from recycled PET. A 1989 patent disclosed the use of a titanium/germanium polymerisation catalyst system.[39]

Quite recently (1998) AKZO-Nobel have developed new titanium catalysts based on TiO_2–SiO_2 compositions made by a technique previously well known in the synthesis of specialised *ceramic* metal oxide compositions. This is the controlled co-hydrolysis in an aqueous alcoholic solution of a mixture of titanium (and zirconium) alkoxides, either alone or with lower alkyl silicate esters, to give a mixed inorganic network molecule.[40] The alcohol is a monohydric lower alcohol containing one to six carbon atoms. Normally the TiO_2 prepared for use as a white pigment or delustrant (such as that used in PET apparel fibres) is made by the controlled hydrolysis of acidic derivatives such as titanium tetrachloride, $TiCl_4$. Such materials are not active catalysts, but the oxide networks made as described in the AKZO patents can be very active as polymerisation catalysts. Either TiO_2 alone, or as a mixture with SiO_2 or TiO_2/ZrO_2 compositions can all be used. Not every formulation is active: only certain ranges rich in Ti or Zr are good catalysts. The preferred compositions are effective PET polymerisation catalysts at low levels (10–40 ppm based upon the weight of BHET) and do not give the yellow discoloration in the presence of ethylene glycol and hydroxyethyl chain ends that plain titanium alkoxides, such as titanium tetraisopropoxide, do. This invention constitutes something of a breakthrough in polymerisation catalyst chemistry and no doubt more will be heard about it in the near future.[41,42]

In order to facilitate the polymerisation reaction, it is customary to apply high vacuum at the polymerisation stage to remove the volatile excess glycol. A recent DuPont process eliminates the need for vacuum altogether by using a special advanced agitator design and a brisk stream of inert gas (nitrogen or carbon dioxide) to remove the volatiles.[43–45] When the desired molecular weight is reached, the vacuum is released with inert gas (usually nitrogen), since the melt will rapidly discolour if oxygen is admitted at 290 °C, the bottom valve of the autoclave or resin kettle is opened, and the molten polymer is extruded under inert gas pressure as a ribbon or a bundle of thick strands, either onto an internally cooled roller or else into a long water bath. In either case, the quenched, solidified PET polymer is either ground up or chopped by mechanical knives into short diced lengths. In some cases the molten polymer strands are processed under water in a simultaneous chipping and moulding device which converts the molten polymer into small spherical particles. At this point, a variety of treatments lie ahead. The polymer chips may simply be dried (very thoroughly, down to few ppm of moisture) and taken to storage hoppers ready for melt-spinning. Again, they may be treated further to raise the molecular weight in a solid phase polymerisation (SPP) process.

3.3.6 Solid phase polymerisation

SPP is used when a higher molecular weight is needed than is simply practicable by melt polymerisation. The polymer chips are firstly intensely dried and annealed at a gradually increasing temperature up to the point of maximum crystallisation rate (which is around 160–170 °C for PET) to encourage a high level of polymer chip crystallinity. This process has to be done with some care as the water-quenched polymer chips are almost wholly amorphous and it is most important not to allow them to fuse or sinter together during the annealing step. The reason for this is that once the crystallisation process starts, it is quite exothermic and the chips may locally fuse as a result. The process of SPP is well explained in the



3.1 (a) A typical DSC trace for commercial PET polymer flake; (b) DSC of the same material after quenching from the melt. From *Preparative Methods in Polymer Chemistry*, Sorensen *et al.* ©2001 John Wiley & Sons, reprinted by permission of John Wiley & Sons Inc.

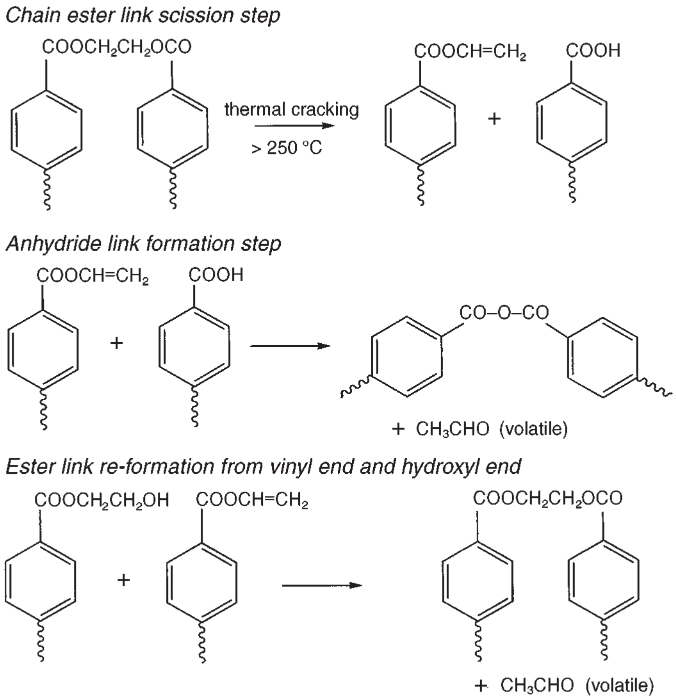
textbook article by Sorensen, Sweeney and Campbell from which the differential scanning calorimetry (DSC) diagrams shown in Fig. 3.1 are taken.[46]

Figure 3.1(a) shows a typical DSC trace for commercial PET polymer flake. The T_g inflexion is at 83.9 °C and there is a weak endotherm due to a phase transition at 176 °C and a T_m at 246 °C. Figure 3.1(b) shows the same polymer after it has been quenched (or rapidly chilled) from the melt. Note that now there is a lower T_g transition at 78.2 °C, a strong crystallization exotherm peaking at 167 °C and a T_m endotherm at 245.8 °C. It is noticeable that the enthalpy of melting has fallen from 40.57 J/g in Fig 3.1(a) to 36.34 J/g in Fig 3.1(b), as a result of the lower order of crystallinity.

Annealing raises the effective softening point by many degrees. The annealed chips are then heated in a stream of hot inert gas or else agitated in a vacuum drier to remove small traces of glycol and other volatiles. Two main types of SPP apparatus are used: either a fluidised bed reactor where the polymer chips are agitated using a brisk flow of nitrogen or another inert gas, or a twin-cone rotary vacuum drier. A system for an integrated annealing and SPP process has been described.[47] One commercial process for making PET bottle resin uses a steady downward plug flow of polymer chips through a tall tower, up which a blast of hot inert gas flows in a countercurrent mode.[48] Because the reaction is done in the solid phase, volatile polymerisation by-products have to diffuse only a short way (typically about 3 mm) to the surface of each of the polymer chips. When they reach the surface they are instantly carried away, either by the gas flow or the high vacuum. The volatiles do not have to form bubbles in a deep, viscous melt and rise to its surface before they can escape. Although solid state diffusion is slower than diffusion through a liquid, the distances involved are much shorter so the overall effect is to raise molecular weight quickly. Since the reaction temperature is below the softening point, the chips do not sinter together and the lower reaction temperature disfavours degradation reactions. All *melt* polymerisations reach an equilibrium state where the chain-forming and chain-breaking reactions balance each other and no net chain growth occurs. Solid-state polymerisation works because it allows chain growth to proceed while minimising chain-breaking, owing to the different kinetics and activation energies of the two different sets of reactions. Usually, melt-polymerised PET has an IV (intrinsic viscosity, a measure of molecular weight) of about 0.67 (for the significance of this, see later). It is quite possible by using the SPP process to raise the IV to 0.80–1.10. High IV polymer is needed for PET soft-drink bottles, which are made by a high-speed, stretch, blow-moulding process that is mechanically very severe. PET bottle resin polymer has IV ~ 0.90. Interestingly, recycled PET bottles are nowadays ground up, dried and melt-spun into polyester yarn for fibrefill or for carpet yarns. One carpet manufacturer at least[49] says that the so-called 'food grade PET polyester', made from recycled beverage bottles, gives a more hard-wearing polyester carpet yarn! A reason could be the higher yarn IV, which would increase fibre toughness and work-to-break parameters (polyester fibres are usually regarded among carpet manufacturers as inferior to nylon for both durability and fibre resilience). When melt-spinning high-tenacity fibres, it may also be necessary to use a SPP polymer with IV > 0.8.

3.3.7 Side reactions and problems with PET melt polymerisation

Nothing in this world is perfect, and melt polymerisation of PET has its share of problems. We have mentioned the fact that chain-breaking reactions occur in addition to chain-forming ones. The degradation of PET is largely a thermal cracking process by which the PET chains break by eliminating a free carboxyl unit, thus leaving a vinyl ester end. The mechanism is generally thought to result from a McLafferty rearrangement, involving a six-membered ring transition state.[50] The vinyl ester end can react with other chain ends to evolve vinyl alcohol in its tautomeric form as acetaldehyde.[36] An acid anhydride link can be formed, at least as a transient species, and acetaldehyde displaced, or the vinyl ester end may react with a hydroxyl chain end to re-form the ester link. Acetaldehyde is always produced during the thermal degradation of PET at over 250 °C. Since melt spinning can take place at up to 300 °C, it will be realised that controlling degradation rates is of great importance in running a robust spinning process. A schematic of the degradation process is shown below:



Vinyl ester ends cause many other problems, too. They act as cross-linkers and gelling agents. They polymerise, and the polymers thermally degrade to give yellow or brown polyenes that discolour the final polymer. It is because vinyl ends form intensely yellow-coloured complexes with metals such as titanium and tetravalent tin that they preclude efficient polymerisation catalysts like titanium tetra-alkoxides or dibutyltin oxide being used in PET polymerisation (see Section 3.3.5).

Another, quite separate, side reaction is the tendency of two hydroxyls from the glycol ends (or BHET ends) to couple by dehydration, forming a diethyleneglycol (DEG) unit in the chain. This does not directly affect the polymer chain length, but it does introduce a 'foreign' DEG unit. This unit reduces crystallinity, and lowers softening point, thermal stability and hydrolytic stability. It is impossible to completely eliminate DEG formation and around 1.0–1.5 mole% is always present. Depression of the polymer melting point (ΔT_m) as measured accurately by Differential Scanning Calorimetry DSC can be used to estimate DEG content. An empirical rule,[51] based on the van't Hoff equation, states that:

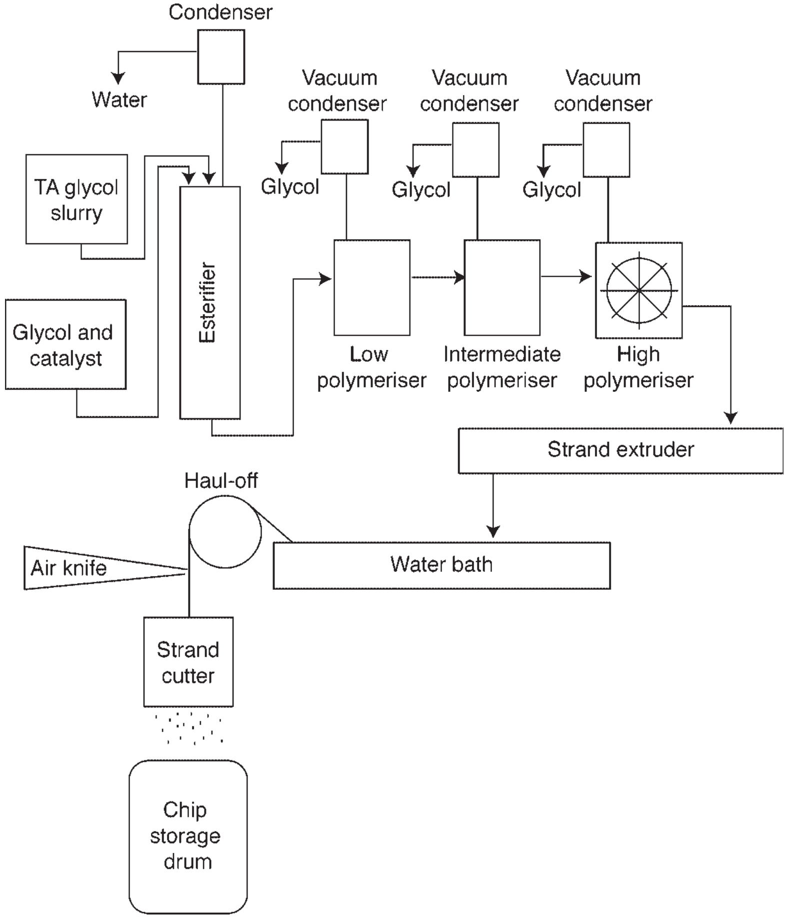
$$\Delta T_m \approx -2.2m\ ^\circ\mathrm{C} \qquad [3.3]$$

where m is the molar percentage concentration of DEG.

The final problem concerns cyclic oligomers. PET forms a stable cyclic trimer with three PET repeat units joined into a macrocyclic ring.[52,53] It can be extracted from PET chip with hot xylene as a well-defined crystalline compound. Whenever the extracted polymer is re-melted, the same level (≈ 1.8 % w/w) of trimer reforms. Any melt-processed PET will always have some cyclic trimer in it. The presence of trimer does little harm to the fibre, but it can be a major nuisance during melt-spinning and fibre dyeing. It exudes to the hot polymer surface and coats spinneret plates on the melt-spinning units. It can even build-up enough to cause breakdown of the molten threadline. During dyeing, it exudes from the fibres (which have a high surface/volume ratio) and, depending on the dyebath temperature, can float in the dyebath liquor, coating the dyeing equipment and generally interfering with the process. Since it cannot be removed permanently, processes have had to be designed to allow for its presence.

3.3.8 Continuous polymerisation

The outline process that was described previously is a batch process and, for large amounts of PET polymer, it would be very uneconomic to make polymer in the volumes needed in this way. Starting around 40 years ago, continuous polymerisation (CP) processes have been developed for PET and have now been brought to a high level of sophistication. Some of the latest CP lines can make as much as 20 tonnes h^{-1} PET polymer. The actual details of the process are quite complex and may also contain highly proprietary information on such things as the specifics of agitator design, so it is only possible to give a broad overall



3.2 Schematic of a typical PET continuous polymerisation unit.

description. Several schematic CP process descriptions and diagrams have been published.[54]

A typical CP train consists of a series of units, each designed to complete one part of the polymerisation process. The first stage is the *esterifier,* where glycol and PTA are reacted in a typical DE process to make BHET mixed with low oligomers. The output is still quite fluid and is pumped to the prepolymeriser or *low polymeriser*. In a large unit, the process may be divided into two stages with a first-stage and an *intermediate polymeriser*. Here vacuum is applied and the increasingly viscous melt is pumped to the finishing stage or *high polymeriser*. The melt is agitated, for example, in a wiped-wall reactor (as shown in Fig. 3.2) so that a continually regenerated thin film of polymer is constantly re-exposed to vacuum, to encourage rapid disengagement of volatiles such as excess glycol and final traces of water.

One of the key design features of any CP plant is to ensure scrupulously that there are no ‘dead spaces’ where stagnant polymer can accumulate and thus become ‘overcooked’, causing it to degrade to a carbonaceous material which contaminates the polymer stream as ’black specks’. The polymer emerging from the finishing stage has by now reached the target molecular weight, which is usually of the order of IV = 0.65. Molten polymer may be pumped directly to a melt-spinning unit in a so-called *CP-spin-draw* unit, which is thus completely integrated. Raw materials go in at one end; and drawn, finished polyester fibre comes out at the other. However, to take account of variations in demand and permit process flexibility, it is more usual to strand or belt cast the molten polymer, and chip and dry it for further processing (e.g. SPP) or hold it in storage until needed. Figure 3.2 shows a strand extruder, with an integrated cutter; the air knife blows off excess water from the wet strands emerging from the water quench bath.

3.3.9 Physical properties of PET

PET is a semicrystalline polymer, and its physical parameters have been repeatedly determined over many years. Table 3.1 gives a summary of the most recent widely accepted values.[55–58]

3.3.9.1 Intrinsic viscosity and molecular weight

The relationship between polymer IV and the molecular weight is given by the well-known Mark–Houwink equation :

$$[\eta] = KM_v\alpha \tag{3.4}$$

where $[\eta]$ is the IV; K, α are constants that depend upon the viscometry solvent; and M_v is the viscosity average molecular weight. Solvents historically used for

Table 3.1 Physical parameters of PET

Crystal habit	Triclinic, one chain per unit cell
Cell parameters	alpha = 100°; beta = 117°; gamma =112°
Cell parameters	$a = 0.444$ nm; $b = 0.591$ nm; $c = 1.067$ nm
Cell density (calculated)	1.52 g cm^{-3}
T_m (DSC)	260–265 °C
ΔH_f	140 J g^{-1}, 33.5 cal g^{-1}
T_g (solid chip, DSC)	78 °C
T_g (drawn fibre, dynamic loss)	120 °C
Specific gravity, undrawn fibre, amorphous	1.33
Specific gravity, crystalline, drawn fibre	1.39

Table 3.2 Mark–Houwink constants for PET

Solvent	K,10^{-4} dL g^{-1}	α
OCP	6.31	0.658
P/TCE	7.44	0.648
HFIP	5.20	0.723
PFP/HFIP	4.50	0.705

OCP = 2-chlorophenol
P/TCE = phenol/1,1,2,2-tetrachlorethane mixture, usually 60/40
HFIP = 1,1,1,3,3,3-hexafluoroisopropanol
PFP = pentafluorophenol

PET have been 2-chlorophenol or a 60/40 w/w mixture of phenol and tetrachlorethane. Neither of these solvent systems is entirely satisfactory, particularly forhigh IV (e.g. SPP) polymers, where it is often necessary to heat the polymer for long times at over 100 °C to dissolve it. The high degree of chip crystallinity (see above) is one reason for this. Unfortunately, under these conditions, polymer degradation due to the acidic nature of the solvents can take place.

Better solvents are hexafluoroisopropanol or a 50/50 v/v mixture of hexafluoroisopropanol (HFIP) and pentafluorophenol. While expensive and highly acidic, they will dissolve even highly crystalline PET at 25 °C with very little chain-breaking, and viscometric results are more likely to be reliable. A list of Mark–Houwink coefficients for all four solvents is included in Table 3.2.[59] Since PET is a typical step-growth polymer, its polydispersity (MW_w/MW_n) is close to the theoretical value of 2.00, but this can change if chain branching agents are incorporated (see Section 3.9.4).

3.4 Cyclohexanedimethanol polyesters

3.4.1 Introduction

The polyester from CHDM and terephthalic acid was originally commercialised by Eastman Kodak in 1958 in the form of a staple fibre.[60] It also achieved success in high-end polyester carpet yarns. The fibre trade name is *Kodel*®. In later years (1968), Eastman began the manufacture of PET fibre under the name *Kodel 400*; the original *Kodel* then became *Kodel 200*. *Kodel* was used in staple fibre-fill applications. Eastman left the staple fibre business in 1993. The main sales volume for their unique polyester today is as moulding resin or extruded sheet plastic called PCT. However, Eastman Chemicals still sells the polymer to fibre spinners for carpet yarn, where its superior resilience and better wear properties compared with PET is appreciated. Eastman still hold all licences for the trade name *Kodel*.[61]

3.4.2 Cyclohexanedimethanol and CHDMT polymers

As noted earlier, an up-to-date review of cyclohexanedimethylene terephthalate (CHDMT) polyesters has been published.[10] However, although it was published back in 1968, the most comprehensive article on CHDMT polyester *fibres*, their physical properties and fibre processing is still that published by Martin and Kibler.[9] Cyclohexanedimethanol is a unique diol that was the basis of Kodel fibre. It is not a single compound but a mixture of *cis* and *trans* isomers. The synthesis starts with dimethyl terephthalate, one of the raw materials for PET, which is hydrogenated in methanol solution over a palladium catalyst to reduce the aromatic ring, giving a 98 % yield of dimethyl cyclohexane-1,4-dicarboxylate (dimethyl hexahydroterephthalate) as a mixture of *cis* and *trans* isomers.[62] This, in a separate stage, is then hydrogenated at very high pressures over a copper chromite catalyst[63] to give a 96 % yield of the diol, which is a 68/32 mixture of *trans* and *cis* forms .The mixture forms a sticky solid with a melting range of 45–50 °C. The pure *cis* diol melts at 43 °C and the pure *trans* diol at 67 °C.

In contrast to PET, the use of CHDM diol does *not* cause the formation of yellow colours with titanium compounds, since on thermal cracking no vinyl esters are formed. Thus it is possible to use highly active titanium tetralkoxides (tetrabutyl or tetra-isopropyl) both as ester interchange and polymerisation catalysts in the polymerisation reaction with DMT. Unlike PET polymerisation, owing to the very high boiling point of CHDMT, it is not necessary to use a large molar excess of diol in the polymerisation reaction – as little as 5 % molar excess will still give a high molecular weight polymer. The final polymerisation temperature under high vacuum is 300–310 °C. The product is a copolyester incorporating both the isomers, but (remarkably) no eutectic effect is seen and no minimum melting point. Both diol isomers can be separated and purified by physical and chemical means and made into the crystalline terephthalate homopolyesters. The pure *cis* polyester melts at 251–256 °C and the pure *trans* at 312–318 °C, the statistical mixture of diols as isolated giving a mixed polymer melting at 290–295 °C. A melting point curve plotted for the terephthalate copolymers varying between 100 % *cis* and 100 % *trans* diol is a monotonically rising curve without any minima. Likewise, the T_g of pure *cis* polyester is 60 °C and the pure *trans* T_g is 90–95 °C, and the copolymer T_g curve rises monotonically over the range.[7]

3.4.3 Physical properties of CHDMT

Both the pure *trans* terephthalate polymer and the pure *cis* form exist in the triclinic crystal system, although in the *cis* form the *c*-axis is much more skewed in relation to the fibre axis. The two sets of parameters are shown in Table 3.3. A copolymer mixture of the two isomers shows a gradual distortion of the *trans* lattice with increasing *cis* content. This explains why there is no minimum melting point in the composition diagram.[64]

Table 3.3 Crystal parameters for CHDMT

Parameter	Pure *trans* polyester	Pure *cis* polyester
a (pm)	63.7	60.2
b (pm)	66.3	60.1
c (pm)	142	137
α (degree)	89.35	89.14
β (degree)	47.11	53.08
γ (degree)	114.36	112.5
Crystal density (g cm^{-3})	1.265	1.303

Physical data such as nuclear magnetic resonance (NMR) suggest that the *trans* CHDM diol units exist in a chair ring form with the two ester links in the di-equatorial conformation. The *cis* form of diol in the chair conformation must have one ester link in an *axial* position. It could also allow the ester units to lie in equatorial positions if we allow a boat form of the cyclohexane ring. Martin has suggested that the *cis* form can undergo ring-inversion relatively easily. Crystallisation of CHDMT is relatively rapid and, because its T_g is higher than that of PET, the maximum crystallisation rate occurs at a higher temperature.

CHDMT polymer has a high melting point, so it has to be melt-spun at temperatures around 305 °C. All aliphatic terephthalate polyesters show signs of thermal cracking above 260 °C. In the case of CHDMT, the β-hydrogen atom in relation to the ester group is also a tertiary one, so that thermal elimination of a carboxyl group leaving a vinylidene-cyclohexane unit would seem mechanistically favoured. This could explain why the polyester from CHDMT and 2,6-NDA (naphthalene dicarboxylic acid) is impossible to melt polymerise, because its T_m is above its decomposition temperature.[65] In the case of CHDMT moulding resins, special stabilisers are added to reduce IV drop at moulding due to thermal degradation. The polymer processing temperature window is relatively narrow. In addition, the melt viscosity of CHDMT polymer at spinning temperatures is higher than that of PET of normal fibre grade IV, which might be expected to cause local degradation due to viscous heating under high shear. As with other crystalline polyesters, such as PET, CHDMT polymers can be readily polymerised to high molecular weight by solid phase polymerisation.

3.4.4 CHDMT: fibre properties and stability

Fibres can be melt-spun as for PET but there are many differences in processing conditions. The spinning temperature is high, at around 300 °C for the usual 70 % *trans* content polymer. It can be shown that for a similar inherent viscosity, the molecular weight for CHDMT is approximately half that of PET. This is probably due to the effect of the bulky CHDM units in the polymer chain. According to Martin and Kibler,[9] the melt viscosities of CHDMT at 295 °C and

PET at 278 °C are very similar for η_{inh} values between 0.4 and 0.8. However, the actual *molecular weight* of the CHDMT is much less than that of PET at the same η_{inh}. This implies that the CHDMT polymer chains must be stiffer than those of PET.

Fibres may be spun and hot drawn and heat set in the 100–200 °C range, but it is not desirable to draw to a low extension (10 % elongation) as this gives a brittle fibre. The best compromise seems to be to draw to about 30 % elongation to give a tenacity of 2.5–3.0 g/denier (2.8–3.3 g $dtex^{-1}$). Yarns of this type have a resilience of about 85–95 % recovery from a 2 % elongation, which explains why CHDMT makes better carpet fibres than does PET. In woven fabrics, the pilling performance of CHDMT is also much better than that of PET, a fact explained by the lower equivalent molecular weight of the CHDMT polymer.

CHDMT fibres are much more resistant to hydrolysis than PET under similar conditions The bulky groups surrounding the CHDM ester links presumably hinder attack by water molecules as well as the whole polymer being more hydrophobic than PET. On the other hand, oxidative stability at 200 °C in air is markedly inferior to PET, the problem being the oxidatively vulnerable tertiary hydrogen atoms in the CHDM units, which have already been mentioned. It is for this reason that antioxidants have to be added to PCT moulding resins.

3.4.5 CHDMT as a textile fibre

As can be seen from Tables 3.1 and 3.3, the densities of CHDMT fibres are less than those of PET so it should have a better coverage power per unit weight of fabric. The dyeability of CHDMT fibres with disperse dyes is much easier than for PET. Medium shades can be obtained at the boil and only deep shades need the use of a carrier; even then, a mild carrier, such as butyl benzoate, is sufficient. Pressure dyeing above the T_g gives deep shades as would be expected. The reason for the comparative ease of disperse dyeing compared with PET may be because the chain structure, even when well crystallised, has more internal free volume than that of PET owing to the bulky *trans* cyclohexane rings. The dyeing and finishing of CHDMT fibres were described in detail by Forrester[66] and Ivey.[67] *Kodel 200* CHDMT staple fibres were used in blends with wool and cotton and gave good results according to Forrester. However, in later years the two main uses of CHDMT fibres have been fibrefill for pillows, sleeping bags, duvets and cushions and as a bulked polyester carpet yarn. In both these cases the superior resilience over PET is the main advantage. Evidence that this resilience is due to the presence of the cyclohexanedimethanol structure comes from a 1968 DuPont patent (US Patent 3 418 276) due to E. F. Izard where polyesterether analogues of ‘Fiber-O’ (see Section 3.2, p. 97) were made using the bis(*p*-carboxyphenyl) ether of CHDM. Polyesters made from this somewhat complex diacid and ethylene glycol were found to have a superior tensile strain recovery compared with a normal PETcontrol. For carpet yarns, the ability to be dyed readily is a very favourable property. As mentioned earlier, while CHDMT polymer is largely manufactured nowadays as a moulding resin, there remains a demand for fibrefill and carpet yarn. How this demand will survive competition with newer fibres such as PTT in the same markets remains to be seen.

3.5 Poly(butylene terephthalate) (PBT)

3.5.1 Introduction

A more accurate name for this polymer would be *poly(tetramethylene terephthalate)*, but ‘PBT’ is a well-established acronym in the engineering moulding resins business. It is another of the fibre-forming polyesters that dates back to Whinfield and Dickson’s time in 1941. Its history has been one of ups and downs: originally developed as a textile fibre, it later became much more important as a highly crystallisable injection moulding polymer and an engineering resin. Nevertheless it maintains a fibre presence in the market, chiefly as bulked continuous filament (BCF) carpet fibre, where its resilience is important.[68]

3.5.2 Butane-1,4-diol

An essential raw material for PBT is butane-diol. It is still made commercially by a process dating back to the days of W. J. Reppe at I G Farbenindustrie in pre-World War II Germany. Butane-1,4-diol was used in I G’s melt-spun polyurethane fibre called *Perlon-U*. In the Reppe process, one mole of acetylene reacts with two moles of formaldehyde to give 2-butyne-1,4-diol ($HOCH_2–C\equiv C–CH_2–OH$). This is then hydrogenated to butane-1,4-diol. While simple in principle, there are many operational subtleties involved in running a commercially successful process. The catalyst for the formaldehyde reaction is a bismuth/cuprous acetylide mixture[69] and the hydrogenation step is best done in two separate stages with different catalysts, going via 2-butene-1,4-diol, rather than proceeding directly to the end product in a one-shot reaction.[70]

A different route has been commercialised by ARCO[71] based on the hydroformylation of allyl alcohol over a rhodium catalyst to give 4-hydroxybutanal, $HOCH_2CH_2CH_2CHO$. This is reduced to butanediol, but the process has to be carefully controlled to prevent side-reactions.[72] Allyl alcohol can be made by rearrangement of propylene oxide, which is now made on a large scale by direct oxidation of propylene. A third butanediol route has been piloted by Mitsubishi Chemical Industries,[73] who react butadiene with acetic acid and oxygen over a palladium catalyst to form 1,4-diacetoxy-but-2-ene. This diester is hydrogenated[74] and subsequently saponified to the desired butanediol. The latter, incidentally, melts at 20 °C when pure, so due precautions must be taken to steam heat trace and insulate all bulk storage and shipping facilities outside to prevent the product freezing in cold weather.

3.5.3 Manufacture of PBT

PBT is traditionally made using the ester interchange (EI) route from DMT, because heating TA directly with butanediol causes loss of the diol by formation of the very volatile tetrahydrofuran (THF). Both batch and continuous polymerisation processes[75–77] are used. Because no vinyl ester ends are formed, titanium catalysts can be used both for EI and polymerisation. The final reaction temperature is around 250–260 °C, so thermal degradation of PBT is reduced and generally higher molecular weight polymers can be obtained by melt polymerisation than for PET. The PBT polymerisations are 'cleaner' than PET ones because the major thermal degradation product is THF, which simply volatilises away. No colour-forming reactions are present, although severe loss of THF can upset the reaction stoichiometry. Melt polymerisation of PBT gives a very white polymer. As with PET, cyclic oligomers are formed in PBT polymer to about the same level, 1.4–1.8 % w/w. However, in this case, the oligomers are an equal mixture of dimer and trimer,[78] together with tiny amounts of higher cyclic oligomers.

PBT Polymerisation:

$$n\,\mathrm{CH_3OCO{-}C_6H_4{-}COOCH_3} + (n+1)\,\mathrm{HO{-}(CH_2)_4{-}OH} \longrightarrow$$
$$[\mathrm{{-}O{-}(CH_2)_4{-}OCO{-}C_6H_4{-}CO{-}}]_n + 2n\mathrm{CH_3OH} \qquad [3.5]$$

Formation of THF from a 4-hydroxybutyl ester end:

$$\mathrm{Ar{-}CO{-}O{-}CH_2CH_2CH_2CH_2{-}OH} \longrightarrow \mathrm{Ar{-}CO{-}OH} + \text{tetrahydrofuran} \qquad [3.6]$$

3.5.4 Physical properties of PBT

Unlike PET, PBT exists in two polymorphs, an α-form and a β-form, which are interconvertible with mechanical stress.[57,79,80] Both systems are triclinic and the cell parameters are shown in Table 3.4 The melting point of PBT is 222–224 °C (depending on degree of crystallinity), with a heat of fusion (ΔH_f) of 140 J g^{-1}.[81] Its T_g is usually quoted[82] as 45 °C. The annealed (highly crystalline) polymer density is about 1.33 g cm^{-3}, while the amorphous polymer has a density[83] of 1.26 g cm^{-3}. The relaxed α-form of the polymer is believed to have the three C–C bonds in the C_4 glycol unit arranged in a *trans–gauche–trans* conformation, while the stretched β-form has an all-*trans* arrangement of the same three bonds.[84]

3.5.5 Polymer molecular weight

PBT is usually made to a number average molecular weight value of 20 000–50 000 daltons. Polymer IV is measured in 2-chlorophenol (OCP) or phenol/tetrachlorethane and the Mark–Houwink parameters [85,86] are shown in Table 3.5.

Table 3.4 Crystal parameters for PBT

Cell parameter	α-form (unstretched)	β-form (stretched)
a (nm)	0.482	0.469
b (nm)	0.593	0.580
c (nm)	1.174 (1.165)*	1.300
α (degree)	100 (98.9)*	102
β (degree)	115.5 (116.6)*	120.5
γ (degree)	111	105
Cell density (g cm^{-3})	1.41	1.37

*These results by I. M. Ward and co-workers.[80]

Table 3.5 Mark–Houwink constants for PBT

Parameter	*K* (dL g^{-1})	α
OCP solvent (25 °C)	6.62×10^{-5}	0.915
P/TCE solvent (30 °C)	1.17×10^{-4}	0.870

3.5.6 Melt-spinning and drawing PBT fibres

The spinning parameters for PBT fibre are similar for those for PTT, which will be described in more detail shortly. Both polymers are melt-spun around 250 °C. Drawing is done in a conventional manner and to avoid repetition, no more need be said about PBT processing. Where yarn properties differ markedly from PTT, it will be pointed out.

3.6 Poly(trimethylene terephthalate) (PTT or PPT)

3.6.1 Introduction

An excellent comprehensive review of poly(trimethylene terephthalate) and its chemistry and fibre processing has recently been published[87] by Chuah. Historically, Whinfield and Dickson in 1941 discovered poly(trimethylene terephthalate) along with PET and PBT and it is disclosed in their original patent.[3] The material was recognised for many years by textile chemists as a fibre-forming polymer affording fibres that had excellent physical properties and outstanding resilience. The lack of an economic source of pure 1,3-propanediol (PDO) was an insuperable obstacle for many years, but recently the situation has changed entirely and 3GT fibres are now a commercial fact.

There seems to be a little confusion on an acronym for this polyester. Shell prefers to use the term PTT (poly(trimethylene terephthalate)) but DuPont and some earlier trade literature sources call it PPT (poly(propylene terephthalate)). The latter is, strictly speaking, a misnomer, since the term ‘propylene glycol’ is conventionally applied to 1,2-propanediol. We shall use the Shell nomenclature henceforth and call the polymer PTT, to avoid any possible ambiguity. Furthermore, this acronym emphasises the essential *three-carbon* glycol unit.

3.6.2 Synthesis of PDO and the manufacture of PTT

3.6.2.1 PDO synthesis

Introduction

There are three main routes to PDO: two synthetic and one based on a biochemical (fermentation) route. A detailed report on the economic prospects for both PDO and PTT polymer was completed in 1999.[88] Degussa and Shell first developed the completely synthetic methods, which have now become commercially viable.

The Degussa process

Degussa uses the older process, the addition of water under pressure to acrolein, using an acidic ion exchange resin to give 3-hydroxy-propanal.[89]

$$CH_2{=}CH{-}CHO + H_2O \longrightarrow HOCH_2CH_2CHO \qquad [3.7]$$

The hydroxyaldehyde is not isolated as such but is hydrogenated in aqueous solution over a Raney nickel catalyst, promoted with other trace metals such as platinum.[90] The starting material, acrolein, has been manufactured by Degussa since the late 1930s, originally by vapour-phase condensation of acetaldehyde with formaldehyde. A later (1959) process makes acrolein by the vapour-phase oxidation of propylene.[91] One problem with the Degussa acrolein hydration reaction is the unavoidable presence of acrolein dimer (2-formyl-2,3-dihydropyran) which reacts with the PDO to form adducts and hemiacetals that are immiscible with PDO and cause turbidity. A method of treating the crude PDO by solvent extraction with cyclohexane to remove these impurities has been disclosed.[92]

The Shell hydroformylation process

The more recently introduced Shell process uses the hydroformylation reaction (carbon monoxide plus hydrogen) of ethylene oxide to give 3-hydroxypropanal, using synthesis gas and a transition metal catalyst. The aldehyde is then reduced to propane-1,3-diol. One of the first patented processes was by Beavers (Eastman Kodak) who used a rhodium or ruthenium catalyst.[93] Shell improved upon the earlier work by using a cobalt catalyst and there has been much patent activity lately concerned with improved hydroformylation catalysts and reaction conditions.[94–97] The hydrogenation of 3-hydroxy-propanal to PDO has also been improved with better catalysts and reaction conditions. Haas and co-workers[98] use a platinum or ruthenium catalyst, while Shell workers disclose nickel–molybdenum.[99] Further improvements result from purifying the crude hydroxy-aldehyde in aqueous solution over active carbon or silica before the hydrogenation step.[100,101]

The first commercial PDO plant using the Shell technology was actually opened in 2000 in Geismar, Louisiana. In 2003 it was announced[101a] that it would be uprated to supply propane-1,3-diol to a new 50/50 venture formed between Shell and the Société Générale de Financement du Quebec called PTT Poly Canada who are building a 95,000 tonne/year PTT polymer plant in Montreal, Quebec.[101b]

The modified Shell process

A somewhat different process has been described in a 2001 Shell patent[102] where the starting material is essentially methyl 3-hydroxypropionate (methyl hydracrylate) rather than 3-hydroxypropanal. The ester is made by reacting ethylene oxide with carbon monoxide and methanol in the presence of a dicobalt octacarbonyl catalyst (methoxycarbonylation reaction). The hydroxy-ester is hydrogenated, without isolation, using a copper–zinc oxide catalyst. Greater process efficiency is claimed, because the methyl ester cannot react with itself (as does 3-hydroxypropanal) to form acetals and hemiacetals. These reduce the yield and contaminate the final product.

The DuPont fermentation process

DuPont has taken a bold and original step for its source of PDO. As an interim measure it either purchased PDO from Degussa or licensed the Degussa process while their fermentation route was under development.

The DuPont process, which is still being perfected, is a modified enzymatic fermentation route using corn sugars (largely glucose) as feedstock to give PDO directly.[103,104] This is an ambitious, large-scale application of 'green chemistry'. One of their collaborators is Tate & Lyle, the well-known UK-based sugar exporting firm. Yeast converts sugars into the phosphate ester of dihydroxyacetone ($HOCH_2COCH_2OH$) and thence to glycerol. It has been known for many years that certain bacteria can perform (in effect) the reduction of glycerol to PDO under anaerobic conditions. The difficulty has been running a commercially viable high-yield fermentation process without the bacteria being adversely affected by the toxicity of high levels of PDO. There is much patent activity in this area. An early example by Unilever uses *Citrobacter* in an anaerobic fermentation of glycerol to

PDO.[105] Another patent specifies the use of *Clostridium butyricum* as a more tolerant micro-organism for the fermentation.[106] In collaboration with Genencor International, DuPont began using genetic engineering to produce novel strains of the bacterium *Escherichia coli,* which was genetically modified to contain genes from baker's yeast (*Saccharomyces cerevisiae*) and the bacterium *Klebsiella pneumoniae,* which give improved fermentation conversions. Genetically engineered bacteria with inserted genes for a diol dehydratase enzyme were claimed[107,108] and modified *Klebsiella pneumoniæ.*[109] A recent patent[110] claims a micro-organism that will operate at PDO levels of 105 g L^{-1}.

Isolation of the final propane-1,3-diol from the fermentation broth mixture usually involves either solvent extraction or distillation. Several routes with a lower energy consumption have been patented. One method due to Archer Daniels Midland Co, uses ion exclusion resins to separate the product from the broth impurities.[111] A recent DuPont patent claims the use of molecular sieves.[112] Recently, in June 2003, DuPont was awarded a Presidential Green Chemistry Challenge Award[113] for this PDO biosynthetic process. In May 2004 Tate & Lyle plc and DuPont announced the formation of a new joint US venture called Dupont Tate & Lyle BioProducts LLC to manufacture industrial chemicals and intermediates from renewable resources such as corn (maize) rather than petroleum. PDO would be one of the first products, using the new bio-based process. The plant will be built at Loudon, Tennessee, and will be completed by the end of March, 2006.[113a]

3.6.2.2 The PTT polymerisation process

PTT is polymerised in a unique way that differs significantly from both PET and PBT processes.[87] Either PTA or DMT can be used as a starting material, but Shell prefers to use the less-expensive direct esterification route based upon PTA. In this respect, the process is like that for PET. However, unlike PET, more active catalysts such as $Ti^{(IV)}$ or $Sn^{(IV)}$ can be used as polymerisation catalysts.[114–6] As with PBT, yellowing is not a serious problem with such catalysts because of the absence of vinyl ester ends. The unusual feature of the reaction is that it is carried out semi-batchwise ('batch-on-batch'), using a 'heel' of low molecular weight polymer and oligomers left behind from the previous batch as a reaction medium for the next. This is because TA is insoluble in hot PDO, so the uncatalysed direct esterification step is run at 250–270 °C under pressure. PDO itself boils at 214 °C. When esterification is complete, the mixture of oligomers is partially transferred to a polymerisation vessel, leaving the 'heel' behind for the next esterification batch. The tin or titanium catalyst is then added and the final polymerisation is run under vacuum at 260–270 °C. The final melt polymer IV is 0.70–1.00. For IVs exceeding 1.0, polymer chips can be annealed and crystallised at 180–210 °C and solid phase polymerised at 180–210 °C in a current of inert gas such as nitrogen or argon.

DuPont used a continuous polymerisation process[117] at its facility in Kingston, North Carolina.

As is usual in melt polymerisations, there are side reactions. Two harmful degradation products can result from the usual McLafferty rearrangement and pyrolysis of the PTT ester links, analogous to the degradation of PET.[118] The products are allyl alcohol and its oxidation product acrolein. Both are toxic and irritant, acrolein being particularly unpleasant and lachrymatory. Addition of triaryl phosphites and hindered phenol antioxidants is claimed[119] to minimise the formation of acrolein. Special precautions have to be taken to dispose of the vapours of such by-products during polymer processing. Again, PTT forms cyclic oligomers: in this case it is the dimer, which can be isolated in the pure state as a crystalline solid, mp 254 °C. Exactly as with PET, ether-link formation takes place by dehydration of 3-hydroxypropyl ester ends, and this causes the formation of bis(3-oxypropyl)ether links in the main chain, which lower polymer T_m.

3.6.3 Physical properties of PTT

PTT has a particularly interesting crystal structure. Once again the crystal system is triclinic, but along the *c*-axis, two polymer chains lie with the glycol units twisted into *gauche–gauche* conformations so that the chains form tight zigzags as seen in the *ac* and *bc* planes. Crystal parameters[120–122] are given in Table 3.6. PTT has $T_m = 228$ °C; $\Delta H_f = 30$ kJ mole repeat unit (146 J g^{-1}); $T_g = 45$ °C; cold crystallisation temperature = 68 °C.[123–126]

3.6.4 Polymer molecular weight

PTT crystallises very much faster then PET, although not quite as fast as PBT. This means that the quenched polymer chips are highly crystalline and do not dissolve at all easily in the usual polyester solvents. As a result, Shell uses HFIP at room temperature as a viscometry solvent. A phenol–tetrachlorethane (P/TCE) mixture can be used but the temperature has to be carefully raised to 110 °C to ensure complete dissolution. Mark–Houwink constants[127–128] are shown in Table 3.7.

Table 3.6 Crystal parameters for PTT

Parameter	Value
a (nm)	0.459
b (nm)	0.621
c (nm)	1.831
α (degree)	98
β (degree)	90
γ (degree)	112
Crystal density (g cm^{-3})	1.441 (calc)

Table 3.7 Mark–Houwink constants for PTT

Solvent	Temperature (°C)	K: 10^4 dL g^{-1}	α
HFIP	35	5.51	0.71
50/50 P/TCE	30	8.2	0.63
60/40 P/TCE	20	5.36	0.69

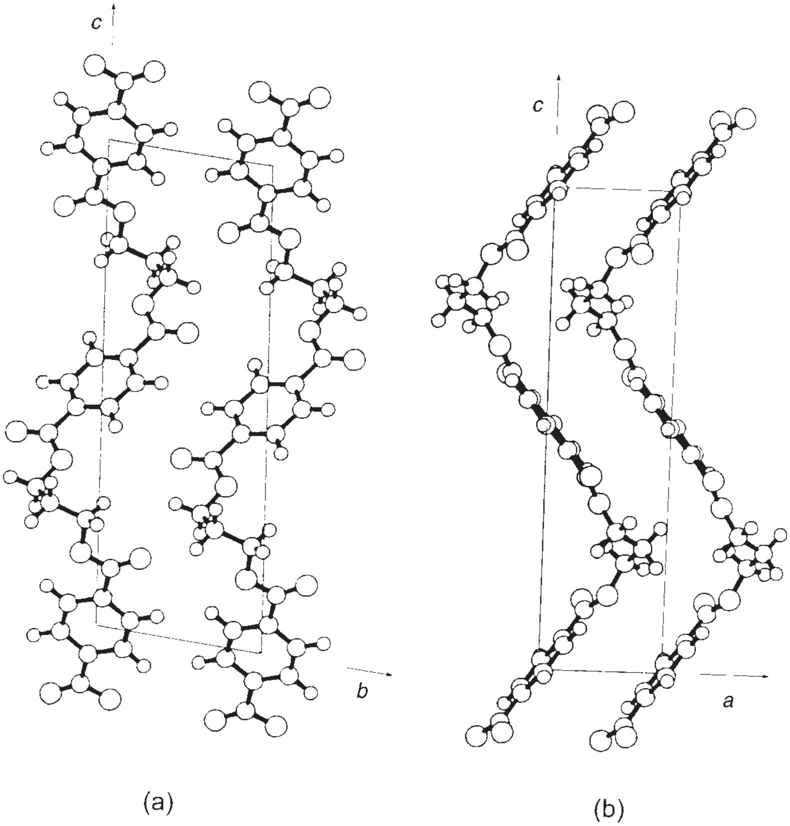
3.6.5 PTT resilience

Of the three major polyester fibres (PET, PBT and PTT), PTT has by far the best resilience, that is, the best elastic recovery from deformations.[129] According to DuPont information[130] on the PTT fibre *Sorona*®, PTT flat yarn recovers 100% from elongations as high as 120%. It is vastly superior to PET and two or three times better than nylon 6,6 in this respect. PBT fibre, by comparison, recovers 100% from elongations of about 112%. Resilience is a valuable property in both textiles and carpet fibres. It is known that in the very early days of PET fibre, fine denier polyester filament yarns were experimentally made into ladies' hose to compete with nylon 6,6. The results were disastrous, because PET has poor elastic recovery properties from the elongations met with in hosiery, the result being that the hose quickly went 'baggy' around the wearer's knees! Had PTT been available, the polyester hosiery story might have been very different. Again, from DuPont information, PTT gives extremely high fibre bulk in conventional draw texturing processes and thus yields superior covering power for the same weight of fibre.

The excellent recovery properties of PTT are due to its crystal structure. It has a very low crystal modulus[131] (2.59 GPa, 550 psi) and the zigzag structures (see Fig. 3.3) give a tightly wound helical structure to the polymer chains so that they can be imagined as behaving like coil springs on elongation. This is a naïve explanation, but it is approximately true and easily understood. It is the double-*gauche* conformation of the two C–C bonds in the trimethylene chain that allows this structure to form. By contrast, PET is more like a fully extended chain and its crystal modulus[132] is much higher (107 GPa, 1.55×10^5 psi). PBT is an intermediate case: it is more elastic than PET because the four-carbon chains are not fully extended and likewise contain *gauche* conformations.

3.6.6 Melt-spinning and processing PTT fibres

According to Chuah[87] the PTT polymer for melt spinning has an IV in the range 0.80–0.92 ($M_n \approx 16\,000–20\,000$). Melt-spinning is carried out in a conventional way at an extrusion temperature in the range 250–265 °C. The polymer chip must be dried at 130 °C to a moisture content below 30 ppm. PTT crystallises readily, so there is no need to anneal or pre-crystallise the polymer to prevent chip-sintering during drying, which is a potential problem with PET. The rheological profile of



(a) (b)

3.3 (a and b) X-ray study of a PTT polymer crystal structure. Reprinted from *Polymer*, **20**, Desborough I. J., Hall I. H. and Neisser J. Z., '3GT', p. 545, 1979, with permission from Elsevier.

0.92 IV PTT at 265 °C under the shear rates typical for melt spinning (10^3–10^4 s^{-1}) is very close to that of 'normal' IV (0.67) PET at 290 °C. However, shear thinning is present to a greater extent.

The Shell polymer is spun into partially oriented (POY) filament yarn, into bulked continuous filament for carpet fibre[133] and into staple fibre, all under the brand name *Corterra* ®. PTT fibre is much softer and has a better drape than normal PET fibre in apparel end-uses. It is very suitable for false-twist draw texturing[134] and staple fibres make non-woven fabrics of exceptional softness.[135] With a low T_g (45 °C) deep shade carrierless dyeing is possible at the boil with disperse dyes.[136]

3.7 Biodegradable polyester fibres

3.7.1 Introduction

Polyesters from hydroxyacetic acid (glycolic acid) were investigated early in the 20th century but their great ease of hydrolysis made them unsuitable for use as

Table 3.8 Biodegradable polyester properties (homopolymers)

Polymer	T_m and T_g (°C)	Modulus (GPa)	Degradation time (months)
Polyglycolide	T_m 225–230; T_g 35–40	7.0	6–12
Poly-L-lactide	T_m 173–8; T_g 60–65	2.7	Over 24
Poly-DL-lactide	Amorphous; T_g 55–60	1.9	12–16
Polycaprolactone	T_m 58–63; T_g –65	0.4	Over 24
Polydioxanone	Depolymerises: T_g –10	1.5	6–12

textiles and industrial yarns and work was soon abandoned. Very much later, in the 1960s, it was realised that this apparent weakness could be exploited as a useful property in what later became a rapidly growing specialised area, that of biomedical polymers. A very good review article on the topic of synthetic biodegradable polymers as medical devices has been published in recent years by Middleton and Tipton.[137] A more general review article on environmentally degradable polymers, which includes references to polylactide, polyglycolide, etc. has been recently published,[138] together with a third article specifically concerning biomedical polymers.[139]

The earliest market opportunity was dissolvable sutures, which need no further surgical intervention to remove them. Suture materials have quite strict technical requirements if they are to be safely and effectively used. These are listed below:

1. The polymer must maintain strength long enough to allow the tissues to heal.
2. The polymer must not be too strong or it may simply tear the tissue: its strength has to be compatible with the end-use.
3. The material must not produce an inflammatory or toxic reaction.
4. The material should be metabolised completely, leaving no trace, and it must produce only harmless metabolites.
5. It should be easily processable into sutures.
6. It should have a long shelf-life.
7. It must be able to be undergo sterilisation regimes without degradation.

The earliest biomaterials were all polyesters but, since then, other useful polymers have been developed, particularly in the area of controlled drug release. However these do not concern us here. A summary of the main monomers and the properties of their homopolymers is set out in Table 3.8. Degradation times are usually measured under simulated ‘physiological conditions’, i.e. pH 7.4 with a phosphate buffer at 37 °C.

3.7.2 Polyglycolide (PGA)

The polyester from self-condensation of hydroxyacetic acid is usually called polyglycolide after its dimeric lactone, glycolide. Polymerisation is usually done by a ring-opening polymerisation (ROP) of the lactone,[140] often with a Sn(II) salt such as stannous octoate. PGA is a highly crystalline polymer that melts at 225–230 °C and has a T_g of 35–40 °C. It is a strong stiff polymer with a modulus of about 7.0 GPa. PGA was first commercialised as a suture material under the name Dexon® in the late 1960s by Davis & Geck (Sherwood-Davis & Geck since 1995). Because of its high level of crystallinity, it is insoluble in common polyester solvents, except acidic ones such as hexafluoroisopropanol. It loses about 50 % of its initial strength in 2 weeks and 100 % in 4 weeks but takes 4–6 months to vanish completely. PGA is too stiff to make monofil sutures; instead, braided sutures made of finer denier multifilaments are used to make them more flexible. A bioerodible ABA tri-block copolyesterether with a PEG block capped at both ends by PGA segments has been found to give a much more flexible monofil.[141]

3.7.3 Polylactide (PLA)

Polylactide is derived from the dimeric lactone of lactic acid (lactide), and this can exist in D, L, racemic (DL) and *meso* forms. The naturally occurring variety is the L-form. The racemic form is a synthetic mixture of D and L-lactides, while the meso form is made up of one molecule of D and one of L in a cyclic dimer. Only the stereochemically pure forms give highly crystalline polyesters. They have structures analogous to isotactic polypropylene. Poly(DL)-lactide is amorphous and is much more easily degraded, which makes it more attractive in drug-delivery systems. Pure poly-L-lactide is about 37 % crystalline and melts at 175–178 °C. It degrades much more slowly than the amorphous form and can take up to 2 years to disappear completely. Copolymers of L-lactide and DL-lactide are used to graduate the biodegradation rate. The relationship between biodegradation rate and polymer composition is non-linear. For example, a copolymer of 50 % glycolide and 50 % DL-lactide degrades faster than either homopolymer. Copolymers of glycolide with L-lactide containing 25–70 % glycolide are amorphous owing to the disruption of chain regularity because of the copolymer effect. Ethicon markets a suture material made from 90 % glycolide and 10 % L-lactide under the trade name *Vicryl*®. This is absorbed completely in 3–4 months, but its strength retention is longer than that of pure glycolide.[142–3] A typical synthesis of polylactide or lactide–glycolide copolymers is given in a US Patent by Okuzumi and co-workers.[144]

3.7.4 Polycaprolactone (PCL)

Caprolactone is the seven-membered ring lactone of ε-hydroxycaproic acid and can be made by a Baeyer–Villiger oxidation of cyclohexanone. In the presence of a stannous octoate catalyst it undergoes ROP to the homopolymer polycaprolactone. This melts at 59–64 °C and has a very low T_g (well below 0 °C). It also has a low modulus but forms strong elastic fibres that are biocompatible. Because it is much more hydrophobic than either lactide or glycolide polymers, it has a long degradation time, of the order of 2–3 years. It is often combined with other monomers to reduce the degradation time. A block copolymer of caprolactone and glycolide is marketed by Ethicon[145,146] under the brand name *Monacryl®*.

3.7.5 Polydioxanone (PDO)

Another monomer that undergoes ROP is 2-dioxanone, originally made by the reaction of disodium glycoloxide with chloracetic acid. This monomer can be polymerised with organometallic catalysts such as diethylzinc or zirconium acetylacetonate. It gives an alternating polyester–ether structure and forms a highly crystalline (55 %) polymer with a low T_g (–10 °C). It makes soft and flexible fibres well suited for sutures, but has the disadvantage that it readily depolymerises on heating and has to be melt-spun at as low a temperature as possible. It is a very biocompatible material and loses about 50 % of its strength in 3 weeks; it is fully absorbed in 6 months. It is marketed by Ethicon[147] as 'PDS filament for sutures'.

3.7.6 Polytrimethylene carbonate (TMC)

The cyclic carbonate ester of trimethylene glycol, made by reacting trimethylene glycol with phosgene, alkyl chloroformates or dimethyl carbonate[148–150], easily undergoes a ROP reaction and can form useful copolymers with glycolide and lactide. Typically they are made as ABA tri-block copolymers with terminal PGA segments. Davis and Geck market a glycolide-TMC copolymer suture under the name *Maxon®*. These copolymers are more flexible than pure PGA and lose 80% of their strength in 2 weeks but then decline more slowly, maintaining 25% of their strength after 7 weeks. They are fully absorbed within about 12 months.

3.7.7 Sterilisation and packaging

All suture materials must be rendered sterile[137] before packaging ready for implantation and this is done either by a chemical treatment with ethylene oxide gas or by irradiation with gamma rays or E-beam. Ethylene oxide is highly toxic, and all traces must be removed from the package before it is sealed.

Irradiation with ionising radiation causes damage to all α-hydroxyacid polymers, and the level must be held to no more than about 2 Mrad. Since the degradation of these materials is primarily due to hydrolysis, they must be kept scrupulously dry. The packaged sterilised sutures are thoroughly vacuum dried and maintained in an anhydrous state by internal desiccants. They are usually stored in a freezer at around –20 °C to ensure an adequate shelf-life.

3.7.8 Mechanism of degradation

The actual breakdown of the polyesters *in vivo* is quite complex, although it is simpler for sutures than it is for the biomaterials used in drug release because fibres have a much higher surface to volume ratio. Basically there are two mechanisms operating: *bulk erosion* and *surface erosion*, and these have different kinetic effects on strength loss. The process is well described in a comprehensive article[151] by von Burkersroda *et al.* There are always two separate processes operating. One is the rate of diffusion of water into the material *in vivo,* and the other is the rate of chain-breaking reactions (hydrolysis). If the rate of hydrolysis is faster than the rate of ingress of water, the polymer will surface-erode, a highly desirable state of affairs for a drug-release polymer. If the rate of chain breaking is slower than the rate of water diffusing into the material, then the latter becomes the rate-determining step and bulk erosion takes place. All commercial sutures degrade by bulk erosion, but the exact mechanism of strength loss is also a complicated process. All sutures are semicrystalline materials, so hydrolytic attack occurs first in the amorphous regions since these are more easily penetrated. The fibre is still held together by the crystalline domains or regions which are as yet unattacked, even though the overall molecular weight may have fallen appreciably. Eventually, there is a catastrophic loss of strength and the structure falls apart. Finally, the fragments of monomer and oligomers are slowly broken down and metabolised in the body into harmless by-products, eventually to carbon dioxide and water. This is why the final disappearance can take many months even though the zero-strength time may be only a few weeks.

3.7.9 Disposable fibres

A whole new area for biodegradable polymeric materials based upon non-petroleum source biomass-derived raw materials has recently started to develop. The topic has been comprehensively reviewed[138] by Stevens. There are two separate and distinct areas here – polymeric materials that are compostable, environmentally friendly and minimise environmental damage and those derived from natural renewable resources (biomass). These areas often overlap. A significant market for biodegradable fibre-forming polyesters has opened up with the emergence of Cargill Dow Polymers as a large-scale manufacturer of cheap L-lactide, derived from fermentation of cornstarch.[152] Poly(L-lactide) is highly crystalline, and a less brittle fibre and film result if a little imperfection is introduced into the polymer chain to break up the regularity.[153] The lactide was originally intended for biodegradable and compostable polylactide packaging film materials under the name *Natureworks*®, but one fibre manufacturer at least (FIT Inc.) is interested in the implications for disposable fabrics (such as towels, nappies, wipes, etc.), where non-wovens usually predominate. J. Dugan, of that company, says that polylactide fibre has many good textile properties and could have a significant market in the disposable fabrics area. He has also used lactide polymer as a matrix for an ‘islands in a sea’ type of bicomponent fibre (see Section 3.11) with PET to make PET microfibres by hydrolysis of the lactide.[154]

Another, much older, naturally derived polymer is *Biopol*®, a copolymer made up of various poly-β-hydroxyacid ester units, notably the copolyester from 3-hydroxybutyric acid (PHB) and 3-hydroxyvaleric acid (PHV). These polymers belong to a class of polyesters called poly(3-hydroxyalkanoates) and the area has been recently reviewed[155] by Ramsay and Ramsay. It has been known since the 1920s that certain bacteria, when starved of nitrogenous food sources, will build up poly(hydroxybutyric acid) and its homologues and store it as an energy source in the form of solid granules in the cells, much as higher organisms store fat globules. An early patent reference[156] to PHB is one by Baptist of W R Grace in 1962. *Biopol*® was originally made from bacterial sources by ICI on Teesside, UK in the early 1970s, when ICI was in the process of developing large-scale fermentation reactors to produce single-cell bacterial protein for winter cattle feed supplements. This project was not a commercial success, so the original protein fermentation pilot plant was adapted to produce bacterial polyester on a comparatively large production scale.[157]The chief micro-organism used was *Alcaligenes eutrophus,* and the food source was usually glucose.[158–161] As much as 80 % dry weight of cells was polyester under optimal fermentation conditions. In 1990 ICI underwent a corporate reorganisation and divested a large part of itself under the name Zeneca. Zeneca (now AstraZeneca) in turn divested itself of *Biopol*, which was acquired by Monsanto, who, in continuing the work, made some important changes. Most notably, it was found that PHB copolymers could be made from genetically modified *higher plants* such as *Arabidopsis thaliana* (leaves) and *Brassica napus* (seeds) and harvested by simple solvent extraction or expression, much as one would use for rapeseed oil. Monsanto also divested itself of the product in 1998, and it has now been taken up by Metabolix Inc. in Cambridge, Mass., who obtained a US Dept. of Energy grant in 2001 to continue the studies.[162]

Biopol is a crystalline thermoplastic with a melting point in the range 170–190 °C. Its structure is analogous to that of isotactic polypropylene, since all the side groups project on the same side of every chain. Like a peptide, the chain has a helical conformation, but unlike peptides, this is due to non-bonded interactions between the carbonyls and the methyl groups. There are no hydrogen bonds, and this helix formation is unique. One practical problem with *Biopol* is that it has a pronounced tendency to embrittle by secondary interlamellar crystallisation. So far, *Biopol* can hardly be called a commercial success, but it has been very thoroughly investigated. A review[163] of PHB polymer and copolymer production by Poirier *et al.* was published in 1995. Again, the author has a personal interest, for while at ICI Fibres in 1977, he was asked to try to melt-spin PHB fibres on a small scale from some of the very earliest samples of ICI's polymer. This was not successful owing to the very high molecular weight of the material. PHB has not been widely investigated as a fibre-forming polymer, although there is talk of biodegradable fishing net monofils. It is less suitable for sutures, for example, since it does not break down readily by simple hydrolysis *in vivo*. It *does* break down both aerobically and anaerobically when exposed to certain enzymes (lipases), as when composted or exposed to marine environments, so it is likely to be of greater use as a disposable, environmentally friendly, thermoplastic polymer. A recent patent[164] describes the use of copolymers of 3-hydroxy and 4-hydroxalkanoates in medical devices such as sutures, bone screws, etc. These materials have been described[165] by Hori *et al.* and can be produced by a biosynthetic route[166] using recombinant bacteria such as *Escherichia coli.*

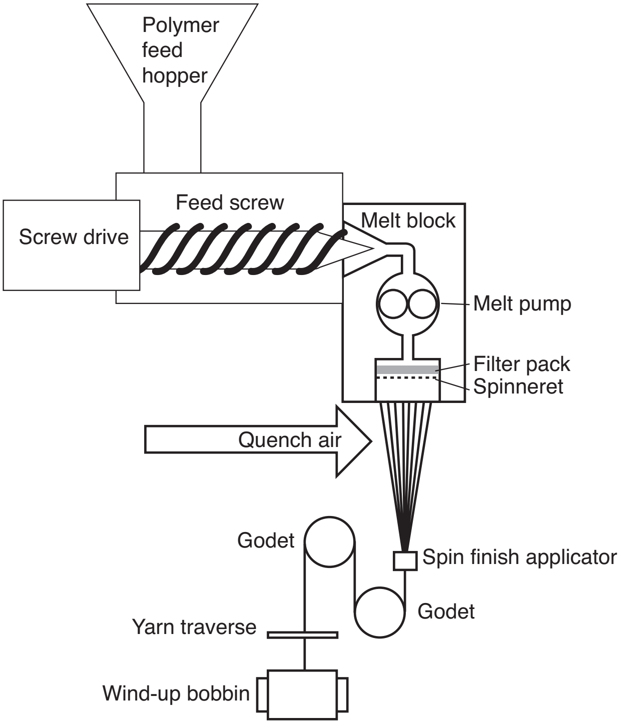
3.8 Melt-spinning polyester fibres and associated processing

3.8.1 Introduction

This is a large topic and, for detailed descriptions, the reader is referred to specialised publications dealing with the subject. Good accounts will be found in Reese's chapter[1] and in Davis and Hill's article[167] on fibre spinning. This work can give only a broad outline of the processes, and most of the discussions will deal solely with PET melt spinning, by virtue of its enormous volume. All synthetic fibres fall into two main categories: continuous *filament yarn* (F/Y) and *staple fibre*, which is discontinuous and cut to short lengths for blending with natural fibres such as wool and cotton. This blending is done just prior to the carding stage, and the blended carded (combed) fibres are then twisted together ('spun') in modern versions of a yarn-spinning process that dates back many millennia.

3.8.2 Filament yarn melt-spinning

Filament and staple polyester are melt-spun under different conditions, and their subsequent fibre processing is quite different. The melt-spinning process is simple in theory, yet very complex in practice if optimum fibre properties are to be achieved. A diagram of a schematic F/Y melt spinner is shown in Fig. 3.4. Rigorously dried polymer (moisture content < 30 ppm), stored in a sealed feed hopper and sparged with dry nitrogen, is melted at a temperature some 15–25 °C above its crystalline T_m in a device such as a screw-extruder. The polymer melt passes from the extruder under a positive back-pressure to the melt block. Sometimes a coarse screen filter is interposed between the end of the screw extruder and the block. The heated block has a number (2–8) of spinning packs mounted within it, although only one is shown in the diagram. Each spinning pack has its own pump, filter and spinneret assembly. The polymer melt is precisely metered by a positive displacement gear pump which delivers a fixed amount of polymer melt per revolution. The melt is filtered immediately prior to the spinneret to remove any foreign bodies that would plug the spinneret holes by forcing it through a filter pack either made of particles of sand or aluminium oxide grains, or,



3.4 Schematic diagram of typical F/Y melt spinner.

more usually these days, through a shattered metal filter. Finally the melt is forced through tiny holes, typically 0.007–0.015 inch (0.180–0.400 mm) in diameter in a spinneret plate. The whole pack assembly is heated electrically to the designed spinning temperature (usually 280–300 °C) so the pack seals and gaskets are designed to function at this high temperature and seal against polymer leaks under pressures that can approach 5000 psi. Ideally, in a well-designed melt spinner, the thermal history of the whole polymer melt is uniform, hence no dead spots, stagnant zones or circuitous melt pathways should exist. Differing thermal histories lead to variations in yarn dye uptake, as a result of slightly different thermal degradations of the polymer. This can lead to unacceptable non-uniformity in the final dyed fabric.

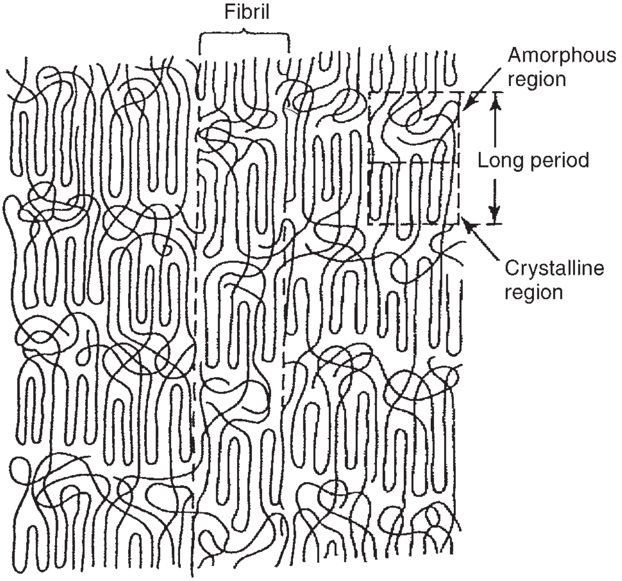
The molten threadlines emerge from the spinneret and solidify as they fall. The cooling process is accelerated by a controlled flow of non-turbulent quenching air. Passing next around a take-off roll or 'godet', the bundle of filaments are wound up on a yarn package or sent directly to other processing steps. One very important parameter is the thickness of the solid as-spun filament, and this is measured by the *denier count*, which is *the weight in grams of 9 km* of yarn. The official metric system uses the *decitex count*, which is the weight of *10 km* of yarn (hence decitex is 1.11 × denier); but it seems that the textile industry in much of the world (particularly the USA) resolutely retains the denier count, a measurement dating back to the Lyons silk industry in 18th century France.

Denier is decided by a combination of the polymer density, the polymer throughput in grams per hole per minute (fixed by the number of holes and the metering pump calibration and speed) and the wind-up speed in m min^{-1} at the godet surface. The polymer throughput per hole is usually in the range 1.0–5.0 g $hole^{-1}$ $min.^{-1}$ The linear speed (jetting velocity) of the molten polymer emerging from the spinneret is much less than the haul-off speed at the godet: this ratio is referred to as the *draw-down factor*. The stretching in the semi-molten state induces molecular order and orientation in the fibre and develops the tensile properties. The degree of orientation is measured on the spun filament by determining the optical birefringence. This is often done manually on a small sample of fibre with a polarising microscope and an optical device called a Berek Compensator. As the wind-up speed increases, so does the birefringence in an exponential curve: at a wind-up speed of 3500 m min^{-1}, a typical PET spun yarn has a birefringence of about 50×10^3 units.[167]

There are three regimes of F/Y spinning speed. Speeds below 1000 m min^{-1} are considered low-speed spinning. Medium-speed spinning is run at 1000–4000 m min^{-1}, while high-speed or *high-stress* spinning is run at over 4000 m min^{-1}. Very high spinning speeds introduce so much molecular orientation that the yarn needs little further drawing.[168] Such a process is the ‘POY’ process, from the acronym for ‘partially oriented yarn’. One of the major technical break-throughs in the 1970s was the introduction of high-speed yarn winders that would give large cylindrical yarn packages or ‘cheeses’ (typically 7 kg of yarn) and would run at over 4000 m min^{-1} (150 mph). The yarn traverse device was a major stumbling block, for without a reliable high-speed traverse to keep pace with the increased wind-up speeds, the process could not run. The engineering problem was the traverse bar drive carrying the yarn guide, which had to reverse *instantaneously* at the end of each cross stroke with no trace of ‘dwell’, or else the package would build up at the edges and the end yarn would simply slough off the yarn package. Solutions were found; nowadays, take-up speeds are even higher, as much as 8000 m min^{-1}, which is a speed of 300 mph.[169–171]

3.8.3 Filament yarn drawing

Although molecular chain orientation has been partly introduced by the draw-down, the main increase in order is usually brought about by a separate *drawing* process.[172] Fibre-forming polymers of adequate molecular weight all show the phenomenon of *cold drawing* on stretching. The undrawn fibre (or a strip of film) will neck down and elongate, and crystallisation will often occur, evident from a change in lustre in the drawn filament due to its optical anisotropy. PET fibres in



3.5 Morphology of PET fibre showing various features. Reprinted from Mark, 'Polyester fibres' in *Encyclopedia of Polymer Science and Technology* ©2003 John Wiley & Sons, reprinted by permission of John Wiley & Sons Inc.

the as-spun state are generally *amorphous*. They have molecular orientation but only become crystalline with *oriented crystallites* when fully drawn. Polymers such as PBT and nylon 6,6 form crystalline spun fibres, but they still need a drawing stage to induce the full molecular orientation. It is the combination of molecular orientation and the presence of polymer chain crystallites to 'lock' this orientation into place, which governs such important parameters as tenacity, elongation at break and heat-shrinkage. In order for drawing to be effective, the fibre has to be elongated several fold, the ratio of yarn feed velocity to draw-roll haul-off speed being the *draw ratio*. It can be anything from about 1.5 up to 6.0. At higher draw ratios the yarn shrinkage falls and so does the elongation to break. The *draw point* where fibre necking takes place has to be stabilised and located at a fixed point. In the early days this was done by a stationary heated metal pin, around which the yarn passed. The pin drawing temperature is set at about 10 °C above T_g (i.e. about 85–90 °C for PET) and since at this temperature the polymer is in a rubbery state, the chains are free to move at a molecular level and can reorganise and reorient themselves under the mechanical stress of the drawing process. The drawing step is quite exothermic, as can easily be demonstrated by cold drawing a strip of undrawn PET film and carefully touching the film to the lower lip. Cold-drawing is somewhat thermodynamically analogous to the adiabatic compression of a gas. Hence, once the drawing process starts, little additional heat is needed to keep it going. To stop the drawn yarn from having an unacceptable degree of heat shrinkage, the yarn has to be *heat-set* by passing it over a long hotplate at about 130–140 °C, which is well above the effective T_g (125 °C) of the drawn, oriented and crystallised yarn. The heat setting stage encourages the final development of maximum molecular order and crystallinity; it can be considered as a continuous annealing step. A diagram of the morphology of an oriented, partly crystalline PET fibre is shown in Fig. 3.5.

This simple drawing system was adequate when draw speeds were low (500 m min^{-1}), but as speeds rose considerably, it was necessary to use separately heated feed rolls and draw rolls to achieve the same effect at much higher speeds. (The heated rolls allowed longer contact times for thermal transfer, the yarn being usually wrapped four or five times around each roll and a small idler roll.) The draw ratio has a major effect on yarn elongation and tenacity. As one might expect, high draw ratios give high-tenacity yarns with higher yarn moduli and lower extensions to break; low draw ratios give lower tenacities with much more extension. A semi-empirical rule connecting elongation to break (e_b) and engineering tenacity (t) has been established[173] which says:

$$t = K/e_b^{\alpha} \qquad [3.8]$$

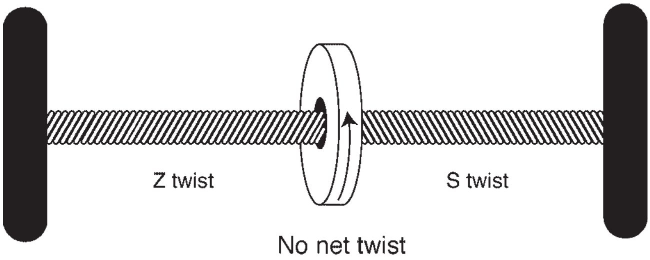
where K and α are constants. Experimentally, $\alpha \approx 0.3$. K is a measure of the inherent fibre strength and is related to the molecular weight.

Heavy-duty industrial yarns for tyre cords and for uses such as car safety belts are drawn under conditions favouring maximum yarn modulus, tenacity and minimum stretch (see Section 3.8.5).

3.8.4 Filament yarn texturising

Drawn filament yarn can be treated in any number of ways. It may simply be wound onto a yarn package, or twisted on a ring frame as ‘flat yarn’ or sent for a yarn texturising process. Many apparel yarns need to be texturised or ‘bulked’ to give desirable aesthetics and textile properties, particularly for women’s wear markets. This may be done either in combination with drawing (‘draw-bulking’) or as a separate process. Draw-bulking or ‘draw textured-yarn’ (DTY) often uses POY yarns as a feedstock, since the required draw ratio is low, only about 1.6-fold. The number of bulking processes is high and reference to specialist sources is recommended for those wanting detailed process descriptions. Several excellent publications, books[174] and various websites[175–176] are available. The descriptions given here are derived from information available from these various sources.

Probably the most important F/Y texturing process is *false twist bulking*. This is a method of producing in the final yarn a distinct spiral crimp that is permanent and gives the yarn a greatly increased bulk and stretchiness without seriously altering the tensile properties of the basic fibre. The expression *false twist* refers to a process which inserts no *total* twist. In the early 1930s a ‘true twist’ process for bulked acetate rayon filament yarn was devised. This involved inserting a high degree of



3.6 Principle of false twist bulking.

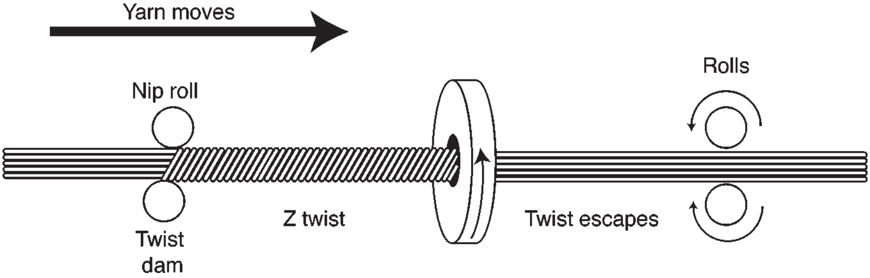
twist into flat yarn, steam setting the twisted yarn under pressure, and then untwisting it. Since the yarn had been heat set into a spiral conformation, during the de-twisting stage, the filaments, in trying to maintain their spiral 'set', simply separated from each other and bulked up to give a textured yarn. Obviously such a process is both cumbersome and time-consuming. Not long afterwards, in early 1934, British Celanese Ltd developed the *false twist* bulking process for cellulose acetate fibres. After World War II, first nylon and then polyester yarns were textured using the false twist bulking process and it has since gone on from strength to strength.

3.8.4.1 The principles of false twist bulking

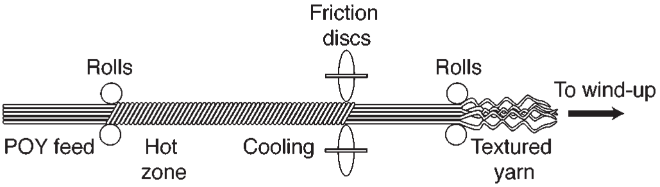
If a bundle of filaments fixed at both ends is grasped in the middle and twisted, there will be no *overall* twist in the yarn since a Z twist will run one way to the fixed end and an S twist will run the other. Releasing the twist in the middle will cause both sets of twist to unwind and cancel out (see Fig 3.6).

It is because the process puts no total (or net) twist into the yarn that it is called a *false* twist process. But if we consider each *half length* of our yarn bundle, the twists are real. Now consider a machine in which a continuous yarn is run through the twisting device (Fig. 3.7). On the downstream side, the twist runs down to the wind-up unit. On the upstream side of the twister, as the yarn runs through it, it untwists as soon as it passes the twister on the downstream side, but fresh twist is constantly applied to the upstream region. An equilibrium is set up with twist being applied to the upstream side. This twist will run back as far as it can and a snubber pin is fitted to act as a twist dam to block the twist progressing any further. Without this dam, the twist would run back to the feed yarn package and cause the feedstock yarn to snarl up.

Now imagine a hot tube or hot plate interposed on the upstream side between the snubber pin and the twister. We can heat set the upstream twist in place into the yarn. The yarn twist deformation will be locked in, and torsional forces applied during twisting will relax with the heat. The yarn is now tension free but permanently deformed into a helical conformation. As the yarn runs through the twister, it tries to untwist on the downstream side but this, in effect, is being back-twisted in the opposite sense. Each individual filament then snarls up and separates



3.7 False twist bulking.



3.8 Friction false twist texturing.

out, giving a yarn with no overall twist but with plenty of lively spiral crimp and elasticity. This gives an attractive bulky, stretchy yarn (see Fig. 3.8).

It was common at one time to combine a separate polyester yarn drawing process with the bulking step, in a two-stage draw-then-bulk process. With the increasing use of POY feedstocks, which need only a low draw ratio, most draw bulking now uses a one-stage process. At one time, the bulked yarn packages from the false twister used to be stabilised by steaming them batchwise in an autoclave. This was slow and labour intensive, so now twin-heater draw-bulker units are used. The bulked yarn is heat set to stabilize the crimp continuously in the second heater before it is wound onto the final yarn package.

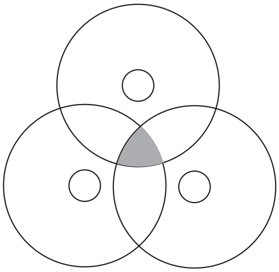
3.8.4.2 Pin twisters

There are two methods of applying false twist. The older device is the pin twister and the later one the friction twister. The pin twister is a small stainless steel tube with a tiny synthetic sapphire pin (made from fused aluminium oxide) fixed transversely across the bore of the tube. The yarn is looped once around the sapphire pin. The tube is rotated along its axis and as it rotates, it applies a positive twist to the yarn. The level of twist needed is high (approximately 1000 twists m^{-1}) so that if the yarn is running at today's productive speeds, which can be over 1000 m min^{-1}, the rotation speed of the twister tube would have to be extremely high, more than 1 000 000 r min^{-1}. This would produce truly formidable mechanical problems, and twister pins were made as tiny as possible and driven by friction wheels or belts or held suspended against magnetic drive wheels, all to eliminate bearings and their problems. It was generally reckoned that 800 000 r min^{-1} was the highest practicable speed for a pin twister drive. Pin texturing gives a high-quality bulked yarn because the twist drive is 100% positive, and there is no chance of twist escaping, leaving un-bulked regions ('shiners') in the yarn, but for the reasons outlined, the overall yarn process speed is much lower than for the friction twisting bulking process. A typical speed range would be 100–300 m min^{-1}.

3.8.4.3 Friction twisters

British Nylon Spinners in 1953 devised an ingenious solution to the engineering problems of the pin twister – they eliminated it completely! Instead, they developed the *friction bulking* process, in which the yarn itself is twisted by running it against the moving surface of a friction bush rotating at high speed. Since the yarn diameter (the usual polyester feed yarn count is 50–300 denier) is very small compared with that of the bush, a very high 'gear ratio' (100 : 1) is readily achieved and the drive bush can now rotate at much more reasonable speeds. The original BNS process used a hollow bush with the yarn running against its *internal* surface. The internal edges were smoothly contoured so that the yarn could be drawn away at right angles to the axis of the bush. These days, bush drives have been superseded by a multiplicity of six to nine friction *discs,* which are arranged in an interleaved cluster around the yarn as in Fig. 3.9. The yarn path follows a zigzag course between the discs, whose edges are carefully radiused to an optimum curve. The yarn follows an angled path over the edge of the friction disc which propels it forward. It will be realised that friction drives, bush or disc, are not 100 % positive, unlike a pin drive. Twist can escape by yarn slippage on the disc edge surface. In practice, this is found not to be a serious problem. It allows twist equilibrium to be established and is more accommodating to yarn variability.

Friction disc texturing gives a more runnable process, particularly at high speeds. Since the disc drives need not run at enormous rotational speeds, the



3.9 Arrangement of friction discs.

machines are quieter and less subject to mechanical wear and tear. The discs themselves are made from a variety of materials, ceramic (usually Al_2O_3) metal (aluminium, coated with diamond) and polyurethane being the main ones. The plain ceramic and metal-diamond discs are hard materials and tend to be harsh, causing mechanical wear damage to the yarn. The latest coated ceramic discs are better but the disc edge surface can change its frictional characteristics with wear and thus alter the degree of twist and bulk. Soft polyurethane discs are probably preferable: they have a high level of yarn friction and, being softer than the yarn, usually do not damage it. However, for the same reason they wear out quite rapidly and need to be replaced on a regular basis, which all adds to process costs. Usually there is a ceramic or metal entry and exit disc with a number of polyurethane working friction discs (typically four) stacked in between, a configuration known as 1–4–1. The type of disc surface affects the disc configuration; for a hard material disc the configuration would be 1–7–1.

A recent patent[177] discloses important modifications to the process parameters needed to produce draw textured yarn (DTY) via a friction disc process for POY made from PTT. There are major differences between POY derived from PTT and PET, most notably the *rapid yarn crystallisation* of PTT. This causes many difficulties in the draw texturing process. The modified process conditions allow a robust DTY process to run successfully.

Another method of friction bulking yarns is the use of crossed flat belt drives, where the yarn is held between two flat belts arranged at an angle which causes the yarn to move progressively along as it acquires twist. A detailed description of the process is given in Takai's patent.[178]

3.8.4.4 Modern draw texturing machines

Modern machines from such established manufacturers as Rieter and Barmag have reached a high degree of sophistication, with widespread use of computer control of heaters, yarn tension and friction disc drive speeds. Since the process is mechanically severe, yarn overheating is possible and streams of cooling air are applied at appropriate points. Spin finishes are usually applied to feedstock yarns, some of which can fume off when hot, so fume extractors are built into the unit. The output bulked yarn is usually wound on paper cones, since much DTY goes into knitted fabrics and the knitting machines use cone packages for feed yarn supply. The latest modern draw-bulking units have automatic doffing equipment to remove the full cones and replace them with empty cones, which are automatically strung up.

3.8.4.5 Other F/Y bulking methods

Many other methods have been used to make bulked filament yarns, some very ingenious. There is not the space to cover them in detail, but they include *edge* *crimping*, where the yarn is passed over a hot knife-edge which induces an asymmetric shrinkage in the yarn, which in turn develops bulk on relaxing. There are bulking techniques that depend on bicomponent fibres and these will be discussed later in connection with multi-component fibres. Air-jet and steam-jet bulking are similar processes where a feed yarn is heated in a turbulent jet of hot air or steam, which tangles the filaments and blows them into loops, then heat sets the tangles, so that the yarn bulks up after relaxing. Air-jet textured yarns or ATY can be used in a variety of fabric weights from very lightweight apparel up to heavy duty materials for soft luggage fabrics. The feed stock yarn, very often POY, is overfed into a special turbulent flow air-jet: and water is usually sprayed on immediately before the jet to lubricate the yarn. Detailed descriptions of the ATY process can be obtained from the Udo Schweizer website.[176]

We have discussed so far (at least by implication) light denier apparel filament yarns, but there is a large market in BCF carpet yarns. These are heavy-decitex fibres which are bulked by passage through a highly turbulent blast of steam above the fibre T_g, similar to the air-jet bulking mentioned above. The turbulence blows the yarn about and entangles the filaments, then sets these tangles into place, giving a desired permanent crimp as the cooled yarn relaxes. Polymers such as PET do not have a high resilience as carpet fibres, but 3GT (PTT) yarn which has $T_g = 45$ °C lends itself very well to the BCF process and has excellent bulked yarn resilience. It is to be expected that it will eventually make big inroads into the polyester and nylon carpet yarn areas.[179,180]

3.8.5 Industrial filament yarns

High-tenacity yarns for industrial use, such as tyre cord, have to be melt-spun and drawn to give a high-modulus, low-heat-shrinkage, low-extension, high-tenacity product (usually called HMLS yarns) and special spinning and drawing conditions are needed. Some industrial yarns are made by a continuous polymerisation spin-draw route. Since industrial yarns are often made to higher IV than apparel yarns, higher spinning temperatures will be needed. To develop the high tensile properties, the yarn drawing may need to be done in a two-stage process to develop the exact characteristics required.[181,182]

Very low work loss (mechanical hysteresis) is important in car tyres running at high speeds, because the constant flexing of the cord could build up serious heating if cord internal work loss were excessive. Tyre cord is a highly specialised product and completely integrated continuous polymerisation, spinning and drawing plants ('*Cp-spin-draw*') have been developed for its production at dedicated facilities. Tyre cord polyester has special requirements and these will be discussed in Section 3.9.3. Other uses for high strength polyester industrial yarns are reinforcing fibres for V-belts, hoses, and in crane slings and motor-car seat belts.

3.8.6 Staple fibres

The demands of staple fibre are very different from those of filament yarns. The fibres are melt-spun using a large diameter, high-throughput extruder as the polymer melter. The melt is then metered via a high-capacity metering pump through a filtered staple spinning pack with a spinneret plate containing a large number of holes, many hundreds at a time. The bundle of fibres is hauled off via a series of godets (to prevent slippage) but not wound up; instead the yarn is deposited loosely via an air-ejector into a large yarn drum or 'can'. When the yarn can is full, the fibre bundles from many cans are combined into a thick 'tow' which may have a yarn count of 1–5 million decitex. This thick bundle of fibres is then drawn on a massively constructed drawframe (massive because the mechanical forces involved in drawing such a thick bundle of fibres are considerable) using many sets of feed rolls and draw rolls. It is heat set in a steam-heated hot-box. The drawing is often done in two or even three stages. The drawn tow then passes to a crimper, often of the stuffer-box type. Here the tow is over-fed into a heated wedge-shaped compartment which compresses it into a concertina crimp. The stuffer box has a weighted or sprung trap door so that excess amounts of yarn are released mechanically and in this way the degree of crimp is controlled.[183] The bulked tow is finally cut to the desired staple length by one of several proprietary designs of continuous staple cutter.[184] The loose cut fibre is then compressed with a hydraulic press into bales. A schematic diagram of a staple line is shown in Fig 3.10. A large staple unit can produce 200–300 tonnes staple fibre per day, which is later blended with cotton, wool or other natural fibres.

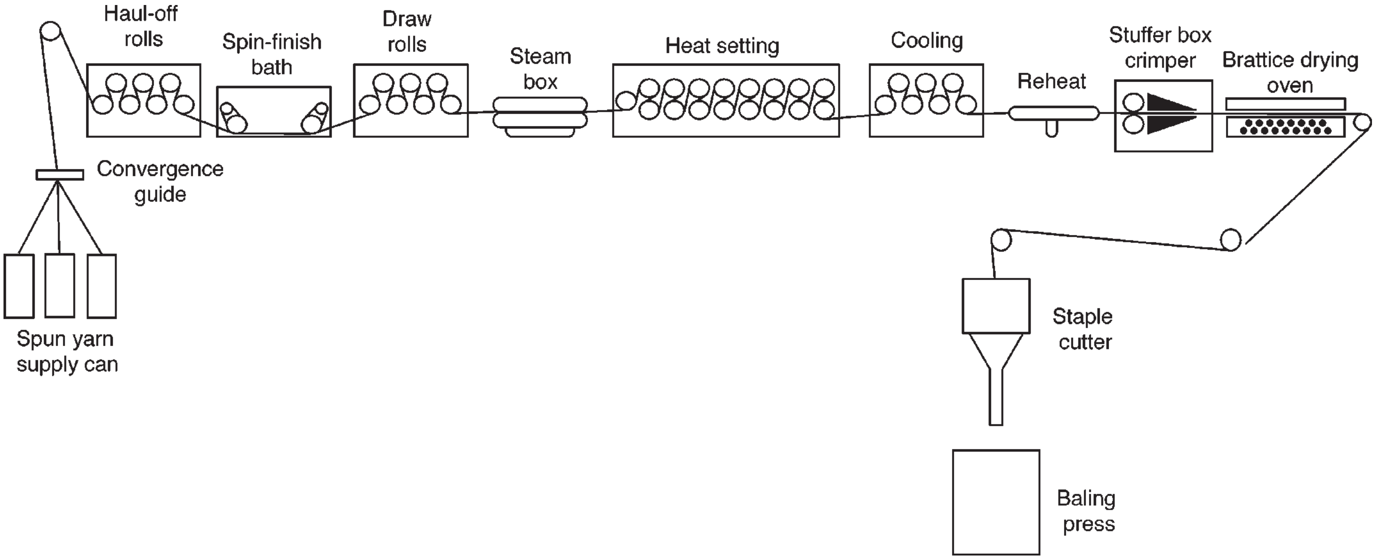
3.9 Modification of polyester fibres

3.9.1 Introduction

Plain PET fibre on a yarn package is unlikely to suit every one of the very many different markets for which it is used. It is often necessary to modify the fibre in various ways. This is a broad topic, covering both chemical and physical modifications to both polymer and fibre. We shall here deal with just a few of the more important variations possible on this theme.

3.9.2 Spin finishes

All fibres need to be treated with surface finishes that alter the frictional characteristic of the yarn surface. Without these spin finishes, the various processing steps such as drawing, texturising and textile processing would be impossible, because so many of them rely on specific frictional properties on the fibre (for example, friction bush texturising). Spin finishes are often water emulsions of various surface-active agents, either non-ionic or anionic, with various lubricant mineral



3.10 Diagram of staple draw frame, showing only a single-stage drawing. Two of even three drawing stages are frequently used.

oils. The finish formulation is complex and something of an art as well as a science.[185] Application of the finish is made early in the process, before the cooling threadline from the melt spinner hits the first godet. In the early days, the finish was usually applied as a water emulsion from a lick roll rotating slowly in a bath of finish. As spinning speeds increased, the finish was applied directly via a hollow ceramic guide in a neat oil formulation and metered at precise levels from a metering pump. High-speed texturizing processes using POY feed yarns have particular requirements: they must not fume badly nor pyrolyse in the heater tubes of the texturising machine. Polysiloxane oils are often used in these special formulations.[186] Staple fibre is usually sprayed with emulsified finishes or else the whole tow is immersed in a bath of finish, and this may need to be repeated at intervals along the process chain. Some staple processes use a drawing stage with the tow immersed in a hot bath of emulsified spin finish.

3.9.3 Tyre cord treatments

Polyester tyre cord is a particularly demanding market. For many years, car tyres used high-tenacity rayon and later nylon for tyre cords. Both fibres bonded well to rubber and were not seriously affected by the rubber vulcanisation process. Greater technical demands on car tyre performance caused rayon to drop out in favour of nylon, but in countries such as the USA, the nylon-reinforced tyres were found to suffer from an irritating fault known as ‘flat spotting’ which was associated with the relatively low T_g of nylon. PET cords with their higher T_g did not suffer from this defect but there were problems to be overcome before commercially successful PET tyre cord could be introduced. For example, the cord had to be strong enough and have a low mechanical hysteresis to prevent temperature build-up on constant cyclical flexing. Suitable spinning and hot drawing conditions overcame these problems, as has already been discussed. Secondly, the polyester cord suffered IV drop and strength loss through in-rubber degradation during the tyre manufacture. During the manufacture of tyres, the polyester tyre core is subjected to some drastic conditions. As the rubber is moulded onto the tyre, the rubber is simultaneously vulcanised; and this process uses various accelerators, activators and catalysts, some of which are organic amines which cause severe aminolytic degradation of the polyester chain. In addition, the process is carried out at 175 °C in the presence of steam. While PET is fairly resistant to strong aqueous *ionic* bases at moderate temperatures, it has been known for many years that *non-polar* covalent, weak bases, such as ammonia, hydrazine and simple aliphatic amines, can easily diffuse into the hydrophobic PET structure and cause aminolytic breakdown, particularly in the presence of steam.[187] Steam lowers the effective T_g of the fibre and degradation reactions rates depend on a $(T_{\text{actual}} - T_g)$ factor. Obviously, lowering the T_g raises the reaction rate at constant temperature.

To maintain the high strength engineered into the tyre cord, it is essential that the IV drop should be minimised. It was found[188] that the rate of in-rubber degradation of the tyre cord was directly related to the level of free COOH groups on the chain ends. These seem to be autocatalytic under the vulcanisation conditions, and if they could be reduced from their usual level (about 30–40 microequivalents of COOH per gram of fibre), a reduction in IV drop should result. This was shown to be so and for some years a process[189] was employed whereby the molten polymer, shortly before extrusion from the melt, was treated with epoxy compounds, such as phenylglycidyl ether (1,2-epoxy-3-phenoxy-propane) to esterify the errant COOH end groups. This process typically reduced the carboxyl ends to about 10–15 microequivalents gram. However, the glycidyl ethers were later found to be carcinogenic and the process was then abandoned in favour of the somewhat drastic alternative of melt-injecting ethylene oxide gas under high pressure into the molten polymer during the last stages of polymerisation.[190] This reduced the free COOH end group concentration by forming harmless BHET ends and the in-rubber cord strength loss at moulding was significantly reduced. However, a third problem surfaced: the reduced carboxyl ends adversely affected the adhesion of the PET cord to the rubber with conventional cord adhesive systems; usually a resorcinol/formaldehyde/latex mixture. The final solution was a proprietary activated adhesive finish[191] which could be applied to the tyre cord yarn and would run safely through the tyre cord process, giving a strong cord-to-rubber bond at the tyre moulding step. These various developments helped Celanese Corporation and its associated companies to achieve dominance in the polyester tyre cord market in the USA until the recent drastic corporate restructuring.

3.9.4 Low-pill staple polyester

PET staple blends with wool and cotton were highly successful from the very first introduction of PET in the 1950s. However, before long consumers noted an irritating problem, particularly with wool/PET blends: the formation of small fuzzy balls (called ‘pills’) on the surface of the woven fabric, which clung remarkably tena-ciously. The phenomenon became known as ‘pilling’. It is, in fact, common to all staple fibres (whether they contain PET or not) and is made worse if the level of yarn twist is low, so that the fabric has a rather loose structure. Usually, for pure woollen fabrics and knits, the pills rub off harmlessly, because wool is a relatively weak fibre. PET is a strong fibre (PET staple fibre tenacity is typically ≈ 3.5 g dtex^{-1}) and pills do not rub off: they cling, with deleterious effects to fabric aesthetics. In order to reduce pilling, the IV of the polyester was reduced to make weaker fibres that do not form pills, simply because any pills formed disappear during wear. A polymer IV = 0.42 was selected as the best compromise for a low-pill PET staple fibre, but it caused many practical problems at melt-spinning. The melt viscosity was so low, and the molten threadline so fluid that the process became difficult to run unless controlled very closely. To give a trouble-free and robust melt-spinning process, a way had to be found to raise the effective melt viscosity of the polymer while maintaining the low IV and relatively weak fibres. One method adopted was to introduce *branching points* into the polymer chain by adding a multifunctional component (either a polybasic acid or a polyhydric alcohol) so as to produce a star-branched polymer. Such polymers are known to have higher melt viscosities for the same (nominal) polymer IV. The branching agent was added at a low level (*ca* 1 mole%) and pentaerythritol (also dipentaerythritol and trimethylolpropane) was the polyfunctional additive of choice.[1] Too much additive leads to gel formation by forming cross-linked polymer networks, but this is not a problem at low levels as used here.

An alternative solution to this problem is to melt-spin a fibre of normal IV which contains a degradable copolymer unit that partially hydrolyses during normal textile processing. An ingenious example[192] is that of DeMartino and co-workers where a PET copolyester containing about 10% w/w polyethylene glycol units (MW ≈ 1500 Da) is melt-spun into staple fibre. During pressure dyeing at 160 °C, the hydrophilic PEG segments allow partial hydrolysis of the polyester chain, reducing the final IV to approximately 0.40 and giving a low-pill, dyed fibre. A similar idea has been recently described by Akzo Nobel workers[193], where the polyalkylene glycol is added as a separate blended phase rather than incorporated as a copolymer.

Another technique was used by Dupont in its *Dacron 64* basic-dyeable polyester (see Section 3.10.3). The copolymerised additive, which allows cationic dyebility, is sodium 5-sulphoisophthalate, and it acts as a cross-linking agent, since it forms an ion pair structure with associated [Na^+] and [SO_3^-] ions inside the hydrophobic PET structure. These tend to associate by coulombic or dipole interaction forces and hold the polymer chains together, thus raising the melt viscosity and allowing a lower IV polymer to be spun under normal conditions. It is of interest that when the sulphonate group is attached to a polymer side chain, the resulting copolyesters do *not* have unusually high melt viscosities. An example of such an additive is dimethyl 5-[2-phenoxy]ethoxy isophthalate, derived from 5-hydroxyisophthalic acid, which when sulphonated at the terminal phenyl group could be copolymerised into polyesters at relatively high levels without excessive melt viscosities.[194]

3.9.5 Non-circular cross-section (NCCS) fibres

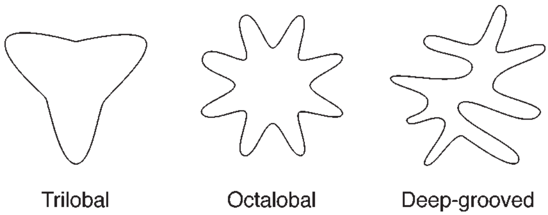
Synthetic fibres such as PET and nylon are normally round in cross-section, yet no natural fibre has a perfectly circular cross-section! Wool is scaly and irregular, cotton is ‘dog-bone’ shaped, and silk is roughly triangular. Consequently, in the early 1970s people began to study the effect of NCCS fibres on yarn and fabric aesthetics, appearance and ‘feel’. Fortunately, melt spinning lends itself quite well to production of NCCS fibres by varying the shape of the spinneret orifices, provided the melt viscosity is high enough that surface tension effects do not cause the filament to resume a circular shape. Since the NCCS holes had to be tiny (approximately 0.4 mm overall), machining a multiplicity of them and keeping them all to uniform size and shape is no small engineering problem, particularly in the very hard metal alloys used for spinneret plates. Spark-erosion machining was one fabrication method used. Nowadays, this problem has been solved by laser-etching. Sometimes it is possible to arrange an array of tiny circular holes in a matrix pattern to make up the final shape – on extrusion, the individual molten filaments fuse into one filament of the desired cross-sectional shape.

In the early days, much of this work was entirely empirical, but gradually there emerged some rules of thumb. One of the earliest cross-sections used was the trilobal section made by extrusion through a T or Y-shaped hole and looking rather like a blunted three-pointed star. Multilobed cross-sections have quite different yarn appearances. For example, trilobal yarns are glittery as the incident light reflects off the fibre surfaces, while octalobal yarns give an opaque matte effect, since the light is effectively absorbed by multiple reflections from the many faceted angles. Many polyester carpet yarns are trilobal in section, since this cross-section assists in soil-hiding. It is argued that a cylindrical fibre tends to act as a lens and magnifies the appearance of dirt in the tufts. Some nylon carpet yarns use a roughly square section filament with four holes along it to act as optical soil-hiding devices. Sharp-edged filaments in textile yarns have the rustle and high frictional characteristics of silk, where the property is called ‘scroop’ and is a highly prized feature of pure silken fabrics. Gradually, the principles learned in the early days of NCCS fibre research have been applied to commercial yarns, and many filament yarns for both apparel and BCF carpet yarns and staple for carpet fibre now use non-circular cross-section filaments.

One new patented process gives a deeply indented and longitudinally grooved fibre cross-section, spun from a castellated spinneret hole, the so-called 4DG® (for ‘deep grooves’) fibre process. It can be used for all thermoplastics, including PET and nylon, and was originally developed by Eastman who later licensed it to Clemson University. Such fibres have a very high surface area per unit length in comparison with cylindrical fibres. A 6 denier per filament (dpf) 4DG® fibre has the surface area equivalent to a 37 dpf round fibre and is much softer and more pliable.[195] These odd-shaped fibres have excellent capillarity and wicking properties for removing surface moisture and are suggested for many uses such as nappies, sanitary towels, filter media, antiperspiration shields, shoe liners and medical applications such as wound coverings.[196,197] They can be made hydrophilic or hydrophobic by suitable permanent yarn finishes. Examples might be a crosslinked polyethanoxylate-acrylate ester (hydrophilic) or a fluorinated alkyl acrylate polymer (hydrophobic). Various NCCS yarn cross-sections, including the 4DG® one are shown in Fig. 3.11.

3.9.6 Antistatic and antisoiling fibres

Antistatic and antisoiling fibres are topics that tend to go together because they have interrelated causes. Synthetic fibres in general and PET in particular are *hydrophobic* materials. PET has a moisture regain of 0.4% at 60% relative



3.11 Non-circular cross-section fibres.

humidity (r.h.) Hence, it is difficult to wet and rapidly builds up static electrical charges by friction, because there is no water present to leak away the voltage produced. In modern centrally heated, well-insulated homes, particularly in Scandinavia and North America during the winter months, the atmosphere can become very dry (5–10% r.h. is not uncommon) and it is possible to build up potentials as high as 50 kV by rubbing a polyester fabric, for example by walking with PVC shoe soles on a polyester carpet. Such a potential, if discharged by grasping a grounded (earthed) door-handle, would give a very unpleasant, even dangerous, electric shock. Static charges also attract dust and dirt, particularly if it is oily, since the PET surface is oleophilic. Oily soil removal is still perceived to be a problem for polyester carpets.

The way around all these problems is to increase the moisture uptake of the polyester by combining it with hydrophilic or humectant materials in some way that does not allow them to be simply washed off. One additive that has been used repeatedly is poly(ethylene oxide) (PEG) which is a stable, functional, highly hydrophilic, water-soluble and humectant polymer:

$$\mathrm{HO{-}CH_2CH_2O[CH_2CH_2O]_{\mathit{n}}{-}OH} \qquad [3.9]$$

PEG polymer can be made with molecular weights of anything from a few hundred daltons up to several million. Early workers made block copolymers of PET with PEG of molecular weights *ca* 500–2000 Da, and it was possible to permanently incorporate enough PEG without drastically reducing PET properties, thus greatly improving the fibre moisture uptake but at the expense of a severe reduction in the light stability of dyed fibres.[198] Other processes used a PET/PEG melt blend[199] which mitigated the dye light stability problem and also acted as a soil hiding additive, since the PEG near the fibre surface leached out with aqueous treatments (such as dyeing and laundering), leaving a network of fine holes that retained moisture and scattered light, making the fibre more visually opaque. A similar method was the use of PET containing a dispersion of a phosphate ester of PEG.[200] Yet another technique was a PET/PEG block copolymer supplied in an aqueous dispersion as colloidal sized particles. When this was padded and baked onto the fibre as a textile finish, the co-crystallisation of the PET segments in the block copolymer with those in the fibre polymer made the treatment surprisingly washfast.[201] The most satisfactory technique is probably to make a bicomponent fibre (see Section 3.11.3) with a thin coating of a PET/PEG copolymer on a PET core in a core–sheath configuration. This does not affect fibre properties and minimises the light fastness issue.[202]

Other ways of improving fibre conductivity are to add actual conductive pathways to the fibres. Very fine metal fibres have been incorporated into carpet fibres, while another technique is to use a bicomponent core–sheath filament with a very fine conductive thermoplastic polymer core filled with carbon black. Unfortunately these are both suitable only for dark coloured floor coverings, since they show up in pale coloured carpets and rugs. Another technique uses a semi-liquid core of an ionic conducting polymer, such as a low softening point polyester-ether or poly-*N*-alkylated polyamide, containing ionic salts, such as quaternary ammonium compounds.[203] Other techniques are to use proprietary semipermanent antistatic coatings based upon cationic fabric finishing resins such as quaternary salt polymers derived from poly(dimethylaminoethyl methacrylate) or DMAEM.

3.10 Dyeing polyesters

3.10.1 Introduction

Dyeing synthetic fibres is another wide topic and there are some excellent publications that deal with the process in a comprehensive manner. A very good one of particular interest to textile chemists is the book[204] by Waring and Hallas. When PET first appeared on the market, it caused many new problems for traditional dyers, since it had no functional groups to give it any affinity for the usual dyestuffs. Natural fibres such as wool, cotton and silk (and later nylon, a synthetic) were well understood and they had good dye affinities, owing to multiple fibre functionalities such as $-NH_2$, $-COOH$ and $-OH$. The only way to dye polyester was to first force a dye into the fibre and then rely on van der Waals forces to hold the dye in place. Classic cationic and anionic dyes for wool and silk or direct dyes for cotton all had water-solubilising groups such as $-NR_3^+$ and $-SO_3^-$ groups. Such dyes had little or no affinity for the hydrophobic PET.

3.10.2 Disperse dyes

The nearest equivalent to polyester in those early days was cellulose acetate (acetate rayon) and cellulose triacetate. A relatively new class of dye called a *disperse dye*[205] could be used. These dyes were first developed in the middle 1920s for use on acetate rayon. The first ones were the *Ionamine*® dyes which had a hydrolysable sulphonate group to act as a temporary solubilising functionality. During the dyeing process, this group was removed and the dye precipitated out as a very fine dispersion in the dyebath which migrated onto the fibre substrate. Later, simple dyes devoid of ionic groups, but with slightly hydrophilic groups such as

–OH and –CH_2OH, were developed for both acetate rayon and triacetate. These substitutents gave the dyes a slight degree of water solubility. They were actually dispersed (hence the name) with a surfactant (such as sulphated ricinoleic acid) as fine particles in an aqueous suspension. The dyes were perforce of low molecular weight, and when they were applied to PET this led to problems due to loss of dye by sublimation. PET fabrics usually need to be *stentered* (that is, heat set on a pin frame) after dyeing to remove creases. Since acetate rayon has a poor heat resistance, it was never heated, so dye sublimation was not previously recognised. It was a big headache for PET dyers. It became clear that special dyes would need to be developed especially for PET, based on improved versions of the acetate rayon and triacetate dyes.

As the polyester fibre market flourished, so these novel dyes rapidly advanced, being based upon well-understood dye chemistry. To prevent excessive sublimation, the dyes were made to a higher molecular weight. Typical chromophores were anthraquinones, which gave crimsons, blues and dark greens, while selected azos were used for yellow and orange or red shades. Usually these dyes were most successful if slightly water-soluble, and the ethanolamino group (–$NRCH_2CH_2OH$), and its O-benzoate or O-benzene sulphonate ester were often incorporated to give a slight degree of polarity and increased solubility in polyester, but without any ionic or highly hydrophilic character. The higher molecular weight dyes reduced dye sublimation, but at the cost of much slower dyeing and poor dyebath exhaustions. The hydrophobic nature and high level of crystallinity in drawn PET fibres made them much more resistant to penetration than acetate rayon or even triacetate. As a result, pressure dyeing at over 135 °C and the use of dye carriers became widely adopted.

One chromophore breakthrough came in the mid-1950s with the development by Dickey and co-workers of novel heterocyclic azo dyes based on 2-amino-5-nitrothiazole.[206] Diazo coupling in acidic solution with suitable substituted anilines gave stable, light-fast, brilliant azo blues for the first time and these had good affinities for PET. Bright red disperse dyes were also made using the same chromophore.

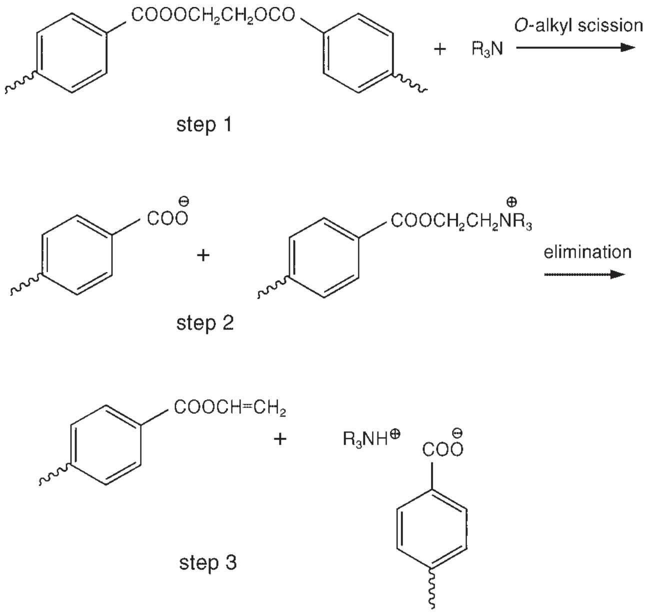
A new problem that became important was the so-called *gas-fume fading* of disperse dyes. This was found to be due to bleaching of the dye by reaction with oxides of nitrogen (NOx) and even traces of ozone in living rooms. These arose from a large increase in the use of oil and gas-fired central heating systems and the growing tendency to insulate homes and seal off all the draughts, all of which exacerbated a problem that had not been evident previously. It was later solved by selecting those dyes whose chromophores were resistant to NOx oxidation. Anthraquinone dyes were very vulnerable. Certain additives such as diphenylacetamidine act as inhibitors of gas fume fading by reacting preferentially with NOx. They can be incorporated by ‘dyeing’ them into the fibre along with the dye itself.

As already mentioned, to speed up dyeing rates, carriers were introduced, which were solubilising agents that temporarily swelled the fibre and allowed the dye to penetrate into the structure. There, the dye molecules would reside in the amorphous regions between the crystallites, since the crystallites were too densely packed with ordered polymer chains in a crystal lattice to allow dye molecules to penetrate them. Typical carriers are molecules such as *o*-phenylphenol (2-hydroxybiphenyl) and they became widely used, since they greatly improved the economics of dyeing polyester. The alternative dyeing method was pressure-dyeing with superheated aqueous dye liquors at 135–150 °C (well above the T_g of drawn PET fibre).This was a capital-intensive process, for the pressure dyeing vessels were large and expensive. Only the larger dyehouses could afford them. Eventually, pollution problems with dyehouse waste led to use of carriers being severely restricted in many places. Pressure dyeing is now the norm, the dyeing industry having undergone drastic shrinkage in many Western countries. This is one reason why non-PET polyester fibres such as PBT and PTT are so attractive to the dyer. Both have T_g values about 45 °C, so they can be dyed to heavy shades at the boil, and show good dyebath exhaustion, all without the need for expensive pressure equipment.

The very reluctance of polyester to dye has been turned to commercial advantage. Polyester carpets are now widely advertised against nylon carpeting because they are *stain resistant***,** particularly to food stains such as tomato sauce and coffee. The argument is that if a fibre does not readily dye, neither should it easily stain. An example is the announcement by Shaw Industries for their *Corterra*® carpets, which are advertised as wearing like nylon but without the need for stain-resist treatments. It is claimed that food stains (mustard, coffee) can be sponged away with hot water only.[207]

3.10.3 Anionic and cationic dyes for polyester

Since much polyester was originally used in blends with wool, it was natural that attempts should have been made early on to modify PET to make it dyeable with anionic (acid) dyes. The most popular theme was to incorporate a basic additive by copolymerising a hydroxy-amine or an amino acid into the PET structure. All such attempts led to failure, as the copolymers were discoloured, yellow or brown, and of low IV. In some cases, grossly degraded tarry substances were the only product. Many years ago, the author and his colleagues devoted much time and effort at ICI Fibres to this problem and achieved partial technical success. The reason for the early failures was revealed when it was shown that PET above 200 °C reacts with tertiary amines to generate a quaternary ammonium salt, as a result of O-alkyl scission. This salt rapidly decomposes, generating vinyl ester ends which, as we have already seen, are the first step in many subsequent degradation reactions:



The O-alkyl cracking reaction seems to be general for all terephthalate polyesters. PBT does not degrade as severely as PET; there are no vinyl ester ends formed to generate colour and the spinning temperatures are lower, around 240 °C. IV drop is still a problem but it is more manageable. To make a melt-spinnable PET product, any acid-dyeable basic additive must not be allowed to interact with the polyester at the usual PET melt-spinning temperatures (≈ 285 °C).

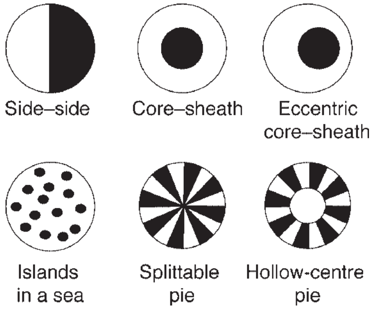
It was found that adding an amine to PET fibre was not sufficient to achieve good dyeability. PEG copolymers with a basic additive dyed to much deeper shades with the same level of additive. As with other PEG copolymers of PET, the dye light fastness was adversely affected, but this was much less of a problem if the PEG was melt blended *as a separate phase* rather than existing as a copolymer. A chance observation showed that certain polyamides containing additional in-chain tertiary amine groups, when melt blended with both PET and a high molecular weight PEG (MW ≈ 20 000) formed a three-phase mixture in which the polyamide was dispersed inside the PEG and this in turn dispersed inside the PET. Thus, the interactive phases were prevented from intermixing in the melt. The mixture was melt-spun at 270–275 °C into fibres that had an outstandingly high affinity for acid dyes. They gave deep shades with a wide range of anionic dyestuffs; even high molecular weight direct cotton dyes showed good dyeability.[208] The reason for the beneficial effects of PEG on acid dyeability is not definitely known but is probably due to its positive effect on fibre *hydrophilicity.* Acid dyes are sulphonic acids and the SO_3H group is usually associated with a hydration shell of *water molecules.* The argument is that sulphonic acid dyes will not adequately penetrate the polyester fibre unless they can take this hydration shell with them.

Patterned jacquard knit fabrics have been produced with mixtures of the dyeable variant and normal PET. These could be cross-dyed to give patterned effects from one dyebath containing both acid and disperse dyes. However, dyeability alone is not the sole criterion of eventual success. The process was deemed to be too complex and expensive for a commercial product, and the light stability of the dyed fabrics was still felt to be inadequate. A subtle but annoying problem was the fact that it was not possible to dye two primary colours side by side. While the plain PET was not stained by the acid dyes, there was no way to 'reserve' the acid-dye variant to *disperse* dyes. If a mixture of a blue acid dye and a yellow disperse dye was used, the result would be stripes of green on yellow, not blue on yellow, for the yellow dye naturally had good affinity for *both* kinds of fibre.

Greater success was achieved by DuPont, who incorporated an acidic co-monomer, the sodium salt of 5-sulphoisophthalic acid, into PET to render the polymer dyeable with cationic dyes.[209,210] This class of dye had a reputation for poor light-fastness, but when polyacrylonitrile (PAN) fibres were first introduced into textiles, they usually contained some copolymerized methacrylic acid to give them affinity for cationic dyes, and new dyes were developed especially for acrylics. Cationic dyes on PAN give shades of excellent light-fastness.[211] Hence the cationic dyeable PET was successfully launched as *Dacron 64* in the form of a low-pill staple product. As already mentioned, the presence of the pendant sulphonate group acts as an ionic dipolar cross-link. This increases the melt viscosity of the polymer quite markedly. Thus, it is possible to lower the polymer IV to ≈ 0.56 and still melt-spin under normal conditions, giving a low-pill fibre variant. The fibre also has a greater affinity for disperse dyes because of disruption of the PET structure. Continuing this theme, there are 'deep dye' variant PET fibres, often used in PET carpet yarns, which are copolymers of PET with chain-disrupting copolymer units such as polyethylene adipate or isophthalate. They have less crystallinity and a lower T_g, so they may be dyed at the boil without the use of pressure equipment or carrier, at the cost of some loss of fibre physical properties. As stated earlier, the new polyesters such as PTT may well solve many of these old-established dyeing problems.

3.10.4 Mass dyeing

Since much polyester, particularly staple fibre, is dyed to dark colours such as black and navy blue, which are expensive to apply from a dyebath, quite often the fibre is made from mass dyed or mass-pigmented polymer where the colouring matter is added at the polymerisation stage. Obviously, very thermally stable pigments or dyes have to be used. For black, special fine opaque pigment grades of carbon black are used, and this may need to be toned by adding small amounts of navy blue or very dark green melt dyes in order to remove any traces of brown, which is usually felt to be unpleasant and unacceptable. Mass dyeing is only economic if the demand is large enough to warrant it.



3.12 Cross-sections of various bicomponent fibres.

A more recent development is the so-called 'dope dyeing' (a term dating back to the acetate rayon industry), where a range of melt-dyed colours are produced by colouring white polymer immediately before melt-spinning by adding calculated mixtures of master-batch pigmented polymer or neat dyestuff. This can be conveniently done by adding the dye in the form of pills or granules containing a specific amount of dye at a calculated feed rate to the molten polymer during the melt-spinning process,[212] or by adding the colouring agent as a liquid dispersion in a very high boiling point (over 300 °C) inert oil, either during polymerisation or at melt-spinning.[213] The latter process is said to be of particular value in melt coloration of POY feedstock yarns.

3.11 Bicomponent fibres and microfibres

3.11.1 Introduction

Bicomponent fibres or 'heterofil' fibres are filaments made up of two different polymers. There are many geometrical arrangements. The three main heterofil geometries are side–side, core–sheath (both concentric and eccentric) and the multiple core or 'islands in a sea' configuration. The two polymer components, while different, paradoxically do not have to differ in chemical nature. They can differ only in physical parameters such as molecular weight. Usually it is desirable that the two components have good mutual adhesion, but not always. Polyolefines with polyesters or polyamides do not bond well and this is exploited in the formation of microfibres (see Section 3.11.7). The so-called 'splittable pie' configurations are used in their production (see Fig. 3.12).

3.11.2 Side–side bicomponent fibres

Side–side bicomponent fibres can be used to produce self-bulking yarns. Two PET polymers of different molecular weights, spun as a side/side heterofil, will, on drawing, produce a self-bulking fibre after relaxing because the two spun birefringences will differ. The relaxed yarn will curl up for the same reasons that a bimetallic strip with different expansion coefficients will curl up and a spiral crimp will result. A self-bulking fibre can also be made by co-spinning PET with a PET copolyester containing a branching agent in a side–side configuration.[214]

3.11.3 Core–sheath bicomponent fibres

The core–sheath (c/s) configuration is very adaptable because many different polymers may be applied as a sheath over a solid polyester core, thus giving a variety of modified surface properties while maintaining all the major fibre and textile properties of PET. An early patent by Shima and co-workers uses an eccentric core–sheath configuration to achieve spiral crimp in a yarn.[215] A recent patent by Chang and co-workers teaches the use of side–side or eccentric c/s bicomponent fibres to achieve a self-crimping yarn made from poly(trimethylene terephthalate) where one component is a melt blend of PTT with a small amount of polystyrene.[216]

We have already mentioned the antisoil/antistatic fibre made by using a PET/PEG block copolyetherester coating on a polyester core. A widely used c/s heterofil has a normal PET core with a lower softening-point sheath polymer (typically a PET/isophthalate copolyester). When such fibres are laid randomly in a non-woven structure and heated to a temperature above the softening point of the sheath polymer but below the fusion point of the core polymer, the fibres will adhere wherever they cross and touch. This may be done either by heated calendar rolls or simply in a forced draught hot air oven. The result is a stable non-woven fabric.[217] A new development is a biodegradable, non-woven material for disposable fabrics made by thermally bonding a polylactide core bicomponent fibre with a low-melting sheath polymer such as polyethylene.[218]

3.11.4 Multiple core bicomponent fibres

The multiple core or ‘islands in a sea‘ type of heterofil is mainly of interest in connection with microfibres, which are dealt with in Section 3.11.7.

3.11.5 Hollow fibres

Hollow fibres are yet another type of c/s heterofil: one in which the core is composed of air! They are usually made in the form of crimped staple fibre and spun from a modified staple spinning pack.[219] With advances in melt-spinner design, more complex geometries[220] are available. One patent describes a multiple-core circular polyester staple fibre with six outer hollow cores arranged around a central one.[221] Hollow fibres in the form of filament yarn have specialised uses in markets such as medical devices, but the largest volume market for hollow fibre is staple fibrefill for pillows, duvets, quilts and thermal outerwear. The desired quality is 'loft' and the lighter and more bulky the fibre, the better. Thermal insulation is a very desirable quality. Hollow polyester fibres are very well suited to this particular end-use: the air entrapped in the hollow cores adds significantly to their insulating properties; more hollow air cores increase this effect. The fibres are frequently crimped by a stuffer-box process or may be made as bicomponent hollow fibres which develop spiral crimp on drawing.[222] Such filler fibres are frequently treated with a permanent polysiloxane finish (called a 'slickening agent') that makes them slippery, so that they slide over each other easily and resist clumping. In this form, they can compete with goose down as a thermally-insulating filling material. For some end-uses, such as fabric interlinings, it may be desirable to stabilise a filled hollow fibre structure by incorporating an additional thermally bondable bicomponent fibre.[223]

3.11.6 Heterofil spinning

Bicomponent filament structures all depend on two separate streams of molten polymer being brought together in such a way that the desired heterofil configuration is achieved. There are many ingenious methods of accomplishing this in the patent literature, most depending on various flow-divider devices which subdivide a single split stream into numerous smaller streams.[214,224] More exotic flow configurations, suitable for microfibre production, are disclosed in patents by Moriki and Ogaswara[225] ('islands in a sea') and Kessler and Birken[226] ('splittable pie'). All heterofil spinners need two separate supplies of polymer, and usually two side-by-side extruders to supply the separate melts to the bicomponent spinning pack, where they are separately metered and filtered at the correct rates to achieve the final configuration. Differences in melt viscosity and density must be allowed for in the process, particularly with side–side configurations or the extruded filaments may be hydrodynamically unstable and exhibit 'kneeing' or 'wriggly' extrusion. A great deal of technology has been devoted to perfecting the process over the past 30 years, and now heterofil fibres are widely used and are becoming relatively cheaper to produce. At a recent conference on non-wovens in Toronto, Canada, one source said[227] that the annual quantity of bicomponent fibres of all types produced in North America was 250 000 tonnes, of which roughly half was used in non-woven fabrics.

3.11.7 Microfibres

By microfibres, we mean any individual fibre with a gauge of less than 1.0 dpf. By way of comparison, the normal filament yarn polyester is around 3.0–5.0 dpf. Microfibres are many times finer than a human hair and much finer than the finest silk: allowing for different densities, their diameters are generally less than 10 μm. A typical polyester microfibre has a titre of about 0.5 dpf. Such very fine fibres in the form of yarns have many excellent textile properties. They are very flexible, giving a soft ‘hand’, and add excellent drape to fabrics. The extremely high density of fibres per unit area in a typical microfibre fabric makes it inherently windproof and waterproof. There are only very tiny gaps for air to blow through and the fabrics are largely unwettable because surface tension effects prevent water from penetrating the interstices in the fabric. However, as water vapour from perspiration can still easily pass out, these fabrics are comfortable to wear. Their fabric properties make them ideal for women’s wear, sportswear, active wear and outdoor wear. They even have (radiant) heat-insulating properties, because the filaments are of the same order of dimensions as the wavelength of infrared radiation. A 0.5 dpf polyester filament (density ≈ 1.4 g cm^{-3}) has a diameter of about 7 μm, right in the middle of the IR wavelength range (2–20 μm). Hence the radiation is efficiently scattered by the microfibres and radiation loss of body heat reduced.

Microfibres lend themselves very well to desirable fabric aesthetics. Dyed fabrics seem to have very solid, bright colours, owing to the fine size of the individual filaments. They are frequently semi-matte in appearance without the need for extra treatments such as sand-washing. One disadvantage they do have is vulnerability to damage from careless ironing. The thermal capacity of the tiny filaments is very low, so it is easy to overheat them. They also have a tendency to snag easily and, as with all fine fabrics, they need to be handled with care.

3.11.8 Melt-spinning microfibres

The very first commercial microfibres were produced in Japan[228] in the 1970s and were made by spinning a bicomponent fibre with polyester fibrils dispersed in a matrix polymer in the ‘islands in a sea’ configuration (Okamoto *et al.*[229]). This was drawn into fibres, processed into fabric, and finally the matrix polymer was dissolved away, leaving very tiny polyester fibrils. These were processed into a synthetic suede material marketed as *Ultrasuede*®. The polyester fibrils were extremely fine, less than 1 μm in diameter. The process was relatively expensive, but the product was successful. During the mid-1960s, the author and his colleagues at ICI Fibres[230] worked quite extensively on melt blends of PET in a matrix of nylon 6,6. This gave the ‘islands in a sea’ structure, and, by dissolving the nylon away in 90 % formic acid, very fine discontinuous fibrils of PET were left. However, the thrust of the work was aimed at a very different target, so the idea of polyester microfibres was not pursued. At the same time, Robertson[231] at Firestone Tire and Rubber Co. was working on similar blends of PET in nylon-6 as a solution to the problem of flat-spotting (see above) in nylon tyre cords. Breen in the USA had also been working independently on blends of PET with soluble matrix polymers with the idea of making microfibres using PET blends and other thermoplastics.[232,233] Numerous variations on this theme later followed. One ingenious idea by Sato and co-workers[234] used a blend of PET in a PET-sulphoisophthalate copolymer rich in SO_3Na groups, which dissolved away readily in aqueous base, leaving the unaffected PET.

There are many patents in the literature, mostly on ingenious static devices for melt-spinning multiple fibres with the 'islands in a sea' configuration. This is usually done by a multiple series of flow-divider plates that take the initial side/side polymer flow (as in a heterofil spinner) and subdivide it and cross over the flow many times before the spinneret plate, so that each spun filament emerges with the desired structure. Some examples are further ideas of Okamoto and co-workers[235] and Dugan.[236] More recently, the dissolvable 'sea' or matrix polymer has been made of such materials as polylactic acid (already mentioned), thermoplastic starches or water-soluble copolyesters. Good review articles on microfibres have been written by Robeson,[237] Murata,[238] and Isaacs.[239]

Another method of making microfibres is the so-called 'splittable pie' technique where a bicomponent fibre of special configurations as shown in Fig. 3.12 is spun from two incompatible polymers that adhere only poorly. On subjecting these fibres to mechanical stress, as during staple carding, they split apart to form bundles of microfibres with a wedge-shaped cross-section. The filament geometry with the hollow core centre (as in Fig. 3.12) is more easily split apart than the 'solid' example, but involves a more complex bicomponent melt-spinning pack. PET/polypropylene or PET/nylon 6 are examples of suitable polymer combinations. Such microfibres are frequently used in non-woven fabrics such as filter materials and specialty fabrics such as cleaning cloths for microelectronic components and polishing cloths for lenses and delicate optical instruments. Many developments in these exotic fibres have come from Fiber Innovation Technology Inc. of Johnson City, TN, USA.[240]

Finally, with the steady advancement in melt-spinning techniques, combined with very high-speed spinning processes (around 7000–8000 m min^{-1}), it is now possible to make fully oriented yarns (FOY) in an integrated process with an individual filament titre of ≈ 0.3 dpf. Special spinning and quench arrangements to cool the molten threadline are needed at these extremely high spinning speeds. The whole topic of high-speed spinning has been dealt with thoroughly in recent specialised publications.[241–243] Various ways to modify the melt-spinning process have been employed. Richardson at ICI[171] use a heated shroud followed by an air quench; Koschinek and co-workers[170] use a carefully programmed airflow profile while Muller uses very small spinneret holes and a minor amount (0.05–5.0% w/w) of an immiscible amorphous polymer added to the melt before spinning[244] which, one may speculate, promotes plug flow through the spinneret holes. Schippers and co-workers[245] use a high-speed spin-draw process with an added radiant heater while Ruzek and Bruckner use a co-linear stream of hot air surrounding each extruding filament by use of a modified core/sheath bicomponent fibre spinneret in addition to a subsequent cold air quench.[246]

3.12 World markets, future trends and conclusion

The total world market for all synthetic fibres in 2002 was around 36 000 000

Table 3.9 World volume estimates of synthetic fibres

Fibre type	World volume in 2002 (estimate; tonnes)
Polyester	21 400 000
Nylons and aramids	4 400 000
Spandex	400 000
Acrylics	2 800 000
Polyolefines	6 800 000

Source: *DuPont Annual Report, 2001*

tonnes. Of this total, some 21 400 000 tonnes is polyester (see Table 3.9) and the rate of consumption is still growing, although at the time of writing (2003) the rate of increase is smaller than the 8% per year that was common hitherto. Over the past 15 years, there have been many cataclysmic changes in the polyester producing fibre business. The gradual eclipse of the textile industry in the USA and much of Western Europe, and its geographical shift to Asia and other places, such as Central America and parts of Eastern Europe, has brought about these changes. Old-established, integrated chemical firms such as ICI, Hoechst, Monsanto and Eastman have disappeared completely from the fibre-producing scene. DuPont, alone of the old leading chemical firms, remains in the USA, having acquired ICI's PET polymer-producing facilities in 1998. In February 2002, DuPont[247] set up its fibre and textile interests as a separate concern under the name *Invista.* Recently (November 2003) it been announced[248] that Koch Industries will acquire *Invista* in the near future.

The new fibre producers buy polyester polymer on the open market as a commodity item and convert it into fibre and yarn. They have revolutionised the polyester market and superseded the old order. Koch Saba (KoSa) will, for example, buy 3GT polymer from Shell and spin *Corterra*® fibres and market them, although Shell retains the trade mark; KoSa proposes[249] to build its own polymer plant in Mexico. New giant firms such as Wellman Industries and KoSa in the USA and others in the Far East now dominate the picture.[250] The emergence of China as a major consumer and as a growing producer of polyester fibre will undoubtedly have a further large effect on world markets.

The market for polyester fibre will certainly continue to grow overall, although as a major commodity item it is likely to be affected very much more than in the past by global economics and trade cycles. Certainly, the price of raw materials such as crude oil and natural gas will have an effect on process costs and markets. Nevertheless, there is still a trend to replace other fibres, both natural and synthetic, with polyester. Nylon is still losing overall markets to polyester. At present, nylon dominates polyester in domestic carpet yarns, but PET has a growing share of the contract carpet trade simply because it is cheaper. The new microfibres and newer easy-to-dye polyesters with excellent resilience (such as PTT) are expected to make big inroads into floor coverings and the apparel markets over the next few years. It was confidently expected that PTT would have an immediate impact on the carpet business (one place where PET polyester suffers) in 1999–2000 when *Corterra*® was first launched. So far, this has not happened, but fibre price and availability, as always, are major factors. In the long term, there are, as we have seen, new non-oil-based biomass-derived processes in commercial production for making not just intermediates for polyesters but even the polymers themselves. The effect of recycling polyester such as soda bottles into fibrefill and carpet yarns may also have unpredictable effects.

For some 40 years, people in the polyester fibre business (and this includes the author, who spent 20 years of his working life there) have been aware of, and have had to endure, a popular sentiment that polyesters were somehow a cheap and inferior substitute for the supposedly superior 'natural' fibres. This never was true: natural fibres have many serious deficiencies. It is well known that cotton shrinks, linen wrinkles, silk turns yellow, and wears really quite badly, while wool creases, shrinks and is devoured by moths! Polyester has boosted the overall performance of natural fibres in the form of blended yarns and fabrics for many years. For example, polyester filament yarn charmeuse fabric is an ideal silk replacement, with excellent wash-wear properties, for fine fabrics in women's markets such as lingerie and blouses. The latest and newest generation of polyester fibres which are now emerging, such as microfibres and the highly resilient and stain-resistant PTT fibres for carpets, and those that will follow, will meet in their own right the market demands of a new generation of fibre consumers. In a constantly changing world, they will meet the challenge: maybe not always in ways we can foresee at present, but meet it they most surely will.

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4

Acrylic fibres

R. COX
Acordis Acrylic Fibres

4.1 Introduction

The textbook definition of an acrylic fibre is one that contains at least 85 % by mass of acrylonitrile comonomer in the polymer chain.[1] All commercial processes for the manufacture of acrylic fibres are based on free radical polymerisation, as this technique gives the required combination of polymerisation rate, ease of control and properties such as whiteness, molecular weight and linearity. This polymerisation technique also allows the incorporation of other comonomers, which impart important fibre processing properties, and in most cases, dye sites for coloration purposes.

Acrylic fibres vary from virtual homopolymers of acrylonitrile, which tend to be used for industrial or high-performance related end-uses, to fibres containing up to 15 % (but typically 5–10%) of comonomers for more typical textile end-uses. The comonomers used all contain ethylenically unsaturated groups and well over 200 such monomers have been listed.[2] However, only about 15 such molecules are actually used in commercial products, of which various combinations of only 8 make up the vast majority. These are listed in Table 4.1.

A second category of acrylonitrile-based fibres also exists and they are known as ‘modacrylic fibres’. These contain by definition less than 85 % by mass acrylonitrile (but a minimum of 35 %) in the polymer chain and hence at least 15 % comonomer. The comonomer content tends to be much higher than this and is typically around the 40 % mark. The comonomers used are almost all based upon halogenated ethylenically unsaturated molecules that impart excellent flame-retardant properties to the polymer. The most commonly used comonomers in this category are vinylidene chloride, vinyl bromide and vinyl chloride.

Acrylonitrile and polyacrylonitrile were both first synthesised in 1893,[3] but it was not until 1938 that fibres of polyacrylonitrile (PAN) were announced.[4] This delay in the industrial exploitation of PAN polymers was due primarily to the fact that the polymer could not be melted without degradation, and no solvents were known to allow solution processing.

Once a number of suitable polymer solvents had been found in the late 1930s

Table 4.1 Polymer composition of acrylic fibres

Monomer	Neutral comonomer	Acid comonomer
Acrylonitrile, 85–100%, typically 90–94%	0–14%, typically 6–9% methyl acrylate vinyl acetate methyl methacrylate acrylamide	0–1% sodium styrene sulphonate sodium methallyl sulphonate sodium 2-methyl-2-acrylamidopropane sulphonate itaconic acid

and early 1940s then the commercial development of acrylic fibres began in earnest. The manufacture of acrylic fibres grew steadily throughout the 1950s and 1960s and peaked during the mid 1980s when annual capacity reached 2.4 million tonnes. During the 1950s at least 18 companies introduced acrylic fibre products, most of which were based in Western Europe and the USA. During the 1970s there was rapid growth of acrylic fibre production in Japan, Eastern Europe and developing countries and by 1981 an estimated overcapacity of 20% existed. The result of this was a steady decline in production since 1981 which is showing signs of steadying out, particularly as demand and capacity in emerging countries such as China increase. The geographical location of manufacture has, however, changed dramatically during this time, resulting in many of the pioneering companies withdrawing from the market (e.g. DuPont and Hoechst).

Acrylic fibre polymers cannot be melt-spun as the polymer degrades before its melting point. It is for this reason that acrylic fibres are one of the major raw materials for carbon fibre manufacture. Acrylic fibre polymers are therefore all spun from solvents.

The common solvents that have been used in the manufacture of acrylics and the polymer concentrations used for the spinning dopes are listed in Table 4.2. These very powerful polar solvents are able to disrupt the considerable hydrogen bonding that is present between the (alpha) hydrogen atoms and the nitrile groups, and the dipole bonding between pairs of nitrile groups, both of which result in chain stiffness within the acrylic polymer.

4.2 Chemical intermediates

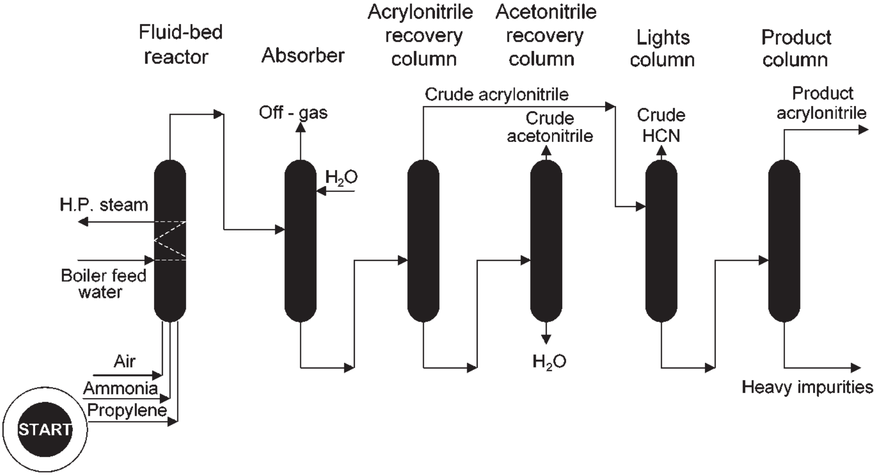
Acrylonitrile (also called acrylic acid nitrile, propylene nitrile, vinyl cyanide and propenoic acid nitrile) can be manufactured by one of three commercial routes. These are based upon propylene, acetylene and ethylene. However, at the present time virtually all acrylonitrile is manufactured from propylene using the Sohio process.[5] This is a heterogeneous vapour-phase catalytic process using selective oxidation of propylene and ammonia, commonly referred to as the propylene ammoxidation process (eq. 4.1):

Table 4.2 Solvents used commercially for spinning acrylic fibres

Solvent	% Polymer
Dimethylformamide	28–32
Dimethylacetamide	22–27
Aq. sodium thiocyanate	10–15
Aq. zinc chloride	8–12
Dimethyl sulphoxide	20–25
Nitric acid	8–12
Ethylene carbonate	15–18

$$H_2C{=}CH{-}CH_3 + NH_3 + \tfrac{3}{2}\,O_2 \xrightarrow{\text{catalyst}} H_2C{=}CH{-}CN + 3H_2O \qquad [4.1]$$

The Sohio process uses a fluid-bed reactor in which propylene, ammonia and air contact a solid catalyst at 400–510 °C and 50–200 kPa pressure. It is a single pass process with about 98% conversion of propylene. Some 1.1 kg of propylene is used per kg of acrylonitrile produced. Useful by-products from the process include hydrogen cyanide (about 0.1 kg per kg of acrylonitrile), which is used primarily in the manufacture of methyl methacrylate and acetonitrile. Acrylic fibre quality (99.2 % minimum) acrylonitrile is obtained by fractionation of the crude acrylonitrile mixture. Improvements in this process have been introduced over the past 40 years as new and more efficient catalysts have been developed. These catalysts are multicomponent mixed metal oxides mostly based upon bismuth–molybdenum oxide or antimony–iron oxide. Figure 4.1 is a process flow diagram for the Sohio process.



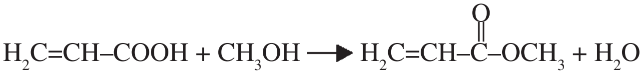
4.1 Process flow diagram of the commercial propylene ammoxidation process for acrylonitrile – Sohio process. Source: Jacqueline I. Kroschwitz, editor, *Encyclopedia of Chemical Technology*, Vol. 1, p. 357 ©1991 John Wiley & Sons, reprinted by permission of John Wiley & Sons Inc.

The structure of acrylonitrile is best represented as the resonance structure:

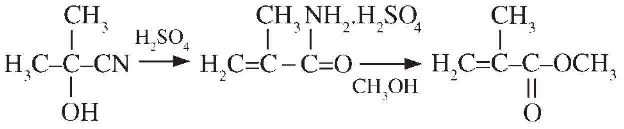
$$\mathrm{CH_2{=}CH{-}C{\equiv}N{:}} \longleftrightarrow \mathrm{CH_2{=}CH{-}\overset{+}{C}{=}\overset{-}{N}{:}} \longleftrightarrow \mathrm{\overset{+}{C}H_2{-}CH{=}C{=}\overset{-}{N}{:}} \qquad [4.2]$$

Acrylonitrile undergoes a wide range of reactions at its two chemically active sites, the nitrile group and the carbon–carbon double bond. Acrylonitrile must be stabilised with a hydroquinone inhibitor in order to prevent polymerisation, which occurs readily, particularly in the presence of light. Polymerisation is initiated by free radicals, redox catalysts or bases and can be carried out in the liquid, solid or gas phase. Homopolymers and copolymers are most easily produced using liquid phase polymerisation.

Some of the comonomers used in the manufacture of acrylic fibres can be synthesised from the chemicals produced from the Sohio process, while others are derived from closely related processes. The ester methyl acrylate is commonly used in acrylic fibres and is obtained by the esterification of acrylic acid. Methanol, acrylic acid and a catalyst (often sulphuric acid) are fed into a reactor at about 80 °C and the ester is separated by distillation (eq. 4.3). Another very important comonomer, methyl methacrylate, is manufactured by treating acetone cyanohydrin with concentrated sulphuric acid at 100 °C to form methacrylamide sulphate. This is fed directly into aqueous methanol from which the methyl methacrylate is isolated by steam distillation and then purified by distillation (eq. 4.4). Methyl methacrylate is a colourless liquid with a characteristic sweet odour, b.p. 100.5 °C.



$$\mathrm{H_2C{=}CH{-}COOH + CH_3OH \longrightarrow H_2C{=}CH{-}\overset{\overset{O}{\|}}{C}{-}OCH_3 + H_2O} \qquad [4.3]$$

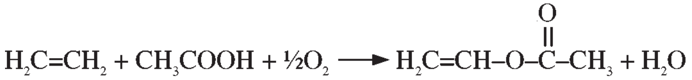


$$\mathrm{H_3C{-}\underset{OH}{\overset{CH_3}{C}}{-}CN \xrightarrow{H_2SO_4} H_2C{=}\overset{CH_3}{C}{-}\overset{NH_2.H_2SO_4}{C}{=}O \xrightarrow[CH_3OH]{} H_2C{=}\overset{CH_3}{C}{-}\underset{O}{\underset{\|}{C}}{-}OCH_3} \qquad [4.4]$$

Acrylamide is prepared by the controlled hydrolysis of acrylonitrile. This reaction used to be achieved by the use of sulphuric acid, but the development of suitable catalysts has replaced this process. A typical process is one in which a <10 % aqueous acrylonitrile mixture is fed into a reactor containing a copper–chromium oxide catalyst at 85 °C (eq. 4.5). Acrylamide is separated from the solution by crystallisation. Acrylamide is a white crystalline solid, m.p. 84–85 °C:

$$\mathrm{H_2C{=}CH{-}CN + H_2O \longrightarrow H_2C{=}CH{-}\overset{\overset{O}{\|}}{C}{-}NH_2} \qquad [4.5]$$

The main comonomer used in acrylic fibre manufacture today is undoubtedly vinyl acetate. This is a colourless liquid with a b.p. of 72.5 °C which has a pleasant, sweet odour. It was traditionally manufactured by the reaction of acetylene with acetic acid, but this has been almost completely replaced by a more economical process in which a mixture of ethylene and acetic acid in the gaseous phase is oxidised over a palladium catalyst at a pressure of 0.5–1 MPa and a temperature of 150 °C –200 °C (eq. 4.6). The exit gases are quenched and vinyl acetate is separated by distillation.



$$H_2C{=}CH_2 + CH_3COOH + ½O_2 \longrightarrow H_2C{=}CH{-}O{-}\overset{\overset{\displaystyle O}{\|}}{C}{-}CH_3 + H_2O \qquad [4.6]$$

4.3 Polymerisation techniques

The commercial processes used to manufacture acrylic fibres are all based on free radical techniques, as these allow the control over the process necessary to produce polymers that can be turned into fibres with all the correct physical, chemical and aesthetic properties. Other techniques have been reported in the literature[6,7] but these have been of no commercial interest to date. They are based upon anionic polymerisation but the resulting polymers suffer from quite significant drawbacks. The colour of the polymer is fairly poor owing to side chain reactions, dyesite end-groups are not incorporated, and only certain comonomers can be used. Two different free radical techniques are used commercially and these are known as solution polymerisation and aqueous dispersion or slurry polymerisation. The techniques are quite different and the resulting fibres are also distinctly different. However, there are a number of parameters that are of fundamental importance for the spinning of good fibres and for the final end-use properties that are common to both polymerisation processes. Two other types of free radical polymerisation are possible, the more fundamental of which is the bulk polymerisation method. This technique is, however, restricted by the autocatalytic nature of the polymerisation. The other technique is known as emulsion polymerisation and is used primarily for modacrylic compositions where a high level of a water-insoluble monomer is used or where the monomer mixture is relatively slow reacting.

4.3.1 Properties required in acrylic polymers for fibre end-uses

4.3.1.1 Molecular weight

The molecular weight and the distribution of molecular weights are key polymer properties and are used by all manufacturers as key quality control measures. The molecular weight of the polymer must be low enough that the polymer is readily soluble in the spinning solvents, yet high enough to give a dope of moderately high viscosity. Typical commercial acrylic polymers for textile purposes have number average molecular weights in the range 40 000–70 000. The weight average molecular weight is typically in the range 90 000–170 000, with a polydispersity index between 1.5 and 3.0. Higher molecular weight polymers are used for specific end-uses in which fibre strength and modulus need to be higher; for example, cement reinforcement and carbon fibre precursor.

The solubility of the polymer and the rheological properties of the dissolved polymer as a dope differ for dry-spinning and wet-spinning and for solvent type. These differences are due to the different comonomers used, the concentration differences, molecular weight differences and, of course, solubility differences for each solvent. Molecular weights are adjusted to maximise spinning performance in each case. The critical parameters affecting spinning performance are polymer concentration and polymer viscosity. It is desirable to have as high a polymer concentration as the solvent allows as this minimises the volume of solvent to be recovered. However, the polymer concentration is inversely related to the viscosity average molecular weight and so it is equally desirable to have as low a molecular weight as fibre properties will allow. The molecular weight is affected by all of the variables in the polymerisation including initiator concentration(s), unreacted monomer concentration, comonomer type and concentration, reaction temperature and time.

4.3.1.2 Dyeability

Fibre dyeability is another property that is critically dependent on molecular weight; this is because most acrylic fibres use a redox initiator system that results in sulphonate and sulphate end-groups. Thus, the dye-site content is inversely proportional to the number average molecular weight of the polymer. A critical balance must therefore be established between the molecular weight requirements for rheological properties and the distribution required for good dyeability. Where such a balance cannot be achieved, and in polymer systems that do not use a redox initiator system, it is usual practice to incorporate one of various ionic dye-site monomers into the polymerisation recipe.

4.3.1.3 Fibre whiteness

Most acrylic fibres are used in textile end-uses and so a good white fibre base is important not only for achieving good whites but also for achieving the brightness associated with coloured acrylics (dyed or pigmented). Acrylic fibres have a slight tendency to yellow and this is associated with side chain reactions between adjacent cyano groups. Much effort is therefore put into maintaining good fibre whiteness and this is achieved by attention to the polymerisation details, the addition of fluorescent additives to the polymer and the removal of as many impurities as possible from the recovered solvents.

In terms of polymer control, high monomer concentration (low conversion)[8] minimises the side chain reactions. Redox couples such as sodium nitrite with sodium bisulphite[9] have been effective in aqueous polymerisation because they are cost effective, are required in very low concentrations and produce acid end groups into the polymer chain. Alternatives such as organic peroxides or azo compounds are less effective, are more expensive and do not produce the required acid end groups on the polymer chain. In solution polymerisation, substitution of carboxylic acid dye-sites by the more thermally stable sulphonic acid dye sites has been particularly effective.

4.3.2 Polymerisation methods

Virtually all acrylic fibres and, of course, all modacrylic fibres contain at least one comonomer. Even fibres designed for industrial end-uses and that are nominally homopolymers usually contain at least 0.5 % comonomer. An example of this is *Dolanit*, manufactured originally by Hoechst then by Acordis for industrial end-uses, which bases its polymer upon 99.5 % acrylonitrile and 0.5 % methyl acrylate.

An understanding of the kinetics of copolymerisation is therefore of fundamental importance if the final polymer composition is to be predicted and, of course, controlled. Four free radical polymerisation techniques can be used to manufacture acrylic fibres. Of these only two are used commercially for acrylic fibres (solution polymerisation and aqueous dispersion polymerisation) while a third (emulsion polymerisation) tends to be used for modacrylics.

4.3.2.1 Bulk polymerisation

This technique is not used commercially because of the autocatalytic nature of the reaction and the very high viscosity that is formed at relatively low conversions (40–50%), although the patent literature does refer to two Montefibre patents that claim that this autocatalytic behaviour can be controlled.[10,11] The heat of reaction is controlled by operating at relatively low (<50 %) conversion levels of monomer; free radical initiators are therefore chosen that have extremely high decomposition rate constants. The rate of addition of these initiators is then used to control the rate of polymerisation.

Acrylonitrile polymer is insoluble in its own monomer owing to its highly polar and pseudocrystalline structure. As a result of this, the polymer particles are precipitated from the reaction medium as soon as they are formed, giving a milky white appearance. The polymerisation is autocatalytic even under isothermal conditions. Three simultaneous propagation reactions have been shown to account for the autoacceleration.[12,13] These are chain growth in the continuous monomer phase; chain growth of radicals that have precipitated from solution onto the particle surface; and chain growth of radicals within the polymer particles.

4.3.2.2 Aqueous dispersion polymerisation

This technique is the most widely used process in the industry today and redox initiation is normally used. This type of initiator generates free radicals in the aqueous phase at relatively low temperatures. A number of different redox systems have been used but the most common consist of an oxidiser (ammonium or potassium persulphate), a reducing agent (sodium bisulphite), and ferric or ferrous iron as the catalyst. The normal operating conditions are pH 2–4 at temperatures of between 35 and 60 °C. The mechanism for radical formation is generally accepted to be:

$$\begin{aligned} S_2O_8^{2-} + Fe^{2+} &\longrightarrow Fe^{3+} + SO_4^{\bullet} \\ HSO_3^{-} + Fe^{3+} &\longrightarrow Fe^{2+} + HSO_3^{\bullet} \end{aligned} \qquad [4.7]$$

Two different free radicals are formed, which react with monomer to initiate chain growth. The sulphate and sulphonate groups derived from these radicals are therefore always positioned at the chain ends and usually serve as dye-sites in the final fibre. The dyeability of the fibre is therefore strongly dependent on the molecular weight of the polymer, which must of course be carefully controlled. This control is usually achieved by the addition of excess sodium bisulphite or a similar compound, and is due to the transfer of radical activity from one species to another with formation of a non-ionic end group. This is best expressed by:

$$P_m\bullet + HSO_3^{-} \longrightarrow P_mH + SO_3^{-}\bullet \qquad [4.8]$$

where P_m denotes a polymer chain of length m units. The sulphonate radical anion can then initiate the growth of a new polymer chain.

Full mechanistic studies of aqueous dispersion polymerisation have been carried out by a number of authors.[14] The reference cited is a summary of this work. It is widely accepted that when inorganic radical initiators are used, the initiation and primary radical/polymer growth occur in the aqueous phase. However, chain growth in the aqueous phase is minimal because the polymer formed quickly becomes insoluble in the water. When this critical molecular weight is reached, the polymer chains aggregate and collapse to form particle nuclei. Some of the radicals that continue to be formed in the aqueous phase can then be captured on the particle surface by a sorption mechanism. As the particle surfaces are also saturated with monomer, polymerisation continues in the swollen layer and the sorption becomes irreversible as the chain end grows into the particle. This phenomenon is known as particle nucleation and growth. Polymerisation is very rapid and 80 % conversion to polymer can be achieved within 20 minutes. However, in practice, residence times of between 40 minutes and 2 hours are quite typical.

The resulting polymer is washed and separated by filtration prior to storage. Depending upon the polymer solvent to be used in fibre spinning, the polymer will be dried for organic solvents but may be stored wet for aqueous salt solvents. Polymer blending may take place prior to the polymer dissolution stage in which a spinning dope is formed.

4.3.2.3 *Solution polymerisation*

This technique is widely used in commercial processes and offers cost advantages in as much as the polymer does not need to be isolated, washed and dissolved. The polymerisation takes place in a homogeneous medium in which the polymer is formed in a suitable solvent for the polymer. The solvents commonly used are highly polar in nature. Examples are dimethylformamide (DMF), dimethylsulphoxide (DMSO) and aqueous sodium thiocyanate (45–55% solution).

Although this polymerisation technique offers the advantage of directly forming a spinnable dope after removal of monomers, it does pose some difficulties. The first of these are that it is difficult to achieve high molecular weights because some of the solvents used have very high chain-transfer constants, C_s. For example, DMF has a value of $C_s = 2.8 \times 10^{-4}$ at 50 ºC and so chain termination is quite frequent. The value for dimethylacetamide (DMAc) is even higher. Other difficulties arise when non-volatile monomers such as ionic dye-site monomers are used. The difficulties are due to the unreacted monomer being hard to remove and the low solubility of the monomer in the solvent. The final restriction is that the monomers vinyl acetate and vinyl chloride cannot practically be incorporated because the reaction rates are so slow.

Some commercial processes use thermally activated initiators such as azo-di-isobutyronitrile or benzoyl peroxide, both of which decompose to form two free radicals. However, the parent molecules are slow acting under the reaction conditions used. Typical half-lives can be 10–20 hours at 50–60 °C. This does not, however, necessarily pose problems in modern reactors, which tend to be continuous steady-state reactors that can be run under pressure at temperatures as high as 80 °C. This allows residence times of 1–3 hours to be achieved. Other processes favour rapid-acting redox initiators such as ruthenium salts with an oxidising agent such as potassium persulphate.[15]

The kinetics of solution polymerisation are fairly straightforward, as there is only a single phase to be considered. A typical reaction scheme would be:

(a) Radical formation (I = azo or peroxide initiator; R• = free radical):

$$\mathrm{I} \xrightarrow{k_d} 2\mathrm{R}\bullet$$

(b) Chain initiation (AN = acrylonitrile; P_1• = chain with degree of AN polymerisation, DP = 1):

$$\mathrm{R}\bullet + \mathrm{AN} \xrightarrow{k_i} \mathrm{P}_1\bullet$$

(c) Chain propagation ($P_n\bullet$ = chain with DP = n; n includes 1):

$$P_n\bullet + AN \xrightarrow{k_p} P_{n+1}\bullet$$

(d) Radical transfer to monomer, solvent, additives:

$$P_n\bullet + XY \xrightarrow{k_{ct}} P_nY + X\bullet$$

(e) Termination by radical recombination:

$$P_n\bullet + P_m\bullet \xrightarrow{k_{tr}} P_{n+m}$$

(f) Termination by radical disproportionation:

$$2P_nCH_2\overset{\bullet}{CHCN} \xrightarrow{k_{td}} P_nCH = CHCN + P_nCH_2CH_2CN$$

(g) Termination by metal ion (such as ferric):

$$P_n\bullet + FeCl_3 \xrightarrow{k_{tm}} P_nCl + FeCl_2$$

The rate of polymerisation, R_p, is

$$R_p = k_p\,[AN]^x\left(\frac{k_d f[I]}{k_{ct}}\right)^y$$

where f is the initiator efficiency, and x and y are exponential factors that characterise the rate dependence on the monomer and initiator concentrations respectively.

4.3.2.4 Emulsion polymerisation

The mechanism of this polymerisation technique has been fully studied by a number of researchers.[16–21] The technique involves stirring the monomers in water along with a suitable emulsifier and a radical initiator. It has been shown that the emulsifier disperses a small portion of the monomer in aggregates of 50–100 molecules. These micelles have a diameter of about 5 nm. The majority of the monomer, however, stays suspended in droplet form with a diameter of 1000 nm. Radical formation occurs in the aqueous phase as described in aqueous dispersion polymerisation. These radicals are rapidly absorbed into the monomer micelles. Polymerisation proceeds rapidly, converting the micelle into a polymer particle nucleus. This particle nucleus continues to grow in size, being supplied with monomer by diffusion from the monomer droplets.

The resulting polymer particles are often less than 1 μm in diameter, which is smaller than the particles formed in bulk and aqueous dispersion polymerisation. (In those techniques the particle size tends to be between 20 and 50 μm.)

In these tiny 1 μm particles, radical recombination is much more likely to occur. As a result, chain growth begins when the first radical enters the particle by absorption and ends when a second radical enters. On average, only half the particles contain a growing radical at any given time. This unique property is very important because it allows high rates of polymerisation and very high molecular weight polymers to be formed.

Although this technique is not widely used commercially for acrylic fibre polymer production, there are many references to its use in the patent literature. Patents covering flame-retardant modacrylics in which vinyl chloride is used as the comonomer are the most notable of these.[22,23] This technique is used for this particular modacrylic polymer because the acrylonitrile–vinyl chloride monomer pair polymerises slowly and gives low molecular weight products by conventional techniques.

4.3.3 Copolymerisation kinetics

Acrylic fibre producers need to be able to predict not only the overall polymer composition but also the sequencing of the various monomers used and the compositional heterogeneity (within a polymer chain and from chain to chain). In order to make these predictions it is important to have an understanding of the relative reactivities of the various monomer pairs. Table 4.3 lists the reactivity ratios for the most commonly used monomer pairs.

In the copolymerisation of monomers 1 and 2, four possible rate constants exist (equations 4.9–4.12):

Table 4.3 Reactivity ratios for acrylonitrile copolymerisations

Monomer pair	r^1	r^2	Temperature (°C)
Vinyl acetate	4.05	0.06	60
Methyl acrylate	1.5	0.84	50
Vinyl chloride	3.6	0.05	50
Vinylidene chloride	0.91	0.37	60
Methyl methacrylate	0.15	1.20	60
Sodium styrene sulphonate	0.05	1.50	40
Acrylamide	0.87	1.35	30
Styrene	0.04	0.37	50

$$\sim\!\sim\!\sim\; m_1\bullet + m_1 \xrightarrow{k_{11}} \sim\!\sim\!\sim\; m_1m_1\bullet \qquad [4.9]$$

$$\sim\!\sim\!\sim\; m_1\bullet + m_2 \xrightarrow{k_{12}} \sim\!\sim\!\sim\; m_1m_2\bullet \qquad [4.10]$$

$$\sim\!\sim\!\sim\; m_2\bullet + m_1 \xrightarrow{k_{21}} \sim\!\sim\!\sim\; m_2m_1\bullet \qquad [4.11]$$

$$\sim\!\sim\!\sim\; m_2\bullet + m_2 \xrightarrow{k_{22}} \sim\!\sim\!\sim\; m_2m_2\bullet \qquad [4.12]$$

The overall rate of polymerisation is determined by the values of the four possible rate constants. The polymer composition, however, will be determined by the reactivity ratios r_1 and r_2, which are derived as follows:

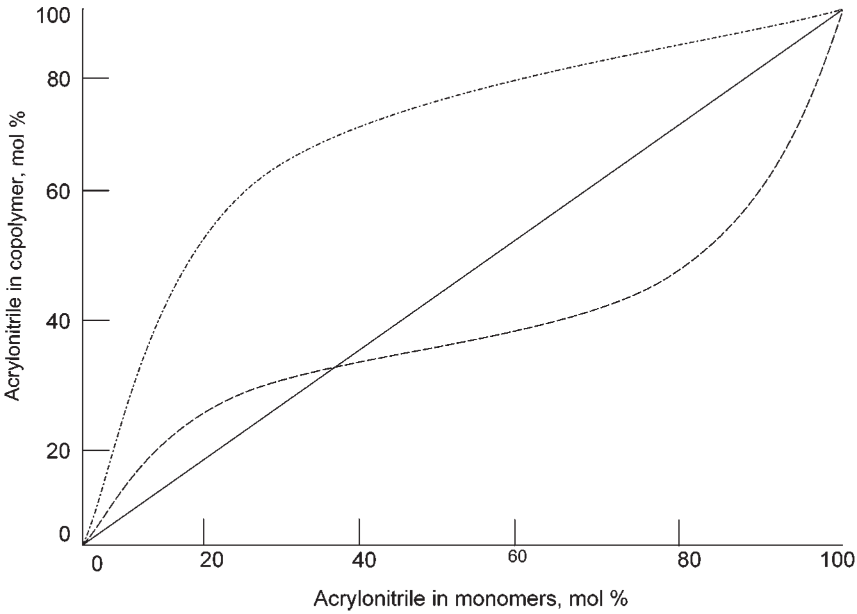
$$r_1 = \frac{k_{11}}{k_{12}}$$

$$r_2 = \frac{k_{22}}{k_{21}}$$

A value of r_1 greater than 1 indicates a tendency for the monomer 1 to incorporate in blocks, whereas a value of r_1 less than 1 indicates a tendency for monomer 1 to alternate with monomer 2 along the chain. If r_1 and r_2 are both less than 1, then the monomers tend to incorporate in an alternating sequence.

Many acrylonitrile monomer pairs have values of r_1 much larger than r_2. A good example of this is the acrylonitrile–vinyl acetate monomer pair in which $r_1 = 4.05$ and $r_2 = 0.061$. These values mean that the acrylonitrile radical chain end will react with another acrylonitrile monomer molecule much faster than it reacts with a vinyl acetate monomer molecule at the same concentration. The resulting polymer will therefore be much richer in acrylonitrile than the monomer mixture. Any chain ending with a vinyl acetate radical will also react much more quickly with an acrylonitrile monomer than with another vinyl acetate monomer. The overall result is that the vinyl acetate is incorporated poorly and virtually no vinyl acetate blocks are formed. However, acrylonitrile blocks are very likely. Three typical copolymer composition curves are given in Fig. 4.2. These are quite different and emphasise the importance of an understanding of monomer pair reactivity ratios.

Some polymer systems are based upon more than two monomers. For example, *Courtelle* fibre manufactured by Acordis in Grimsby, UK, incorporates methyl acrylate at 6 or 8 % and the dye-site monomer sodium 2-methyl-2-acrylamidopropane sulphonate (AMPS) at 1 %. Copolymer composition can be predicted for this system quite reliably by assuming that the component reactions involve only the terminal monomer units of the chain radical. A series of binary reactivity ratios can then be derived.



4.2 Three principal patterns of copolymer composition *vs*. monomer composition found in free-radical copolymerisation of acrylonitrile. Acrylonitrile is monomer 1; monomer 2 is vinyl acetate (r_1/r_2 = 4.05/0.61) (·–·–); methyl acrylate (r_1/r_2 = 1.5/0.84) (–––) and styrene (r_1/r_2 = 0.04/0.37) (——). Source: Jacqueline I. Kroschwitz, editor, *Encyclopedia of Chemical Technology*, 2nd edn, Vol. 1, p. 356 ©1985 John Wiley & Sons, reprinted by permission of John Wiley & Sons Inc.

4.3.4 Commercial processes

The use of an aqueous medium for the polymerisation is by far the most widely used technique. The reasons for this are quite simple: water acts as a convenient heat transfer and cooling medium, and filtration or centrifugation easily recovers the polymer formed. Some manufacturers use an aqueous-based polymer solvent system as the polymerisation medium (e.g. 45–55% sodium thiocyanate) which offers the advantage of directly forming a spinning dope. Solid polymer is never isolated in these systems.

The most common type of reactor used at the present time is the continuous stirred tank employing a steady-state system. This technique has replaced the semi-batch polymerisation process which was used in the early years of acrylic fibre production and is today restricted to some acrylic specialities of low volume. The continuous stirred tank reactors tend to be built in series and are often run continuously for many years, being shut down only for maintenance or in times of low production. Short-term polymer production requirements are often managed by changes to residence time in the reactors rather than the starting up and shutting down of reactors, as reactor start-ups can cause major polymer quality disruptions.

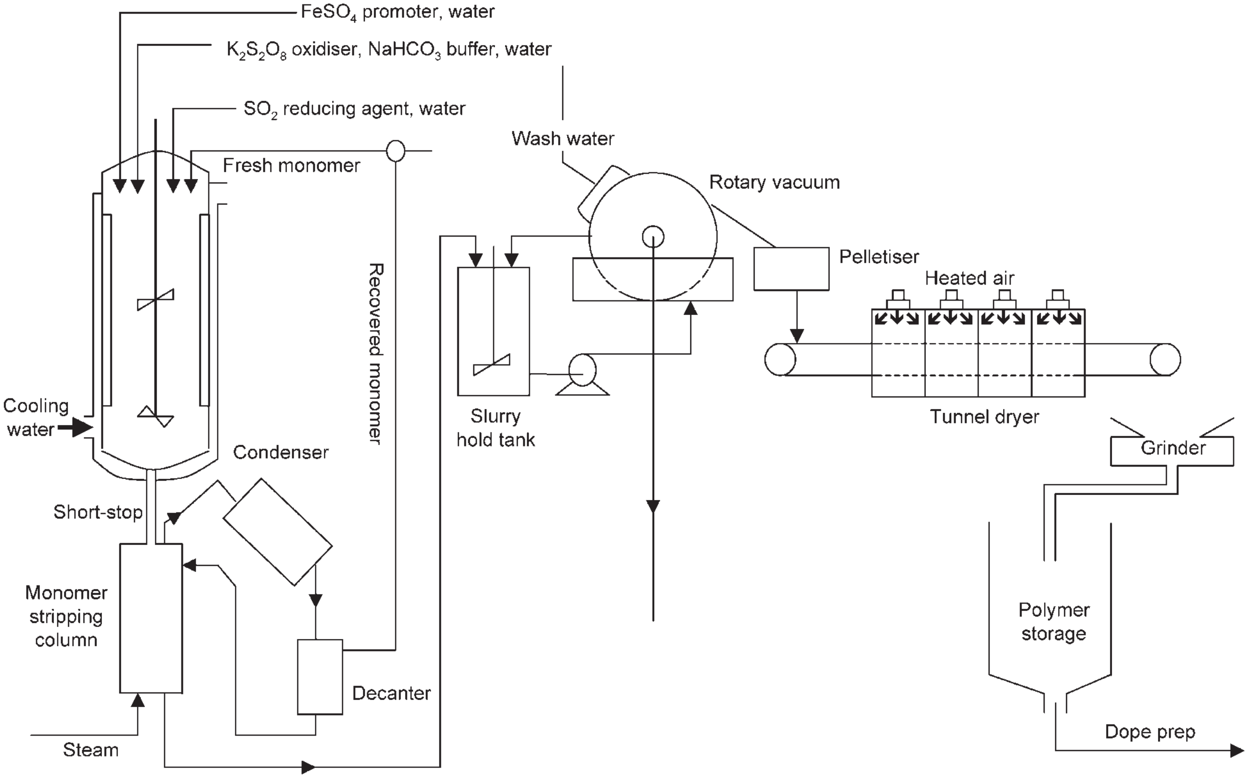
For aqueous dispersion reactions, the reactors tend to be manufactured from aluminium. This is to prevent the build-up of polymer on the walls of the reactor. The aluminium surface slowly dissolves because of the acidic nature of the reaction medium and it is necessary to determine the reactor wall thickness periodically in order to determine when new reactors are required. In solution polymerisation, the reactors need to be of specific grades of stainless steel in order to withstand the strong solvating properties of the solvents used.

A schematic of a continuous stirred tank reactor is given in Fig. 4.3. To start up a reactor, it is charged with a predetermined amount of reaction medium, usually solvent or pH-adjusted water. Monomers and initiators are then fed in, in the required amounts, and the temperature/pressure conditions established. For aqueous dispersion systems, monomer concentrations are higher than for solution polymerisation techniques because the system runs at a lower viscosity. A more refined technique, however, is to charge the reactor with overflow from a reactor already operating at steady-state conditions. This minimises the start-up time. The reactor feeds are then metered in at a constant rate for the entire course of the production run, which can last for many years. The advantages of this process over the semibatch process are that control of molecular weight, dye-site level and polymer composition are greatly improved.

A typical aqueous dispersion process would involve feeding a monomer mixture composed of acrylonitrile and up to 10 % of a neutral comonomer, such as methyl acrylate or vinyl acetate, continuously into the reactor. In addition, aqueous solutions of potassium persulphate oxidiser, sulphur dioxide reducing agent and sodium bicarbonate buffer are also fed into the reactor. The feed rates of these reactants and water can be varied to give a particular throughput, but reactor dwell times of 40–120 minutes are quite typical, with water to monomer ratios of 3–5. Reaction temperatures are typically 60 °C to 80 °C, which means that atmospheric conditions can be used. The conversions are typically 80%.

For redox-initiated polymerisations, the resulting polymer is then mixed with a material such as oxalic acid or ethylenediaminetetraacetic acid (EDTA) as it leaves the reactor, in order to stop the reaction quickly. The reaction is stopped in this case by removal of the iron within the redox couple. An alternative approach is to raise the pH, which will also stop the redox couple. This step is known as the short-stop stage. In some processes, the aqueous dispersion of polymer then enters into the monomer stripping stage, which is designed to recover unreacted monomers. In other systems, the slurry is washed and then dried. The drying process acts as a monomer removal and recovery stage.

This latter technique tends to be favoured for those processes in which the fibre-spinning process is from an organic solvent rather than from an aqueous-based solvent. One method is to feed the short-stopped slurry into the top section of a baffled separation column. The separation of monomer is achieved by passing a



4.3 An aqueous dispersion polymerisation process used in the manufacture of acrylic and modacrylic fibres. Source: Jacqueline I. Kroschwitz, editor, *Encyclopedia of Chemical Technology*, 2nd edn, Vol. 1, p. 358 ©1985 John Wiley & Sons, reprinted by permission of John Wiley & Sons Inc.

current flow of steam introduced at the bottom of the reactor. The monomers are recovered and recycled into the polymerisation process by condensing them from the overhead stream and then decanting them from the water layer. The virtually monomer-free slurry is then taken from the bottom of the column and separated from the water by a filtration process (usually a rotary vacuum filter). The resulting polymer cake is stored prior to blending and dissolution in the spinning solvent. This storage method is used for systems in which the fibre spinning is wet-spinning from *aqueous* solvents. Alternatively, for *organic* solvent-based fibre spinning, the polymer is dried and stored prior to dissolution. Which route is followed depends entirely on the polymer solvent used for the fibre spinning process. For example, Acordis uses this aqueous polymerisation technique in its Kelheim and Barcelona (now owned by Fisipe and no longer making acrylic fibres) plants. However, in Kelheim, the polymer is dried, stored and blended prior to dissolution in dimethyacetamide solvent while in Barcelona it is stored wet prior to dissolving in the aqueous sodium thiocyanate solvent.

For solution polymerisation, reactor start-up from empty involves the reactor being charged with buffered solvent, monomers and initiators, chain transfer agents and colour improvers. The temperature of the reaction will be chosen to suit the solvent used but the boiling point of acrylonitrile is 79 °C and so most reactors in solution polymerisation are run under a slight pressure. The speed of the reaction is controlled to ensure that side chain reactions (which can lead to poor polymer colour) are minimised. For the same reason, the reaction is not allowed to run to completion. Typical residence times will be 2–4 hours. The resulting polymer leaves the reactor and enters a multistage de-monomerisation process prior to being stored and blended.

4.4 Fibre production techniques

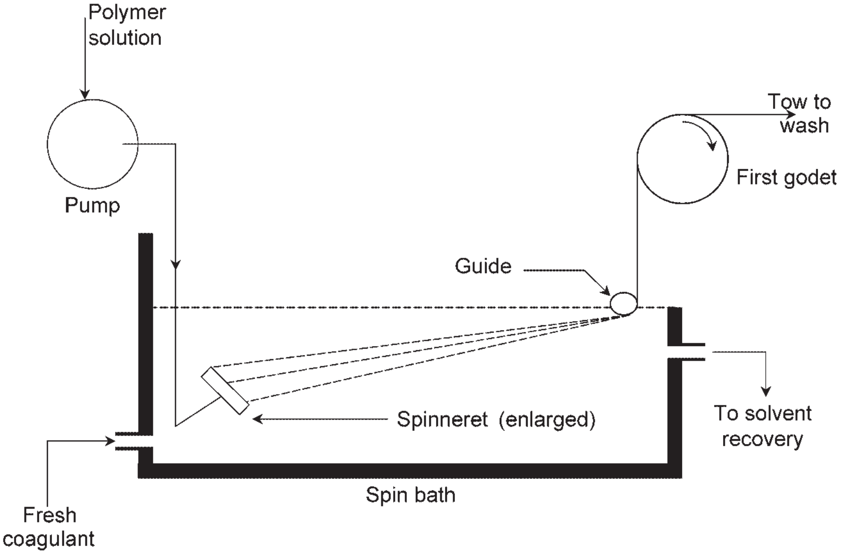
Commercial fibre spinning processes fall into two categories – wet-spinning and dry-spinning. Much effort has been put into trying to develop a melt-spinning process for acrylics and some speciality fibres can be spun from what are known as plasticised melts. However, the vast majority of acrylic fibres are spun either by dry-spinning, in which the fibre is formed by removal of the solvent in hot air, or by wet-spinning, in which the fibre is formed by a diffusion process in which solvent is exchanged for non-solvent. The reason why melt-spinning is not commercially viable is because all of the acrylic polymers made for fibre spinning begin to decompose before their melting points. The apparent disadvantage can, however, in some cases be turned to an advantage. This slow decomposition that takes place at elevated temperatures prior to the melting point actually facilitates the manufacture of carbon fibres. This involves the fibre decomposition being carried out in a slow and controlled oxygen-deficient process, which results in carbon fibre being formed.

We have seen from the description of the polymerisation techniques that the acrylic polymer can either be formed in a solvent solution or as a solid polymer that is isolated. Clearly, the solution polymerisation technique results in a polymer solution that is essentially ready for fibre spinning, while the slurry polymerisation technique requires the isolated polymer to be dissolved in an appropriate solvent. The polymer solution is known as a spinning dope and a considerable amount of technology is applied to this dope before it can be turned into a fibre.

However, the dry or semi-dry polymer resulting from slurry polymerisation must first be dissolved. This is a critical process as it is very easy to form polymer gels that once formed, are almost impossible to remove other than by filtration. In order to form gel-free dopes it is necessary to disperse the polymer in cold solvent (typically 5 °C) in order to form a fine slurry. At this temperature, the solvating properties of the solvent are minimised. The polymer is then dissolved by the application of heat and shear in a dope mixer or heat exchanger. The temperature requirements differ from solvent type to solvent type, as does the polymer concentration. Table 4.2 details typical polymer concentrations for the commonly used solvents. A typical dope temperature will be about 70 °C.

Economic considerations require that polymer concentrations and fibre extrusion rates are as high as possible. However, limitations exist and these are based upon the limits of polymer solubility, the viscosity/pressure required to pump the dopes through the spinnerets and the required fibre physical properties. Polymer solubility is limited by the solvent strength required to maintain a gel-free spinning solution at the temperature of the process. The concentrations given in Table 4.2 are optimised for each solvent. In wet-spinning, the jets are designed with thin plates containing many thousands of holes. One side of the spinneret contains the warm/hot polymer solution while the other side is immersed in the cold non-solvent. Back pressures on the spinneret face do therefore need to be fully understood and they do limit the conditions that can be used. Finally, the viscosity can be reduced in order to reduce pressures and thereby increase spinning speeds, but the properties of the fibre formed will vary significantly as these conditions are changed. There is also a minimum polymer concentration below which there is simply not enough polymer to form a fibre network in the fibre formation process. All of these factors have been fully explored by each of the pioneering companies that developed the various technologies in the 1950s/1960s and optimised for their process.

Polymer dopes of an appropriate concentration (for the solvent used) and viscosity (for the spinning technique) are common to both wet and dry-spinning. For both processes it is very important that the polymer dope is filtered and de-aerated prior to fibre spinning. Filtration is commonly achieved by passage of the polymer dope through a series of filters, which start off quite coarse and become finer as the polymer dope nears the spinneret. De-aeration is a function of time/pressure and air-free dopes usually emerge from the filtration processes. Various polymer additives are often introduced at an appropriate point in the filtration process. Common examples are titanium dioxide, which acts as a delustrant, and carbon black, which acts as a pigment.



4.4 Simplistic schematic of an acrylic fibre wet-spinning bath. Source: J. C. Masson, *Acrylic Fiber Technology and Applications*, p.73, by courtesy of Marcel Dekker Inc.

4.4.1 Wet-spinning

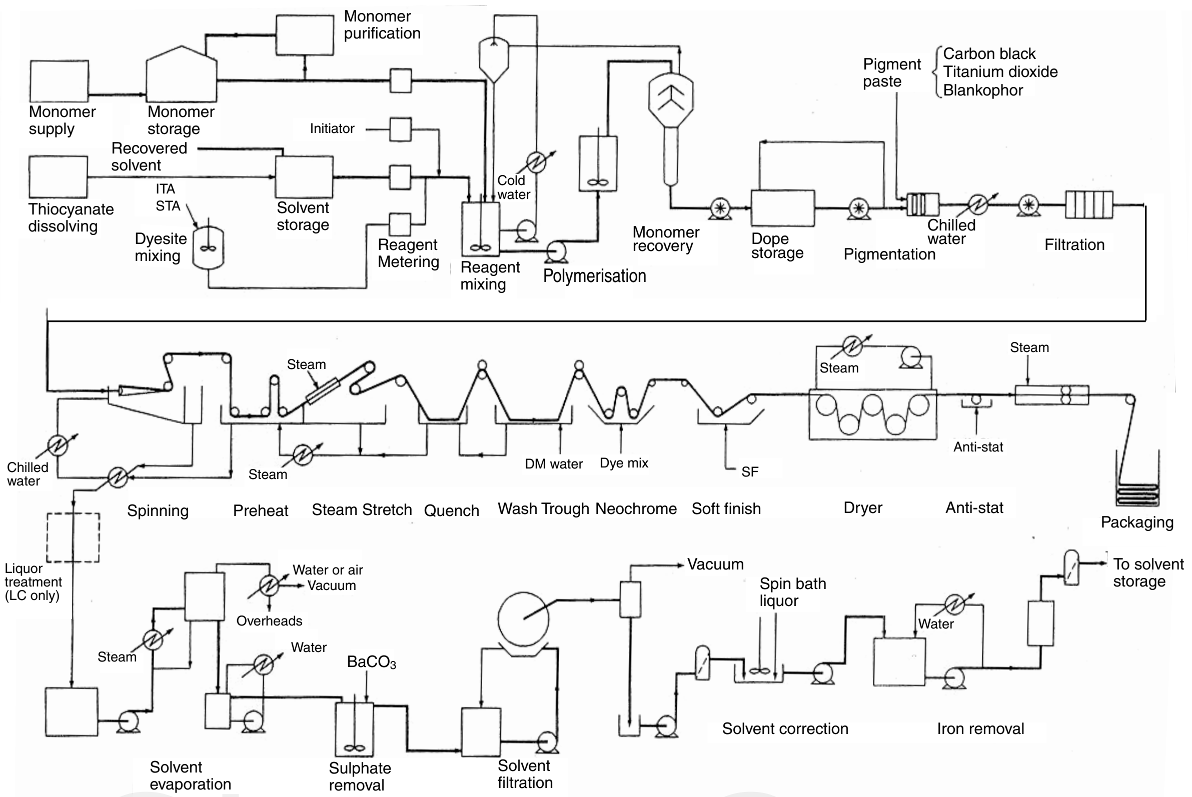
In wet-spinning the finely filtered and deaerated dope is spun through a spinneret into a dilute version of the polymer solvent. This dilute version of the polymer solvent acts as a non-solvent and allows the controlled formation of the fibre by a slow diffusion process. Polymer solvent is exchanged for non-solvent, which allows the polymer to come out of solution through a process simply known as coagulation. Figure 4.4 is a simplistic diagram to illustrate the basic design principles of the spin bath in wet-spinning.

The spin jets are usually made of precious metals in various alloys and come in many different designs. However, the basic principles are the same. Hole diameters vary from 0.05 to 0.38 mm and hole numbers vary from a few thousand up to 360 000. The length of the hole is also critical as fibre formation and fibre properties are influenced by the hole diameter/hole length ratio (known as the aspect ratio). Work within Acordis on their wet-spinning process has shown that the rate of dyeing and the fibre tenacities are influenced to a small extent by the aspect ratio and the cone angle used within the spin jet holes. These influences have been attributed to the polymer alignment that takes place as the polymer solution is accelerated and constricted as it moves down the capillary length. It is for this reason that the jet face containing the holes tends to be quite thin, which in turn limits the dope pressures that can be passed through the jet face. Jet designs also vary from simple circular jets containing a small number of holes but which tend to be used in large clusters (perhaps 20 jets in one bath) to the large strip jets pioneered by Courtaulds (Acordis), which contain as many as 360 000 holes.

The fibre microstructure is established in the spin bath and this is the critical part of the whole fibre-spinning process. The important part of this process is the transition from a liquid to a solid phase within each individual filament. Two liquid to solid phase transitions are possible in the spin bath. The first one is precipitation of the polymer to form a solid phase and the second one is the formation of a gel-state solid. All wet-spinning processes have been optimised so that the gel-state solid is formed. In this gel state, hydrogen bonding and dipole bonding between the polymer and solvent are present, which results in a very elastic structure. This facilitates subsequent fibre stretching in which the fibre physical properties are developed by orientation mechanisms. The microstructure formed from gel-state fibre is also much finer than that formed from precipitated polymer. In general, gelation occurs more rapidly at high dope solids and lower temperatures.

The fibre emerging from the spin bath is a highly swollen gel, containing both solvent and non-solvent. It is taken up by the first godet (driven roller), which is designed to give an exit velocity higher than the velocity of the polymer solution through the spinneret. This imparts a slight stretch to the fibre – usually somewhere between 1.5 and 2 times – which is known as the jet stretch. After the take-up godet, the fibres need to be washed to completely remove the remaining solvent, stretched in order to develop the tensile properties of the fibre, and dried to remove the water and to collapse the fibre. The sequence in which these processes take place varies from technology to technology; many companies have also developed on-line dyeing with cationic dyestuffs, which are applied to the gel state fibre. All fibre processes will also incorporate the application of a soft finish and an antistatic agent and some processes also incorporate an in-line steaming stage in order to fully develop the required fibre physical properties.

The basic steps are common to all wet-spinning processes but the designs for each technology can be quite different. Figure 4.5 is a simple schematic, showing one of the many variants possible. The stretching operation can be done in hot water over a series of small nip rollers, each one with a progressively higher velocity, or it can be done in steam over a very short distance. The stretching operation may also be done early in the fibre-making sequence and significantly before the residual solvent has been washed out, or it may be done late in the process, after the majority of the residual solvent has been removed. These various options account for the subtle differences in the properties of the resulting fibre. For example, the way the fibre tensiles are built as a result of the tension under stretch will be influenced by the amount of residual solvent (which has a plasticising effect) present during the stretching process. The overall stretch ratios commonly used are between 3 and 12 times and this process orients the polymer chains within



4.5 Schematic diagram illustrating solution polymerisation and fibre spinning. DM is demineralised water, ITA is itaconic acid, LC is Latent Crimp (a bicomponent fibre made by Acordis), SF is soft finish, STA is a polymerisation control agent. Source: Copyright Acordis UK Ltd.

each fibre, thereby developing the fibre tensiles and shrinkage potential. Although it is accepted that the as-formed fibres do not have a fibrillar structure, it is possible to see the development of a sub-structure as a result of this orientation process, which gives the appearance of a fibrillar structure. The individual polymer chains form into groups with amorphous and semicrystalline structure and it is these groups and the relationships between groups that give this fibrillar appearance.

The washing operation is designed to remove the majority of the polymer solvent (but not all) and is usually carried out by a counter current flow of hot water. The fibre is well formed at this stage but still in the gel state. This gel state allows dyes to be introduced into the fibre if required and this dyeing operation only requires water and dyestuff at 50–100 °C to contact the fibre for a few seconds in order for fully coloured fibres to be obtained.

The final operations in the wet-spinning of acrylic fibres involve the application of suitable soft finishes and antistatic agents, fibre drying and crimping. These operations are all very important. The choice of soft finish to be used will reflect the process by which the fibre is to be converted into a product for a specific end-use. For producer-coloured fibres that are to be converted into knitwear, the finish applied has to allow good fibre processing in terms of static control and fibre cohesion but then go on to give the finished article the soft hand desired to make the garment attractive to the final consumer. This is because the fibre will not see any wet processing until the consumer washes it. Other conversion routes will use ecru fibre and so the finish chosen only has to aid fibre conversion into yarn, as other finishes will be applied at the yarn/fabric dyeing stage. Fibre finishes used on acrylics tend to be a mixture of cationic and non-ionic polymers so that they have some chemical affinity with the fibre. Modified fatty acids with chain lengths of between C14 and C20 are very common in this type of processing route.

Fibre drying is a critical process in terms of developing the final tensile properties of the fibre and the inherent fibre shrinkage. Some manufacturers dry under tension, others tensionless. In either case, significant fibre relaxation and structure collapse takes place and each manufacturer will have optimised drying profiles for each fibre type that they make. Drying under tension allows some degree of control to be imposed on the structure developed as the fibre collapses and also allows full collapse of the fibre while retaining some shrinkage.

After drying, an antistatic processing aid is applied, followed by fibre crimping. The fibre is then usually collected as a continuous tow form into cans. It can then be baled for tow to top conversion or cut into staple.

4.4.1.1 Fibre formation in detail

The formation of acrylic fibre using wet-spinning technology has been studied in great detail by all of the companies involved in acrylic fibre production. A good understanding of the thermodynamics and kinetics of a phase-separating polymer solution is important if product optimisation is to be achieved. The individual steps that need to be understood can be described by the terms diffusion and phase separation. These determine the structure of the resulting polymer.

Fibre structure is controlled by the diffusion of solvent from the polymer solution as the dope leaves the spinneret and by the counter-diffusion of the non-solvent into the polymer solution. These diffusional processes are driven by concentration differences along and within the fibre as coagulation proceeds. The relative rates of solvent to non-solvent diffusion set the driving force for phase separation and the rate of phase separation. Like any diffusion process, the independent variables for wet-spinning are rate of extrusion, concentration and temperature. The rate at which the polymer is extruded into the spin bath, including the jet stretch element, will affect the rate of diffusion of solvent into the spin bath and therefore fibre properties. However, the relative diffusion rate of solvent out to non-solvent in remains constant.

The concentration of the polymer dope and the relative concentration of the solvent/non-solvent coagulant affect the diffusion rate during coagulation. Higher polymer concentrations have been shown to increase the resistance of the boundary layer to diffusion and hence movement of solvent and non-solvent through the boundary layer is slowed down. The boundary layer is dependent upon the surface tension of the liquid layer, which covers the fibre tow, and this boundary layer has to be overcome for diffusion to take place. The relative rate of diffusion of the solvent out to non-solvent in also increases with increasing polymer concentration.

The number of variants in terms of solvent/non-solvent ratio in the spin bath is infinite, ranging from 0 % to 100 % of each. Obviously the extremes are of no interest to commercial processes but many options are available between these extremes. It is generally accepted that as the solvent to non-solvent ratio increases, then the diffusion rate of solvent and non-solvent decreases and the relative diffusion rate of solvent to non-solvent increases.

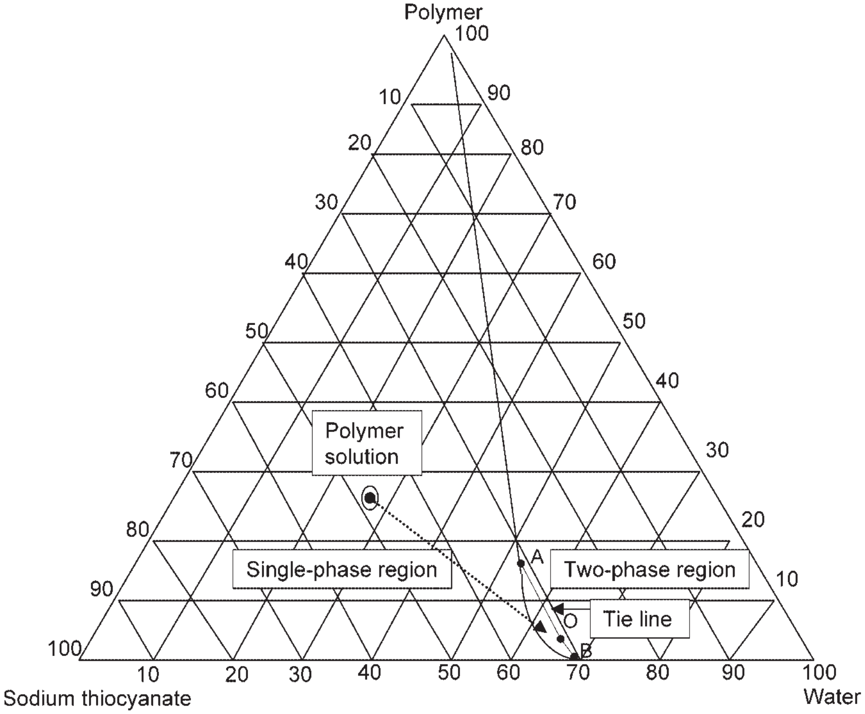
Temperature is a critical control factor in this diffusion process. The range of temperatures used in the wet-spinning of acrylic fibres is from –1 to +50 °C for the spin bath and +25 to +120 °C for the spin dope. As expected, as the temperature of the coagulant increases, then the diffusion rates of solvent and non-solvent increase. This is also true for an increase in the polymer dope temperature. However, in both cases, while the overall rate of diffusion increases, the relative rate at which the solvent diffuses out changes more than the rate at which non-solvent diffuses in. Capone[24] covers these issues in some detail.

All of these control factors are used to optimise fibre spinning in terms of economics and fibre properties. For a given polymer type, the combination of these control factors will be changed for different decitexes, tenacities, etc., to produce fibres with specific target properties. Product changes during spinning do therefore require changes to the coagulation conditions and the planning of product changes is therefore an important issue.

The final factor that needs to be considered in this overview of diffusion is the rate at which fresh spin bath liquor is introduced. As fibre spinning progresses, solvent from within the polymer dope is exchanged for non-solvent in the spin bath liquor. The concentration of solvent in the spin bath liquor will therefore increase very quickly and it is necessary to replace the spin bath liquor constantly at a rate designed to maintain a constant solvent/non-solvent ratio. This is achieved by having a countercurrent flow of spin bath liquor across the spin bath, whose volume throughput can be adjusted. One complication to be considered in terms of maintaining a constant spin bath concentration is the localised concentration differences that occur, particularly with the larger strip jets. Considerable localised concentration differences can occur unless steps are taken to minimise them.

Given the many variables involved in this diffusion process and the importance of understanding and controlling them, many researchers have derived mathematical models for the overall process. Work by Qian *et al.*,[25] based on Fick's Law, and Qin and co-workers[26] and Terada[27] are just a few of the more recent insights into this important process.

The second step in coagulation is known as phase separation and is the process by which the polymer in solution forms a porous gel network in the solid phase (phase inversion). The best way of illustrating this process is by use of a three-component phase diagram in which the changes that take place in polymer, solvent and non-solvent concentrations can be followed. Figure 4.6 shows a typical phase



4.6 Phase diagram for the sodium thiocyanate/water/polymer three-component system. Source: Acordis UK Ltd.

diagram for the sodium thiocyanate/water/polymer three-component system. This system has been studied in detail by researchers within Acordis and is reported in a PhD thesis by Law.[28] Much of this section is based upon Law's thesis.

The starting point for phase inversion is a thermodynamically stable solution of a polymer in a solvent. This solution is then rendered unstable, usually by changes in temperature or composition. Both of these changes can be considered as 'worsening' the quality of the solvent. If the change is large enough in magnitude, then the solution can become so unstable that precipitation of the polymer occurs. This leads to a two-phase mixture composed of solid polymer and solvent/non-solvent.

This behaviour can be described in thermodynamic terms by changes in the free energy of mixing (ΔG_m). If the free energy of the mixture (G_{12}) is lower than the sum of those of the single components (G_1 and G_2) then a homogeneous solution is obtained:

$$\Delta G_m = G_{12} - (G_1 + G_2) \leq \mathrm{O} \quad [4.13]$$

The term ΔG_m can be calculated from:

$$\Delta G_m = \Delta H_m - T\Delta S_m \quad [4.14]$$

where H_m is the heat of mixing and T is the temperature in kelvin

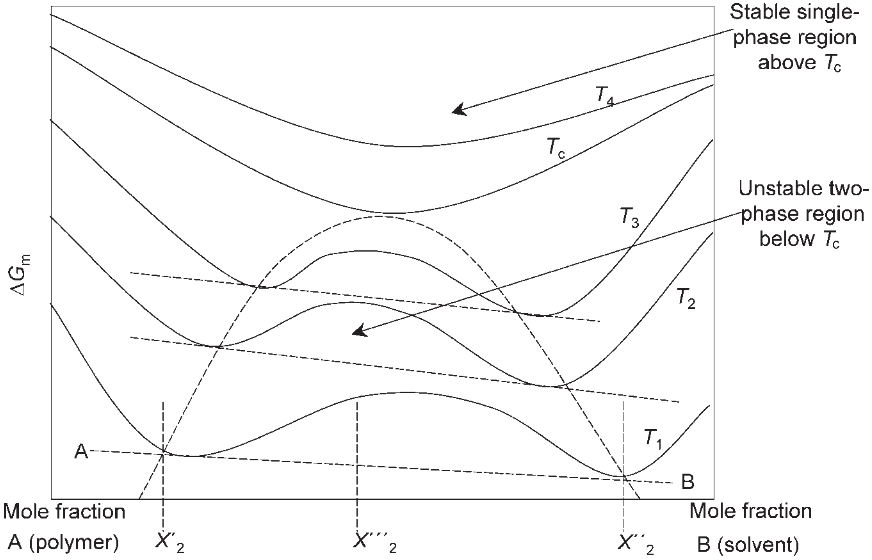
Since the entropy of mixing, ΔS_m is dependent on the relative volume fractions of the components (Φ_1 and Φ_2), then:

$$\Delta \mathrm{S}_m = -R(n_1 \ln\Phi_1 - n_2 \ln\Phi_2) \quad [4.15]$$

where R is a constant

The free energy of mixing is also dependent on the volume fraction of the components. The free energy is also dependent on temperature, through both ΔS and ΔH. Plotting ΔG as a function of composition of the mixture over a range of temperatures yields a family of curves. In systems where the solubility increases with increasing temperature, the free energy curves at high temperatures exhibit a single minimum (concave), indicating that the free energy of mixing is always lower (therefore more stable) for mixtures of solvent and solute than for the two 100 % components lying at $X_2 = 0$ and $X_2 = 100$, i.e. on the ends of the curve at the two y axes. However, as the temperature is reduced, the curves can show two minima, corresponding to lower free energies for separated components within the mixture. These minima define the limit of stability known as the binodal. Where two minima occur, points of inflection are present. When these points are plotted against temperature, a curve inside the binodal is generated, known as the spinodal (Fig. 4.7).

Where minima approach each other, and eventually coincide, is the point where the first and second derivatives of ΔG with respect to volume fraction are zero. This is termed the critical point. Inside the spinodal curve, compositions are instantaneously unstable and phase separation is energetically favourable. This process is known as spinodal decomposition. Between the binodal and spinodal, solutions are metastable and a finite composition change is required (a nucleus) to begin phase separation. This is known as nucleation and growth.



4.7 Schematic diagram of Gibbs free energy of mixing as a function of mole fraction of solute X_2 showing behaviour over a range of temperatures. Source: PhD Thesis, S. Law.[28]

When demixing is brought about by the addition of non-solvent (water), then a three-component system has to be represented. The phase diagram now has to be represented in three dimensions, but for convenience is represented isothermally using triangular co-ordinates. The moves through compositional space are brought about by the addition of non-solvent (water) rather than by temperature. Interpretation is, however, the same. In Fig. 4.6 a polymer solution is represented in the single-phase region and the changes in composition as non-solvent (water) is added are shown by the dotted line until the binodal is crossed.

If we consider the composition at the point at which the binodal is crossed (point O), it can be seen that the mixture has formed two phases. The average composition is still indicated by point O, but the composition of the individual phases is represented by points A (the solid phase) and B (the liquid phase). From the phase diagram it can be seen that the solid phase consists of polymer, solvent (sodium thiocyanate) and non-solvent (water), while the liquid phase is virtually free from polymer. This is typical of wet-spun acrylic fibres and phase inversion membrane systems. The length of the line OA is representative of the volume of the liquid phase as a proportion of the complete tie line AB. Likewise the amount of solid phase can be calculated from the ratio of the length of the line OB to the full tie line. In this way the ratio of the overall amount of non-solid phase to solid phase is obtained, which represents the porosity of the liquid-filled polymeric system. If the liquid is removed without affecting the polymer network then the amount of liquid component will be the pore volume of the solid polymer.

This description does not define the size of the pores within the polymer matrix and an understanding of how to control this pore size is also of great importance to fibre properties. Those companies whose technology in terms of solvent/non-solvent pro-duces a polymer matrix with a high pore volume with pore sizes above a certain limiting value have exploited the ability to on-line dye using this polymer porosity. An example of this is the *Neochrome* technology pioneered by Courtaulds in the early 1960s. Some solvent/non-solvent systems produce polymers with much lower pore sizes and so on-line dyeing is not possible. The wet-spinning process used in the Acordis facility in Kelheim (ex Hoechst) has not been able to exploit the on-line dyeing process. This is because the coagulation conditions used to produce fibre with acceptable physical properties lead to pore sizes at less than a critical minimum, below which dyeability is lost. The gradation of this pore structure from the outside of the fibre to the inside of the fibre will be considered in Section 4.5 covering fibre structure.

One variation on wet-spinning that has been developed by a few companies is a technique known as air-gap spinning or dry-jet wet-spinning. The fibre is extruded into air before being immersed into the normal solvent/non-solvent coagulation bath. The small fraction of a second during which the fibre is exposed to air causes significant changes to the surface of the nascent fibre filament, which goes on to impact the diffusion rates of solvent out, non-solvent in. This in turn will cause some structural changes and hence fibre physical property changes. The technique has been developed for speciality acrylic polymers where a higher polymer concentration and faster linear spinning speeds are required. It has to date only been possible to use this technique with the small circular jets for the manufacture of filament yarns. The hole spacing has to be larger for this air-gap spinning technique, which reduces the throughput capacity; however, the higher polymer concentration and faster spinning speeds compensate for the small jets.

4.4.2 Dry-spinning

Dry-spinning of acrylic fibres was the first technology to be developed commercially. This technology is attributed to DuPont and Bayer, who were both granted patents in the 1940s. The dry-spinning process is fairly simple, with the polymer solvents being removed from the polymer by an evaporation process using hot, inert gases. The search for suitable solvents for acrylic polymers led to two solvents that were suitable for the dry-spinning process. These were dimethyl formamide (DMF) and dimethyl acetamide (DMAc). The requirements of a solvent to be used in dry-spinning are as follows:

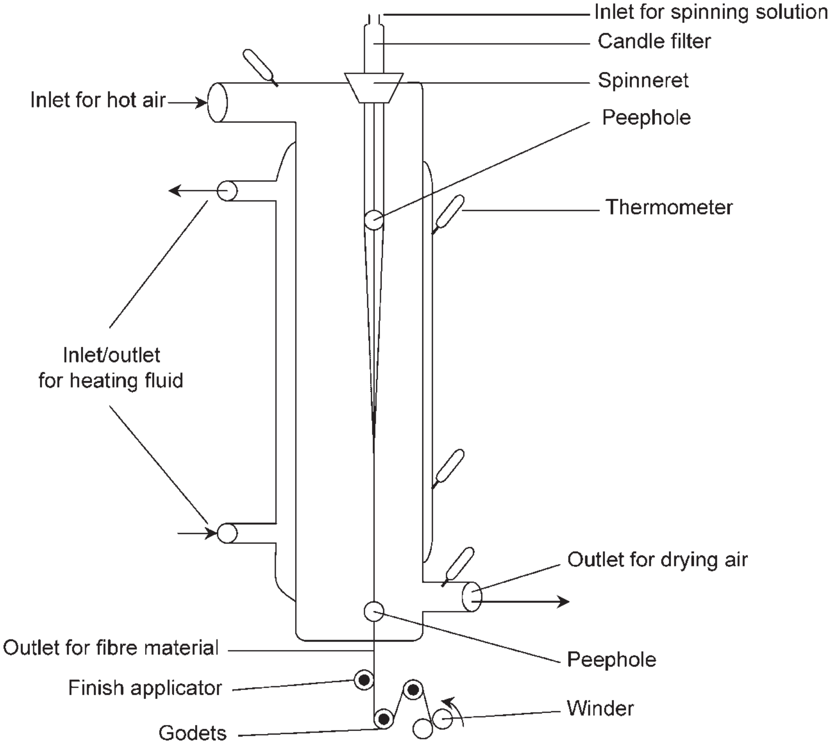
- good stability at the boiling point of the solvent;
- low boiling point;
- no chemical interactions with the polymer;
- good solvating properties;
- low heat of vaporisation;

- low toxicity;
- easy recovery ability;
- low risk of explosion;
- cost effectiveness;
- low possibility of static charge build-up.

While both DMF and DMAc were used commercially for many years, the most suitable solvent for dry-spinning is acknowledged to be DMF and this is used almost exclusively today.

DMF has a boiling point of 153 °C, a heat of vaporisation of 579 J g^{-1} and an ignition temperature of 445 °C. The main disadvantage of DMAc is that it has an ignition temperature of around 320 °C, which means that the spinning tube temperatures (°C) need to be reduced by 30%, which affects productivity by a similar amount. DMAc does, however, produce polymer dopes of higher viscosity and solids content, features which are an advantage.

Like wet-spinning in which the removal of the polymer solvent is the key step, the most important stage in the dry-spinning process is the evaporation of the solvent after spinning. Figure 4.8 shows a typical design for the spinning tube.



4.8 Spinning tube for dry-spinning process (length 6–10 m). Source: reprinted from J. C. Masson, *Acrylic Fiber Technology and Application*, p. 119 by courtesy of Marcel Dekker Inc.

The spinning dope is usually stored at a temperature of 90 °C. As the dope is moved forward towards the spinning tube it passes through a number of filtration stages and is heated up to a temperature of between 130 and 140 °C as it passes through the final candle filters. De-aeration takes place throughout these stages and pigments in the form of stable dispersions in the polymer solvent may also be added if necessary. The pressure of the dope entering the spinning tube is between 0.8 and 1.5 MPa.

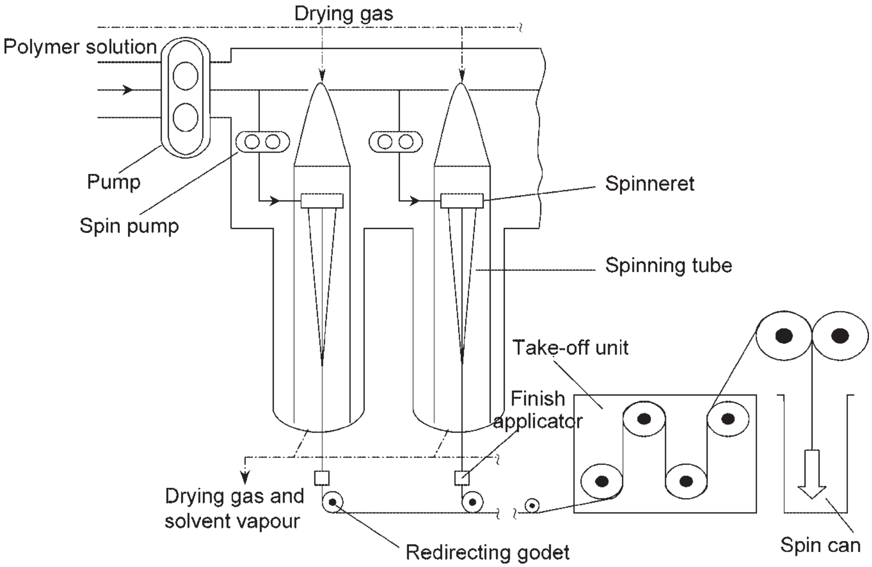
The spinnerets used in the dry-spinning of fibres are fairly simple, consisting of a ring made from stainless steel alloy and containing up to 2800 holes. Hole diameters are usually in the region of 0.1–0.3 mm. For the spinning of continuous-filament yarns, bowl or hat-shaped spinnerets may be used.

Ring spinnerets, however, have the advantage that the hot gases used to evaporate the solvent can be introduced through the centre of the ring as well as from the outside. With bowl-shaped spinnerets the hot gas can be introduced only from around the outside. As the polymer leaves the spinneret it is met by the hot gas at around 300–350 °C and the solvent is evaporated. The hot gas can be air or an inert gas such as nitrogen or in some cases steam. The preferred option is air mixed with nitrogen to reduce the oxygen content to about 8 %. This reduces the explosion threshold and also reduces the yellowing tendency of the fibre. The hot gas provides most of the heat required for evaporation but the spinning tube or cell is also heated independently to ensure that there are no cold spots on which solvent can condense. The hot gas laden with solvent is then recycled and the solvent is recovered continuously as part of the recycling operation.

The spinning cell is often operated under a slight vacuum in order to prevent the gas from escaping through the fibre exit opening. Hot gas flows can be co-current or counter-current. In co-current systems, the gas enters the tube through filters positioned close to the spinneret and is removed at the other end by suction. In the counter-current process, it enters at the bottom of the tube and is removed above the spinning head. One of the most critical quality factors in dry-spinning is to ensure that filaments do not stick together as they are forming. Excessive polymer flow rates and turbulence must be avoided in order to prevent the damp filaments coming into contact with one another. The gas flow rate is usually 1–2 $m^3 s^{-1}$.

A typical dry-spinning line will usually consist of two halves, with up to 35 spinning cells on each half. The throughput of fibre from each cell is normally 8 to 15 kg per hour. Higher outputs are possible by modifications to the spinning heads and gas flows, but the solvent content of the gas must be kept below the explosion threshold at all times.

The resulting fibre is taken up by a godet and finish is applied prior to the fibre being collected in spin cans. Some dry-spinning units will incorporate a water quench trough just after the take-up godet. For filament routes, an oil-based finish is applied to the filaments at the bottom of the spinning tube. They are then drawn off via godet rollers and wound at 200–500 m min^{-1}. For tow end-uses the fibres from each spinning cell on each half of the machine are combined together to form



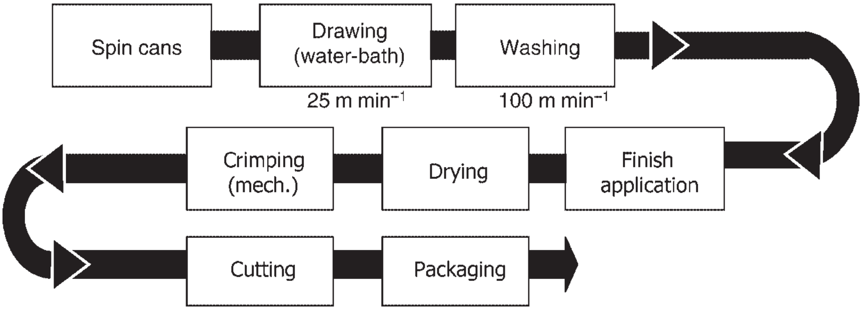
4.9 A typical dry-spinning unit for the production of staple fibres. Source: Reprinted from J. C. Masson, *Acrylic Fiber Technology and Applications*, p. 121 by courtesy of Marcel Dekker Inc.

a large tow of up to 500 000 dtex. These are drawn off by take-off rollers at speeds of 250–450 m min^{-1}, prior to collection in spin cans. Figure 4.9 shows a typical dry-spinning unit for the production of staple fibres.

Dry-spinning is traditionally a two-stage process with a break at the can collection stage. Much effort has been put into designing continuous dry-spinning processes and there has been some success in this area. Some of the more modern units that have been added in recent years by companies such as Bayer are thought to incorporate these more efficient designs. The breakthrough in design that has allowed for a continuous process to be developed came from the ability to move fibre down the line in a tensionless mode. Under the discontinuous process the product is transported under tension; productivity is therefore restricted by the treatment times required to remove the solvent and for drying and, as a consequence of this, the plants were very long (200 m).

However, most units are of the discontinuous type and fit the description given above. The undrawn tow collected in cans after spinning has very poor tensile properties and it has to undergo further processing in order to develop good fibre tenacity and elasticity. Figure 4.10 shows the stages that follow the spin cans.

The first process in the second stage of the fibre manufacture is the drawing process. This is a critical process during which the fibre properties are developed and the final titre (decitex) is established. The key elements of this process are that the fibre contains residual solvent (5–25%) and the fibre temperature is close to the wet glass transition temperature. Nip rollers are used to feed the fibre into the first



4.10 Dry-spinning schematic of downstream operations. Source: Reprinted from J. C. Masson, *Acrylic Fibre Technology and Applications*, p. 137 by courtesy of Marcel Dekker Inc.

part of the wet drawing unit and fibre from a number of cans may be combined together at this stage. The tow passes over a number of rollers in order to form an even distribution of fibres and to prevent fibre slippage. The tow then enters a hot water bath at 98 °C and is submersed for a length of about 4 m. The rollers at the exit end of the drawing unit impart an exit velocity of about 100 m min^{-1} to the fibre tow. A draw ratio of between 1 : 2 and 1 : 10 can be applied depending upon the final end-use for the fibre. After this stretching process the fibres have a boiling water shrinkage of between 15% and 45%, depending upon the draw ratio and comonomer content. The significance of the residual polymer solvent and the draw temperature is that the stress/strain relationship is linear and relatively shallow. This ensures that fibre orientation takes place in a controlled manner as the elasticity and tenacity build slowly. The solvent acts as a plasticiser.

Washing, the purpose of which is to reduce the solvent content of the fibre to <1%, follows this drawing process. On conventional units washing is carried out under tension. Using this method the solvent diffuses out of the fibres into the water occupying the space between the fibres. The water then carries the solvent away and the solvent is subsequently recovered for re-use. The efficiency of these units is quite low at about 20 %. It is therefore necessary to pass the fibre through 20 washing zones at 90 °C in order to achieve the required reduction in solvent content. The overall residence time in the washing unit will vary but is around 300 seconds. The wash troughs are therefore quite long. Washing is followed by finish application during which between 0.25% and 0.5% of a suitable fibre lubricant is applied.

Finally, the fibre is dried. The mode of drying is important, as this is the stage at which the final shrinkage potential of the fibre and the dye rate of the fibre are manipulated. The fibre tow is usually dried at temperatures of between 120 and 170 °C with throughput speeds of 100 to 150 m min^{-1}. The fibre entering the dryer has a shrinkage potential determined by the fibre drawing stage. Drying under tension, usually over heated drums, can retain this shrinkage potential. By altering the tension on the drum dryers along with speed and temperature, the final shrinkage and dyeability can be determined. The drying process also sets the fibre to some extent. As this affects the ability of the fibre to be crimped, then the degree of setting becomes another control variable.

The final stages in the fibre manufacturing process are fibre crimping and, for staple end-uses, fibre cutting. Crimping technology is well established around the stuffer box principles in which feed rollers push the dried tow into the nip rollers within the stuffer box. This allows the tow to fold as it passes through the nip rollers, and these folds are set to varying degrees depending upon the temperature/pressure conditions within the stuffer box. As the tow passes through the nip rollers it buckles, which creates the primary or micro-crimp that is required for downstream fibre processing.

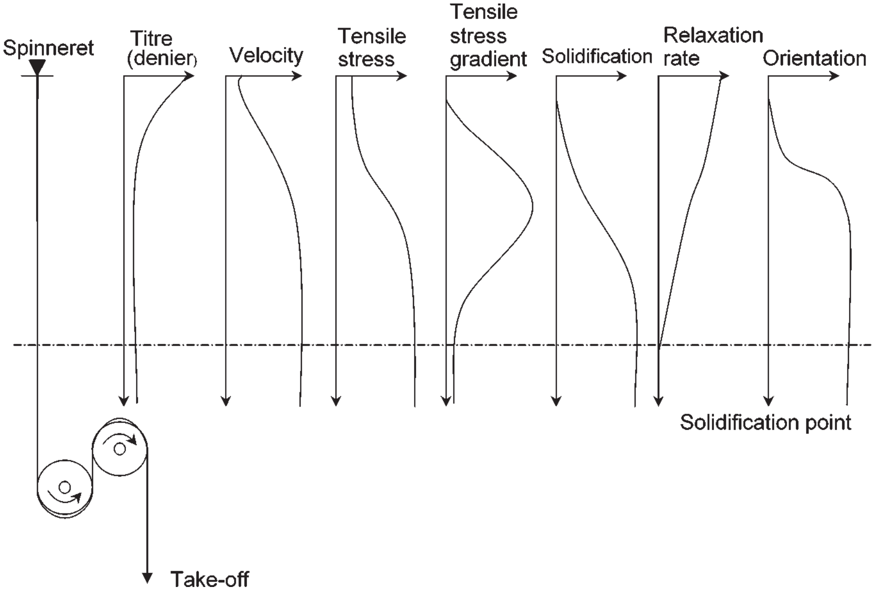
The crimped tow is then collected in large cans for tow to top conversion or is cut to different staple lengths for staple spinning or in non-woven end-uses.

4.4.2.1 Fibre formation in detail

Polyacrylonitrile polymer solutions used in the formation of acrylic fibres have non-Newtonian rheological properties. This means that the polymer solution viscosity decreases as the shearing force increases (pseudoplastic properties) and secondly that the polymer solution is able to store elastic energy (viscoelastic properties). These non-Newtonian properties are very important in the fibre spinning process as we are dealing with the movement of the polymer solution through metal pipework and spinnerets, during which deformation of the polymer solution takes place.

As the polymer solution passes through the pipework, it does so with a parabolic profile. This means that the residence time of the polymer solution near the face of the pipes is longer than that of the polymer solution in the centre of the pipe. In order to compensate for these differences, inline static mixers are used to break up and mix the polymer solution. As the polymer solution passes through the individual holes in the spinneret, the polymer solution undergoes elastic deformation. This involves a certain amount of molecular orientation but the bulk of the work done on the polymer solution is stored as energy. As the polymer solution exits the spinneret, this stored energy is released and the polymer solution expands or bulges. This behaviour is known as the Barus effect and is the main reason why shaped acrylic fibres were for many years very difficult to produce. The fibre is formed effectively by drawing from a semi-spherical reservoir of polymer solution. Shaped acrylic fibres are now produced commercially and the Barus effect is overcome by being able to draw the fibre away from the spinneret very quickly.

As the solvent is evaporated from the polymer solution, a number of changes take place up to the solidification point. These are summarised in Fig. 4.11. The fibre dtex drops constantly until the solidification point is reached. The velocity and tension of the forming fibre increase proportionately. The rate of solidification



4.11 Processes occurring during dry-spinning. Source: Reprinted from J. C. Masson, *Acrylic Fiber Technology and Applications*, p. 115 by courtesy of Marcel Dekker, Inc.

accelerates towards the solidification point and the relaxation rate decreases. The tension, solidification and orientation gradients reach their maximum points while the filament is in the rubber-elastic state.

Technical personnel in the industry often use the term 'spinnability window' and this refers to the limits of certain key factors, outside of which the quality of the fibre is impaired. In dry-spinning, the polymer solution viscosity, polymer solution temperature and take-off speed are examples of such key factors. Low or high-polymer solution viscosity can lead to broken filaments as can too high a polymer solution temperature or too high a take-off speed. Other problems that can impair product quality are rapid evaporation of the solvent, which can lead to vapour bubbles within filaments, and turbulence within the spinneret, which can lead to stuck filaments. Ideal spinnability windows ensure that these problems are minimised.

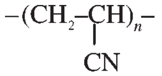
One of the ways in which dry-spun fibres are easily differentiated from wet-spun fibres is by the cross-sectional shape. Dry-spun fibres are dog-bone or dumbbell shaped while wet-spun fibres are mainly round or kidney bean shaped. The reason for the dog-bone shape is easily explained; it is an artefact of the solvent diffusion and evaporation stages that lead to polymer solidification. As the solvent evaporates from the polymer solution, the outer part of the forming fibre solidifies before the inner sections. This causes radial inhomogeneity within each filament, which can be considered in simple terms as a core–sheath structure. Clearly, once the outer section of the filament solidifies, further solvent vapour generated within the core of the filament has to pass through this newly formed solid polymer. As this solvent evaporates from the core of the filament, the mass of the core is reduced and this results in the outer sheath collapsing inwards. The faster the evaporation rate compared with the diffusion rate, the more likely the cross-section of the fibre is to change from circular through bean shaped to dog-bone. This phenomenon occurs to a much lesser extent in wet-spinning in which fibre is formed by a coagulation process. This is why only circular or kidney bean shaped fibres are formed in wet-spinning.

The other major difference between dry-spun and wet-spun acrylic fibres is the absence of the gel-state phase in dry-spinning. The absence of this gel-state phase leads to significant differences in the physical properties of the resulting fibres, which results in dry-spun fibres being preferred for some end uses (for example, *Dralon* in upholstery and awnings because the flexural rigidity is much better) and wet-spun fibres being preferred for apparel end-uses (for example, *Courtelle* or *Cashmilon* in knitwear, where the lower flexural rigidity is a benefit). It is also the reason why on-line dyeing is not possible in dry-spinning but is possible in wet-spinning (cf. *Neochrome* process (p. 192)). Dry-spun fibres can be producer dyed but this is done by the addition of pigments prior to the spinning jets. This leads to coloured fibres with excellent fastness properties as pigments generally have better fastness than cationic dyes, but is a less versatile process in terms of batch quantities per colour and the number of colours available.

4.5 Physical properties and structure of fibres

In order to fully describe the physical properties of acrylic fibres it is important to understand the micro- and macro-structure of these fibres. We need to begin with the structure formed by polyacrylonitrile polymers and copolymers. A comprehensive and in-depth review of the work covering the structural investigation of acrylic fibres is given in a PhD thesis by Law.[28]

Polymerisation of acrylonitrile yields polyacrylonitrile, with the general formula [4.16]:



$$-(\mathrm{CH_2{-}\underset{\underset{\displaystyle CN}{|}}{C}H})_n- \qquad [4.16]$$

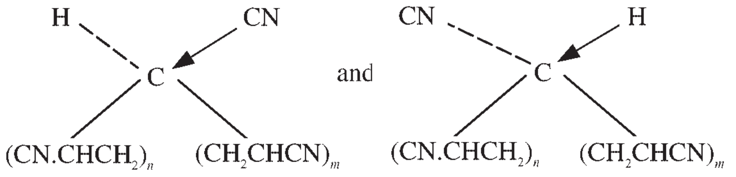
Under almost all polymerisation conditions the polymer predominantly adopts the ‘head to tail’ structure [4.17]:

$$\cdots\mathrm{CH_2{-}CH(CN){-}CH_2{-}CH(CN)}\cdots \qquad [4.17]$$

rather than the less favourable ‘head to head’ structure:

$$\cdots\mathrm{CH_2{-}CH(CN){-}(CN)CH{-}CH_2}\cdots \qquad [4.18]$$

Acrylonitrile is an asymmetric monomer, and following polymerisation every tertiary C atom can be considered as a chiral centre, since adjacent chain fragments have different lengths. There are therefore two possible configurations represented by simply reversing the positions of the hydrogen and nitrile groups:

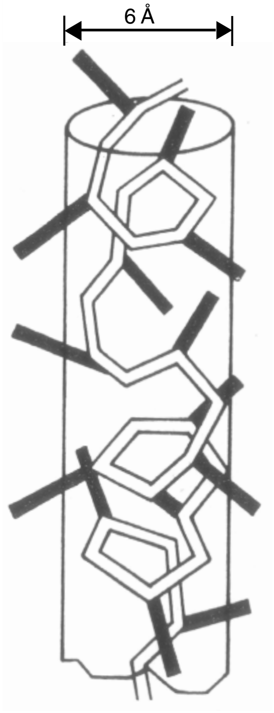


[4.19]

These two types of configuration can theoretically be distributed in several ways along the chain, i.e. isotactic (three consecutive monomer units have the same configuration), syndiotactic (monomer groups have alternating configurations) and atactic (monomer units have completely random configurations). In the case of PAN it has been found that it is quite difficult to influence the type of structure that develops, and a mixture of distributions results.[29–31] The PAN structure is described in this way because it is acknowledged that the distribution of structures found is more ordered than just a random distribution as defined by atactic. The percentage of isotactic and syndiotactic structures is higher than would be expected for a purely random distribution.

One of the dominant features of an individual PAN chain is the presence of the highly polar nitrile groups, which are attached to every alternate C atom in the chain and are therefore able to interact fairly strongly. Interaction between adjacent nitriles on the same chain causes some repulsion to occur. This is due to the fact that the nitrile groups cannot adopt an antiparallel arrangement because the bond angles do not allow this. This tends to twist the chain into an irregular helical formation. It is best envisaged by thinking of the main twisted backbone of the polymer chain fitting within a tube approximately 6 Ångstroms in diameter, with the nitrile groups pointing out from the chain at various angles. It is this structure that is thought to be partly responsible for the lack of a clear melting point for PAN, whereby little freedom is gained on moving from the solid to liquid state. A simple model of this structure has been proposed by Henrici-Olivé and Olivé[32] and is represented in Fig. 4.12. This is a pictorial representation and no direct evidence of this structure has been presented at this stage.

The protruding nitriles are also able to interact with nitriles on adjacent chains. Calculations suggest that the greatest energy can be gained when nitriles are in an antiparallel arrangement, and chains will modify their structure to approach this ideal position. Where chains are highly extended, as in the case of drawn fibres, groups of PAN tubes will approach closely enough to form larger groups, which give rise to the characteristic wide-angle X-ray diffraction pattern. The diffuse halo in the X-ray diffraction patterns normally associated with semicrystalline



4.12 Diagrammatic representation of polyacrylonitrile molecule. Source: Henrici-Olivé & Olivé.[32]

polymers is substantially absent, suggesting extensive order. However, the presence of diffuse scatter throughout the pattern normally associated with an amorphous polymer is present, suggesting some kind of irregularity. The PAN rods are thought to pack in a hexagonal structure. This is based on the ratio of intensities of the two equatorial reflections ($\sqrt{3}$: 1) and the observation of six X-ray diffraction peaks on irradiation parallel to the chain axis.

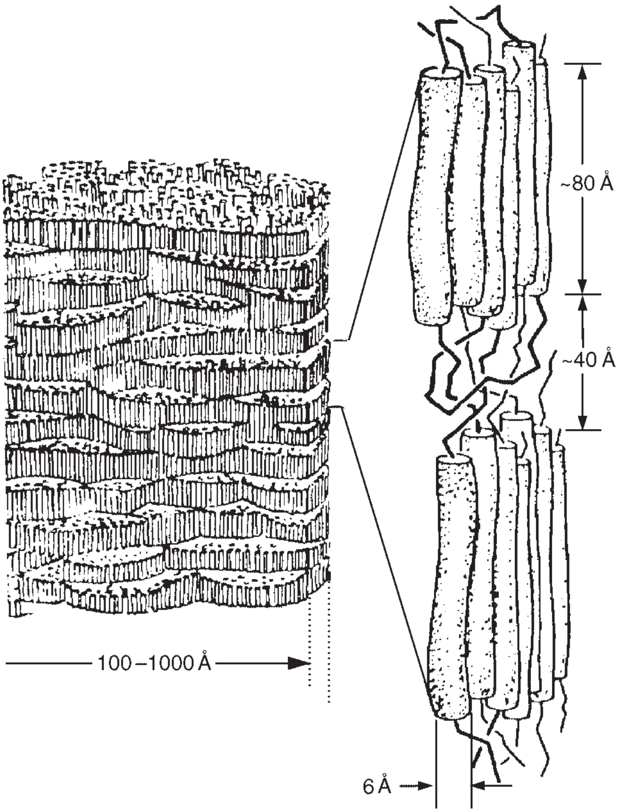
A second key feature of the X-ray diffraction pattern is the presence of diffuse scattering throughout the pattern, which is quite different from the diffuse halo found for conventional semicrystalline polymers, and which arises from disordered, amorphous material akin to the scattering of a liquid. In the case of PAN the extensive diffuse scattering suggests a single laterally bonded phase with many defects. The theory of paracrystallinity has been applied to account for the X-ray pattern[33] and the diffuse scattering ascribed to an inconsistent conformation along the chain length. Paracrystallinity is described as a single ordered morphology containing many defects. Work by Bohn *et al.*[34] showed that the 5.2 Å spacing increased above the glass transition temperature, which is inconsistent with a two-phase model. However, the debate continues with some workers in the field proposing evidence for a two-phase structure.[35]

The debate over the morphology of copolymers of PAN is also still not fully resolved. The behaviour of copolymers of PAN is thought to arise from the 'base' morphology described previously with a secondary morphology arising from the need to accommodate comonomer units within the base structure. Minami[36] contends that vinyl acetate enters a distinct amorphous region, and this is supported by Gupta and Chand.[37] They observed little change in the Bragg spacing when the comonomer was incorporated and concluded therefore that it could not be residing in the crystalline region. This is consistent with the general theory proposed by Flory.[38]

However, Frushour,[39] who showed that only on incorporation of a large amount of comonomer was the X-ray pattern disrupted, revealed a more complete picture. He went on to argue that the paracrystalline phase could tolerate a certain amount of defect material. He further showed that the molar volume of the comonomer played a role in the disruption. This was demonstrated by use of a novel plasticised differential scanning calorimetry (DSC) technique, in which the plasticiser, water, reduces the melting point of PAN below its decomposition temperature, thereby allowing 'melting' thermograms to be obtained. Using this technique, he was able to show that a reduction in melting temperature was noted on incorporation of only small amounts of comonomer, and that the level of reduction was related to the amount of comonomer and its molar volume. The fact that X-ray techniques pick up changes in structure only after much larger inclusions of comonomer was interpreted by arguing that diffraction techniques access more extensive ordered regions, whereas the DSC technique is sensitive to individual dipolar interactions. The fact that comonomer units modified the melting behaviour in a way typical of crystalline polymers is strong evidence for their presence in the crystalline or paracrystalline phase. The proposed morphology of PAN polymers is illustrated in Fig. 4.13.

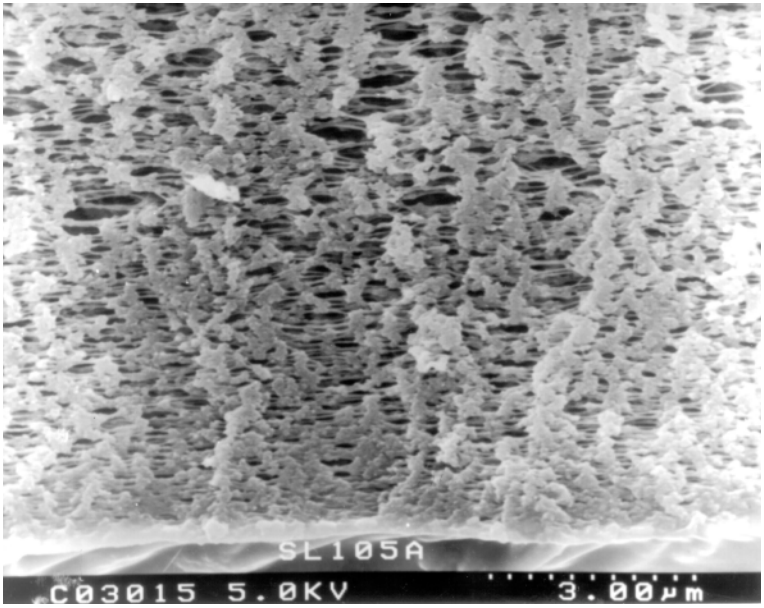
The macrostructure of acrylic fibre changes significantly from first formation to dried, finished product. In dry-spun fibres we have seen that the first formed outer dense skin cannot accommodate the decrease in internal volume as the solvent evaporates and so the as-formed circular cross-section will collapse to form a dog-bone shape. The internal structure across these filaments is fairly uniform with the only visible structure occurring at the interface between the first formed outer skin and the bulk of the internal polymer. Wet-spun acrylics, which are formed by a diffusion process, show considerable structure across their cross-section and this internal structure can be manipulated significantly during the fibre-forming and subsequent processes.

The structure was first comprehensively characterised by Craig and co-workers.[40] By a combination of transmission electron microscopy (TEM), mercury porosimetry, density and surface area measurements, the pore and matrix structures of a range of PAN fibres were described. The TEM photographs showed a continuous network of polymer rods connected by nodes, and a porous structure interspersed. A gradation in pore size was also noted, with smaller pores towards

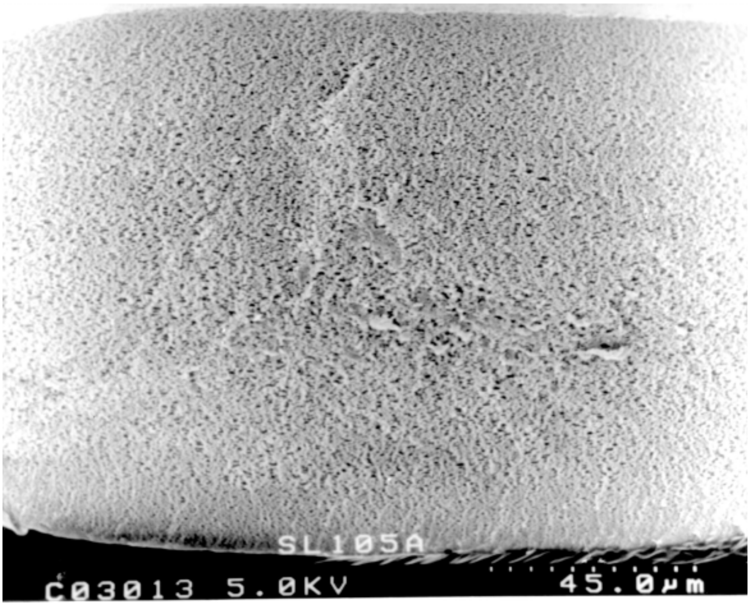


4.13 Diagrammatic representation of two-phase morphology of polyacrylonitrile. Source: Warner, Uhlmann and Peebles.[35]

the outside of the filament. In a later paper, Knudsen illustrated how the various coagulation variables affected the size of the pores, and that those conditions that favoured a slower precipitation led to a finer structure.[41] Work by the author using cationic dyes and disperse dyes of differing molecular size and volume on fibres prepared under differing conditions led to suggested pore sizes being postulated for the Acordis wet-spun fibre.[42] One of the drawbacks of the on-line dyeing of gel state fibres is that uneven dyeing across and down a continuous tow can occur. This is commonly referred to as 'streakiness'. Many factors can influence the degree of streakiness observed in a tow, and it is known that dyestuff selection is one of these factors. This work by the author suggested that the kinetics of the dyeing process were influenced by the pore gradation observed within wet-spun acrylics and that the molecular volume of the dyestuffs was a critical factor. The observed time constants for dyeing of individual dyes and then pairs of dyes changed as the pore size decreased and those dyes with a large molecular volume were the first to be affected. Figures 4.14 and 4.15 illustrate this structure.



4.14 Pore structure within wet-spun acrylic fibre (1). Courtesy: Acordis UK Ltd.



4.15 Pore structure within wet-spun acrylic fibre (2). Courtesy: Acordis UK Ltd.

Having said this, it is this structure that accounts for the ability of never-dried wet-spun acrylic fibre to be on-line or gel-dyed. This porous structure in the never-dried state has a surface area of up to 190 m^2 g^{-1} and is able to be dyed by simple exchange of imbibed water for dye/water from the dye bath at temperatures of 50–60 °C within a time of less than 2 secs.

The level of orientation achieved during fibre formation can be controlled by the take-up draw, but it is invariably low, as measured by sonic modulus. The porosity present in wet-spun acrylics has been shown to close up on drying, leaving a very low pore volume on complete removal of water. Recent work[43] on the effect of hot water stretching on the porosity of wet-spun fibre has also shown a reduction in surface area from 190 m^2 g^{-1} to about 90 m^2 g^{-1} during this operation. Clearly, the stretching operation also causes a partial loss of porosity.

This gradation in porosity/structure from the outside of the fibre to the centre, which is seen visually, has been studied and modelled mathematically by a number of workers. Paul[44] stated that diffusional interchange with the bath was the key step and showed that the ‘coagulation front’ spread from the outside of the filament at a rate proportional to the square root of time. This follows the classical Fickian diffusion model. He found that the rate of precipitation decreased as the concentration of solvent in the bath increased, which is the expected result as the concentration gradient driving the diffusion is reduced. The data has been used to construct a constant flux ratio model, which has been shown to fit experimental data quite well.[45]

The lack of a measurable melting point (using conventional techniques) in acrylonitrile homopolymers and copolymers used for spinning fibres can be attributed to the structure adopted by the polymer chains and the strong interactions between the nitrile groups. Thermal instability of this chain structure begins at temperatures above 180 °C with autocatalytic cyclisation through the nitrile groups, along with some decomposition to gaseous products such as HCN and NH_3 taking place. The term autocatalytic cyclisation is used because the process starts with either a free radical being formed from an initiator group or an ionic species being formed from a copolymer group such as itaconic acid. The nitriles zip up to adjacent nitriles in a sequence, until sterically this reaction cannot go any further. It is thought that the free radical then transfers to an adjacent chain and the whole process starts again.

It has been possible to determine the melting point by using exceptionally high heating rates and a value of 320 ± 5 °C is accepted.[46] These experiments involved observing the complete loss of crystallinity as determined by X-ray techniques.

Acrylic fibres do, however, undergo thermal transitions at lower temperatures. Various transitions have been reported at temperatures between 39 and 180 °C. However, it is generally acknowledged that acrylic fibres undergo two transitions in this range. The first one, identified as the glass transition temperature, occurs at 80–100 °C for typical acrylic fibres containing vinyl acetate or methyl acrylate comonomers. During this transition, the fibre goes from a glassy solid to a rubber-like structure. The second transition occurs at around 140 °C but the precise cause of this transition is still under debate. Low molecular weight molecules with high dipole moments, of which water is a typical example, have been shown to interact strongly with nitrile groups. These interactions can result in a sharp reduction in the first observed thermal transition. A whole range of temperature reductions for different acrylic polymers has been recorded. Some of these reductions are as high as 50 °C. However, for conventional acrylic fibre polymers, reductions of around 15–20 °C are the norm.[47–49]

This reduction in the glass transition temperature in the presence of water is very significant, as it is one of the factors that contribute to the ease with which acrylic fibres can be dyed. Commercial fibres designed for dyed textile end-uses have a wet glass transition temperature of around 80 °C and this facilitates rapid dyeing with cationic dyestuffs at the boiling point of water. It is interesting to observe the kinetics and thermodynamics of the dyeing process of acrylic fibres. Virtually no dyestuff will penetrate the fibre surface at temperatures below 75 °C, but as the wet glass transition temperature is approached, the diffusion rate of dye into fibre increases dramatically. This increase is so large that it is necessary to control the rate of diffusion by the use of chemical retarding agents. A number of different mechanisms have been used to achieve this. Readers wishing for more information on this topic are referred to a textbook on the theory of coloration.[50] This large change in diffusion rate is due to the generation of free volume within the polymer structure, which is achieved by segmental mobility.

Although this reduction in the wet transition temperature is advantageous to the dyeing operation, it does also lower the resistance of the fibre to deformation. The hot wet modulus of acrylic fibres is a measure of the fibres' ability to resist deformation under tension and has been studied by many workers. Work by the author in which different acrylic fibre types were compared as well as the effect of various fibre formation variables showed that the hot wet modulus could be manipulated significantly.[51] Fibres with structures laid down under high draw conditions in combination with slow fibre precipitation rates gave the highest hot wet modulus values. Low values of the hot wet modulus have been correlated to aesthetic values such as poor yarn/fabric bulk and fabric creasing. Creases can appear in acrylic fabrics during the dyeing process if the fabric is cooled too rapidly through the glass transition temperature range. Dyebaths are therefore cooled very slowly from 100 to at least 60 °C. This cooling process can take several hours and is a significant cost issue. The creases develop as the structure returns to a glassy solid from a rubber-like structure.

Acrylic and modacrylic fibres are sold predominantly as tow and staple products with a small quantity of continuous filament fibre being sold as a speciality product. Fibre linear densities of between 0.84 and 17 dtex are produced, with the most common values being 1.7 for staple and 3.3/5.0 for tow to top conversion. Linear densities of below 1.0 are classed as microfibres. For the cut staple route, fibre lengths of between 25 and 150 mm are used. Fibre lustre can vary from bright

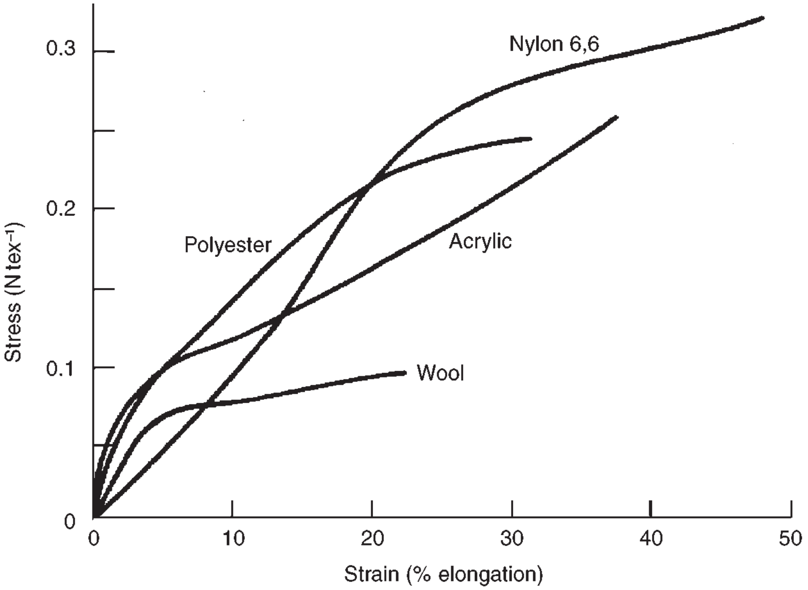
Table 4.4 Physical properties of acrylic and modacrylic fibres

Property	Acrylic	Modacrylic
Specific gravity	1.14–1.19	1.28–1.37
Tenacity (N tex^{-1})		
dry	0.09–0.33	0.13–0.25
wet	0.14–0.24	0.11–0.23
loop/knot tenacity	0.09–0.3	0.11–0.19
Breaking elongation (%)		
dry	25–45	25–45
wet	29–61	
Initial modulus (N tex^{-1})		
dry	3.5–4.9	2.6–3.5
wet	3.1–4.9	
Elastic recovery (%)		
2% stretch	99	95–100
10% stretch		70–95
20% stretch		
Electric resistance	High	High
Static build-up	Moderate	Moderate
Flammability	Moderate	Low
Limiting oxygen index	0.18	0.27
Char/melt	Melts	Melts
Resistance to sunlight	Excellent	Excellent
Resistance to chemical attack	Excellent	Excellent
Abrasion resistance	Moderate	Moderate
Index of birefringence	0.1	
Moisture regain (std %)	1.5–2.5	1.5–3.5

fibre, which contains no delustrant, through semimatt (or dull), which contains about 0.2% to matt (0.4%) and even supermatt (up to 1%). Titanium dioxide is the most commonly used delustrant.

The physical properties of acrylic and modacrylic fibres are given in Table 4.4. Typical acrylic fibres have specific gravities of between 1.14 and 1.19. The elastic properties compare favourably with wool and are quite different from cotton. Tensile strengths are considerably lower than polyamide and polyester synthetics but are higher than wool and similar to cotton. This combination of elastic properties classifies acrylics as ‘compliant’, which correlates to a soft or wool-like handle. High-tenacity variants can be produced (tenacities of up to 1.4 N tex^{-1}) by stretch orientation but these tend to suffer from fibrillation. This can be a particular problem in dyed products as the abrasion that can lead to fibrillation manifests itself as a lightening of the shade. Typical stress–strain curves for various fibres are given in Fig. 4.16.

Other notable physical characteristics are high electrical resistance, moderate flammability, excellent resistance to sunlight, chemical and microbiological attack and a moisture regain of 2–3%. These properties are thought to be due to the dipole effects between the nitrile groups within polymer chains and between



4.16 Typical stress–strain properties of acrylic and other fibres at 65% r.h. and 21 °C. Source: Jacqueline I. Kroschwitz, editor, *Encyclopedia of Chemical Technology*, 2nd edn, Vol. 1, p. 343, ©1985 John Wiley & Sons, reprinted by permission of John Wiley & Sons Inc.

chains. The strong dipole bonds created between these nitriles along with the hydrogen bonding between the electronegative nitrogen and tertiary hydrogen atoms form a strong barrier to melting or solvation. In addition to this, the repulsive forces within chains present barriers to bond rotation, so that even when solvation or melting occurs there is only a small increase in entropy. Acrylic fibres are therefore insoluble and unswollen by most chemical solvents. This is why highly polar solvents such as dimethyl formamide, dimethyl sulphoxide, ethylene carbonate and aqueous sodium thiocyanate are used for fibre spinning.

As would be expected, some of these properties dictate the end-uses into which acrylics are consumed. For example, the excellent UV stability, good fibre tenacities and resistance to microbiological attack have led to an extensive use of dry- and wet-spun acrylic fabrics in awning and convertible car roof fabrics, while the excellent chemical resistance and lack of a melting point in dry-spun homopolymers lends itself to hot gas filtration end-uses. Dry-spun fibres also tend to have excellent flexural rigidity properties, which favours their use in upholstery. Bayer's *Dralon* trade name is almost synonymous with furniture fabrics. The wet-spun acrylics are used extensively in apparel end-uses where the comfort factor afforded by acrylic fibres is the major asset.

Table 4.5 summarises the chemical resistance of acrylic fibres, as well as giving a comparison with the other fibre types. This chemical resistance is a function of the physical structure described above.

Table 4.5 Chemical properties of fibres

Chemical agent	Acrylic/modacrylic	Nylon	Polyester	Polyolefin	Cotton	Wool
Weak inorg. acids	Resistant	Fair	Resistant	Resistant	Hydrolysed hot	Resistant
Strong inorg. acids	Dissolves in conc. HNO_3, H_2SO_4	Poor	Resistant, but degrades in 96% H_2SO_4	Slowly oxidised	Hydrolysed, oxidised	Resistant
Dilute alkalis	Resistant	Good	Resistant	Resistant	Resistant	Degrades easily
Concentrated	Degrades hot	Good	Degrades hot	Resistant	Swells	Degrades easily
Oxidising agents	Resistant	Resistant	Resistant	Moderately resistant	Degrades in conc. H_2SO_4 Degrades in conc. bleaches	Degrades Degrades
Reducing agents	Resistant hot					
Dry-cleaning solvents	Insoluble	Insoluble	Insoluble	Insoluble	Insoluble	Insoluble
Non-polar solvents	Insoluble					
Polar solvents	Soluble in DMF, DMSO, DMaC, ethylene carbonate	Soluble in 90% formic acid	Some	Insoluble		
Heat resistance	Degrades slowly above 200 °C	Degrades slowly > 200 °C; melts at 250–255 °C	Excellent: melts at 250 °C	Degrades slowly and melts at 150–170 °C	Excellent below 150 °C; burns at 390 °C	Degrades above 150 °C; chars at 300 °C
Stability in sunlight	Excellent	Good	Good	Must be stabilised	Fair–degrades	Fair–degrades
Resistance to insect attack	Resistant	Resistant	Resistant	Resistant	Attacked by silver-fish	Attacked by moths
Resistance to biological agents, e.g. mildew, fungus, bacteria	Resistant	Resistant	Resistant	Resistant	Not resistant to rotting	Resistant

4.6 Chemical variants

During the 50 years that acrylic fibres have been commercially available, there have been many fibre and chemical variants manufactured. Some of these variants fall within the definition of an acrylic fibre (< 15% comonomer) and some fall outside of this definition (> 15% comonomer). Those products that contain less than 85% acrylonitrile are termed modacrylics.

Many of the product variants that have been developed are not available today. Some have been withdrawn for economic reasons, some for legislation reasons (e.g. some flame-retardant fibres) and some have simply been withdrawn because the parent company has left the business. A good example of this last case is the bicomponent fibre *Orlon 21*, which used to be manufactured by DuPont.

The wide range of variants is possible for four reasons. The first reason is that acrylonitrile is readily polymerisable with ethylenically unsaturated monomers, of which there are many. The second reason is that it is possible to blend different acrylonitrile polymers together, in many cases without phase separation occurring, to produce fibres with special properties. The third reason is that it is possible to control the structure of the fibres as they are formed within the spinbath. This allows many useful product variants to be produced. The variants produced by structure modification within the spinbath will be dealt with in Section 4.7 (fibre variants). The fourth reason is that it is possible to add functional additives to the polymer prior to fibre formation.

Chemical variants are important to any business for two reasons. They usually perform a function in addition to the usual textile properties and they sell at premium prices. They are therefore an important part of a company's product portfolio because they add value to the business.

4.6.1 Copolymer variants

Acrylic and modacrylic fibres invariably contain one or two copolymeric units based on comonomers. Even fibres described as homopolymers usually contain a small amount (0.5%) of a copolymeric unit. These copolymeric units are added for a variety of reasons:

- To produce fibres with desirable textile properties.
- To produce fibres with flame-retardant properties.
- To produce fibres that can be dyed easily.
- To produce fibres that can be oxidised to produce carbon fibre.
- To produce bicomponent fibres.

4.6.1.1 Asbestos replacement fibres

Asbestos replacement fibre for use in reinforcing concrete and tarmac is a good example of a fibre engineered to give specific properties. The properties required

Table 4.6 The chemical resistance of Dolanit 10 fibre

Titre	(dtex)	1.5
Staple length	(mm)	6.12
	on request (mm)	4
Fibre cross-section		Kidney shaped
Lustre		Bright/ecru
Density	(g cm^{-3})	1.18
Extension	(%)	8–12
Fineness related tensile strength	(cN tex^{-1})	80–87
Starting modulus	(cN tex^{-1})	min. 1500
(Conversion 1 cN tex^{-1} = 11.8 N mm^{-2})		
Resistance to acids	Very good – after 8 weeks at 2 °C in • sulphuric acid (50% solution): 85% tenacity remains • nitric acid (30% solution): 93% tenacity remains	
Resistance to alkalis	Very good – in pH13 caustic soda for 24 h at 80 °C approx. 93% tenacity remains	
Heat resistance	Good – after 200 h at 150 °C: approx. 75% tenacity remains. Short-term processing temperatures of up to 200 °C; does not melt	
Hydrolysis resistance	Very good – after 350 h at 130 °C: 95% tenacity remains	
Resistance tests	The tests were performed on individual fibres and thus represent tough testing conditions	
Moisture	Maximum 2% (higher moisture content available on request)	
Burning behaviour	Fibre cement slabs containing type 10 are non-combustible, do not develop any toxic gases and meet the requirements of class As of DIN Standard 4012 Part 1 for building materials	
Applications	Fibre cement and related products	

Source: Acordis Kelheim Acrylics

in a fibre to replace asbestos are high tenacity and modulus, resistance to alkali degradation, retention of modulus in warm-moist conditions and good bonding of the fibres to the cement or tarmac.

Virtual homopolymers of acrylonitrile are usually used for this purpose. They contain up to 0.5% of units based on a comonomer (e.g. sodium methallyl sulphonate or methyl acrylate) and are made with a high molecular weight (100 000 to 500 000). These high molecular weight polymers are usually given high draw ratios in spinning in order to produce fibres with tenacities and moduli in the higher range required. One of the best examples of this type of fibre is *Dolanit 10* manufactured at the Acordis Kelheim facility. Table 4.6 gives details of the acid and alkali resistance on the tenacity of *Dolanit 10* and it is easy to

Table 4.7 Flame-retardant fibres

Product	Producer	Halogen monomer	(%)	Other monomer	Comments
Dolan 88	Hoechst	VCl_2	(16.7)	Methyl acrylate sulphonate	Stopped production
Dralon MA	Bayer	VCl_2	(36.1)	Sulphonate	
Dynel	Union Carbide	VCl	(60.0)		Stopped production
Kanecaron SE	Kanegafuchi	VCl	(50.8)		
Lufnen	Kanebo	VCl_2	(35.6)		
SEF	Monsanto	VCl_2 VBr	(23.2) (11.8)	Sulphonate	
Teklan	Courtaulds	VCl_2	(45.6)	Sulphonate	Stopped production
Velicren FRS	Enichem	VCl_2	(36.9)	Sulphonate	Stopped production
Verel	Tennessee Eastman	VCl	(39.1)	Substituted acrylamide	Stopped production

understand why this type of fibre is used for these purposes. The polymer structure retains the bulk of its properties for a very long time.

4.6.1.2 Flame-retardant fibres

Flame-retardant fibres can be achieved by incorporating high percentages of halogen monomers into the fibre. Typical incorporation levels are between 34–51 mole %, thereby classifying all flame-retardant acrylics as modacrylics. Monomers used are one or more of:

- Vinyl chloride (VCl): $CH_2=CHCl$
- Vinylidene chloride (VCl_2): $CH_2=CCl_2$
- Vinyl bromide (VBr): $CH_2=CHBr$

Many other monomers have been reported in the patent literature as flame-retardants for acrylonitrile (AN) polymers, but none of them has been commercialised.

Polymerisation of modacrylics is generally done under pressure as all three halogen monomers have boiling points near to or below ambient temperature. They are usually batch processes due to the unreactive nature of the monomers. Vinyl chloride has reactivity ratio values of r_1 (AN) 2.55–3.65 and r_2 0.02–0.07, vinyl bromide has similar values. However, vinylidene chloride is much more reactive with values of r_1 (AN) 0.44–1.04 and r_2 0.28–1.8. For vinyl bromide or chloride, it is necessary to maintain a large excess of the monomer in the reaction mix, typically >80%, in order to incorporate the correct levels (AN =100, VBr = 180). Vinylidene chloride need only be added in slight excess.

The flame-retardant polymers manufactured commercially are all spun using a wet-spinning process. Most modacrylics have either antimony trioxide or antimony pentoxide added to enhance flame retardency. These are added in the form of a pigment at levels of 3% or more. Table 4.7 gives details of the most recent commercial flame-retardant fibres but most have been withdrawn since 1990. *Kanecaron* is by far the most important commercially with an annual capacity of over 40 000 tonnes.

There has been significant debate for a number of years about the environmental and health and safety impact of not only these flame-retardant polymers but also all flame-retardant textile processes. A working party was set up a few years ago to assess these issues and a published report[52] summarises the conclusions. As a result of this report there is renewed effort to investigate and develop new classes of flame-retardant monomers and additives. This work is likely to concentrate on phosphorus–nitrogen chemistry and nanocomposites, thereby avoiding the use of halogens and heavy metals.

4.6.1.3 Acid dyeable fibres

Most commercially available acrylic and modacrylic fibres contain some form of basic dyeable end groups. These acidic end groups emanate from either the redox initiator system used in polymerisation, as discussed earlier, or from sulphonate comonomers added as dye-sites. All of these fibres dye easily with the various ranges of cationic dyestuffs developed for this purpose. However, there is a niche market for acrylic fibres that are dyeable using acid dyes (wool/polyamide dyestuffs). Such fibres require the incorporation of monomers that function as bases. Three types of basic monomers have been used commercially. They are pyridines (e.g. 2-vinyl pyridine), tertiary amines (e.g. *N*,*N*-dimethylaminoethyl methacrylate) and quaternary ammonium salts (e.g. 2-hydroxy-3-methacryloylpropyl trimethylammonium chloride). The main difference between these bases is the dyeing pH that can be used. Pyridines require a pH of 1 to 2, tertiary amines pH 3 and the quaternary ammonium salts up to pH 6. Clearly, a more neutral pH is desired for ease of dyeing.

There are only a few fibres available today that are acid dyeable. *Cashmilon AD* from Asahi (who no longer make acrylic fibres) and *Dralon A100* and *A800* from Bayer are the most well known. They are used almost exclusively for producing piece dyeable stripes or heather effects in blends with conventional acrylics.

There are several difficulties associated with making acid dyeable polymers and with the performance of the resulting fibres:

- The monomers are either non-volatile or have very low vapour pressures. This makes recovery of the monomer after polymerisation very difficult. The favoured polymerisation technique is a batch process so that as high a conversion rate as possible can be achieved.

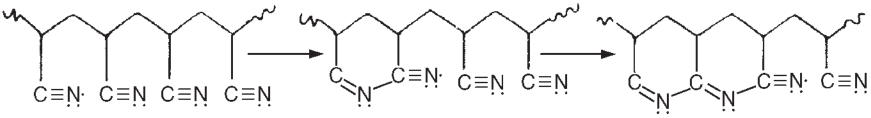
- The redox initiation system commonly used produces acidic end groups in the polymer chain. It is therefore necessary to neutralise these or to use an initiator system that does not produce acid end groups.
- The dye-site monomers are expensive.
- The resulting fibres have reduced heat stability because of the presence of the amine groups. They also have a poor fibre colour.

4.6.1.4 Carbon fibre precursor

Acrylic fibres are the major fibre type used as the precursor for carbon fibre production. However, in order to produce a fibre suitable for this process it is important to stabilise the exotherm that occurs in the early stages of oxidation and which of course is an important part of the process used to manufacture the carbon fibre. The carbonisation process involves three or four stages. The first step is the oxidation process in which the continuous fibre tow is held to length while it is heated to 250 °C in an air atmosphere. It is held at this temperature for about 90 minutes and the speed of the tow through the oven is about 200–300 m h^{-1}. The fibres incorporate about 8% oxygen into their structure during this process and lose an equal weight in low-temperature volatile species (finish, etc.). The second step is known as the low-temperature or tar removal step in which the tow is heated to between 600 and 800 °C for a few minutes in a nitrogen atmosphere. This burns off the bulk of the acrylic fibre residues. The third step is known as the high-temperature phase in which the fibre is heated to 1300 °C for a few minutes in a nitrogen atmosphere. This is the step in which the carbon fibre structure and properties are built. The resulting carbon fibre is known as low-modulus carbon fibre and a fourth step is possible in which the fibre is heated to temperatures as high as 3000 °C. This forms the high-modulus/graphitic carbon fibre.

It is important to be able to control the exotherm in the oxidation phase and this is done by stabilising the mechanism by which cyclisation occurs. This stabilisation is achieved by allowing the fibre to form a ladder polymer in the early stages of the carbonisation process. The ladder polymer is formed by nitrile polymerisation and is initiated by a free radical or ionic mechanism (Fig. 4.17).

The ionic process is initiated by the incorporation of nucleophilic agents such as itaconic acid, methacrylic acid or vinyl bromide into the polymer. The Acordis carbon fibre precursor (CFP) business uses the itaconic acid route. This comonomer reduces the temperature at which the nitrile polymerisation starts and as such moderates the exotherm. This fibre also incorporates methyl acrylate (MA) as a comonomer and although this comonomer has been shown not to catalyse the exotherm, it is known to interrupt the nitrile polymerisation.[53] Maslewski and Urbanska[54] have shown that there is a relationship between the precursor fibre strength and modulus and the carbon fibre strength and modulus. It is therefore desirable to produce polymers with higher molecular weights and fibres with higher stretch ratios for this end-use.



4.17 First stage carbon fibre–nitrile polymerisation. Source: Gupta, Paliwal and Bajaj, *Rev Macromol Chem Phys*, 1991, **C31**(1), 13.

Commercial polymerisations for carbon fibres generally use radical initiators, usually azonitriles, and all conventional spinning processes, dry, wet and dry-wet, have reported fibres suitable for precursor end-uses. Fibres for conversion to carbon fibre generally need to be very uniform and straight. This means that it is not possible to put high levels of crimp into the continuous tows as this can cause flaws in the carbon fibre. As the carbonisation process operates at a much slower line speed than the manufacturing rate of the fibre, it is not possible to have a continuous process. It is necessary therefore to package the tow at the end of the fibre-making stage and then to feed this into the carbon fibre process. The fibre tow needs to be packaged differently from conventional fibres because of the requirements for low crimp levels. The tow is therefore usually collected on creels or in containers in which the tow is simply plaited in without the bale pressing/packaging. Two different tow sizes are available depending upon the spinning process used. The Acordis product is manufactured in large tows of 36–53 ktex while other manufacturers manufacture tows of around 12 ktex. These tow sizes make significant differences to the economics of the carbon fibre making process.

The end-uses in which carbon fibres are being utilised continue to expand. Recent developments include the use of carbon fibre brake systems for aeroplanes and high-performance motor vehicles. They are also used for concrete reinforcement, as a replacement for metal rods that tend to corrode with time, and in a very recent development in which only the surface of the fibre is carbonised. The core of the fibre is retained along with its fibre properties. This produces a very useful fibre that can be used in more conventional textile conversion processes. The outer layer of carbon acts as a flame and heat barrier.

4.6.1.5 Bicomponent fibres

DuPont first introduced bicomponent acrylic fibres to the market in 1958. The much-lamented type 21 fibre was made by dry-spinning a polyacrylonitrile homopolymer and a copolymer of acrylonitrile with sodium styrene sulphonate (SSS) through a bicomponent jet. The jet technology required to produce true bicomponent fibres is critical, with the two polymers needing to be kept separate to a late stage and delivered to each hole in the jet face side by side, thus forming side-by-side bicomponent filaments. Polymer rheologies are also very important, as flow characteristics also need to be matched. This type of technology is best suited to the small dry-spinning jets but pose huge design problems with the larger wet-spinning jets. These jets contain much larger numbers of holes and it is extremely difficult to engineer true bicomponency in such jets. Monsanto claims such a jet is possible.[55] Acordis has experience of the *Kasen* bicomponent jet that contained up to 20 000 holes.

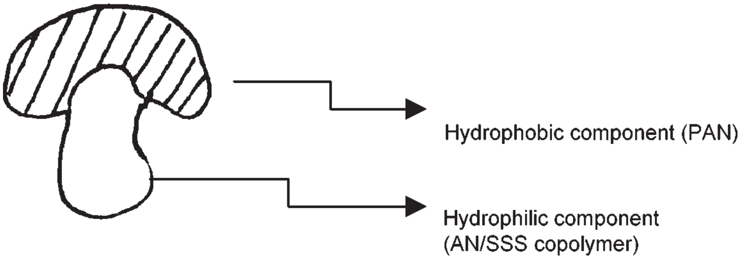
The alternative to true bicomponent fibres is random bicomponent fibres that have about 50% of the bicomponent character of a true bicomponent fibre. These are however, much easier to manufacture. The composition of individual filaments will vary from 100% of polymer A or polymer B to equal quantities of A and B. This is achieved by the multi-layering of the two polymers prior to the spinjet and this is an example of the mixing of two polymers without phase separation occurring. Each filament consists of a single phase with variable composition throughout the fibre. This type of approach does not require the two polymers to be kept separate up to the jet face. *Courtelle LC* fibre manufactured by Acordis is an example of this type of approach.

The acknowledged benefit of bicomponent acrylic fibres is that they produce yarns and fabrics with enhanced bulk. This extra bulk is generated by the chemical crimp formed by the differential shrinkage within the two polymer types. When the fibre is subjected to wet finishing and subsequent drying the two polymers will shrink differently, thereby setting up tension within the fibre cross-section. The tension is relieved by the formation of a helix down the fibre length. Yarn/fabric bulk is formed from regular fibres by the mechanical crimp in each filament preventing the close alignment of filaments, thereby creating space between them. The chemical crimp generated within bicomponent fibres will add to the mechanical crimp given to the fibres during the crimping process. Extra bulk is therefore created.

This chemical crimp in bicomponent fibres can be generated during the fibre manufacturing stage or it can be generated at the yarn spinning or dyeing stage. This is known as latent crimp and can be used to generate interesting effects. *Courtelle LC* fibre is a good example, with the chemical crimp being generated in the yarn relaxation stage. This fibre has a random bicomponency and is made by mixing together two polymers, one based upon the regular *Courtelle* polymer (AN/MA/AMPS) and the other a special polymer made from acrylonitrile and acrylamide.

Further classification is important with bicomponent fibres in order to differentiate between water-reversible and non-water-reversible bicomponent fibres. The concepts behind water reversible crimp are best explained by reference to DuPont's *Orlon 21*. We have already seen that this fibre was manufactured by bringing together two different polymers at the jet face. These polymers were designed with a large difference in hydrophilicity. The acrylonitrile virtual homopolymer is essentially hydrophobic while the acrylonitrile/sodium styrene sulphonate polymer is quite hydrophilic. These two polymers therefore respond quite differently to water; the AN/SSS polymer will absorb water and swell/expand, while the AN polymer will be essentially unaffected.

When these two polymers are brought together at the jet face and fibre formation



4.18 Cross-section of *Orlon 21* fibre. Source: Reprinted from J. C. Masson, *Acrylic Fiber Technology and Applications*, p. 172 by courtesy of Marcel Dekker, Inc.

begins to take place by evaporation of the polymer solvent, the resulting fibre has a mushroom shape. This is due to the polymers responding differently to the evaporation of the solvent, the stem of the mushroom being the AN/SSS polymer and the cap being the AN polymer (Fig. 4.18).

The fibres are given mechanical crimp as normal and they enter the textile chain behaving in much the same way as regular fibres. However, once the resulting yarn or fabric is subjected to a wet processing operation then the chemical differences between the two polymers have a significant effect upon the resulting yarn/fabric. The ionic groups within the AN/SSS polymer absorb water and the polymer expands. Upon drying, the two halves of the bicomponent fibre dry at different rates and shrink to different extents. The hydrophilic AN/SSS polymer shrinks significantly more than the AN polymer. This differential shrinkage causes tensions down the fibre filament and these are released by the formation of a helix. However, the crimping force generated by this helical crimp is quite low and it will be retarded if the clothing is dried under tension, e.g. on a washing line. This crimp is therefore maximised by tumble-drying in which relaxation takes place in a tensionless environment. This phenomenon is known as water-reversible shrinkage because the effect is reversed when the yarn/fabric is given a wet treatment. The yarn/fabric will thin or extend as the hydrophilic polymer absorbs moisture and then shrink again as the yarn/fabric is tumble-dried. This is a very desirable property in acrylic textiles because it ensures that the fabrics retain their shape, dimensions and bulk throughout their product lifetime. Regular acrylic yarns/fabrics have a tendency to thin/extend through wash/wear cycles and this can be a disadvantage.

Orlon 21 was a great success in the USA, where tumble-drying was the normal way in which clothes were dried. However, in Europe, where it was more likely that clothes were dried on a washing line, this product was never very successful. DuPont left the acrylics business in 1991 and sold this technology and trademarks to Monsanto (now Solutia). The product manufactured by Solutia uses a different technology and behaves in a different way from the original *Orlon 21*. The Solutia product is known as *Type A21* and is manufactured using their wet-spun technology.

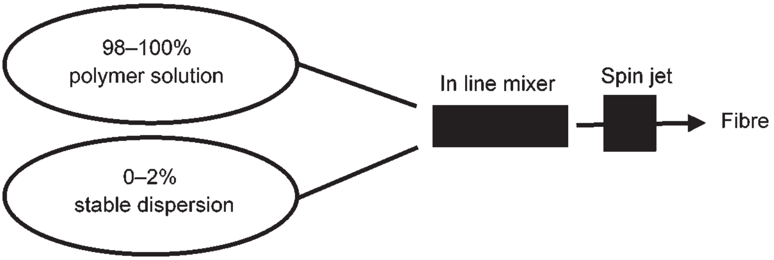
Clearly, this means that the degree of bicomponency will be lower. However, the benefits of using this *A21* fibre in knitwear are almost identical to those attributed to *Orlon 21* and so Solutia has engineered an excellent fibre.

4.6.2 Functional additives

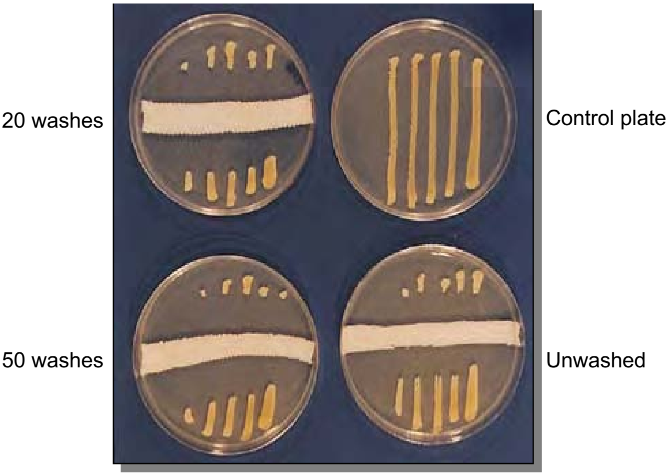
The late 1950s through to the mid 1970s were a very innovative time for acrylic fibres, with many product variants being developed. However, the acrylic fibres business overall went into decline during the late 1970s and early 1980s and product developments of any significance were infrequent. As an outcome of the restructuring of the business, those companies that have remained have been very active since 1995 and we have seen a resurgence in the development of innovative acrylic fibres. The desire to develop new functional fibres is driven by the added value that can be achieved by such products. Many of these products have been made possible by developments in other areas of chemistry, particularly zeolite chemistry and microencapsulation chemistry.

Several of the functional fibres that have entered the market in the last few years are produced by adding stable dispersions of the functional chemical to the polymer solution prior to fibre formation. This is very similar to the masterbatch approach in melt-spinning. These stable dispersions can be added in the same way that pigments or delustrants are added, i.e. to the polymer solution prior to filtration, or much later in the process using late injection principles (Fig. 4.19). The 'pigmentation' approach means that all of the spinning machines are supplied with the functionalised polymer and so large quantities of fibre will need to be produced (10 tonnes minimum). The late injection technique allows much smaller quantities of fibre to be made as the additive is usually injected into individual spinning machines just before the spin jet. The material can be supplied from a ring main with individual injectors and filters supplying individual machines or each machine may have its own supply. This allows for increased flexibility and much smaller minimum quantities (500 kg in some instances).

- Antimicrobial additives are added prior to the fibre spinning stage
- Additives are therefore locked inside the fibre



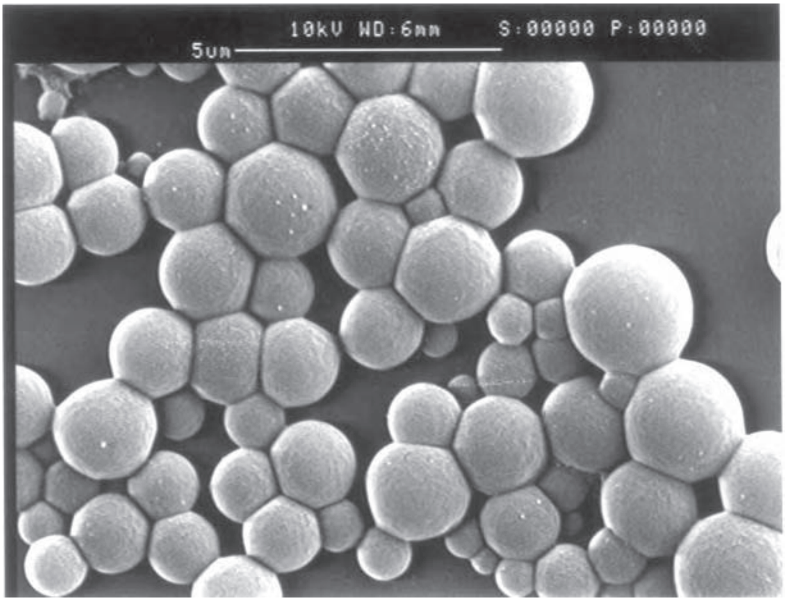
4.19 Late injection scheme. Source: Acordis UK Ltd.



4.20 Antibacterial performance of a 70% cotton/35% *Amicor* fabric using Swiss SNV195920 protocol. Source: Acordis UK Ltd.

Functionalised fibres are available that offer protection from ultraviolet or infrared radiation. This is usually achieved by the addition of pigments such as titanium dioxide in which the surface of the pigment has been functionalised so that it interacts with sunlight. Fibres are available that have the ability to control bacteria (bacteriostatic) and fungi (fungistatic) when blended with other fibres that are biodegradable, such as cellulose. By blending 30% of a fibre such as *Amicor Pure* from Acordis with cellulosic fibres, the resulting yarns/fabrics are protected from bacterial and fungal growth. Figure 4.20 shows the results of testing a 70% cotton/30% *Amicor* fabric to the SNV195920 protocol. This is an internationally agreed protocol for testing the antibacterial performance of articles. Figure 4.20 shows the growth of bacteria on the agar plates and on the test fabrics, one of which has been washed 20 times and one 50 times. These effects can be durable to dyeing and finishing and subsequent laundering, depending upon the chemistry of the antimicrobial additive. Some of these antimicrobial fibres incorporate free organic molecules as the functional additive; others use zeolite structures. These are known as leaching and non-leaching types, respectively. Zeolites have the ability to support different metal ions, such as zinc or silver, which are held by ionic interactions and which are able to generate free metal ions. It is these free ions that have the antimicrobial activity. The latest technology in this area uses pigments in which the surfaces of the pigment molecules have been modified with different metal ions.

Fibres are available that incorporate microencapsulated materials such as free waxes or perfumes. An interesting product is the *Outlast* fibre made by Acordis under licence to the owners of the technology – Outlast Technologies Inc., to whom the ownership of the original patents[56,57] has been transferred. This fibre

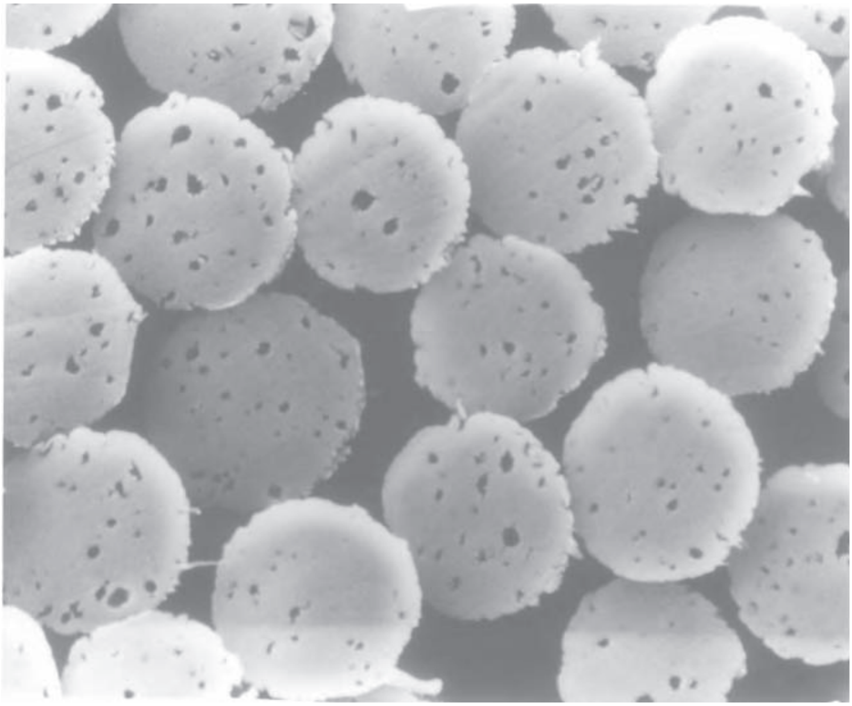


4.21 Microencapsulated phase change material used in *Outlast* fibre. Source: Acordis UK Ltd.

incorporates large quantities of microencapsulated phase change material. These microcapsules are about 2 μm in size and are shown in Fig. 4.21. The phase change materials are hydrocarbons that have melting points around body temperature. They are therefore able to respond to the body temperature by absorbing heat and changing phase from a solid to a liquid and vice versa. This responsive fibre is therefore able to offer real benefits in the perception of comfort. It has the ability to influence the microclimate between the skin and textile; by minimising the swings in skin temperature, moisture generation is also influenced and this adds to the comfort benefits. Figure 4.22 shows the cross-section of the *Outlast* acrylic fibre manufactured by Acordis.

Other speciality fibres that are on offer include moisture-absorbent fibres, an example of which is the *Dunova* fibre manufactured by Bayer. The porous structure is formed in the polymer by the addition of water-soluble polyols, such as glycerol, of lower volatility than the spinning solvent. These materials are added to the spinning dope prior to the fibre formation, separate as a dispersed phase during spinning, and are later removed in the washing processes. The voids that remain give the fibre greatly enhanced water absorption properties.

A new acrylic fibre variant called *A.H.F.* has been announced by Mitsubishi Rayon. It is made by mixing together acrylic and cellulose diacetate polymers at the fibre-making stage. Clearly, a common solvent is required for this approach and this is thought to be dimethyl acetamide. The current product announced by Mitsubishi Rayon is based upon a 70 : 30 mixture of acrylic/diacetate polymers



4.22 Cross-section of *Outlast* acrylic fibre. Source: Acordis UK Ltd.

and the acetate is understood to be randomly dispersed in the acrylic polymer matrix. The resulting wet-spun fibre is claimed to have the characteristic dry feeling of acetate along with enhanced moisture-permeable effects. One of the other benefits of this new product is that it has deodorising properties, particularly with ethanoic and isovaleric acids. The significance of these acids is that they are present in perspiration. Antibacterial properties can also be obtained by the addition of chitosan to the polymer mixture.

The need to control the static electricity that develops during the processing of acrylic fibres into yarns and fabrics is of fundamental importance. Acrylic fibres are essentially insulators and static will build up during processing unless it is dissipated. This is done routinely by the surface application of an antistatic processing aid. These antistatic finishes will move the specific resistance of the acrylic fibre from around 10^{15} Ω cm down to 10^{10} Ω cm. Such processing aids tend to be cationic surface-active agents. It is, however, possible to move the resistance of the acrylic fibres into the region of semiconductors (specific resistance as low as 10^{-3} Ω cm) by a number of techniques. The first technique involves forming a layer of metal on the surface of the fibre by a vacuum deposition technique. Aluminium has been successfully deposited onto the surface of acrylic fabrics to offer a surface resistance of 1.5×10 Ω cm. Chemical plating processes have also been used to form metal coatings on yarns and fabrics with similar semiconductor properties.

Other techniques have involved the incorporation of copper compounds into the fibres. By soaking in copper sulphide solution, it is possible to anchor the copper ions through the cyano groups in the polymer chain, thereby allowing copper(I) ions to be available. The final technique involves applying resins to the fibre/fabric surface that contain π-electron conjugate polymers. Further details on these antistatic and electroconductive fibres can be found by reference to a Toray Research publication on functional fibres.[58]

Insect and mite-repellent fibres are available that prevent the development of mites within fabrics and in some cases repel insects (e.g. mosquitoes). These properties are imparted by the impregnation into the fibre of acaricidal agents such as benzyl benzoate or repellent agents such as *N*,*N*-dimethyl toluamide.[59]

Many deodorising fibres have been developed and there are five basic mechanisms by which they work. These can be categorised as follows:

1. Sensory deodorising, in which volatile natural oils such as lemon or lavender are incorporated into the fibre.
2. Chemical deodorising in which the malodour is chemically deactivated. Additives such as iron sulphate can be used to remove sulphur smells; oxidising or reducing agents, chemicals that undergo addition or condensation actions (e.g. glyoxal), or ion exchange additives can also be used.
3. Deodorising through chemical adsorption using, for example, specific activated carbons or zeolites containing specific chemicals (e.g. $KMnO_4$).
4. Deodorising through physical adsorption. Neutral activated carbons and clays and zeolites are commonly used additives.
5. Biological deodorisation. Enzymes, bacteria and yeasts that break down malodours have been used.

4.7 Fibre variants

All acrylic fibre manufacturers make the usual range of fibre variants in terms of decitex, kilotex, staple length and lustre. These usually range from 0.84 dtex up to 15 dtex with staple lengths of 25 mm up to 150 mm in bright, semi-matt or matt lustres. These fibres can be processed through all of the common fibre conversion routes, namely short staple cotton spinning, long staple woollen spinning, tow to top or worsted spinning, air-jet and Dref spinning (core–sheath spinning technology developed by Fehrer) and all non-woven conversion routes including thermal bonding.

These normal products can be made with different shrinkage potentials and dye rates and it is routine practice to be able to manipulate these properties on-line.

4.7.1 On-line coloration

A number of acrylic fibre variants can be made by manipulation to the fibre formation conditions and subsequent on-line processes. One of the most important of these is the ability to producer dye (gel dye) the fibre on line. Three possibilities exist for on-line coloration: gel state dyeing, solution or dope dyeing and tow dyeing. Dope dyeing and pigmentation with coloured pigments is fairly routine and no further comment is offered in this chapter. Tow dyeing is a small speciality product for some manufacturers in which dried fibre tow is fed into a Serracant dyeing machine, which works on the pad/steam fix principle. By far the most significant coloration technique is the gel-dyeing process. Recent figures from one of the major dyestuff manufacturers in the world indicate that over 20% of all dyed acrylic fibres are gel-dyed and that this figure is increasing each year.

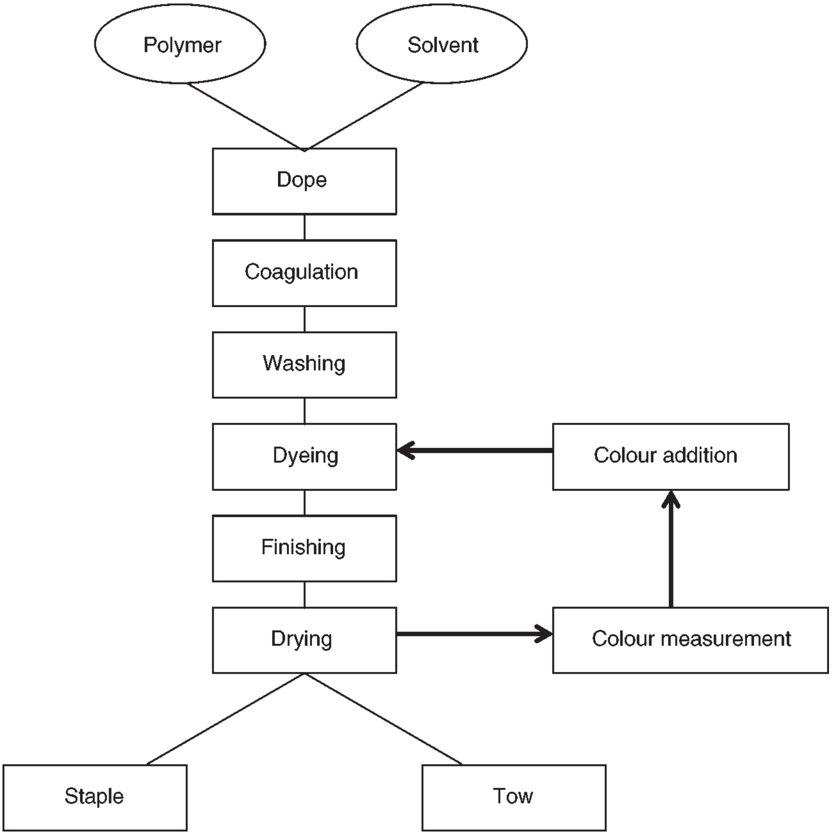
We have already seen that wet-spun fibres prior to drying have a porous structure which can be as much as 60% of the void structure. When the ‘as formed fibre’ is wet, this porous structure acts like a sponge. It is quite easy to exchange water within the fibre for dye/water from an external bath by using simple fluid mechanics principles. This exchange mechanism can occur within a few seconds and at ambient temperatures, although temperatures of between 50 and 100 °C are usually used.

Dye can be applied at almost any stage of the fibre formation process from the coagulation bath through washing and stretching and after stretching. It is, however, advantageous to have a washing stage after the dye application in order to remove any unfixed dyes before the fibre is dried and collapsed.

Liquid cationic dyestuffs, including optical whites and fluorescent dyes which were developed specifically for gel dyeing, are used in this process. Some companies offer coloured fibres from fixed shade cards and some companies produce coloured fibres to specific orders. Acordis in Grimsby has over 12 000 shades on record and offers minimum order quantities of only 1 tonne of fibre. This is achieved by having a very efficient on-line colour correction system in which it is possible to change colours within seconds. This rapid colour change is made possible by having two inline dyebaths fitted with dip rollers that can be raised out of the bath. As one colour run is coming to an end, the second bath is prepared with the new colour. The rollers are lifted on dyebath 1 as the rollers on dyebath 2 are lowered. This allows for a colour change to happen within about 2 minutes and for the new shade to be colour measured and corrected in about 10 minutes. Figure 4.23 is a simplistic diagram of the Courtelle process in Grimsby.

4.7.2 Low-pill fibres

One of the major criticisms aimed at apparel products made from acrylic fibres is the rather poor pilling performance. The mechanism of pill formation in textile fibres is well understood and documented. Pills will form when short lengths of fibre work their way free from the yarn structure and protrude from the fabric surface. Although they are held firmly at one end, the other free end is able to tangle with other free fibres and form small fuzz balls. These lie on the fabric surface and give the fabric a poor, worn appearance. The propensity of any fabric to pill is



4.23 Schematic of an on-line coloration process. Source: Acordis UK Ltd.

influenced by a number of factors – the staple length and decitex of the fibre, the yarn and fabric construction as well as the fibre tensile properties. As it is very difficult to stop short fibre lengths from freeing themselves from the yarn structure, the best way to minimise the problems of pilling is to ensure that the fuzz balls can break away from the fabric surface soon after they have formed.

The acknowledged way of doing this is to produce fibres with reduced knot tensiles (i.e. work to break). As tensile properties are developed in the fibre formation process and subsequent operations, then the skill is to reduce the knot properties without reducing the straight tensiles. The resulting yarns/fabrics will therefore perform in much the same way but as the pills form by entanglements, then the reduced knot tensiles allow the fibres to break at the points of stress within the loops.

Most acrylic fibre manufacturers have the ability to achieve this by a combination of stretch ratios and drying profiles. Regular acrylic fibres will give pill ratings of 3–4 using the European standard pill test. A fabric that does not pill will have a rating of 5 using this technique. Low-pill fibres on offer today will have ratings of 4–5, which is excellent by any standards. There are many low-pill fibres on the market today. Some of the better known ones in Europe are *Dralon Low Pill* made by Bayer, the Montefibre fibre *Leacril NP* and *Courtelle Low Pill* from Acordis, while in the USA, Solutia's *HP* fibre has these properties.

4.7.3 Microfibres

Microfibres have become an important product in most companies' product ranges since 1995 and have allowed many new fabric developments to be brought to market. The reason for this is that fabrics made from microfibres have quite different aesthetics and moisture management properties. Microfibres are manufactured by attention to the fibre-formation parameters and the draw ratios used in the fibre stretching stages. It is usual practice to slow the rate of fibre formation by changes to the conditions used and to draw the fibre by as many as 20 times. The structure of the fibre surface in microfibres is therefore usually much smoother and, for dry-spun fibres, the cross-sectional shape remains circular rather than dog-bone.

The resulting yarns are much finer and contain more filaments per unit length. This influences the handle and drape of resulting fabrics, which tend to be very soft and with excellent drape. The closer packing of the filaments within the yarn structure can facilitate better wicking of water molecules by the resulting fabrics. This is claimed in some fibre types to be due to the dye site end groups in individual fibre filaments packing closely enough to allow for dipole interactions between the water and the negatively charged acid end groups. These performance claims have been substantiated by independent testing[60] of the fabrics, which have shown that acrylic fabrics made with microfibres perform as well as many of the functionalised moisture management polyester fabrics. These fabrics often use finish treatments such as *Intera* to achieve these effects. This licensed technology is described as a semipermanent hydrophilic coating.

4.8 End-use survey

The acrylic fibres business is now very mature, having been established for over 50 years and it can be described as being a truly global business. The business has gone through many periods of rationalisation and significant changes have been seen in the breakdown of global capacities. The world production of chemical fibres in 2001 was 30 112 000 tonnes. The breakdown by fibre type of this volume is given in Table 4.8.

Acrylic fibre production in 2001 was 2 574 000 tonnes, with Western Europe producing some 510 000 tonnes, the USA 240 000 tonnes, Asia (excluding Japan) some 990 000 tonnes and Japan 370 000 tonnes. Table 4.9 summarises the trends in acrylic fibre production from 1980 through to 2001 and gives projections through to the year 2010.

Table 4.8 World production (in thousands of tonnes) of chemical fibres

	1995	1997	1999	2001
Polyester				
Filament yarns	6 408	8 384	10 189	11 234
Staple fibres	5 540	6 783	7 696	8 148
Total	11 948	15 167	17 885	19 382
Polyamide				
Filament yarns	3 139	3 425	3 276	3 255
Staple fibres	601	558	528	428
Total	3 740	3 983	3 804	3 683
Acrylic				
Filament yarns	4	4	5	5
Staple fibres	2 442	2 724	2 516	2 569
Total	2 446	2 728	2 521	2 574
Olefin				
Filament yarns	1 678	1 800	2 543	2 891
Staple fibres	901	1 065	1 181	1 255
Total	2 579	2 865	3 724	4 146
Others				
Filament yarns	136	164	193	222
Staple fibres	111	110	101	105
Total	247	274	294	327
Grand total	20 960	25 017	28 228	30 112

Table 4.9 World production (in millions of tonnes) of acrylic fibres (1980–2001)

	1980	1985	1990	1995	2001	2010 (predicted)
North America	0.42	0.37	0.33	0.35	0.24	0.15
South America	0.05	0.06	0.06	0.05	0.07	0.07
Western Europe	0.69	0.84	0.67	0.62	0.51	0.33
Eastern Europe	0.20	0.25	0.25	0.15	0.09	0.00
ME/Africa	0.04	0.12	0.14	0.23	0.27	0.45
South & South East Asia	0.01	0.02	0.05	0.11	0.16	0.29
East Asia	0.25	0.37	0.44	0.58	0.83	1.33
Japan	0.35	0.38	0.36	0.37	0.37	0.36
World	2.01	2.41	2.31	2.47	2.55	2.98
Idle capacity	0.53	0.19	0.50	0.57	1.16	

Source: CIRFS.

The trends indicated in Table 4.9 suggest that the changes seen in the acrylic fibre production statistics since 1995 will continue and will result in dramatic changes by the year 2010. Production output in North America has fallen from 420 000 tonnes in 1980 to 240 000 tonnes in 2001 and is projected to fall to 150 000 tonnes by 2010. In Western Europe production has fallen from a peak of 840 000 tonnes in 1985 to 510 000 tonnes in 2001 and is projected to fall to 330 000 tonnes by 2010. However, the world production of acrylic fibres has increased steadily from 2.01 million tonnes in 1980 up to 2.55 million tonnes in 2001 and is predicted to rise to 2.98 million tonnes by the year 2010. Obviously, we are witnessing a significant change in the global business with the development of new capacity in East Asia and with significant new capacity projected for South East Asia and the Middle East/Africa regions by the year 2010. It is clear therefore that for the economically developed nations, the growth in acrylic fibre consumption has stopped and in many cases reversed, while in the developing nations it is expanding.

Despite these changes in production statistics, the end-uses for acrylic fibres are well established. These applications fit in very well with the unique properties that acrylic fibres display and which are fully exploited by the fibre conversion routes available. Acrylic fibre demand remains strong because it has a number of major differences from other fibres, which give it a strong differentiation. It has a low specific gravity of 1.18 (cotton is 1.58), which gives bulk and warmth at reduced weight and hence good value. Yarns and fabrics have soft, wool-like aesthetics, and can be dyed at atmospheric pressure with well-developed and very cost-effective dyestuffs. A full shade range is easily achieved with colours being bright and with an excellent colour yield. Yarns and fabrics resist UV fading and biodegradation. The moisture regain level of 2–3% is useful, while allowing rapid drying and good wicking, and fabrics retain their shape after machine washing. The major end-uses for acrylic fibres are knitwear, socks, fleece-wear, handknitting or craft yarns, blankets, upholstery and a number of industrial fields of application.

In terms of fibre conversion routes, acrylic fibres process with high yields through all of the known conversion routes. Three forms of acrylic fibre are sold into the market for conversion into yarns and fabrics: tow, short staple and long staple. The tow to top route using stretch-breaking equipment is particularly cost effective with acrylic fibres and when combined with some of the shorter fibre spinning routes such as Repco spinning, the yarn-making costs are extremely competitive. Short staple fibre is converted through conventional cotton spinning equipment with ring spinning, open-end spinning and air jet spinning being used to manufacture yarns. Long staple spinning produces yarns through the woollen system. As one of the key advantages of acrylic fibres is the cost effectiveness of the on-line coloration process, the processing of coloured fibres is very common for acrylics. This puts some demands on conventional ecru mills in that segregation of coloured fibres from ecru fibres is essential and the sequential production planning of colours is important. Effective cross-blending is also very important, particularly for the shorter routes. Although on-line coloration of acrylic fibres is a great benefit, colour variation down a continuous tow and from tow to tow does mean that cross-blending is essential for good colour continuity. Staple end-uses take care of this cross-blending quite efficiently but in the tow to top conversion route it is very important that measures are put in place to ensure good cross-blending. In tow to top conversion it is usual practice for two tow bales to be fed into one stretch breaker. The resulting broken fibres are collected in cans and these are stored in columns until there is sufficient stock to feed into the subsequent drawing operation. The cans are taken from across the columns as they are fed into the drawing operation, thereby ensuring good cross-blending.

Tables 4.10 and 4.11 summarise the latest data from CIRFS on the end-uses into which acrylic fibres are utilised. These tables cover declared figures for sales of acrylic fibres into staple, tow and tops for Western Europe, Central and Eastern Europe and Turkey for the year 2000. The data are split into spun yarn and non-spun end-uses and it is concluded that these countries shipped 524 905 tonnes of acrylic fibre in the year 2000.

It is clear from these figures that acrylic fibres have made little impact in non-spun areas, with only 13 959 tonnes (2.3%) being used. Of this volume, the most significant is the Wildman process that produces fleece type fabrics for apparel end-uses. This product accounts for 7 715 tonnes of this total, which leaves only just over 6 200 tonnes for other non-spun applications. The reason for the low consumption of fibre into these non-spun end-uses is that, generally speaking, acrylic fibres do not provide any specific properties, including fibre price, that cannot be bettered by other fibres. Clearly, there are some niche end-uses into which acrylics do offer real benefits, but these are low volume areas such as concrete and bitumen reinforcement and hot gas filtration.

For spun yarns, it is clear that acrylic yarns have wide appeal in terms of application; however, with only 79 114 tonnes (18.3%) going into woven end-uses, it is the knitted area that dominates. Of these knitted end-uses there are two

Table 4.10 Acrylic fibre deliveries (in tonnes) for Western Europe, Central and East European countries (CEEC) and Turkey (2000)

Process	Western Europe	CEEC + Turkey
Spun yarn		
Cotton, Schappe & flax spinning	113 256	40 619
Woollen & semi-worsted spinning	21 519	41 754
Worsted spinning	134 803	143 071
Total of spun yarns	269 578	225 444
Of which open-end	33 598	2 763
Unspun yarn		
Filling & wadding applications	2 881	68
Needlepunch carpets	175	
Non-wovens	823	30
Wildman	7 514	201
Other processes	1 778	489
Total unspun	13 171	788
Traders & jobbers	15 026	898
Total	297 775	227 130

Table 4.11 End-use breakdown (in tonnes) for acrylic fibre deliveries to Western Europe, Central and East European countries (CEEC) and Turkey (2000)

End-uses	Western Europe	CEEC + Turkey
Spun yarn		
1 *Weaving*	37 630	41 484
Apparel fabrics	4 802	12 050
Cotton-type fabrics	3 794	3 200
Wool type fabrics	1 008	8 850
Furnishing and household fabrics	28 567	29 434
Blankets	15 387	16 405
Bedding and household fabrics	2 822	3 504
Net curtains and transp. voile	1 270	1 645
Other furnishing fabrics	9 088	7 880
Industrial fabrics	4 261	
2 *Textile narrow fabrics*		
3 *Knitting*	220 266	132 351
Warp, Raschel and Leaver knit	82 505	41 314
Apparel fabrics	79 806	40 141
Net curtains and transp. voile	80	74
Furnishing, household and Industrial	2 619	1 099
Other knittings	137 761	91 037
Hosiery–footwear	7 158	12 665
Underwear	7 928	8 000
Outerwear	120 857	58 297
Furnishing and household	1 639	1 2023
Industrial applications	179	52
4 *Carpets*	5 916	37 090
Backing	Not used	Not used
Pile: tufted	4 969	4 690
Pile: others	947	32 400
5 *Others*	5 766	14 519
Hand knitting	4730	14519
Other processes	1 036	
Total spun yarns (1 + 2 + 3 + 4)	269 578	225 444
Unspun yarn		
For apparel	7 609	234
For furnishing and household	3 527	34
For industrial uses	2 035	520
Total unspun	13 171	788

Source: CIRFS.

that consume the bulk of the volume – apparel fabrics produced by warp and Raschel knitting, and outerwear, produced by flat bed or circular knitting. Other end-uses, which make very worthwhile contributions to volumes, are blankets, furnishing fabrics, hosiery, carpets and hand-knitting or craft yarns.

Of these spun yarns, worsted or tow to top spinning accounts for over 56%, with cotton ring spinning accounting for a further 23.4%. These statistics tie in quite nicely with the major attributes of the acrylic fibre technologies. We have already seen that acrylic fibres have a low specific gravity that allows yarns and fabrics to be made which have a high bulk to weight ratio. If we combine with this the simple and effective on-line coloration capability of the acrylic fibre technology then we have all the makings of a very cost-effective route to market. It is these attributes that have contributed more than any others to the development of the worsted-spinning route. The worsted route is designed to produce yarns with high shrinkage and hence bulk potential as well as fully relaxed yarns. It is also ideally suited for processing of coloured fibres with changeovers from one colour to another quite easy.

We have therefore a whole sequence of technologies that allow finished fabrics and garments to be produced without any need for wet processing. The fibre manufacturer produces coloured fibres and these are converted into high bulk or fully relaxed coloured yarns through worsted spinning. These are, in turn, used in knitted socks or outerwear, or in craft yarns. This is an extremely cost-competitive route to market and is one of the major reasons for the success of acrylic fibres. It also clearly accounts for the split of end-uses. Acrylic fibre manufacturers have also tried to maximise these attributes over the years with fibre variants such as the bicomponent fibres playing to these strengths.

While on-line coloration and knitted end-uses are key to the acrylic business, they are best suited to the wet-spun technologies. However, dry-spun fibres also have physical properties, that allow them to provide desirable fabric properties in certain end-uses. One of the important differences in the physical properties between dry-spun and wet-spun acrylics is the little-discussed property known as flexural rigidity. This is a measure of the ability of a fibre or group of fibres to recover from deformation. It is an important property in short pile fabrics that are used in situations where deformation occurs frequently. Good examples are upholstery and carpets, in which the short tufts or piles can be deformed by people sitting or walking on them. In order for the fabric or carpet to remain aesthetically pleasing it is important that these tufts or piles recover from the deformation quickly and repeatedly. Dry-spun acrylic fibres have this ability and so they find quite extensive use in this type of end-use. The name *Dralon* is not only the name given to the dry-spun acrylic fibre manufactured by Bayer; as already noted it is almost synonymous with acrylic upholstery fabrics.

Other properties associated with acrylic fibres in upholstery end-uses are their ability to be dyed to brilliant shades, excellent light fastness, good abrasion resistance, high resistance to staining and good cleanability. The use of acrylic fibres in carpet yarns has declined significantly since the 1980s as polyamide and polypropylene yarns have become more dominant. However, acrylic fibres are still important in carpet yarns, particularly in certain types of high-quality products such as rugs.

There will be some subtle differences in these statistics for Europe when compared with the USA and the Far East, but the general patterns are consistent. Two notable differences between the USA statistics and Europe will be the consumption of acrylic fibres in the USA into hosiery end-uses and craft yarns. The acrylics council set up in the USA in the 1980s to promote acrylic fibre has worked very hard and with some notable success on the use of acrylics in hosiery end-uses. Acrylic fibres offer a number of performance benefits in hosiery over cotton and wool. They transport moisture away from the skin more efficiently than cotton or wool and they hold less water. These combine to provide wearer comfort and reduce the risk of blisters during high-stress conditions. Within Europe, the use of craft yarns for hand knitting and crocheting has declined significantly since the 1980s. This is due to lifestyle changes within European society. However, in the USA this industry is still very strong and although some decline has been seen, the percentage of fibres consumed in this area is much larger than in Europe or the Far East.

Finally, it is worth noting that acrylic fibres do have some unique properties that allow them to find uses in some industrial products. The outstanding resistance of acrylic fibres to chemicals and their non-melting properties advocate their use in cement and bitumen reinforcement. Fibres used in these areas tend to be nominally PAN homopolymers with high molecular weights although there are notable exceptions to this general rule. This gives them excellent resistance to the highly alkaline wet conditions in cement and the high temperatures found in bitumen end-uses. Similar properties account for the use of certain acrylic fibres in battery plate reinforcement. It is the excellent resistance to hydrolysis by sulphuric acid that is the major attribute of acrylics in this end-use.

The outstanding ultraviolet stability of certain acrylic fibres combined with the dimensional stability of the woven acrylic fabrics allows them to find a niche end-use in awnings, boat covers, outdoor furniture, car convertible roof fabrics and sandbags. The final end-use of note is that of certain acrylic fibres in hot gas filtration. These fibres tend to be PAN homopolymers and they offer excellent resistance to these aggressive environments. A typical example of such an end-use is in power stations that burn fossil fuels.

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5

Polyolefin fibres

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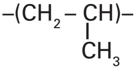
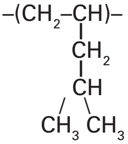
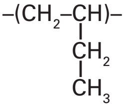
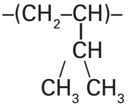
5.1 Introduction

Polyolefin fibres comprise those fibres whose polymer chains are essentially high molar mass, saturated, aliphatic hydrocarbons. The United States Federal Trade Commission approves two names, 'olefin fibres' and 'polyolefin fibres' to describe manufactured fibres in which the synthetic polymer is composed of at least 85% by mass of polyolefin units.[1,2] Chief among polyolefins in commercial importance are polypropylene (PP) fibres and, to a lesser extent, polyethylene (PE) fibres. Both types of fibre are recognised as generic names defined in ISO2076.[1] Their structures are given in Table 5.1. The correct chemical names of PP and PE are, in fact, poly(propene) and poly(ethene) respectively, propene and ethene being the chemical names for propylene and ethylene.

Other polyolefin fibres that have been produced with commercial application in mind are poly(4-methyl-1-pentene), poly(1-butene) and poly(3-methyl-1-butene), although commercial interest in these types of fibre is only marginal.[2] The outline structures of these polyolefins are also shown in Table 5.1. Thus, apart from PE, polyolefins are in practice polymers of α-olefins of general formula, CH_2=CHX, where X represents an alkyl chain. In addition, copolymeric polyolefins, such as ethene–propene and ethene–octene copolymers, have some commercial significance. Blends of different polyolefins are also produced commercially: for example, bicomponent multifilaments, with each filament containing a PP core and a PE sheath. If the fibres are heated, the PE sheath can melt and so bond the multifilaments into resilient monofilament yarns. These bicomponent fibres also find use in non-woven fabrics. Fibres from blends of PP with other polymers, such as nylon and polyester, are also available.

The first polyolefin fibres, from low-density polyethylene (LDPE), were extruded as long ago as the 1930s,[2] but their commercial impact was very limited. Fibres melt-extruded from high-density polyethylene (HDPE), which became available in the late 1950s, were found to possess considerably superior mechanical properties. The processing technology by which Ward *et al.* in the 1970s developed high-modulus PE fibres[3] was licensed commercially to produce

Table 5.1 Structures of some polyolefins

Polymer	Repeat unit
Polyethylene	$-(CH_2-CH_2)-$
Polypropylene	 $-(CH_2-\underset{\displaystyle CH_3}{\underset{\vert}{CH}})-$
Poly(4-methyl-1-pentene)	
Poly(1-butene)	 $-(CH_2-\underset{\displaystyle CH_3}{\underset{\vert}{\underset{\displaystyle CH_2}{\underset{\vert}{CH}}}})-$
Poly(3-methyl-1-butene)	

Tenfor™ and *Certran*™ fibres.[4,5] However, the commercial success of these fibres appeared only limited and their production eventually ceased. Commercial interest in PE fibres increased again when gel-spun PE fibres came onto the market in the early 1990s.

By contrast to PE fibre, PP fibre enjoys a massive acceptance in the marketplace. Its commercial impact started in the 1960s when it began to replace jute fibre in carpet backings and bast fibre in ropes and cords. Since then, PP fibre and tape have been developed for a huge variety of end-uses, including carpet face yarns, geotextiles, textiles for horticulture, filters, sports surfaces, packaging and strapping. During the 1990s, for example, the growth world-wide in PP fibre consumption was at least 6% in any one year. By the year 2000 the total world production of PP in textiles had risen to nearly 6.0 million tonnes[6,7] and accounted for 96% of overall polyolefin fibre production. The equivalent amounts in 2000 for polyester (PET) fibre and nylon fibre were 18.9 and 4.1 million tonnes, respectively.[7] More recently, there has been a spectacular rise of PP fibre use in the non-wovens sector, especially in medical and hygiene applications. Many observers believe that there are still further commercial applications to be explored, principally because some end-users are still unaware of the scope offered by PP fibres.[8] The most tantalising challenge is, arguably, the apparel industry, where the use of PP fibres is quite limited, except in a few specialist sectors such as protective clothing and some military uses.[9] The emphasis in this chapter will be on PP fibres, since they account for by far the greatest market among polyolefin fibres.

It is apparent, then, that each of the many different end-uses of PP fibres demands a different set of technical specifications to be met. The different mechanical properties required will result from the different fibre structures produced by different processing conditions. Thus, to maximise the commercial potential of PP fibres, the importance of the relationship between processing, structure and fibre performance has to be recognised.

The considerable commercial market pull has been complemented in recent years by a significant technological push, arising from improvements in fibre technology, the ability to produce grades of PP using metallocene catalysts, and developments in additives. In future, there will be considerable benefits too from the application of plasma treatment, to alter the surface properties of PP fibres without affecting their bulk properties. Fibres treated in this way are likely, for example, to be used in protective clothing and biomedical applications.

5.1.1 Commercial advantages and disadvantages

The commercial advantages are summarised in Table 5.2. The low densities of PE and PP (both are lighter than water) confer on them very high covering power in comparison with other textile fibres. Moreover, both types of fibre can be produced by melt extrusion, the simplest of all synthetic fibre extrusion technologies and one that is perceived as clean. In addition, there is currently a high performance/cost ratio, notably with PP fibres.[10] Nowadays, however, PE fibre produced by gel spinning accounts for much of PE fibre usage.[11] There is also some interest in PE fibres produced by solid-state extrusion.[12] Detailed accounts of high-performance PE fibres have been published in a sister volume.[11,12]

However, PE and PP fibres do possess some serious inherent disadvantages, which are also summarised in Table 5.2. The low melting points of PE and PP, although they do facilitate fibre processing by melt extrusion, prevent their use in environments with elevated temperatures. PE and PP fibre types produced for outdoor use have to be protected from ultraviolet radiation. The inherent inability of PE and PP fibres to be successfully dyed, unless they contain suitable additives or comonomers to which certain types of dye are substantive, considerably restricts their use for clothing. Because of their high flammability, PE and PP fibres have to be treated with fire-resistant additives for many applications.

Despite many similarities in structure and properties between PE and PP fibres, the commercial production of PP far outstrips that of PE fibres.[6] A number of reasons may be cited. For the majority of textile applications, fibres must be dimensionally stable up to at least 100 °C.[13] This requirement limits the use of melt-extruded PE fibres. PP fibres possess better resilience, with tenacity and

Table 5.2 Commercial advantages and disadvantages of PE and PP fibres

Advantages	Disadvantages
Low density (0.90–0.96 g cm^{-3})	Low melting point (120–125 °C for PE; 160–165 °C for PP)
Good tensile properties	Prone to photolytic degradation
Good abrasion resistance	Inferior shrink resistance above 100 °C
Excellent resistance to chemicals	Poor dyeability
Excellent resistance to mildew, micro-organisms and insects	High flammability
Almost negligible moisture regain	Inferior resilience
Good wicking action	Creep
High insulation	
Comfortable to the skin	

abrasion resistance equal to those of PE fibres.[2] PP fibres also possess better resistance to creep,[13] although it has been pointed out that a considerable improvement in the resistance to creep in PE fibres can be obtained by radiation cross-linking.[3]

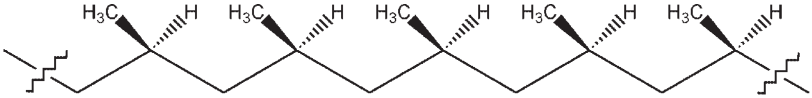
5.2 Molecular configuration

PE chains, which contain no asymmetric carbon atoms, tend to adopt a zigzag form. For PP and other α-olefin polymers, every other carbon atom along the chain backbone is asymmetric. The polymer chain can adopt a variety of configurations. As an example, the three different stereoisomeric forms that PP chains may assume are shown schematically in Fig. 5.1 in fully extended planar projections. In planar projections of isotactic PP chains, all the methyl side groups are situated uniformly on the same side of each chain. In practice, the chains normally adopt a three-dimensional helical configuration, as illustrated in Fig. 5.2. This highly regular structure favours the formation of PP fibres with superior mechanical properties. In syndiotactic PP chains, the methyl groups alternate in a regular fashion between the two sides of each chain. Syndiotactic PP chains can also adopt a helical configuration. In atactic PP chains, the methyl groups are arranged randomly on the two sides of the chain.

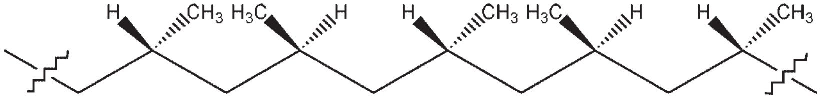
5.3 Production of polyolefins

5.3.1 Ziegler–Natta catalysis

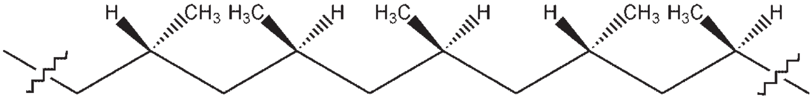
The structures and properties of polyolefin fibres are significantly influenced by the properties of their constituent polymer chains. In turn, these properties reflect the method of synthesis of the chains. In 1953, Karl Ziegler discovered catalysts that promote the polymerisation of ethene molecules to form PE macromolecules



Isotactic – methyl groups same side



Syndiotactic – methyl groups alternate



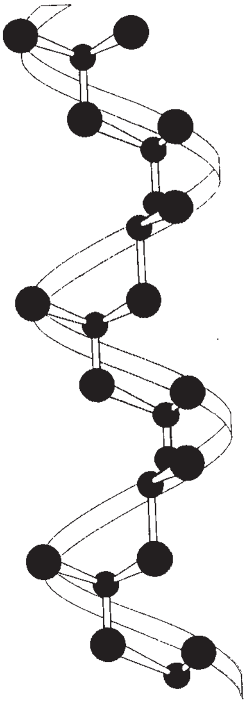
Atactic – methyl groups randomly arranged

5.1 Stereoisomeric structures of polypropylene.

even at low pressure. A year later, Giulio Natta synthesised isotactic PP macro–molecules in the same way, and in the same year PP monofilament yarns were also extruded from the melt.[14]

Ziegler found that, in the presence of a catalyst containing an aluminium alkyl compound and a transition metal halide, ethene could be polymerised at atmospheric pressure and ambient temperatures. Natta, using similar types of catalyst, was able to polymerise a variety of α-olefins, including PP. These polyolefins possessed a high degree of stereoregularity in their polymer chains. Since the 1950s, a wide variety of Ziegler–Natta catalysts has been prepared, in which a Group I, II or III metal alkyl is combined with the halide of a transition metal, very often a titanium halide. Indeed, the nature of the solid catalyst is highly influential in determining the degree of stereoregularity in the polyolefin product.[15] Thus, high stereoregularity is generally favoured by large catalyst particles. The formation of isotactic PP is, furthermore, favoured by the α-form of titanium trichloride rather than the β-form, by the presence of Ti^{3+} ions rather than Ti^{4+} ions, and by shorter alkyl groups in the metal alkyl.[15]

It is considered that, before it has been incorporated into the growing polyolefin chain, each α-olefin molecule undergoes complexation at a transition metal centre. Although various mechanisms for Ziegler–Natta-catalysed polymerisations have

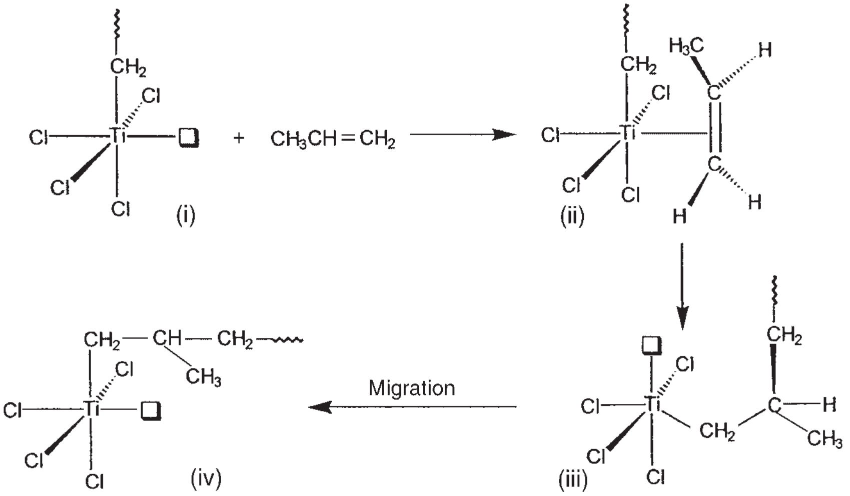


5.2 Helical configuration of an isotactic PP polymer chain.

been proposed, the so-called monometallic mechanism is now the most favoured.[15–17] This mechanism can be conveniently outlined here for PP synthesis with a catalyst containing α-$TiCl_3$ and an aluminium alkyl.[16,18] It is proposed that the Ti^{3+} ion is alkylated after chemisorption of the aluminium alkyl to the $TiCl_3$ crystal surface (Fig. 5.3 (i)). The complex so formed is, therefore, at the catalyst surface. However, at the catalyst surface, each Ti^{3+} is only 5-coordinated, so that a vacant *d*-orbital is present.

An incoming propene molecule can form a π-complex with the titanium through the vacant d-orbital (Fig. 5.3 (ii)). The propene molecule then becomes inserted between the titanium and the alkyl chain (Fig. 5.3 (iii)), whereupon the polymer that is formed returns to its original position (Fig. 5.3 (iv)). Further propene molecules can now in turn be incorporated in a similar fashion. Thus, the growing polyolefin chain is always attached to the transition metal.

For an isotactic polyolefin to be formed, each α-olefin molecule must approach the catalyst surface with the same orientation. Thus, it can be shown that a propene molecule can be accommodated in only one way at the catalyst surface, for it to be sufficiently close to the Ti^{3+} ion in complex (ii). Moreover, the formation of



5.3 Monometallic mechanism for Ziegler–Natta catalysis. The square boxes represent empty coordination sites.

isotactic polyolefin depends on the migration of the vacant *d*-orbital in the titanium back to its original position before another α-olefin molecule is incorporated. Without this migration, a syndiotactic polyolefin would be formed.

The dispersities of HDPE grades produced using Ziegler–Natta catalysts normally range between 5 and 20. Dispersity refers to the ratio of the weight-average molar mass, M_w, of a polymer to the number-average molar mass, M_n. M_w can be as high as 1 000 000 g mol^{-1} but fibres can be produced from grades of such high molar mass only by gel spinning.[3,11] For HPDE grades that can be melt-spun, the highest value of M_w is about 200000 g mol^{-1}.[3]

The dispersities of PP grades normally range between 4 and 8. Thermal cracking of these grades results in a reduction in molar mass and a lower range of dispersities, 3–6, due primarily to the elimination of the high molar mass 'tail' in the molar mass distribution. These modified PP grades, often called controlled-rheology (CR) grades, are especially suitable for forming fibres. For most fibre applications, M_w is in the range 200 000–350 000 g mol^{-1}. However, for the production of monofilaments, M_w may be as high as 600 000 g mol^{-1}, and for the production of melt-blown non-wovens, as low as 150 000 g mol^{-1}.

5.3.2 Melt flow index

Polyolefin grades are normally supplied as granules. An important specification of these grades is the melt flow index, MFI. The MFI is the mass of polymer in grams extruded in 10 minutes at 230 °C under an applied load of 2.16 kg through a standard cylindrical dye in a flat entry extrusion rheometer.[19] Equipment is

Table 5.3 MFI values for different grades of PP

Product	MFI
Monofilaments and tapes	1–11
Staple fibres	9–16
Bulk continuous fibres (BCF)	11–24
Spun-bond PP	20–40
Melt-blown PP	100–1500

Table 5.4 Dispersities of two samples of isotactic PP of MFI 12 g/10 min

M_n (number-average molar mass)	M_w (weight-average molar mass)	M_w/M_n (dispersity)
34 000	261 000	7.7
42 000	211 000	5.0

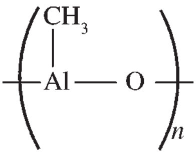
commercially available for the determination of MFI values. Table 5.3 shows some typical MFI values for PP grades of different products.

There is an inverse relation between MFI and the apparent melt viscosity under constant shear stress. Therefore, an increase in M_w results in a reduction in MFI. However, there is no simple relation between MFI and M_w. As an example,[20] two samples of isotactic PP, for both of which MFI is 12 g/10 min, are compared in Table 5.4.

5.3.3 Metallocene catalysis

In the 1980s, interest was kindled in a new range of catalysts, the metallocenes, following the discovery by Sinn and Kaminsky[21] of a new catalyst system which was highly active in the polymerisation of ethene. Subsequently, Kaminsky and co-workers[22] discovered a similar catalyst system for the synthesis of isotactic PP. These catalysts are soluble. (Although soluble Ziegler–Natta catalysts had been prepared, they were found largely to catalyse the production of atactic polyolefins.)

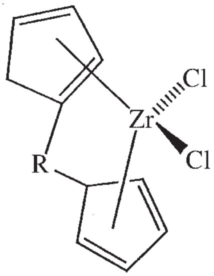
Metallocenes are organometallic compounds based on Group IV transition metals, such as titanium, zirconium and hafnium. Of these, zirconium is the most active, while titanocenes tend to be deactivated at higher temperatures. Metallocenes react with methylalumoxane (MAO), a co-catalyst, to form an active catalytic complex. MAO consists of oligomers, whose structure approximates to:



$$\left(\overset{\overset{\displaystyle CH_3}{|}}{Al}—O\right)_n$$ [5.1]

where $n = 10–30$.

The mechanism underlying catalysis by metallocenes has been discussed by Brintzinger *et al.*[23] The metal in the metallocene molecule is the active centre for polymerisation and is sandwiched between two η^5-cyclopentadienyl (CP) ligands (the symbol η^5 signifies that all five carbon atoms in the CP ring are bonded to the metal atom). In addition, two σ-ligands, usually chlorine atoms, are also co-ordinated to the metal atom. However, molecules of simple metallocenes are too flexible to confer sufficient rigidity to the catalytic complex, and catalytic activity is consequently low. The two CP rings are, therefore, also bridged through one or more carbon atoms or a silicon atom, to provide the rigidity required. The structure of a zirconocene can be represented as:



[5.2]

It should be noted that the two CP rings are not situated directly opposite one another.

The CP rings remain attached to the metal atom during polymerisation, but the chlorine atoms leave the complex during formation of the active catalyst. Alkyl or aryl substituents may be present on the CP rings. Different substituents and different bridging entities alter the structural character of the CP ligand, the metal–CP distance and the CP–metal–CP angle. There is thus considerable electronic and structural versatility in metallocene catalysts.

The activity of the catalyst system is strongly influenced by the CP–metal–CP angle. A short bridge between the two rings reduces this angle, and catalytic activity is increased in consequence. A smaller angle is particularly important for propene polymerisation, although ethene polymerisation can be catalysed where the bridge is much longer.[15] The ratio of MAO to metallocene concentrations is also important: the ratio required for maximum catalytic activity varies among different metallocenes. In addition, the molar mass of the polymer produced is dependent on the structure of the CP ligands. A methyl substituent in the 2-position of each CP ligand, for example, gives rise to polypropylene of much higher molar mass. As with Ziegler–Natta catalysis, the true catalyst site is the metal, with the growing polyolefin chain as a ligand, and there is a vacancy at the metal atom to allow co-ordination of the incoming monomer.

Metallocene catalyst systems are becoming increasingly important for the production of PP. They are more specific and more active than Ziegler–Natta catalysts and can be designed so that only chains of isotactic PP are produced. By contrast, isotactic grades of PP made using Ziegler–Natta catalysts contain small proportions of atactic PP, typically up to 5%. Moreover, metallocene grades of PP possess a narrower molar mass distribution, of dispersity *ca.* 2.5. However, owing to small regio-irregularities in the polymer chains, where individual propene monomers have been inserted in a reverse manner, the melting points of commercial metallocene grades of PP are often about 15 °C lower than PP grades produced using conventional Ziegler–Natta catalysts.[18]

Fibres based on metallocene PP grades possess a number of advantages.[18] The more uniform distribution of PP chain length results in a rheology more favourable for melt processing. Thus, finer fibres may be extruded to create spun-bonded non-woven fabrics with more cloth-like qualities.[24,25] The greater control of fibre processing also leads ultimately to fibres of improved tensile strength. In addition, metallocene catalysts allow the incorporation of special comonomers into PP chains, thus permitting the modification of the structure and properties of PP fibres. These comonomers include flame-retardant units, chromophores, and compounds that, by increasing intermolecular attraction between the PP chains, can improve fibre resilience.[25,26] More recently, an iron-based catalyst has been synthesised whose efficiency in catalysing the polymerisation of ethene matches those of the most active metallocene catalysts.[27]

Polymers of low dispersity can, in principle, be synthesised by ‘living’ polymerisation,[28] in which there is virtually no chain termination or transfer. A living polymerisation of propene has recently been reported,[29] giving rise to PP of dispersities as low as 1.2 ($M_w \sim 42\,000$ g mol^{-1}).

5.4 Polyolefin structures

5.4.1 Arrangements of polymer chains

The simplest approach to the structures of polyolefin fibres is to consider that they consist solely of crystalline regions and amorphous regions. In the crystalline regions, segments of the polymer chains exist in well-defined lattice structures, such that they can be identified by X-ray diffraction. In the amorphous regions, an assembly of random interpenetrating chains may be considered. Degrees of crystallinity in fibres can be estimated by a variety of techniques, including X-ray diffraction, fibre density measurements and heats of fusion.[16,30] A method using Raman spectroscopy has also been recently reported.[31]

However, more recent developments have given rise to the concept of a spectrum of order/disorder, which is constructed around various degrees of organisation both within polymer chains and between them.[32] At one extreme of the spectrum is the truly amorphous structure. If the random assembly of polymer chains which it contains is altered to a more extended conformation, accompanied by a parallel arrangement of chain segments, an amorphous structure with correlation results.[33] This arrangement can exist, however, only below the glass transition temperature, T_g, so will, in practice, not apply to PE and PP fibre technology. Further ordering now gives rise to regular chain conformations, whereby the chains are parallel but displaced along their axes, yet the chains' lateral packing remains irregular. Still further order appears if the axial displacement is lost and there is more efficient lateral packing. This degree of ordering is represented by the paracrystalline structure, which has particular importance in polyolefin fibre technology. As an alternative, conformationally disordered, or 'condis' crystals may result, in which there is regular packing of chains with some degree of conformational disorder.[34] Further ordering gives a crystalline structure with defects, and then finally an ideal crystalline structure.

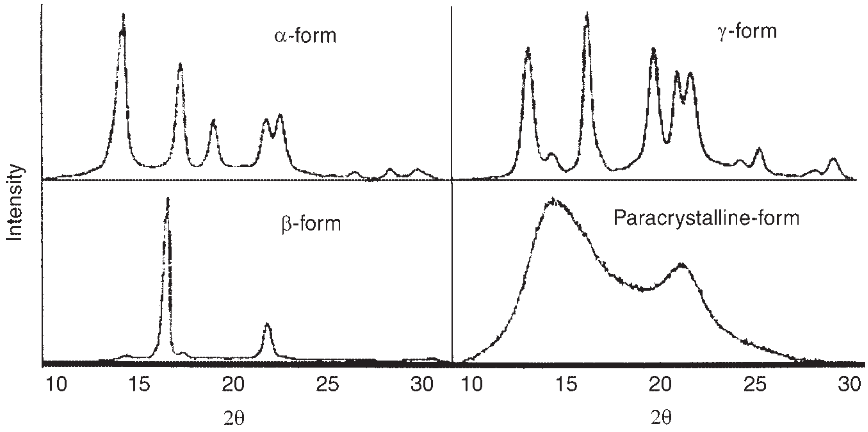
To understand the physical structure of a fibre more fully, further factors have to be taken into account. Thus, the locations of regions comprising the various degrees of order and disorder should be considered.[32] Another factor is the degree of orientation of the polymer chains and even of the bonds and segments that constitute them. To resolve all these aspects is an ambitious task, but considerable progress may be possible using molecular and microstructural modelling techniques.[32]

5.4.2 Crystalline structures

For PP, three different crystalline forms have been identified: α-monoclinic, β-hexagonal and γ-orthorhombic. A common feature of all three forms is the helical conformation of the constituent PP chains. The forms display narrow, sharp peaks in wide-angle X-ray scattering (WAXS) patterns (Fig. 5.4). However, they also display some features that are highly unusual in polymer crystallography.

The α-form is the most stable and also the most important in the context of PP fibres. Its monoclinic lattice has unit cell dimensions $a = 0.665$ nm, $b = 0.2096$ nm, $c = 0.650$ nm, $\alpha = \gamma = 90\,^\circ$ and $\beta = 99.3\,^\circ$. The PP chains lie in the direction of the *c* axis. Isotactic α-PP also exhibits a lamellar branching, which appears to be unique in polymer crystallography.[35] Evidence has been adduced that this lamellar branching is an intrinsic property of isotactic α-PP. In PP fibre extrusion, for example, an additional component whose chain axis is approximately at right angles to the fibre direction may develop at slower fibre take-up speeds.[35]

Crystals of the β-form can be obtained with the use of special nucleating agents.



5.4 WAXS patterns of α, β, γ and paracrystalline polypropylene.

The unit cell dimensions of the trigonal lattice are $a = b = 0.1101$ nm and $c = 0.650$ nm. An unexpected feature of the β-structure is that it is frustrated:[35] the structure does not follow the normal crystallographic convention of structural equivalency.

The orthorhombic γ-form can be obtained by crystallisation of PP at high pressure or of PP with a small proportion of comonomer at low pressure. The γ-form may also be observed in WAXS patterns of isotactic PP with shorter chain lengths. It is hence of interest too in connection with metallocene PP, in which there are shorter isotactic chain lengths on account of occasional regio-irregularities in the chains.[18] The unit cell dimensions of the orthorhombic γ-form are large: $a = 0.854$ nm, $b = 0.993$ nm and $c = 4.241$ nm.[35] A strange feature of the γ-form structure is that it consists of a series of bilayers of chains in a crossed pattern. The chains are tilted at 80 ° or 100 ° to one another.[35]

A paracrystalline, or 'smectic', form has also been identified, whose WAXS peaks are broad and more poorly defined, and only of moderate intensity (Fig. 5.4). The PP chains within the paracrystalline structure also adopt a helical conformation.[36] A liquid crystalline model for the paracrystalline structure has recently been put forward, proposing a 'liquid-like' lateral packing of parallel PP helical chains, together with a high degree of registry in the direction of the chains.[37]

PE generally assumes an orthorhombic crystalline structure, although on stretching in the formation of tape, for example, a monoclinic form may begin to emerge. The unit cell dimensions of the orthorhombic form are $a = 0.741$ nm, $b = 0.494$ nm and $c = 0.255$ nm. The PE chains lie in a planar zigzag fashion in the direction of the c axis. The a and b dimensions, therefore, characterise the side-by-side packing of the chains.[38]

5.4.3 Crystal morphology

The crystallinity in freestanding PE and PP arises from the presence of crystallites, generally of dimension less than 100 nm. The crystallites are made up of thin lamellae, and the direction of the polymer chains lies across the thickness of each lamella. Thus, the chains within each crystallite are folded many times in order that it can accommodate them. The lamellae, in turn, are arranged into spherulitic structures, whose diameter can be as high as a few mm. Each spherulite grows in a radial manner from a nucleus. The arrangement of the polymer chains will be denser and more regular within the spherulites than in the regions between them, so that clearly defined boundaries are observable.

When undergoing elongational strain, as in fibre formation, the spherulites stretch out into ellipsoids. This deformation process is maintained until the lamellae within the spherulites can no longer accommodate the stress imposed on them. They then begin to fragment. The lamellae slide and rotate, and the regularly folded polymer chains within them slip, twist and even unfold.[39] The detailed nature of these changes depends on the orientation of each lamella with respect to the direction of stretch. The deformation of the spherulites eventually results in the formation of small fibrils,[40] which can consist of a hierarchy of structures at different scales from tens of nanometres to micrometres.[41,42] During this transformation, the lamellae break into small fragments, and these fragments commonly form fresh crystalline domains in the new fibrils. Those polymer chains that were originally in the less dense regions outside the spherulites become much more stretched along the fibre axis and, in consequence, are aligned close to one another. Strain-induced crystallisation can then occur, and further crystalline domains are formed.

It is interesting to note that in the formation of PP fibrils, the appearance of 'shish-kebab' structures has been reported,[41,42] in which a central core consisting of extended PP chains (shish) is surrounded by sections with folded chain crystals (kebab). Shish-kebab PE structures have also been reported.[12]

Further deformation is considered to occur through the sliding of fibrils past one another. There is also the stretching of tie molecules, which link the fibrils, and the unfolding of sections of polymer chains by which tie molecules are anchored in the crystal blocks of neighbouring fibrils.[19] Eventually, the deformation stress is too great for the fibre to support, and the sample breaks.

5.5 Fibre production

5.5.1 Introduction

Polyolefin fibres can be produced by melt extrusion processes, which are followed by drawing and other after-treatments such as texturing and entanglement. While this technology is practised on a commercial scale for PP fibre production, PE fibres are now very largely produced using gel-spinning and solid-state extrusion technologies. Since these are already described in a companion book,[11,12] attention in this section is largely concentrated on PP fibre production.

Although the commercial production of PP fibre involves melt extrusion, a number of different melt extrusion processes are used. The choice depends on the type of fibre to be produced and the use for which it is destined. Different processes can be identified for the production of multifilament yarns, monofilaments, staple, tapes and non-wovens. Each of these is now discussed in turn.

5.5.2 Multifilament yarns

Multifilament yarns are produced as partially oriented yarns (POY), fully oriented yarns (FOY) or bulked continuous filament (BCF). The POY process is low cost and allows for greater flexibility in subsequent processing, such as drawing, or more complex processing as in draw-twisting and draw-texturing. POY can be produced in counts ranging from about 40 to 200 dtex, with 0.5–4.0 dtex per filament. An important feature of the POY process is the long length of the quench unit, which can be up to 10 m. Such a long unit is needed to ensure that at the high production speeds used, the filaments are cooled sufficiently before being wound. The filaments are taken off onto winders at speeds of 2000–3000 m min^{-1}.

The POY yarns are then further processed. Drawing is always a part of subsequent processing and, because of the high processing speeds involved, PP grades of sufficiently narrow molar mass distribution are desirable,[18] in order to avoid an excessive number of filament breaks. However, where the molar mass distribution is narrower, the maximum draw ratio achievable is reduced.[19] The processed POY yarns are used for such applications as upholstery cover fabrics, sportswear and socks.

Multifilament yarns may alternatively be produced as FOY yarn. Here the spinning and drawing form consecutive parts of a continuous process. Final winding speeds can be as high as 5000 m min^{-1}. The process is highly versatile, and a large variety of polymer grades can be used to produce yarns with different mechanical properties, depending on the control settings used. For example, high-tenacity yarns destined for technical fabrics, as well as standard yarns for more traditional applications, can be produced by the FOY process.

One difference between the production lines resides in differences in the fineness of the filaments produced: 1–2 dtex for standard yarns but 5–10 dtex for high-tenacity yarns. Another key difference is reflected in the fibre drawing and relaxation conditions, which will exert an important influence on the mechanical properties of the final yarn. Thus, standard yarns possess tenacities of 0.3–0.5 N tex^{-1}, whereas for high-tenacity yarns, values of 0.5–0.7 N tex^{-1} are achieved, and in some instances, even higher. These values exceed those for multifilaments produced by the POY process, even after drawing has been applied (0.2–0.3 N tex^{-1}).

The BCF process combines high-speed spinning, drawing and texturing into one continuous process. The speed of filament production is generally 1500–4000 m min^{-1}. The process is quite similar to the FOY process, except that after drawing, the filaments are textured. The most prominent method of texturing is the stuffer box crimp process. After partial relaxation, the filaments are bulked by overfeeding in steam or hot air into a stuffer box, in which a three-dimensional crimp is induced. The crimped yarn is then ejected onto a cooling drum, from which it passes through an intermingling unit before the final winding stage. The level of crimp achieved depends on such factors as the temperature of the filaments on entering the texturing unit, the duration of the texturing process and the size and shape of the texturing unit.

5.5.3 Monofilaments

Monofilaments, being in excess of 100 dtex, are much coarser than multifilaments. In principle, however, monofilaments can still be produced by broadly the same methods as those used for the production of multifilaments, but monofilaments produced in this way tend to curl.[19] This property renders them unsuitable for many applications. To avoid this problem, monofilaments are often formed at reduced speeds and extruded into water, because the cooling is much more efficient. After travelling a short distance (≤5 cm) in air from the spinneret, the filaments enter a bath of water. The subsequent drawing process may involve as many as three stages, often in a hot water bath or hot air ducts. The most important property required of monofilaments is high tensile strength.[43] Hence, they are produced for technical textile applications, such as belts, ropes and hawsers.

5.5.4 Staple fibres

Staple fibres can be produced by two methods: a two-stage discontinuous process or a single-stage compact continuous process. The two-stage process is generally utilised for high-quality, very fine staple fibre (0.5 dtex per fibre) and also in plants where the throughput is large (>20 000 tonnes per annum). The spinning speed is usually about 2000 m min^{-1}, 10–20 times greater than in the compact process. Spun tow is produced from the first stage. The second stage consists of drawing, crimping and cutting into staple. In the cutting stage, the tow is cut into staple fibres of the required length, whereupon the fibres are packed into bales. An alternative to cutting is converting, in which a sliver of parallel fibres is formed (this is called converter tow); such slivers are then used for worsted spinning. A major drawback to the two-stage process is that a lot of space is taken up for all the equipment required. In particular, the length of the quenching zone is approximately 10 times that used in the compact process.[18] However, a great advantage of the two-stage process is considered to be that each stage can be operated independently under its own optimum conditions.

The single-stage compact process combines all the production stages and is becoming more important economically. Although the spinning speeds are much lower (100–300 m min^{-1}) than those used in the two-stage process, productivity is gained by using spinnerets with a very large number of holes – up to 100 000, arranged in a grid structure. The spinning speeds are sufficiently low that the tow can be continuously fed to a drawing unit.[44] The fibres produced possess a minimum count of 1–3 dtex and so are normally used for carpet yarns and non-woven products. The fineness limit and production speeds of the spun filament are governed by its cooling and the maximum level of drawing that can occur. The single-stage process is economic even for the production of only small quantities of staple and is highly flexible where colour changes are required.

5.5.5 Non-wovens

PP non-wovens can be produced by a multistage process that incorporates the production of staple fibre, described in the previous section. Alternatively, a single-stage operation can be utilised which integrates filament production and the formation of a non-woven fabric. The preferred method of holding the web together is thermal bonding, because of the low melting points of polyolefin fibres. Adhesives often adhere only poorly to polyolefin fibre surfaces because of their low surface energies. Also, much of the adhesive tends to be located away from the contact points between individual fibres and is, therefore, wasted.

There are two important versions of the single-stage process: the spun-bond process and the melt-blown process.[45] In the spun-bond process, bundles of individual filaments or a flat filament curtain are melt-extruded, cooled and stretched, either mechanically or by a current of air. The filaments are then laid down in a random fashion on a conveyor belt and the resulting web is passed through a hot calender, where it is thermally bonded. The method using filament bundles offers greater flexibility of production, but the method using filament curtains offers higher productivity. The PP grades used possess MFIs in the range 20–40 g/10 min, and the density of the spunbond web ranges from 5 g m^{-2} to several kg m^{-2}. Spun-bond webs are noted for their strength.

The melt-blown process is used not only for PP but also for many forms of PE. In the process, polyolefin is extruded through numerous small spinneret holes, located close together. Just below the spinneret holes, a stream of molten polymer is caught in a current of hot air moving at high speed. The molten stream of polymer is thus broken up into an integrated network of very fine (microfibre range) entangled fibres of varying lengths, which are immediately deposited onto a rotating screen. Successful processing depends very much on the correct combination of extrusion conditions and the speed and temperature of the air current. The individual fibres which result from the fragmentation of the molten polymer will possess a fineness in the range 0.01–0.2 dtex. Thus, the melt-blown fabrics, which possess densities in the range 10–500 g m^{-2}, are lighter than spun-bonded fabrics and have lower strength. Their texture, however, renders them excellent for use in filtration and absorption applications such as for industrial wipes, surgeons' masks and gowns, and oil clean-up products.

Production lines combining both processes are now being increasingly used for the formation of SMS (spun-bonded–melt-blown–spun-bonded) multilayer fabrics. These fabrics bring together the desirable properties of spun-bonded and melt-blown materials. The external spun-bonded layers provide good mechanical properties, while the internal melt-blown web provides good filtration and absorption properties. The layers are bonded either thermally or mechanically, depending on the weight and desired application of the SMS product. Thinner webs are bonded by means of heated calender rollers, whereas thicker webs are mechanically needled.

It should be noted that, apart from spun-bonded and melt-blown non-wovens, other types of PP non-wovens are produced. For example, needlepunched PP non-wovens are quite prominent, produced by mechanical interlocking of the loose fibres in a web through the use of arrays of barbed needles repeatedly passing into and out of the web. Hydroentanglement (spun-lacing) technology is also applied, in which the web of loose fibres is entangled by subjecting them to multiple rows of fine, high-pressure jets of water.

5.5.6 Tapes

Tapes can be produced by two methods.[18] In the more common method, a film of polyolefin is extruded and cooled on rollers or in a water bath. The film is then stretched uniaxially, about ten-fold, when it begins to fibrillate. As it fibrillates, it is cut with knives into tapes. Alternatively, the actual fibrillation process may produce tapes of the desired dimensions. The tapes produced possess high tenacities, e.g. up to 6–7 N tex^{-1} for PP tapes, and are used in carpet backings, sacks and bags. In the second method, each tape is extruded separately through an individual slit-shaped orifice. This process is much more expensive and is generally confined to specialist uses, such as dental and medical applications.

5.5.7 Spin finishes

The use of spin finishes to protect polyolefin filaments from wear is an important factor in their processing. A spin finish has several functions. For example, it acts as a lubricant to protect the filament surfaces, it provides good cohesion between individual filaments in a multifilament assembly, and it dissipates any static electricity that may be generated during processing. Static electricity can cause ballooning in multifilament yarns because of electrostatic repulsion between the individual filaments. Static may also distort or even rupture the yarn during processing and cause electric shocks when the processing equipment is touched. Spin finishes also normally contain biocides.

Table 5.5 Surface energies of some synthetic fibres

Fibre	Surface energy (mJ m^{-2})
PP	31
Polyester	43
Polyacrylonitrile	45
Nylon	46

In order to accommodate all these requirements, commercial spin finishes consist of a complex mixture of chemical components, and so spin finishes are generally applied as emulsions. Good accounts of the compositions of spin finishes can be found elsewhere.[19,46]

Different types of fibre, however, possess different individual properties. Moreover, different types of equipment will produce different patterns of wear on a fibre. The spin finish, therefore, must be formulated according to the properties of the fibre processing equipment. Thus, for polyolefins, their low surface energies, as manifest by their hydrophobicity, and low melting points have to be taken into account. Furthermore, different types of spin finish may be preferable at different processing stages.

Even among conventional synthetic fibres, polyolefin fibres possess very low surface energies, which render their complete coverage by emulsified spin finishes particularly demanding. Some values estimated for the surface energies of common fibres are given in Table 5.5, from which it may be noted that the surface energy of PP fibres is markedly lower than those of other common synthetic fibres. For initial wetting of polyolefin fibres, therefore, a spin finish of very low surface tension has to be applied. Yet water, which is one of the components in emulsified spin finishes, possesses a surface tension as high as 72 mN m^{-2} at 20 °C. Thus, special wetting agents have to be included in spin-finish formulations for polyolefin fibres. Moreover, if all the water in the finish evaporates, the degree of coverage of the filaments may be substantially altered.

For multifilament yarns, there is an additional consideration. The spin finish must also penetrate the filament bundles in as short a time as possible. A spin finish of low viscosity is, therefore, required.

Polyolefins exhibit the highest friction among common synthetic fibres, and indeed the heat generated by friction during fibre processing can cause softening, or even melting of the fibres. Thus, an important role of spin finishes in polyolefin fibre processing is the reduction of friction, a role that is assuming increasing importance with the ever-increasing fibre production speeds.

It is not surprising, then, that there is still extensive effort in devising new ranges of spin finishes for the variety of processing routes from which polyolefin fibres are formed. Furthermore, the types of lubricants commonly used in the processing of other synthetic fibres, such as mineral oils and fatty esters of low viscosity,

Table 5.6 Examples of additives for synthetic fibres

Processing additives	Heat stabilisers HCl scavengers
Functional additives	UV stabilisers Flame retardants Colourants Antistatic agents Antimicrobial agents Agents against creep Agents against abrasion

cannot be applied to polyolefin fibres. Although such finishes wet polyolefin fibres well, they also migrate into the bulk of the fibres and swell them. Examples of lubricants currently used for PP fibres are alkoxylated long chain alcohols, alkoxylated triglycerides and fatty acid polyglycol esters.

5.6 Additives

5.6.1 Introduction

Additives are employed to assist the processing of polyolefin fibres and to achieve the fibre properties required. They are either present in the polymer grades supplied to the fibre manufacturer or are incorporated into the polymer melt prior to extrusion. Additives are conveniently classified into two main groups, and examples are shown in Table 5.6. It is clear that additives have a number of roles, and indeed commercially produced polyolefin fibres contain a variety of additives. Care has to be taken, therefore, that the effectiveness of an individual additive is not impaired by any of the other additives present. In some cases, though, there may be synergistic effects. Moreover, all the additives incorporated must withstand the fibre processing conditions used, the subsequent conversion of fibre to the finished article and the end use of the article during its lifetime. Some of the additives listed in Table 5.6 are discussed more fully below. The coloration of polyolefin fibres is discussed in Section 5.7.

Many of the additives listed in Table 5.6 are incorporated to counter the oxidation of the polyolefin chains. Unless these additives are present, polyolefin fibres are highly prone to both thermal and photochemical oxidation. In particular, oxidation is considered to be a major problem in the processing and handling of PP fibres, given the very high fraction of the polyolefin fibre market that they occupy. Oxidation leads to reduced mechanical properties and even undesirable discolorations. It may be accelerated too in the presence of some metals, though the use of chelating agents can often prevent the action of these metals. The mechanisms underlying the oxidation process are complex, so only an outline is provided here. Detailed schemes are given elsewhere.[19,47,48]

The thermal oxidation and resulting degradation of polyolefins occur through chain reactions involving free radicals. The process can be considered in terms of initiation, propagation, branching and termination steps.[47] Initiation occurs through abstraction of hydrogen atoms in the polyolefin chains by excited singlet oxygen molecules:

$$PH + {}^{1}O_2 \rightarrow P\bullet + \bullet OOH \qquad [5.3]$$

Hydrogen atoms linked to tertiary carbon atoms are the most readily abstracted. The products arising from the abstraction reaction may also combine to form a hydroperoxide:

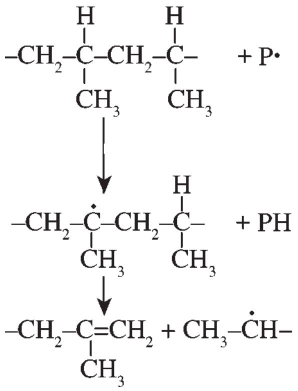
$$P\bullet + \bullet OOH \rightarrow POOH \qquad [5.4]$$

Initiation is followed by a complex series of propagation reactions, from which further hydroperoxides are formed. The number of free radicals in these reactions remains constant. However, the hydroperoxide may be split in a branching reaction, so that the number of free radicals increases:

$$POOH \rightarrow PO\bullet + \bullet OH \qquad [5.5]$$

Termination of the overall process is through several reactions, in which the free radicals combine to form a variety of non-radical products.

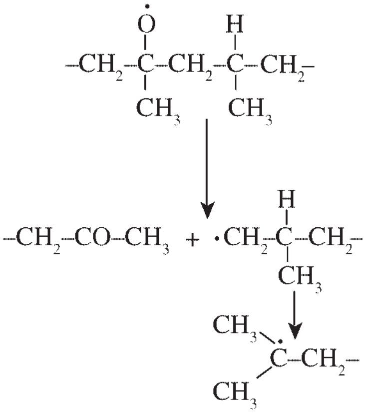
None of the above reaction stages, however, leads to the degradation of the polyolefin chains. Indeed, an increase in molar mass results. Nevertheless, it is well established that polyolefins are susceptible to degradation as a result of oxidation. Clearly, scission of the chains must also occur. The scission of PP chains can be taken as an example:



$$-CH_2-\overset{H}{\underset{CH_3}{C}}-CH_2-\overset{H}{\underset{CH_3}{C}}- + P\bullet \longrightarrow -CH_2-\underset{CH_3}{\dot{C}}-CH_2-\overset{H}{\underset{CH_3}{C}}- + PH \longrightarrow -CH_2-\underset{CH_3}{C}=CH_2 + CH_3-\dot{C}H- \qquad [5.6]$$

An olefin and a new free radical are, consequently, formed. The olefin is even more prone to oxidation than a saturated hydrocarbon, and the new free radical can take part in further oxidation steps.[47]

The alkoxy radical, PO•, can also be degraded. The degradation of PP chains illustrates the process:



[5.7]

Polyolefin fibres are also degraded by weathering at ambient temperatures. Absorption of ultraviolet radiation in the range 300–400 nm triggers photo–chemical oxidation of the polyolefin chains. Photodegradation is initiated mainly by entities formed during manufacture of the polymer, its storage and subsequent fibre processing. These entities include catalyst residues, alkyl hydroperoxides and ketones.[19] Thus, UV radiation can trigger the breakdown of hydroperoxides into free radicals:

$$\mathrm{POOH} \rightarrow \mathrm{PO}\bullet + \bullet\mathrm{OH} \qquad [5.8]$$

The breakdown of ketones is more complex.[19] In the case of PP, it has been proposed that an additional means of initiating photochemical oxidation is through the formation of excited charge transfer complexes between PP and oxygen.[49]

5.6.2 Processing additives

5.6.2.1 Heat stabilisers

Resistance to thermal oxidation is conferred by the addition of antioxidants to the polymer. These antioxidants are oxidised themselves, in preference to the polymer chains. Thus, antioxidants generally remain effective until they have been consumed. Research into the development of more effective stabilisers is currently very active.

An antioxidant may be a primary stabiliser, which scavenges free radicals, or a secondary stabiliser, which decomposes hydroperoxides. Primary stabilisers can terminate the oxidation process by forming free radicals that are not reactive enough towards oxygen molecules to continue the chain reactions. These stabilisers are usually aromatic amines or hindered phenols, though a number of the phenolic stabilisers possess the drawback of assisting fading by gas fumes, such as nitric oxide. Indeed, many polyolefin fibre producers now demand that the polymer grades with which they are supplied are free of phenolic antioxidants.

Secondary stabilisers remove hydroperoxide radicals and prevent the start of new oxidation cycles. They are termed secondary stabilisers because they perform best when primary stabilisers are present.[47] There is a strong synergistic effect between a primary and secondary stabiliser, if the correct combination is made. Secondary stabilisers are drawn from a variety of compounds, containing sulphur or phosphorus: disulphides, thioesters, thioethers and tertiary phosphites and phosphonates.

5.6.2.2 HCl scavengers

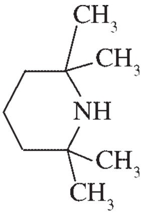
The residues of Ziegler–Natta catalysts in polyolefin fibres can compromise the efficiency of antioxidants present. The catalyst residues can react with phenolic oxidants to produce hydrochloric acid, which may corrode parts of the extrusion machinery. Formation of hydrochloric acid is prevented by the presence of epoxy compounds, dibutyl tin compounds, and calcium and zinc laurates, stearates and benzoates.

5.6.3 Functional additives

5.6.3.1 UV stabilisers

As noted in Section 5.6.1, polyolefins can also readily undergo photochemical oxidation, initiated by UV radiation. In fibrous form, polyolefins possess a very high ratio of surface area to volume; hence polyolefin fibres are especially susceptible to UV light. Moreover, photochemical oxidation is accelerated at higher temperatures. Therefore, without UV stabilisers to prevent photochemical oxidation, the application of polyolefin fibres, and particularly PP fibres, would be severely restricted.

Many factors combine to govern UV stability: fibre processing, the type of UV stabiliser and its concentration within the fibres, fibre count and treatments given to the fibres during subsequent processing. By far the most important class of UV stabilisers in PP fibres are the hindered amine light stabilisers, known as HALS. Many of these stabilisers contain 2,2,6,6-tetramethyl piperidyl groups:



[5.9]

The mechanism of action of HALS stabilisers has recently been reviewed.[50] Essentially, they function as free radical scavengers, though the active functional groups are nitroxyl radicals, formed by oxidation of the amine groups:

[5.10]

During scavenging, the nitroxyl groups are largely regenerated, but the regeneration process eventually ceases: in each regenerative cycle, some of the HALS is lost, and some inefficient radical scavengers are generated as well.[47] However, it has been shown that the addition of hydroperoxides or ketones to PE exerts only a small effect on its rate of photodegradation. It has been proposed that HALS stabilisers can also act by quenching excited polyolefin–oxygen charge transfer complexes which would otherwise initiate photodegradation.[50]

The choice of HALS rests on a number of factors. A HALS with a low molar mass migrates readily from the bulk of the fibre to its surface, especially if the chemical structure of the HALS has little compatibility with that of PP. Not only does migration of the HALS give the fibres a chalky or metallic appearance, but the stabilisation of the fibres against UV radiation also suffers. A HALS of much higher molar mass, although possessing little propensity for migration, may in consequence have limited ability to scavenge radicals. Such a HALS may also have little compatibility with PP. Thus, a HALS with optimal properties will be sufficiently mobile to be effective as a radical scavenger, yet not so mobile that it escapes to the fibre surfaces.

A HALS of high molar mass is arguably the preferred option for fibres, in view of their high specific surface area and the elevated temperatures at which they are extruded and even may be drawn. In practice, combinations of types of HALS with low and high molar mass are often employed, since quite often a synergistic effect results between the two types. Indeed, synergistic combinations of HALS are gaining increasing commercial importance.[51] More recently, a new type of HALS has been launched from Clariant, *Sanduvor PR-31*, which can be grafted to the polyolefin chains under the action of light.

5.6.3.2 Flame-retardant additives

The incorporation of effective flame-retardant additives into PP fibres is crucial for many applications, including automotive, aerospace applications and in floor coverings. Indeed, PE and PP undergo combustion more readily than any other common synthetic fibres.[2] However, for effective protection against ignition to be conferred, the levels of flame-retardant additives can be so high that fibre processing is rendered more difficult, and the physical and mechanical properties of the fibres are impaired. In addition, the effectiveness of UV stabilisers can be reduced by flame-retardant systems, especially those containing halogen atoms, such as decabromodiphenyl oxide and hexabromocyclododecane. Furthermore, there is a risk of the generation of significant quantities of hydrogen chloride or hydrogen bromide from halogenated flame-retardant additives. For these reasons, other flame-retardant additives are now being exploited. These include additives based on phosphorus,[18] aluminium trihydrate and magnesium hydroxide, although to be effective the levels of the metal-based additives have to be especially high.[52] A number of intumescent flame retardants, which function by generating char, have also been evaluated for use with PP, notably ammonium polyphosphate and polytriazinylpiperazine.[52]

A new *N*-alkoxy hindered amine flame-retardant system has been recently launched by Ciba. The product, *Flamestab® NOR™-116*, is designed to act both as a flame-retardant chemical and as a UV stabiliser in polyolefin applications. It is claimed to be effective at levels as low as 1%. The impact on fibre physical and mechanical properties is, therefore, low.

5.6.3.3 Antistatic additives

The importance of spin finishes in reducing static effects during polyolefin fibre processing has already been noted. However, treatments with spin finishes are generally not effective during the subsequent use of the fibres. To extend antistatic properties into fibre use, antistatic agents may be added to the polymer granules before they are melt extruded. These agents must, therefore, be resistant to the elevated temperatures encountered during extrusion, drawing and texturing and must have no deleterious effects on the properties of other additives or on the polyolefin fibre itself. Indeed, they should possess a degree of compatibility with the polyolefin chains. However, antistatic products normally contain hydrophilic groups, which can attract water vapour and consequently lower static charge. The presence of these hydrophilic groups, on the other hand, tends to compromise the compatibility of the antistatic additive with the polymer chains. This is a particular problem with polyolefin fibres, whose chains contain no polar groups.

Antistatic additives are often nitrogen-containing compounds, such as long chain amines, amides and quaternary ammonium salts. Other types of antistatic additive include derivatives of poly(ethylene glycol) and polyhydric alcohols. Whatever their chemical nature, they function by migrating to the fibre surface. The hydrophilic part of the antistatic agent is excluded from the fibre matrix. When enough antistatic agent is present at the surface, electrically conducting paths are formed through the absorption of moisture from the air. If the air itself is dry, the performance of these additives is impaired.

An alternative approach to reducing static charge is to blend the polyolefin fibre with an antistatic fibre, for example, by bicomponent filament extrusion. More recently, however, an antistatic agent has been launched from Ciba, *Irgastat P 22*,[53] which forms a conductive network throughout the fibre and is, consequently, still effective at low levels of humidity in the atmosphere.

Other approaches to dissipating static charge on polyolefin fibres have also been reported.[54] Thus, melt-blown PP fabrics for medical use are treated with conductive agents in order to lower the risk of sparking. Special grades of carbon are also incorporated into polyolefins: the products do not develop any static charge by friction and they conduct charge away to earth without spark formation. To be effective, however, a 15–20% loading of carbon is normally required, and the conductivity is influenced by the degree of crystallinity of the polyolefin fibre host.

5.6.3.4 Antimicrobial agents

Antimicrobial agents are designed to repel, inhibit or kill micro-organisms. Although polyolefin fibres exhibit excellent resistance to micro-organisms, it is still often desirable to incorporate antimicrobial agents into the fibres. The use of antimicrobial agents is particularly important in sportswear, floor coverings and bedding material. Thus, the growth of bacteria on carpets, for example, can present a real danger in hospitals, schools and homes for the elderly. The presence of dust mites in bedding poses a serious problem to those suffering from asthma. Although antimicrobial treatments can be sprayed onto carpets and bedding, their effectiveness is transient. Instead, effort is now concentrated on adding antimicrobial agents to polyolefin granules prior to melt-spinning. However, as with antistatic agents, antimicrobial agents have to be resistant to all the fibre processing stages they encounter, they must not impair fibre performance during use, nor must they reduce the effectiveness of other additives.

Many different antimicrobial agents are available on the market. They generally enter the cell membrane of each micro-organism and disrupt its metabolism, so that its ability to grow and reproduce is impaired. One antimicrobial agent that has been developed for use in polyolefin fibres is a silicon-based polymer containing quaternary ammonium groups, to which are attached long aliphatic hydrocarbon chains.[55] The positive quaternary groups form complexes with the anionic lipoproteins in the cell membranes of the micro-organisms, and they are inactivated.

Antibacterial behaviour is also triggered by the presence of silver in the fibres,[56] and the use of silver for antibacterial treatments is becoming more widespread. Silver ions, in common with a number of other heavy metal ions, are reactive towards proteins. When silver ions are absorbed within the cell structures of bacteria, therefore, they are attracted to groups in the enzymes present in each cell. It is considered that silver ions are particularly reactive towards thiol groups.[56] The enzymes are consequently denatured, the metabolism of the bacterial cells is inhibited and the bacteria are rendered inactive.

5.7 Coloration of polyolefin fibres

In contrast to other types of conventional synthetic fibre, polyolefins cannot be dyed effectively, unless they have been specially modified. Access of dye to the interior of the fibres is limited, there is poor retention of the dye in the fibres, and the evenness of the dyeing is also often poor. The principal factor preventing effective dyeing is the high degree of crystallinity of polyolefin fibres. Another factor is the low affinity between dye and fibre, owing to the weak attraction between the hydrocarbon chains making up polyolefins and the functional groups in the dyes applied.

To overcome these problems, a number of approaches have been tried. Examples are the addition of nickel compounds to enable dyeing with ligand-forming dyes and the inclusion of suitable polymers to allow effective application of disperse dyes or acid dyes.[19] The application of dyes with long alkyl chains has also been attempted. So too has the inclusion into PP fibres of suitable dendrimers and hyperbranched polymers, to act as dyeing promoters.[57] Indeed, it has been reported that the disperse dye, C.I. Disperse Blue 56, exhibits good wet-fastness in PP fibres containing 3% of a stearate-modified hyperbranched polymer, although the light-fastness of the absorbed dye is poor.[57]

Nevertheless, dyeing of polyolefin fibres is still far from being commercially viable. For this reason, polyolefin fibres have to be coloured by pigments, which ideally are uniformly dispersed as tiny coloured crystals throughout the polyolefin fibre matrix. However, polyolefins are far from chemically aggressive, and so there is a wide selection of pigments for numerous shades.[58] The pigments applied must not be thermally degraded during processing of the polyolefin fibres and they must be compatible with other additives present, particularly UV stabilisers. In addition, they should not significantly reduce the mechanical performance of the fibres. Some pigments are known to promote the thermal and photodecomposition of polyolefins; yet other pigments exert a retarding effect.[19]

Many of the pigments applied are organic, in view of their bright shades and greater compatibility with polyolefins. Nevertheless, the white pigment titanium dioxide, especially in its rutile form, is important as a delustring agent, and carbon black, being electrically conductive, confers antistatic properties. Some types of carbon black also possess a degree of antioxidant character.[59] Some brown iron oxide pigments are also used, as they are inexpensive relative to organic pigments.[58]

Pigments consist of tiny crystals, whose cross-section in the case of organic pigments can be as low as 0.05 μm. Such small crystals have an innate tendency to aggregate. Pigment crystal aggregation is highly undesirable in that it reduces overall tinctorial strength and impairs the brightness and clarity of the colour. In synthetic fibre technology, crystal aggregates can cause problems in processing by upsetting the rheology of the molten polymer, clogging the filter pack in the spinneret and hindering fibre drawing. Crystal aggregates also reduce the mechanical performance of the final fibres. It is, therefore, essential to prevent, or at least severely restrict, pigment crystal aggregation in the pigmentation of polyolefin fibres. One approach is the treatment of the pigment crystals by the manufacturer with additives that render the crystal surfaces more compatible with polyolefins. However, the size and shape of the pigment crystals can also be important in reducing crystal aggregation. The problems of pigment crystal aggregation and means of overcoming them are more fully discussed elsewhere.[60,61]

In view of the propensity of organic pigment crystals to aggregate and of the viscous nature of molten polypolefins, uniform dispersions of the tiny pigment crystals are difficult to achieve. As a result, the conditions giving rise to optimum mixing of pigment and polymer tend to be quite different from those required for fibre processing. The achievement of the pigment dispersion, therefore, is often separate from the fibre-forming process. The pigment is first dispersed in a binder, and the coloured predispersion is supplied to the fibre processor.

Predispersions can be supplied in several different forms. The most usual is the master-batch, in which the pigment is predispersed at high concentration (up to 50% or more) in a binder and processed into granular form. The master-batch is then mixed with sufficient uncoloured polyolefin granules to achieve the desired tinctorial strength in the fibre after processing. Traditionally, the binder has been low-density PE, but for the coloration of PP fibres, PP has now become the predominant binder. Moreover, to promote the dispersion of pigment in the binder, low-viscosity synthetic waxes may be incorporated.[62] Occasionally, a predispersion is supplied as a ‘compound’, which is a composition in granular form ready for processing without further addition of polyolefin granules.

5.8 Properties of PP and PE fibres

As with other synthetic fibres, the technological properties of polyolefin fibres are influenced by the grade of polymer, the fibre processing conditions used and the

Table 5.7 Properties of common synthetic fibres

	Tenacity (N tex^{-1})	Initial modulus (N tex^{-1})	Elongation to break (%)	Density (g cm^{-3})	Moisture regain* (%)	Glass transition temperature (°C)	Melt temperature (°C)
HDPE	0.3–0.6	2–5	10–45	0.95	0	–85	120–125
PP	0.3–0.8	2–9	15–35	0.90	0.04	–5	160–165
PET	0.3–0.8	6–12	15–55	1.34–1.38	0.4	70–80	265
Nylon 6.6 (dry)	0.2–0.6	2–5	15–65	1.14	4–5	60–70	265
Acrylic (dry)	0.2–0.3	6–7	20–50	1.16	1.5	95–100	–

*Values of moisture regain at 20°C and 65% relative humidity.

additives present in the fibre. However, the extent to which each of these factors exerts its influence depends on the property of interest. In some examples, such as moisture regain, the chemical structure of the polymer is by far the dominant factor. In other examples, especially fibre mechanical properties, fibre processing conditions are highly influential.

There are two particularly striking differences between the properties of PE and PP fibres and those of other synthetic fibres. There is an almost complete lack of water absorption by polyolefin fibres, and they possess densities lower than that of water, as already noted in Section 5.1. The glass transition temperatures and melt temperatures of PP and PE fibres are appreciably lower than those of other common synthetic fibres. In addition (Table 5.2), PE and PP are very resistant to chemical attack, though, as noted above, they are sensitive to oxidising agents.

Some properties of PE and PP fibres are listed in Table 5.7. Many of these properties are highly influenced by processing conditions, and so the values for them in Table 5.7 are subject to considerable variation.

5.9 Hard-elastic fibres

A number of polyolefins can be processed into fibres with elastic properties, so-called hard-elastic fibres. These polyolefins include PE, PP, poly(4-methyl-1-pentene), poly(1-butene) and poly(3-methyl-1-butene).[2,20] The fibres are capable of high recovery from large extensions, e.g. more than 90% recovery from at least 50% elongation.[2] They are produced by melt-spinning at high levels of spinline stress and little (if any) subsequent drawing, followed by annealing treatments, which may be severe. If the spinline stress is too high, however, structures result with reduced elasticity but increased tensile properties.

The elastic nature of the fibres cannot originate from flexible chain segments, as is the case with true elastic fibres. Instead, the high spinline stress during melt-spinning gives rise to a row-nucleated morphology aligned at right angles to the fibre axis. Annealing produces further ordering into stacked crystalline structures.[63] These lamellae are connected to one another by short tie molecules, which can transfer stress between the lamellae. A detailed review of the structure in hard-elastic fibres has been written by Cannon *et al*.[64]

As the fibre is stretched, so the lamellae splay apart, with the development of a large number of microvoids. The overall density of the fibre is hence considerably reduced by stretching.[19] By contrast, the density of a true elastomeric fibre scarcely changes on stretching. In addition, the elastic behaviour of hard-elastic polyolefin fibres is observed only in the direction of the fibre axis. The mechanism of elastic recovery in these fibres is principally, though not totally, energetic, in contrast to the recovery in elastomeric fibres, which is largely entropic.[2]

A number of applications have been considered for hard-elastic polyolefin fibres, although none appears to have been extensively commercialised. These applications include stretchable sewing threads, stretchable non-woven fabrics and cardiovascular prosthetic devices.[2] One practical problem is the construction of fabric from hard-elastic fibres such that their elastic behaviour can still be utilised in a number of directions.

5.10 Processing–structure–property relationships

5.10.1 Introduction

The extensive commercial interest in melt-spun polyolefin fibres, and especially PP fibres, stems from their mechanical properties. As with other synthetic fibres, there is particular emphasis in this regard on fibre strength, as indicated by tenacity, and fibre stiffness, as indicated normally by initial modulus.[65] Elongation to break is also an important technological property. All these parameters are evaluated from curves relating specific stress to strain, measured at moderate strain rates. They may not, however, always be reliable indicators of practical mechanical performance over very short or very long durations, as experienced respectively by the fibres under impact or under continuous loading. Nevertheless, strength, stiffness and elongation to break are helpful guides towards assessing the mechanical performance of fibres.

It is, therefore, useful to estimate the maximum theoretical values of fibre tenacity and modulus. Maximisation of initial modulus requires a high value of modulus for the constituent polymer chains, a high degree of chain orientation and strong intermolecular forces between adjacent chains.[66] In addition, a high molar mass is desirable to allow greater continuity of the chains along the fibre, and also a narrow molar mass distribution. Chain modulus is higher for those polymer chains whose extension is a result of bond angle opening and bond stretching. The presence of side groups, especially large ones, reduces the strength of intermolecular attraction between chains and is, therefore, undesirable.

The modulus achievable for PE should, then, be higher than that for PP. PE consists of zigzag chains which contain no side chains. On the other hand, PP consists of helical chains which are more readily stretched. Moreover, the methyl side groups reduce the attraction between adjacent chains, by increasing the overall cross-sectional area of each chain. The chain modulus calculated for PE chains is about 300 GPa , whereas for PP chains the value is only around 40GPa.[65] Nevertheless, for melt-spun PE fibres,[3] the maximum value which has been achieved in practice is about 60 GPa. For PP fibres, values up to 6 GPa are obtained for commercial samples, although it has been shown that PP fibres with a modulus of *ca*. 11 GPa can be produced by melt-spinning.[65] However, this value is still less than 30% of the theoretical maximum value. The modulus of gel-spun PE fibres is over100 GPa.[11]

Estimation of the maximum fibre tenacity achievable is more difficult, although one approach suggests that the value should be around 10% of the modulus.[65] On this basis, the theoretical maximum strengths of PE and PP will be *ca.* 30 and 4 GPa, respectively. However, a value as high as 18 GPa has also been suggested for PP fibres.[11] For melt-spun PE, fibre tenacities of 1.3 GPa have been achieved, and the tenacity of gel-spun PE fibres is over 3 GPa.[11] For PP fibres, values up to 0.8 GPa can be obtained commercially, although values as high as 1.1 GPa have been reported.[65] As with the modulus values, these values are far below the theoretical maximum.

The theoretical achievable values for fibre tenacity and modulus are calculated for extended polyolefin chains, aligned in perfect orientation in the direction of the fibre axis. The shortfall of the values obtained in practice can be attributed to the extensive folding of the chains in drawn fibres and, in consequence, the load borne by the small fraction of tie molecules. The achievement of higher values for tensile strength and modulus depends, therefore, on reduction in chain folding. It should be noted that for gel-spun PE fibres, where the chains are better oriented along the fibre axis, the values of fibre tenacity and modulus are indeed higher.[11]

However, it is not clear that the alignment of polyolefin chains can be significantly improved in fibres produced by melt-spinning and subsequent drawing, because of the chain entanglements occurring in the molten state, which are then retained in the solid fibres. In addition, polyolefins crystallise readily from the melt during the extrusion process, yet it is beneficial if an extensive crystalline structure is formed only after the drawing stage, to allow a high draw ratio to be achieved. However, it has been demonstrated for PP that the production of fibres in the paracrystalline state does assist the drawing stage.[67,68]

It is evident then that to achieve improved mechanical performance, attention has to be focused not only on the properties of the polymer grade used, notably its molar mass and dispersity, but also on fibre processing itself. The control parameters involved in melt-spinning which determine the successful formation of fibres (good spinnability) and the resultant fibre properties have been extensively discussed by Ziabicki,[69] who subdivides melt-spinning variables into three groups.

The independent, or primary variables, uniquely determining the course of the spinning process and the resultant fibre structure and properties, include the grade of polymer material, spinning temperature, the number of holes in the spinneret and their dimensions, the mass output rate of each filament, spinning path length, take-up velocity and cooling conditions. Ziabicki also identifies secondary variables, which are related to the primary variables and govern spinning conditions. Examples of secondary variables are filament tex and draw-down ratio. The third group comprises resulting variables, including filament structure, tensile stress at take-up godet and the temperature of the filaments at a given distance from the spinneret.

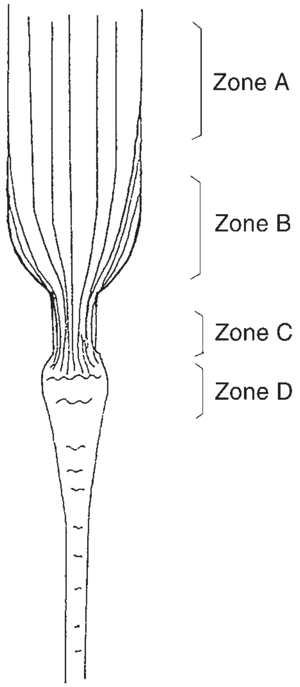
For discussion in this chapter of processing–structure–property relationships, the fibre processing stages may be conveniently considered as follows: the processing of the melt, the solidification of the melt and draw-down of the filaments formed, and the subsequent drawing process. Each of these is discussed in turn.

5.10.2 The polyolefin melt

Once fed into the extruder, the polyolefin granules become molten. By virtue of a screw (or in bench-top equipment perhaps a ram), the melt moves through the barrel of the extruder to the spinneret. The flow of the melt in the spinneret is controlled by a metering pump. During this stage, intimate mixing and a high level of dispersion of the additives has to be achieved. In addition, the polyolefin melt is prone to oxidation, although resistance to oxidation is increased in the presence of suitable antioxidants (as discussed in Section 5.6.2.1). Nevertheless, one study has shown that degradation of PP within the extruder is apparent at 260 °C and above.[67]

It is evident that the flow of the melt through the barrel of the extruder will be influenced by the melt's rheological properties. These properties are particularly important during passage of the melt through each hole in the spinneret and in its egress from these holes. The pattern of flow immediately above each hole, through it and out of it has a major influence on the settings of the melt extrusion equipment.

The passage of the polymer melt is illustrated schematically in Fig. 5.5. The pipe leading to each spinneret hole (zone A) is considerably wider than the hole itself. The melt has a relatively high viscosity and the shear rate it experiences is small. In zone B, immediately above the entrance to the spinneret hole, there is usually tapering of the pipe from its diameter in zone A to that in zone C. The tapering serves to counteract prolonged stagnation of the melt and hence avoid its consequent thermal degradation in the corners of the entry zone. In zone B, the flow pattern is complex and is characterised by a progressive rise of stress, a rapidly decreasing viscosity and a build-up of recoverable viscoelastic strain.[19] The rheological behaviour is predominantly governed by the molar mass and dispersity of the polymer, and the nature and concentration of the additives present. Hence, different grades of polyolefin possess different flow behaviour in zone B. The



5.5 Passage of polymer melt through a spinneret hole.

rheological behaviour of the melt largely determines the angle at which the pipe should be tapered towards the spinneret hole. A taper of 60 ° to 90 ° is commonly used commercially for PP.[19]

In zone C, the shear rate is almost constant. The shear stress decreases in the initial section of the zone but then remains virtually constant. There is, too, a reduction in recoverable strain, because of the reduction in stress and relaxation of the polymer melt. The volume output of the melt is governed by the drop in pressure along the length of the spinneret hole, and in turn this drop in pressure is determined by the dimensions of the hole. In common with many other polymer melts, the viscosities of fibre-forming polyolefins decrease markedly with increasing shear. Thus, the flow of melt through the spinneret hole is greater than that expected if the viscosity had remained constant. The dimensions of the spinneret hole are important factors in melt extrusion, and indeed it is common practice to characterise the hole by the ratio *L*/*D*, its length to its diameter, which for polyolefins is normally in the range 1–4.

The egress of the melt from the spinneret hole (zone D) sees a rapid change from shear flow to elongational flow. The melt is no longer constrained by the walls of a narrow spinneret hole. The melt also begins to cool. There are sharp reductions in shear rate and shear stress, and an increase in viscosity. The release of elastic energy on emergence of the melt from the spinneret gives rise to die-swell (or Barus effect), which is manifest by a dilation of the extruded filament at the exit from the spinneret. It is particularly evident, for example, in PP melts, where the increase in diameter can be two- to three-fold. It thus has a pronounced effect on the speed of spinning, and indeed distortions in the shape of the fibre cross-section may occur. For PP fibre melts, it has been observed that die-swell is reduced for spinneret holes of increased L/D values, increased values of D, and lower flow rates through the melt.[19,70] A theoretical analysis of the die-swell in extruded PP filaments has been published.[71]

The dimensions of the spinneret hole also govern the conditions for the onset of melt fracture, which refers to the distortion of the surface of the extruded melt. Severe distortions may be in the form of helical indentations, and extruded PP melts are susceptible to this phenomenon. Melt fracture is intensified by higher flow rates through the spinneret hole, a low angle of taper on entry to the spinneret hole (zone B), a decrease in *L/D*, reduced temperature of the melt and increased molar mass.[19]

Molar mass distribution also exerts a pronounced effect on susceptibility to melt fracture in extruded PP melts.[48] Molar mass distribution has been shown also to have a significant influence on the elongational flow of high-density PE.[70] When the apparent elongational viscosity, λ, of a PE grade of broad molecular distribution is plotted as a function of distance from the spinneret exit, a minimum is observed. For a PE melt of narrower molar mass distribution, no such minimum is apparent. The same contrast was also noted in plots of λ against the reciprocal of spinning temperature. It was concluded that the unexpected minimum in elongational viscosity in highly disperse PE melts may arise from the wide variation in strain rates in PE chains of such considerably different lengths. Alternatively, the minimum may arise from the formation of liquid crystals.[70]

Another source of instability in the filament melt emerging from the spinneret is draw resonance. This term refers to periodic fluctuations in diameter in the filament melt. Whereas melt fracture appears to commence at a particular value of throughput rate, draw resonance will occur only when the filament is being stretched.[72] The onset of draw resonance occurs, therefore, at a critical draw-down ratio. Both PP and high-density PE are prone to draw resonance, but it appears to be less of a problem with low-density PE. The intensity of draw resonance is influenced by the molar mass distribution of the polyolefin and also by the shear deformation of the melt in the spinneret holes. The presence of additives, such as pigments and stabilisers, can also promote draw resonance. Moreover, additives that exist in solid particulate form during fibre extrusion may cause knots (short irregular sections) in as-spun fibres.

5.10.3 Solidification of the melt and draw-down of the filaments

5.10.3.1 Crystallinity

After the polymer melt has emerged in the form of filaments from the spinneret holes, it rapidly cools. At the same time, the extruded filaments are attenuated because of the extensional force applied to them. On solidification, the rate of crystallisation of polyolefins is innately high and is even further increased by the chain orientation effects occurring during draw-down of the filaments. However, to achieve maximum extension during the subsequent drawing stage (discussed in Section 5.10.4), it is desirable to suppress crystallisation. In the case of PP fibres, however, it has been amply demonstrated that as-spun fibres can be successfully drawn, provided they are in a paracrystalline state, rather than in a true crystalline state.[67,68,73] Paracrystalline PP fibres can be readily obtained by rapid cooling of the melt into a water bath,[74,75] whereas quenching by air often produces PP fibres in the α-monoclinic state. However, under carefully controlled conditions, paracrystalline fibres can also be obtained by air quenching.[67,76] As-spun PE fibres are formed with a well-defined orthorhombic crystalline structure, irrespective of spinning conditions.[75] Poly(1-butene) fibres are formed with a well-defined hexagonal structure in air, but rapid quenching gives instead a tetragonal structure, which then ages to the more stable hexagonal form.[75] As-spun poly(4-methyl-1-pentene) fibres possess a well-defined tetragonal structure.[75]

The rate of crystallisation and the extent of crystallinity in as-spun fibres depend both on the grade of polymer extruded and the extrusion processing conditions.[67,76] The magnitude of the spinline stress has been noted as particularly important in this respect.[67,77,78] It has been observed that an increase in spinline stress increases the crystallisation rate and the overall crystallinity of the as-spun fibres produced. In turn, spinline stress can be increased by raising cooling rate and winding speed and by lowering metering pump speed and spinning temperature. In contrast to this observation, however, some recent work on the extrusion of PP monofilament has revealed that crystallinity can decrease with increase in winding speed.[42] It therefore appears that filament thickness also has a bearing on the crystallinity of the as-spun fibre produced.

The factors governing the rate of crystallisation in the formation of as-spun fibres are complex and are markedly influenced by the rate of cooling of the filaments and the tensile stress at crystallisation. Studies of the onset of crystallisation in the spinline have been reported for PE and PP fibres.[77,78] For example, it has been shown that the crystallisation temperature of PP under melt-spinning conditions is much higher than under quiescent conditions. Moreover, the temperature of the onset of crystallisation is higher with increased spinline stress. Thus, the higher chain orientation arising from elongational flow, together with the draw-down tension in the filament, increase crystallisation rate appreciably.

Spinning temperature also has a part to play. Low spinning temperatures favour the onset of crystallisation but reduce the mobility of the polymer chains. There is a temperature range over which the rate of crystallisation reaches a maximum. For PP, this maximum is generally between 100 and 110 °C, though in the presence of nucleating agents the temperature may be as high as 140 °C.[19]

The influence of molar mass on the rate of crystallisation remains unclear. It is known that PP grades of higher molar mass lead to increased spinline stress,[78] and this increase would be expected to enhance crystallisation rate. Although evidence has been presented to support this argument,[79] other evidence favours the opposite.[19] This conflict may arise from an interaction between molar mass and spinning temperature.

However, it is generally accepted that the degree of crystallinity increases with increasing molar mass. Moreover, the molar mass distribution is also an important factor. A greater proportion of longer chains in PP fibres, for example, promotes the formation of α-monoclinic crystals and raises the degree of crystallinity.

It is noteworthy too that the presence of pigment particles can affect the crystalline structures of synthetic fibres.[80] Thus, as-spun PP fibres coloured with a phthalocyanine pigment have been observed to be in the α-monoclinic form, even when extruded under conditions where the uncoloured fibres are in a paracrystalline state. As-spun PP fibres coloured with a quinacridone pigment can contain both α- and β-forms, though on heating of the fibres, the β-form transforms to the α-form.

5.10.3.2 Orientation

The overall orientation of the polyolefin chains in as-spun fibres is largely determined by the degree of stretching during draw-down (the draw-down ratio). Kitao *et al.* have reported that, at lower draw-down ratios, the chain orientation in as-spun polyolefin fibres increases with increasing draw-down ratio.[81] At draw-down ratios between 8 and 80, however, they report no further increase in chain orientation in PE and PP fibres, although there is an increase in poly(1-butene) fibres. They also concluded that crystalline regions contribute more to overall orientation than non-crystalline regions. Moreover, in addition to the orientation of crystals along the fibre axis, orientation at right-angles to the fibre axis may occur at draw-down ratios of <50. These conclusions have been largely confirmed by Choi and White,[75] who have also reported that crystal orientation is correlated better with spinline stress than with draw-down ratio. They report that at a given spinline stress, the ranking of the crystal orientation is: poly(4-methyl-1-pentene)>poly(1-butene)>PP>PE.

5.10.3.3 Skin–core effect

The as-spun fibres may exhibit a skin–core effect, which tends to be more pronounced the thicker the filament. The outer filament of the skin is composed of polymer chains of higher orientation than those in the core of the filament.[82] The principal factor giving rise to the skin–core effect is the transfer of heat from the surface of a filament, which in turn leads to a temperature gradient across the filament. In consequence, variations in polymer viscosity, along with variations in stress, may occur through the filament cross-section.

The processing of the fibre may be impaired if the skin does not have uniform thickness around the core. Such non-uniformity can arise where fibre extrusion involves polymer of high molar mass, low spinning temperatures, high rate of cooling and high speed of winding of the solidified filaments.[19] The filaments, on relaxation, tend to curl, a tendency that may be further enhanced during subsequent drawing. However, a pronounced skin–core structure can be deliberately encouraged, to produce 'self-crimping' fibres.

5.10.4 Fibre drawing

As-spun polyolefin fibres possess mechanical properties that are much too inferior for practical application. The tenacity and initial modulus of the fibres are too low, and there is also a high, irreversible elongation. However, as with other synthetic fibres, drawing under carefully controlled conditions can markedly improve fibre mechanical performance in polyolefins. Generally, the higher the draw ratio, the higher the tensile strength and modulus of the drawn fibres and the lower the elongation to break. The process can directly follow the melt-spinning operation, as in the production of FOY and BCF, or it can be a separate operation using as-spun filaments wound onto bobbins, as in the production of POY and in the two-stage process for producing staple fibres (Section 5.5.4). Thus, the structure and mechanical properties of drawn fibres are markedly influenced by the structure of the precursor as-spun fibres and the drawing conditions employed.[68,73] Important control parameters for fibre drawing are draw ratio, draw temperatures, draw speeds and the number of draw stages.

Polyolefin fibres can deform in a draw stage either inhomogeneously, where there is a marked necking effect, or homogeneously, without any necking. The type of deformation depends on the structure of the as-spun fibre and the drawing conditions.[19] For example, neck formation in PP fibres is favoured by lower temperatures and increased draw speeds. It is also favoured by higher orientation of the polymer chains and the presence of monoclinic crystals in the as-spun fibre. Drawing of fibres with larger cross-sections is also more likely to involve necking.

Neck formation arises from variation in the distribution of stress along a filament, as a result of tensile deformation during drawing. Such stress variation may arise from small variations in cross-sectional area or from other inhomogeneities along the length of the filament. Once a neck has formed, however, it is essential that the thin portion maintains a constant cross-section, through strain hardening. Strain hardening will occur if there is increased orientation of the polyolefin molecules in the direction of the fibre axis. The angle of the neck is likely to be important in this respect. If there is a sharp neck angle, leading to a more pronounced necking effect, there will be a higher degree of overall chain orientation. However, the draw process may also become unstable.

The drawability of an as-spun fibre is usually considered in terms of the maximum draw ratio to which it can be drawn. Certainly, draw ratio profoundly affects the character of drawn fibres, and several empirical relations have been proposed to relate draw ratio to overall chain orientation.[83,84] Changes in structure as a result of deformation forces of the type that occur during fibre drawing have already been discussed in Section 5.4.3.

Draw temperature is also an important factor, because temperature influences the mobility of the structural units during deformation. Drawing at ambient temperatures, for example, converts as-spun PP fibres with α-monoclinic crystalline structures into more oriented, yet less ordered structures with reduced crystallite size, increased lattice strains and defects that are similar to the paracrystalline form.[85] Subsequent annealing, however, transforms this disordered structure into a highly ordered α-monoclinic structure, with a high overall chain orientation.

Drawing at low temperature can induce the formation of microvoids, which elongate in the direction of the fibre axis as a result of the tensile force applied.[86] The formation of these microvoids occurs in the interspherulitic regions, and their presence lowers the modulus of the fibres.[87] The number of microvoids can be considerably reduced by annealing, with a resultant increase in the fibre modulus.

Drawing at more elevated temperatures can be considered to be similar to a combination of cold drawing followed by annealing.[85] Fibres with highly ordered and highly oriented structures are formed. In contrast to cold drawing, there is no formation of necks and a steady reduction in filament cross-section is observed. The structural changes occurring during drawing at higher temperatures include healing of crystal defects, a reduction in the number of tie molecules, relaxation of the non-crystalline material in each fibre and increased mobility of the polymer chains throughout the fibre.[39]

To explain the effects of temperature on fibre drawing, the concept of crystal mobility temperatures, CMT, has been applied. CMT is the critical temperature above which crystalline lamellae become mobile enough to be oriented. For instance, it has been shown that deformation of as-spun fibres with a spherulitic structure at 90 °C is largely influenced by non-crystalline polymer chains.[87] The CMT is 110 °C and so the crystalline lamellae resist orientation. When the drawn fibres are annealed under tension at 140 °C, however, the lamellae are able to slip and rotate, so that their chain axes are oriented along the fibre axis, and the transformation from spherulitic structure to fibrillar structure is completed.

Speed of drawing (draw rate) is a further factor affecting structural changes to polyolefin fibres. A concept that is often used is 'ease of drawing', which determines the speed of drawing without an excessive number of filament breaks.[19] This consideration is especially important to commercial fibre manufacture, where draw speeds may be higher than 4000 m min^{-1}.[18] Polymers with narrower molar mass distribution are generally easier to draw without filament breaks, although the maximum draw ratio achievable may be low. The inclusion of additives such as stearates, paraffin waxes and silicon-based additives, promotes ease of fibre drawing. Higher draw speeds can be obtained, the maximum draw ratio is increased and the formation of microvoids is reduced.

More than one drawing stage is often needed to achieve the desirable mechanical properties in the final fibre, despite the added complexity in terms of processing. For the drawing of PP fibres, it has been shown that two-stage drawing can provide a route to filaments of high tenacity, where the first stage utilises a high draw ratio at low temperature (≤60 °C) and the second stage utilises a low draw ratio at high temperature (*ca.* 140 °C).[67,68] The as-spun fibre should be in the paracrystalline state. With this two-stage approach, a high orientation of the PP chains could be obtained in the first stage before transformation from the paracrystalline to the α-monoclinic form in the second stage. PP fibres of count <0.6 tex could be obtained with a tenacity as high as 0.85 N tex^{-1}, although the draw speeds in both stages were limited to 200 m min^{-1}. It was suggested, however, that this problem could be eased by integration of spinning with the first draw stage, using an optimised design for this draw stage. The second draw stage could be designed to provide a compromise between achievable mechanical performance and commercially acceptable production speeds, with the possibility of integrating this draw stage with further processing downstream. The advantages of multistage drawing have also been demonstrated by other workers,[88,89] and indeed multistage drawing is widely practised on a commercial scale.

The development of flaws and defects during the drawing of polyolefins, particularly to high draw ratio, has been the subject of recent research, notably by Bassett and Ward and their co-workers. In the drawing of paracrystalline PP fibres at 60 °C, the development of longitudinal defects, often several μm long, has been demonstrated.[86] Moreover, at higher draw ratios (≥7), the drawn fibres were observed to contain transverse bands of defects, which alternated with homogeneous sections along the length of each fibre. As the draw ratio increased, the defect bands increased in length and proportion until they occupied very nearly all of the fibre. The defects have been identified as regions of reduced density.

A similar distinct longitudinal morphology has also been observed in some highly drawn polyethylenes.[90,91] In this case dumbbell specimens were cut from sheets and drawn at 75 °C in tensile testing equipment. A regular morphology of alternating transverse bands and rows of etched pockets was observed, termed Pisa structure by the authors because of their resemblance to the façade of the Leaning Tower. In addition, transverse sections of the highly drawn fibres revealed large voids and some featureless patches – a morphology termed by the authors as mesa structure, in view of its resemblance to features of the North American desert.

Understanding of the formation of these structures is still quite limited. However, a new model of the underlying structure of polyolefin fibres has recently been put forward.[92] The structure, it is proposed, develops as a consequence of the nucleation of an extended network of entangled polyolefin chains throughout the fibres. Subsequent growth into spaces in the network will encounter stresses because of contraction on crystallisation giving rise to density-deficient regions within the fibres.

5.11 Applications

5.11.1 Introduction

By far the most important type of polyolefin fibre in a commercial sense is PP fibre. Although there are specific markets for PE fibres, the PE fibres for these markets are generally produced by gel spinning.[11] Attention, therefore, is devoted primarily in this section to PP fibres.

PP fibres enjoy a wide range of end-uses, and these uses are expected to increase over the coming years.[10] There are several reasons to account for the swing towards PP fibres. Propene is perceived to be a secure raw material for the production of PP, and the ratio of technical performance to cost of fibre is high. PP fibre is uncomplicated to process, is a good substitute for numerous other materials, is quite readily recycled and is considered to have little adverse environmental impact. PP fibres are to be found, for example, in carpets and other household textiles, motor vehicles, geotextiles, healthcare and hygiene products, filters, sacks and bags, cables, ropes, netting and agricultural and horticultural products. Some selected examples of the many applications of PP fibres are now given.

5.11.2 Carpets

PP fibres have very largely replaced jute as the material for carpet backings. Primary carpet backing, the backbone of the carpet, must be able to withstand a number of harsh processing treatments, such as tufting, dyeing and steaming, without loss of strength or undue change in dimension. PP fibres are, therefore, well suited. For the secondary carpet backing, the base of the carpet, PP fibres are again well suited in view of their resistance to moisture. There is no swelling of the fibres that would result from the absorption of moisture, and there is little growth of moulds. Carpet backings normally consist of PP fibres produced by the FOY process, or PP tapes. Both forms provide the high strength required.

PP fibres are finding increasing application too in carpet pile yarns, owing extensively to the texturing processes now available for BCF yarns. The excellent stain resistance of coloured PP fibres is also important, a feature due to the inherent properties of PP and to the presence of the colour in the form of pigmentary particles. Carpet pile can be subjected to many different kinds of spillages, whether in the home, the office, in shops or in transportation, yet the inertness of PP renders the fibres resistant to most types of chemical spillage. The colouristic properties are also largely unaffected by such spillages, and moreover the fibres resist fading by light.

There is still considerable effort, however, in improving the resilience of PP pile yans and their resistance to continuous wear. Some of this effort is centred around the design of suitable profiles for spinneret holes in melt extrusion and the consequent shape of the fibre cross-section (Section 5.13.2).

5.11.3 Household furnishings

PP fibres are applied in a wide range of home furnishings. For example, PP fibres are being used more and more for upholstery cover fabrics in view of their high abrasion resistance. These fibres are produced in POY form or as staple fibre yarns. In addition, mattress duck, made from PP fibres that can be given long-term antimicrobial treatments, can help to alleviate the problems suffered by those especially susceptible to allergies, as with asthma and eczema. Other PP household textiles include bed linen, bedspreads, cleaning cloths, net curtains and bath mats.

5.11.4 Geotextiles

Geotextiles have a wide variety of uses. They can provide reinforcement in roads and stabilisation in embankments, by absorbing forces from which other components in a construction must be protected. They can also provide filtration and drainage of water in foundations and keep materials separate, to prevent intermixing of layers of these materials.

Geotextiles are manufactured from woven and non-woven fabrics, the choice of fabric depending on the function required. Thus, woven fabrics, often from slit tapes, are used where strength and stability are important, but non-wovens are used where filtration, drainage and cushioning are among the principal requirements.

The chemical inertness, high strength, low density and low cost of PP fibre render it an attractive option for many geotextile applications. In addition, for those geotextile applications where the PP fibres are below ground level, their susceptibility to photodegradation is a less serious factor. Nevertheless, there are some problems associated with the use of PP fibre in geotextile applications, one of these being poor creep resistance. Thus, during use, many geotextiles constructed from PP fibres are readily deformable and should, therefore, be used in roles where the stress to them is limited.

A further problem is sensitisation under stress to oxidative degradation. Evidence has been obtained that stress increases the rate of oxidative attack through the promotion of PP chain scission.[93] Furthermore, it has been pointed out that this observation has implications for durability tests and predictions of the lifetimes of PP textiles not only in geotextile applications but in any application where a PP textile is continuously under stress. Indeed, it has been suggested that creep tendency and stress sensitivity to oxidation are related via a common mechanism. Thus, strategies for reducing creep may also reduce stress sensitivity to oxidative degradation, with consequent improvement in durability. The presence of some grades of carbon black in PP fibres appears to be beneficial in this respect.[94]

5.11.5 Motor vehicles

Textile components in a standard car account for 2–4% of its total mass. Some of these textile components are readily seen: for example, carpets, interior trim and boot liners. Many textile components, however, such as tyre cord and airbags, are hidden from view. Components such as seat belts and airbags play a vital role in protecting drivers and passengers in the event of a vehicle accident.

The application of PP textiles in the automotive sector is steadily increasing, owing to the low density and ready recycling of PP. In addition, as already noted, PP textiles generally possess better colour stability than other synthetic fibres and have good resistance to chemicals and staining.

PP textiles, then, are to be found in many parts of a vehicle. Needlepunched, non-woven PP fabrics are used in parcel shelves, boot liners and bonnet liners, door panels and the top decorative layers of floorcoverings.[95,96] Woven and knitted PP textiles are used in door linings. The use of PP textiles in car seats is limited, as the abrasion resistance is considered too low compared with polyester. However, PP fabrics are occasionally used in the side linings of seats. It is expected that the increasing legislation requiring greater emphasis on the recovery and recycling of waste material will promote the growing application of PP fibres in automotive textiles.

5.11.6 Healthcare and medical applications

Polyolefin fibres have found a wide variety of applications in the hygiene and medical sector. Moreover, their uses continue to expand, especially for PP non-wovens. Textiles for healthcare and medical applications are conveniently categorised into four groups:[97]

1. non-implantable materials, e.g. plasters, bandages and gauzes;
2. extracorporeal devices, e.g. artificial lungs, kidneys and livers;
3. implantable materials, e.g. sutures, vascular grafts and artificial ligaments;
4. healthcare/hygiene products, e.g. surgical gowns, cloths, wipes and bedding.

Polyolefin fibres find application in all four groups. They are highly inert in living tissues and may retain their tensile properties over several months or even years *in vivo*. Thus, PP fibres are commonly used in woven and non-woven orthopaedic cushion bandages, applied under plaster casts or compression bandages to prevent discomfort to the patient. PP fibres are also used in plasters and gauzes.

The commonest application of polyolefin fibres in extracorporeal devices is as hollow fibres in mechanical lungs. The porous construction is such that the lung possesses high permeability to gases but low permeability to liquids. Thus, carbon dioxide can be removed from the patient's blood and oxygen can be supplied to it, yet leakage of blood plasma is prevented.

PP fibres are also used in sutures for wound closures. There is minimal tissue reaction, an important factor in contaminated and infected wounds. Moreover, PP sutures retain knots better than do most other synthetic materials, yet because they do not adhere to tissue, they are readily pulled out when the wound has healed. Meshes fabricated from PP fibres may be used to replace abdominal walls and replace hernias, when the suture experiences extensive stress during healing of the wound. PP sutures are generally suitable for repairing blood vessels, such as coronary arteries, where excessive tissue reaction to the suture could lead to reduced cross-section of the blood vessel or the formation of a thrombus within it. Skin sutures usually consist of PP monofilaments.

Textile materials are particularly suitable as soft-tissue implants, in view of their strength and flexibility. Woven or braided porous meshes of PE fibre surrounded by a silicone sheath are often used for fabricating artificial tendons. Non-woven low-density PE is often used for artificial cartilage in the face, ear, nose and throat, as it is considered to resemble natural cartilage quite closely.

Polyolefin fibres are used extensively in healthcare and hygiene products. Thus, woven and non-woven PP is used in surgical gowns. In isolation wards and intensive care units, non-woven PP is used in disposable, protective clothing, worn to minimise cross-infection. Woven and non-woven PE is commonly used in surgical drapes and cover cloths in an operating theatre. The drapes are designed to cover the patient, and the cover cloths to cover the area around the patient. Both types of polyolefin are used in incontinence products, such as nappies. Spunbonded, non-woven PP often forms the inner covering layer, while the outer layer may consist of non-woven PE. Bicomponent fibres, consisting of a PE sheath and PP core, are used for sanitary towels, tampons and incontinence products.

5.11.7 Filters

PP fibres are used extensively in filters, both for solid–gas and solid–liquid filtration systems. Although filtration products used to be typically manufactured from woven fabrics, non-woven fabrics are now being increasingly utilised. Non-wovens are considered to possess greater versatility, in that they can often be readily used on their own or in conjunction with some other material. Moreover, in dry filtration, non-wovens permit greater flow of gas without reduction in filtration efficiency.

Improvements in filtration systems are being driven by the need for higher rates of filtration, improved efficiency of filtration and stricter environmental legislation. These factors have led to the increasing use of PP textiles, with additional factors being their superior chemical and abrasion resistance and low cost of manufacture. In wet filtration applications, woven and non-woven PP textiles are used more than any other types of textile. The rapidly increasing application of melt-blown nonwovens for dry filtration has also promoted the use of PP fibres.

5.11.8 Slit tape products

The commercial importance of PP fibres in carpet backings has already been discussed (Section 5.11.2), but there are also many other outlets for fabrics woven from PP tapes. These outlets include sacks, bags, flexible intermediate bulk containers (FIBCs) and tarpaulins. The same properties which are important for carpet backings are important too for these other products, notably low density, low cost of manufacture and high tensile strength. Many of these products are used in exterior applications; hence effective stabilisers in the fibres against photochemical degradation are vital.

5.11.9 Ropes and netting

PP ropes have extensive maritime use. Because the density of PP is less than that of water, ships' ropes made from PP float on water and can consequently be in constant view. Moreover, PP ropes cannot become waterlogged, as the moisture regain of PP is tiny (Table 5.2). PP lines are evident too in water sports: they connect waterskiers to the boats towing them and are used to separate swimmers in races.

PP netting has a wide range of applications. These applications include safety fences such as those used around building sites and in downhill runs to protect skiers. PP netting is also used in horticulture to control the intensity of light incident on plants and to protect them from insects. It is utilised too as a base in road construction and as a grid to limit the movement of fill materials in construction work.

5.11.10 Sports surfaces

The replacement of grass by artificial sports surfaces is becoming increasingly widespread. In winter, natural grass is prone to severe erosion if used for more than a few hours per week. The erosion can be all too obvious around goalmouths during a football match on a wet day! Even in summer, heavy use of sports surfaces, as in lawn tennis courts, can wear grass away.

Polyolefin fibres are now being increasingly used as artificial grass. While PP fibres have been historically used, the more sophisticated present-day systems often employ PE-based fibres, in order to achieve the required flexibility and performance. Polyolefin fibres are almost completely unaffected by ambient temperature and humidity, in that they retain their dimensions, strength and abrasion resistance. However, the presence of HALS compounds, particularly in

PP fibres, is essential, given the susceptibility of polyolefins to photodegradation. The green colour is provided by pigments dispersed within the fibres, such as chlorinated copper phthalocyanine pigments. The pigment too must be resistant to temperature, humidity and light.

5.11.11 Apparel

PP fibres have had very limited application in the fashion industry. One major drawback is the difficulty in dyeing PP textiles, especially for an industry so heavily involved with trends in fashionable colours. Nevertheless, PP textiles are used in some types of apparel. For example, PP textile garments are often worn next to the skin, because they adsorb little water. Consequently, perspiration can pass from the skin through the PP garment to an absorbent outer layer. The good wicking and low thermal conductivity of PP fibres thus keep the wearer warm and dry. PP fibres are, therefore, used in some types of underwear and socks. They are finding increasing application in sports and leisure wear, such as lightweight outerwear for climbers, walking socks, cycle shorts, swimwear and garments for divers.

5.12 Recycling

The increasing concern about the environment and the consequent legislation passed to protect it are changing the emphasis in the commercial arena from waste disposal to waste management. Thus, there is great interest in renewable materials, recyclable materials and the conversion of waste to energy, as in incineration. For polyolefins, recycling is the most feasible approach: new polyolefin textiles can be fabricated from used or waste polyolefin products. Such products are generated during production of a polyolefin textile and after use by a consumer.

In polymer production, considerable quantities of waste material may accumulate if the product fails to reach a required range of specifications. This waste normally requires no extensive cleaning, nor does it attract substantial costs for its collection. There could, therefore, be real economic benefits to the producer if the waste could be used as a partial replacement for virgin polyolefin. However, in order that it can be accepted by the extruder, the polyolefin fibre waste has to be converted into material of much higher bulk density, through repelletising (densification). Moreover, as little stress as possible must be exerted on the polyolefin material, to prevent any significant changes to its properties. Any pigment in the fibres also has to be segregated, unless the recycled material is destined for applications where the colour is unimportant.

During fabric manufacture, trimmings from the edges of a fabric can be produced, as for example with spunbonded PP. With suitable fibre extrusion equipment, the trimmings may be fed back to the extruder without the need for repelletising. The trimmings have the same additives and colorants as the virgin polyolefin, and the melt flow index is likely to be only slightly higher. The trim should comprise a maximum of no more than 10% of the total throughput rate of the polymer in the extruder, so that the slightly higher MFI will only marginally affect the processing of the polymer blend and the properties of the textile produced.

Recycling of used product, once the consumer has thrown it away, is far more complex. It involves collection of the used product and then segregation of polyolefin fibres from all the other components. Segregation includes size reduction, sorting, separation, cleaning and drying.

The polyolefin eventually isolated may still be contaminated, so that its range of end-uses becomes limited. Fabrics containing recycled polyolefins are, for example, likely to be barred from biomedical, agricultural and even industrial applications, because of concerns about residual contamination. Moreover, especially after prolonged use, the polyolefin may have been partially degraded by heat, light, oxidising chemicals and other agents. The MFI may, consequently, be substantially raised. Indeed, re-extrusion of the polyolefin may also raise the MFI, by reducing the molar mass and narrowing the molar mass distribution.

It is evident, then, that for the successful recycling of polyolefin fibre waste into high-quality repelletised material, factors such as residual contamination, colour and MFI are important. Nevertheless, the increasing demands of environmental legislation are forcing many polypropylene fibre producers to try to increase the proportion of recycled polyolefin in their products. Horrocks and co-workers have investigated the inclusion of recycled waste PP on the performance of geotextile tapes.[98,99] They have noted a significant loss in the strength of PP tape when recycled PP is added, owing to thermo-oxidative degradation. However, if suitable antioxidants are also introduced along with the recycled PP, tapes with acceptable tensile properties can be produced. Christiani *et al.* have carried out rheological analysis of PP melts, to predict the state and level of degradation of PP fibrous waste material, and hence its spinnability.[100] They concluded that a melt-spinning grade of PP could be recycled five times before the properties of the fibre became significantly impaired. After five cycles, spinnability was lost because of marked reduction in molar mass and melt viscosity.

5.13 Future trends

5.13.1 Challenges

What are the future prospects of polyolefin fibres? It seems almost certain that PP fibres will continue to play an important role in textiles, provided that supplies of propene, the source of PP, remain secure and that recycling of PP can be managed economically. There is a possibility too of a resurgence of interest in PE fibres produced by melt-spinning. There are signs of this renewed interest in biomedical applications (Section 5.11.6).

As made evident in Section 5.11, the uses of polyolefin fibres, and in particular of PP fibres, are highly diverse. Yet, despite the obvious advantages enjoyed by polyolefins, there are a number of inherent drawbacks (Table 5.2). Although some of these drawbacks can, in practical terms, be largely overcome (e.g. resistance to photodegradation, through the incorporation of HALS compounds), several still remain. Perhaps, the most prominent is the inability to dye polyolefin fibres successfully.

There is still, therefore, a clear need for further technical improvements in polyolefin fibres. These improvements can arise from superior grades of polymer and advances in processing technology. The impact of metallocene catalysts on the production of polyolefin grades has already been discussed (Section 5.3.3), and indeed catalysts of even greater promise are already being investigated.[27]

The quest to advance processing technology, particularly in the case of PP fibres, to meet such a wide variety of end-uses, continues. Efforts to produce polyolefin fibres that can be readily dyed have been discussed in Section 5.7. There is also considerable activity in the production of PP fibres of greater resilience and even interest in 'smart' PP fibres. The use of systems such as neural networks as a forecasting tool and modelling technique is also attracting interest.[101] From a production viewpoint, a model should quickly be able to predict whether a desired range of fibre specifications is in fact achievable. If the specifications can be met, then the model will enable a production manager to set up the necessary processing conditions rapidly.

The following sections highlight some of these challenges, with particular emphasis on PP fibres.

5.13.2 Improvements in fibre resilience

A major drawback with PP fibres is their poor resilience, and this problem has limited the use of PP fibres as carpet face yarns. In most carpet pile constructions, PP fibres are markedly inferior to nylon fibres in crush resistance and appearance retention. However, a number of approaches are being adopted to overcome the problem.[25] These approaches make use of inhomogeneities deliberately introduced into the fibre during processing or the effects of fibre cross-sections other than circular.

One method is the differential cooling of individual filaments in the quench chamber after they have emerged from the spinneret. By passing cold air at speed in a direction perpendicular to the path of the filaments, a differential filament structure results. The side of each filament facing the air is cooled more quickly than the opposite side, and hence the structures of the two sides differ. This difference can be enhanced on subsequent drawing.

The use of twin extruders also offers a range of possibilities. For example, PP resins of different grades can be extruded through separate metering pumps into a bicomponent spinning manifold. Alternatively, different degrees of crystallinity may be induced through the addition of a small amount of nucleating agent in one

PP melt stream, or the two streams of PP melt can be at different temperatures when they meet.

Another approach is to tailor the cross-section of the PP fibre. Cross-section has a significant impact on the mechanical performance of a synthetic fibre, and indeed on its aesthetic qualities. Both the shape and size of the cross-section are important in this respect. Spinneret holes in extrusion equipment are normally circular. Holes of different shapes will give rise to fibres with profiled, 'exotic' cross-sections. Many of these fibres produced on a commercial scale possess triangular or trilobal profiles, and in both cases fibre resilience is improved.

Yet another approach is to produce PP fibres of helical geometry. During extrusion, turbulence is generated in the PP before the filaments leave the spinneret plate. The molten filaments are then quickly cooled to induce rapid solidification. After drawing and subsequent relaxation, the fibre adopts a helical structure. The structure is composed of sections of helices in clockwise and anticlockwise directions alternately.

5.13.3 Control of fibre processing

It has become increasingly apparent in the PP fibre processing industry that better control of processing is needed. Often a traditional 'one factor at a time' approach is followed: only one process control parameter is varied at a time, while all the rest are kept constant. However, this approach has several drawbacks. Large numbers of experimental trials are needed, and the acquisition of all the data required can take a long time. Furthermore, any significant interactions existing between control parameters may well not be identified.

It has been proposed that a more soundly based alternative is an integrated approach,[76,89] comprising factorial experimental design[102,103] and comprehensive statistical analysis of the results. This approach is well established, having been first formulated by Sir Ronald Fisher many decades ago.[104] Using this approach, we may reliably estimate the level of significance of each of the processing control parameters and identify any significant interactions between them.

5.13.4 Copolymers

Optimised processing, while highly valuable, cannot remove those limitations inherent in the very nature of a polyolefin macromolecule. The limitations can, however, be tackled by adding small proportions of other materials. Additions may be made on a molecular level to produce copolymers, or on a larger scale through blending.

A number of polyolefin copolymers have been available commercially for some time. The introduction of ethene comonomer into a PP chain reduces the degree of crystallinity, and indeed the degree of crystallinity is generally lowest in copolymers containing equal proportions of ethene and propene.[105] Moreover, ethene-rich copolymers exhibit the orthorhombic form of PE and propene-rich copolymers exhibit the α-monoclinic form of PP.[105] The two types of crystal do not exist together in any PE/PP copolymer. The presence of ethene comonomers also broadens the melt temperature range, an effect useful in the production of spun-bonded non-wovens. PE/PP copolymers have also been developed for BCF yarns, and these yarns generally reveal improved resilience over standard PP yarns. Terpolymers are also available, containing propene, ethene and butene. The effects of copolymers in metallocene PP fibres have already been highlighted in Section 5.3.3.

5.13.5 Fibre blends

Although the production of polyolefin copolymers could clearly serve to overcome some of the disadvantages of polyolefin fibres, the approach may not always be viable commercially, unless one or two comonomers are identified that can confer many of the wide range of fibre properties required. An alternative approach is to incorporate other materials into the fibres to produce these properties, and indeed the incorporation of a variety of additives (Section 5.6) and of pigments (Section 5.7) has already been highlighted. In PP fibre technology, however, there is also considerable interest in utilising blending to produce fibres of enhanced mechanical performance. Thus, improvements can be achieved by the presence of fillers, such as glass or carbon fibres, but there are difficulties associated with processing. Blending with filler fibres can create a melt of increased viscosity, and it is consequently more difficult to obtain a uniform distribution of the filler in the PP fibre matrix. The extrusion equipment tends to be subjected to greater wear and tear, and the filler fibres are prone to fragmentation during processing. In addition, the reinforcing effect of the filler fibres will not be transferred to the PP fibre matrix unless there is good interfacial adhesion between the filler and PP phases.

Some of these difficulties may be less pronounced if fillers containing particles or fibres of nanometre dimensions are used. For example, the incorporation of nano carbon fibres as a minor component has been shown to provide PP fibres with some improved mechanical properties.[106] However, whatever property they confer, the blending of nano-materials into a polyolefin requires care: where significant pressure is experienced by the nano-material, its particles are liable to compact into aggregates, and the nano-scale benefits are lost. Nevertheless, there is currently considerable research activity in the application of nano-materials that will enhance specified fibre properties without impairing other properties, and it is likely that developments on a commercial scale will result.

An alternative approach is to blend polyolefin fibres with a small proportion of a thermotropic liquid crystalline polymer (TLCP), which exhibits liquid crystalline properties in the desired melt temperature range. This strategy has been discussed for PP fibres.[88] As with PP, a TLCP can be melt extruded. These TLCPs generally possess chains containing rigid rod-like structures, which can be readily aligned in the direction of flow during melt extrusion. Thus, TLCPs exhibit surprisingly low viscosities when in the liquid crystalline state, a property that would facilitate PP fibre extrusion. Not only can improvement of PP fibre mechanical performance be provided, but also less energy is likely to be used during melt extrusion, owing to the reduced viscosity of the melt that the TLCP component confers. The PP blend fibre can also have lower thermal shrinkage[107] and better resistance to creep. However, care has to be taken to prevent fragmentation of the TLCP component during the drawing stage.

In these blends, the TLCP component exists as tiny fibrils inside the PP matrix. Other matrix/fibril bicomponent fibres, in which the PP component forms the matrix, are also attracting interest. Among these are PP/PE fibres designed to improve fibre handle, and blends of PP and polyester to enable dyeing. Skin–core bicomponent fibres have also been developed. One example is a fibre with a PP core and a PE sheath, which has application in spun-bonding technology. The lower melt temperature of the PE sheath, compared with the PP core, allows bonding of the web at a lower temperature without affecting the mechanical properties of the core PP.

5.13.6 Auxetic PP fibres

Auxetic materials possess a negative Poisson's ratio, ν: in contrast to most materials, they become thicker when stretched, with an increase in void volume. This behaviour contrasts with that of hard-elastic fibres (Section 5.9), whose diameter remains constant on fibre stretching, before decreasing.[20] A wide variety of auxetic materials have now been produced since the successful synthesis of auxetic polymeric foams in 1987.[108] Among these materials are auxetic versions of PP,[109] ultra-high molecular weight PE[110] and, recently, PP fibres.[111]

It has been demonstrated that auxetic fibres can be processed by melt-spinning with some novel modifications. In particular, a low processing temperature seems to be required throughout the extrusion equipment. Indeed, it has been reported that a temperature as low as 159 °C can achieve the formation of auxetic PP fibres.[111] The fibres were not subsequently drawn. The Poisson's ratio obtained for these fibres was -0.60 ± 0.05. The auxetic behaviour of these PP fibres was, therefore, found to be more pronounced than that of PP rods, reported previously,[109] for which $\nu = -0.22$. Characterisation by scanning electron microscopy revealed that the PP fibres possessed a modified version of the typical auxetic polymeric microstructure of nodules connected to one another by fibrils.

While it is clear that considerable development of auxetic PP fibres is yet required, applications for them can already be envisaged. Auxetic PP fibres may find application in composite materials, owing to enhancements in fibre fracture toughness, increased energy absorption capabilities and reduced fibre pull-out.[112] A further application may be for drug release materials, where the auxetic fibres contain wound-healing particles trapped within the pores of the fibre structure. If a wound, covered by a bandage containing these fibres, swells as a result of infection, the stretching of the fibres will be accompanied by an increase in their width. This auxetic effect will enlarge the pores in the fibres and enable the release of a wound-healing agent.

5.13.7 Plasma treatments

The application of plasma treatments offers exciting technological developments for the future, especially as equipment on a commercial scale is becoming increasingly available. With this technique, fibre surfaces can be modified, while the fibre bulk remains unaffected.

Plasma is an electric glow-discharge of a gas. There are many everyday examples of plasmas, such as fluorescent lighting and neon signs. In these cases, the objective is to produce light, but plasma can equally be utilised for modifying solid surfaces. The plasma atmosphere comprises a mixture of ions, free radicals, electrons and UV radiation. The interactions of all these species with one another and with a solid surface, therefore, constitute a complex process.

A variety of different gases may be used for plasma treatments, and even mixtures of gases have been tried. Depending on the nature of the gas and the conditions under which the plasma is generated, different effects may be experienced by the solid surface. In the case of synthetic fibres, a number of possible effects can be identified. Thus, plasma treatment with a noble gas such as helium or argon may alter the detailed topography of the surface, to generate roughness on a micro-scale and increased surface porosity. Plasma treatment may, additionally, alter the chemical nature of the surface through the introduction of various functional groups within the polymer chains at the fibre surface. Gases such as oxygen, nitrogen and ammonia may give this effect. Plasma treatment may cause the deposition of a very thin polymeric coating on the fibre surface. This polymeric coating has a highly crosslinked structure. Hydrocarbons and fluorocarbons can, for example, bring about plasma polymerisation.

Plasma treatments may be given under atmospheric or vacuum conditions. In processing terms, plasma equipment operating under atmospheric conditions can be incorporated in a production line,[113] but modification of the fibre surface is often less stable and less reproducible. Vacuum plasma treatments, on the other hand, require more sophisticated equipment but provide stronger, more stable fibre surface modifications.[114]

There are a number of attractions in the application of plasma treatments to polyolefin fibres. Coating techniques traditionally provide means of adapting fabric surfaces to confer particular desired properties, but polyolefin textile surfaces are more difficult to coat successfully than many other synthetic fibre surfaces. Thus, plasma treatment offers an alternative approach, which is also, importantly, a ‘clean’ technology in an environmental sense.

For any application of polyolefin fibres which requires good interaction with more polar environments, notably aqueous environments, the hydrophobicity of the fibre surface becomes a disadvantage. With the aid of suitable plasma treatments, such as oxygen plasma treatments, the fibre surfaces become more hydrophilic owing to the introduction of polar groups at the surface. This modification confers, for example, greater biocompatibility, given that the majority of fluids in the body are aqueous based. Greater hydrophilicity is, therefore, advantageous for such applications as scaffolds, wound dressings and blood filters.

The mechanisms by which oxygen and other gases confer increased hydrophilicity on polyolefin fibre surfaces are far from completely resolved. It has, however, been demonstrated that, when PP is treated with oxygen plasma, there is negligible insertion of oxygen as a result of reaction with active sites on the polymer.[115,116] It appears, instead, that there is formation of a surface layer of a random copolymer consisting of oxidised and unaltered segments. The layer, once formed, then rearranges itself over time, to lower the free energy at the fibre surface.

Polyolefin fibre surfaces may also be made more oleophobic. This increased resistance to oils can be useful in some filtration systems. Increased hydrophobicity can be conferred by plasma treatment with a fluorocarbon, such as tetrafluoromethane or hexafluoroethane. Although these gases are expensive, very little is required for surface modification. Fluorocarbon plasma treatments cause the deposition of fluorinated plasma polymers. One report has shown that a variety of fluorinated functional groups are present at the fibre surface.[117] These groups include $–CHF$, $–CF_2–$, $–CF_3$ and even $–CH_2–CF_2–$.

An important technological aspect is the durability of plasma treatments. It is known, for example, that the wettability of PP films treated with ammonia plasma gas decreases over a period of time. However, durability can often be enhanced through pretreatment with helium or argon gas plasma, which increases the mechanical resistance of a fibre surface through cross-linking of the polymer chains at the surface.[3]

Another important result of plasma treatment is manifest as changes in the topographical nature of the fibre surface. Different changes of the surface topography can be effected by different plasma gases and varying conditions of exposure. It has been shown, for example, that extended exposure to oxygen plasma causes pitting of PE fibre surfaces.[3] This pitting is helpful in promoting adhesion between PE fibres and resin in composites, because the pitted structure can be penetrated by the resin to confer better mechanical keying.

To obtain a clearer understanding of the effects of plasma treatments on polyolefin fibre surfaces will require a combination of sophisticated experimental techniques. While changes in wettability can be readily assessed by the determination of contact angles of drops of water on a fabric, it has also been shown that environmental scanning electron microscopy can be utilised to determine the contact angle of water (and oils) on individual fibres in the fabric.[118] Furthermore, advanced microscopy techniques are needed to study the changes in surface topography, and indeed the value of atomic force microscopy in this respect has recently been reported.[119] For studying the chemical changes induced at the fibre surface, X-ray photoelectron spectroscopy is a valuable tool.

5.14 Conclusion

In commercial terms, by far the majority of melt-spun polyolefin fibres are PP fibres,[6,7] and these look to have a bright commercial future. Their technological advantages render them well placed to meet the variety of innovative demands they are likely to face over the coming years. At the same time, many of their inherent disadvantages are being steadily overcome by the use of suitable additives, as discussed in Section 5.6. Nonetheless, in order to meet future technological demands, improvements in polyolefin fibre performance will continue to be required.

The achievement of these improvements can embody a number of approaches. Thus, systematic experimental design techniques, of the kind outlined in Section 5.13.3, will provide useful ways of gauging which fibre processing conditions, and which combinations of them, have significant influences on a set of required technological applications. Processing conditions to meet these specifications can then be optimised. Following optimisation, neural networks and other suitable techniques can be applied as forecasting tools to link polyolefin fibre processing and performance.[101]

However, useful though all these techniques are, the future of polyolefin fibre processing on an industrial scale will need to be underpinned by even more detailed understanding of the structural changes occurring during fibre processing. While it is evident that considerable progress has been made over the last decade or so, notably with polyethylene,[90–92] the application of advanced microscopic techniques, such as scanning probe microscopy and environmental scanning electron microscopy (ESEM) should help to progress our understanding still further. Particularly exciting are the possibilities that ESEM offers for real-time *in situ* studies of polyolefin fibre drawing.

The next few years may also see further innovations in the effectiveness of additives, particularly flame-retardant, antimicrobial and antistatic additives, and even antioxidants. The dyeing of polyolefin fibres still remains one of the most elusive challenges.

Finally, the coming years are bound to witness more stringent demands and legislation for the recycling and regeneration of synthetic fibres; the recycling of polyolefin fibres has been already discussed in Section 5.12. Moreover, the technologies used for the production of polyolefin fibres will require to be ‘clean’. However, in comparison to many other synthetic fibres, polyolefin fibres are arguably well set to meet these important environmental challenges.[120]

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