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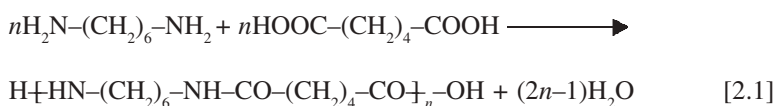
Nylon polymers can be formed in many ways. The four most important for industrial polymers are:

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.

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

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

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:

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

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).

$$n HN(CH_2)_5 CO + H_2O \longrightarrow n H_2N(CH_2)_5COOH \qquad [2.3]$$

$$nH_2N(CH_2)_5COOH \longrightarrow H[HN(CH_2)_5CO]_n\text{–}OH + nH_2O \quad [2.4]$$

$$nHN(CH_2)_5CO \longrightarrow [HN(CH_2)_5CO]_n \quad [2.5]$$

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:

$$[HN(CH_2)_{10}CO]_n \quad [2.6]$$

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]

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

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 °C, 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:

$$[HN(CH_2)_4NHOC(CH_2)_4CO]_n \quad [2.8]$$

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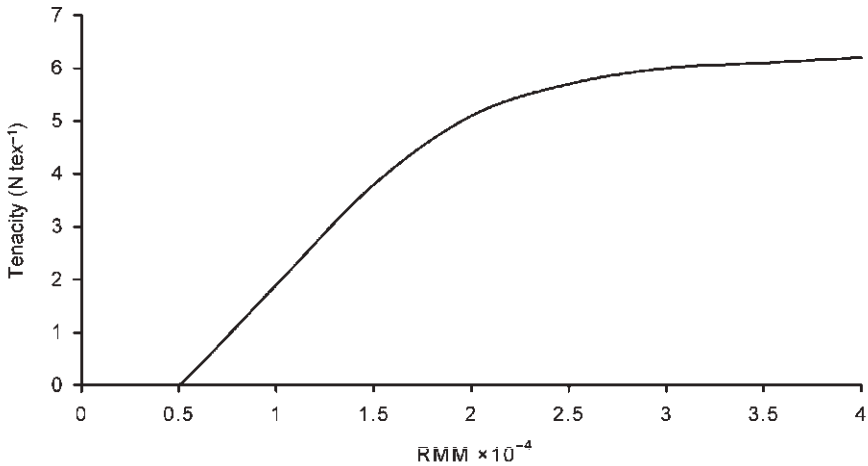
2.1 Schematic graph of the effect of the polymer relative molecular mass (RMM) on the nylon fibre tenacity.

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

$$n_x = p^{x-1}(1 - p) \qquad [2.10]$$

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:

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

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:

$$P_w = \frac{(1 + p)}{(1 - p)} \qquad [2.12]$$

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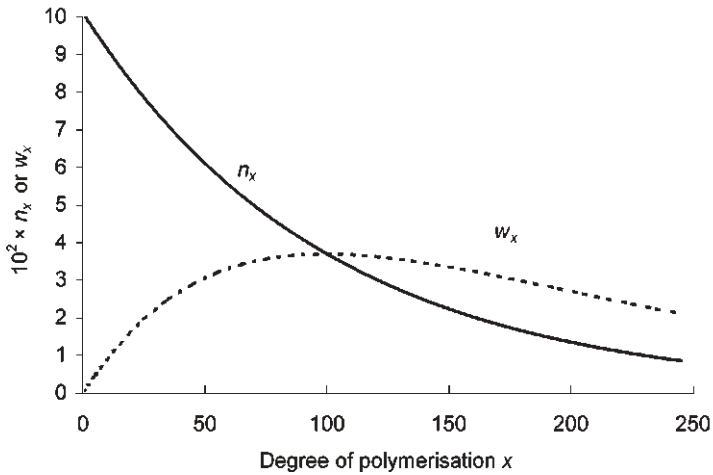
2.2 Most probable molecular mass distribution for nylon showing variation of mole and weight fraction for $p = 0.99$.

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:

$$-NH_2 + HOOC- \rightleftharpoons -NHOC- + H_2O \qquad [2.13]$$
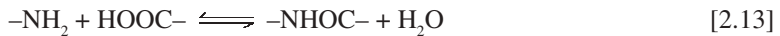
The equilibrium constant for the reaction is therefore:

$$K = \frac{[-NHOC-][H_2O]}{[-COOH][-NH_2]} = B \exp \{-\Delta H_a/RT\} \qquad [2.14]$$

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 °C there will be residual water content within the polymer. For nylon 6,6 at equilibrium at 280 °C 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.
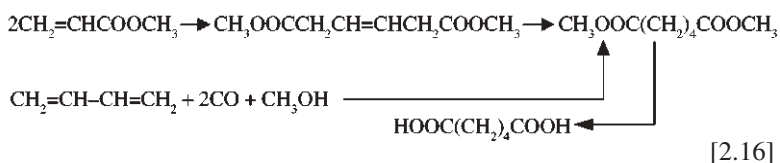
2.3.5.1   Adipic acid

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]
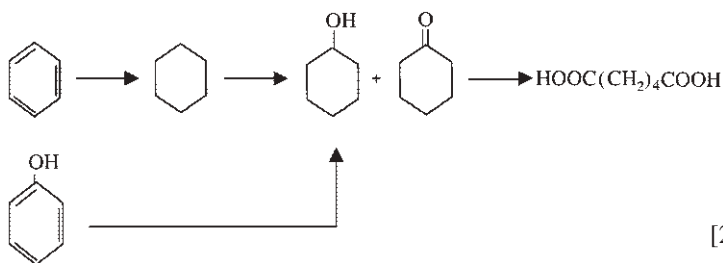
An alternative route to adipic acid involves the dimerisation of methyl acrylate (methyl propenoate) to form dimethyl hexenoate. This is carried out either electrolytically or by coupling using a transition metal catalyst; the latter process was patented by ICI.[27] Hydrogenation and hydrolysis of dimethyl 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:

$$2CH_2=CHCOOCH_3 \rightarrow CH_3OOCCH_2CH=CHCH_2COOCH_3 \rightarrow CH_3OOC(CH_2)_4COOCH_3$$

$$CH_2=CH-CH=CH_2 + 2CO + CH_3OH$$

$$HOOC(CH_2)_4COOH$$

[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):

$$HOOC(CH_2)_4COOH \rightarrow H_2NOC(CH_2)_4CONH_2 \rightarrow NC(CH_2)_4CN \quad [2.17]$$

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

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:
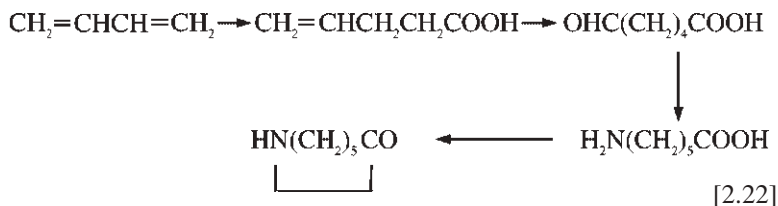

$$[2.20]$$
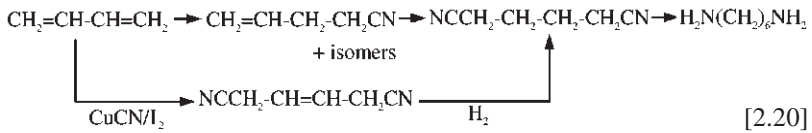
2.3.5.3   Caprolactam

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):

$$\text{(cyclohexanone)} \xrightarrow{(NH_3OH)HSO_4} \text{(cyclohexanone oxime, NOH)} \xrightarrow{\text{Oleum}} HN(CH_2)_5CO \qquad [2.21]$$
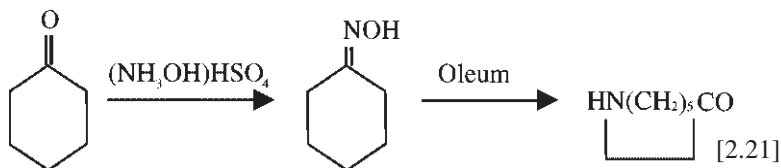
DSM has developed a hydroxylamine phosphate oxime process (HPO). An aqueous mixture of nitric and phosphoric acids is reduced with hydrogen using a palladium catalyst to form the hydroxylamine phosphate, which is then reacted with the cyclohexanone dissolved in toluene.[33] The oxime is formed in the 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:

$$CH_2=CHCH=CH_2 \rightarrow CH_2=CHCH_2CH_2COOH \rightarrow OHC(CH_2)_4COOH$$

$$HN(CH_2)_5CO \longleftarrow H_2N(CH_2)_5COOH \qquad [2.22]$$

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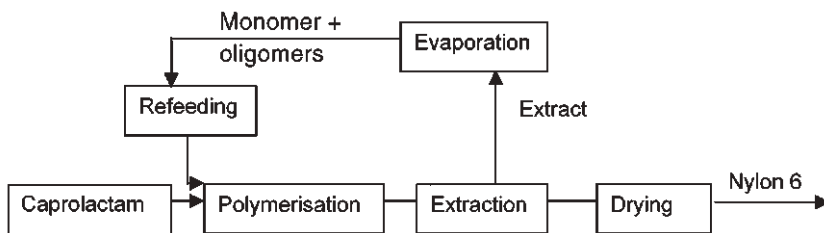
2.3 Block flow diagram of a continuous nylon 6 polymerisation process.

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-tempera-ture 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]
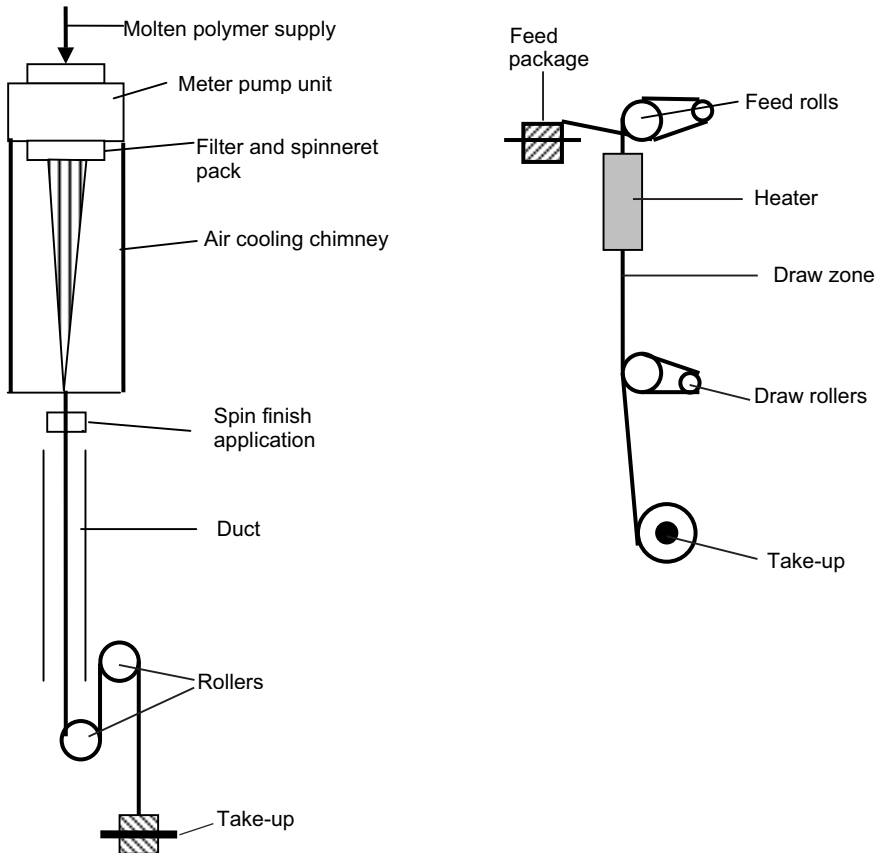
The concentration of oligomers in the polymer for nylon 6 can be as high as 10 %. Most of this is unreacted caprolactam but some cyclic dimer and higher oligomers are present. The oligomers may be removed by hot aqueous or vacuum extraction. The aqueous extraction can be used only if the polymer emerging 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

Molten polymer supply

Meter pump unit

Filter and spinneret pack

Air cooling chimney

Spin finish application

Duct

Rollers

Take-up

Feed package

Feed rolls

Heater

Draw zone

Draw rollers

Take-up

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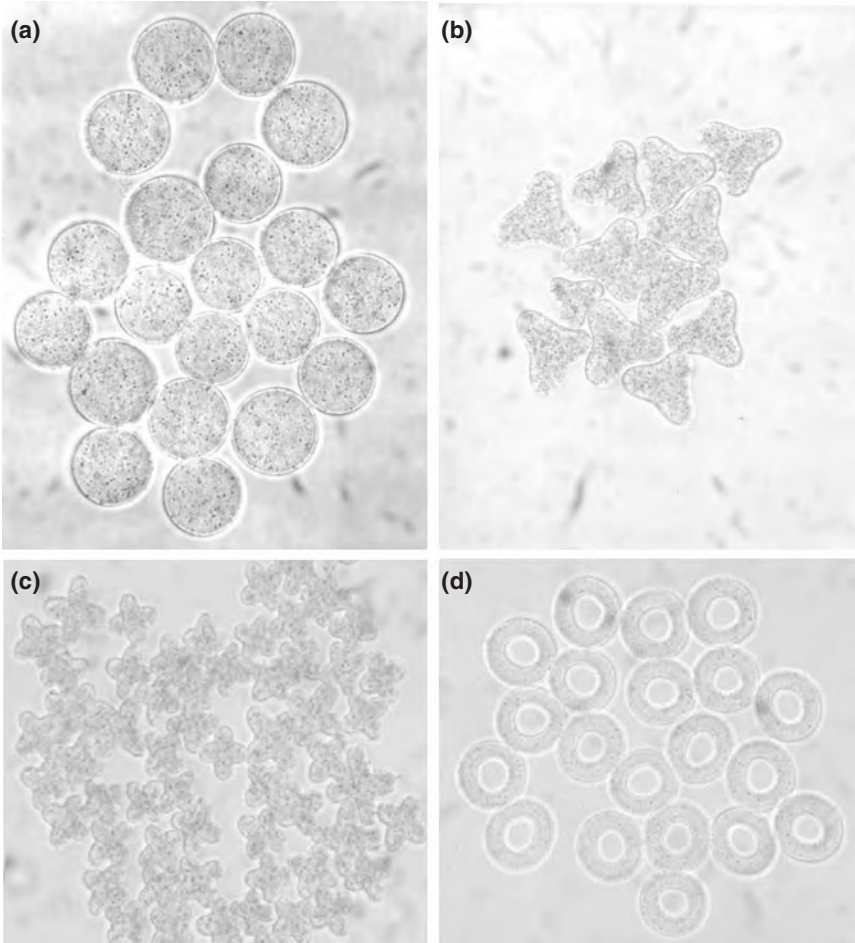
2.5 Nylstar *Meryl*® nylon fibres with (a) round cross-section; (b) trilobal; (c) tetralobal; and (d) hollow cross-section (by courtesy of Nylstar; *Meryl* is a registered trade mark of Nylstar).

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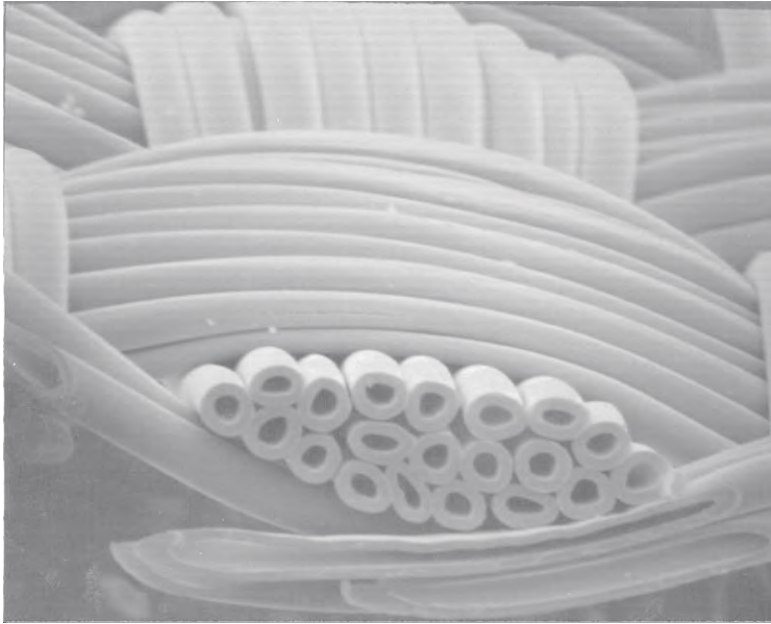
2.6 Nylstar *Meryl*® *Nexten* hollow fibres in a woven fabric (by courtesy of Nylstar; *Meryl* is a registered trade mark of Nylstar).

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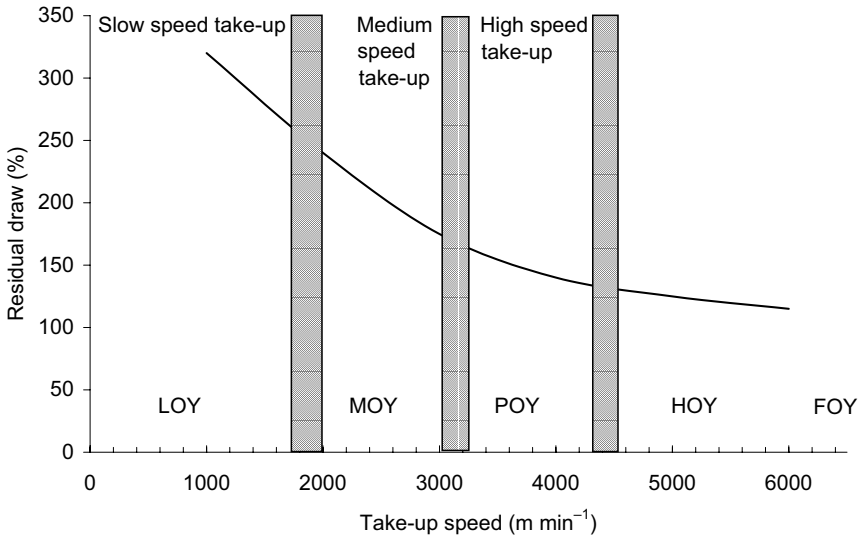
2.8 Dependence of the residual draw ratio of nylon on the take-up speed.
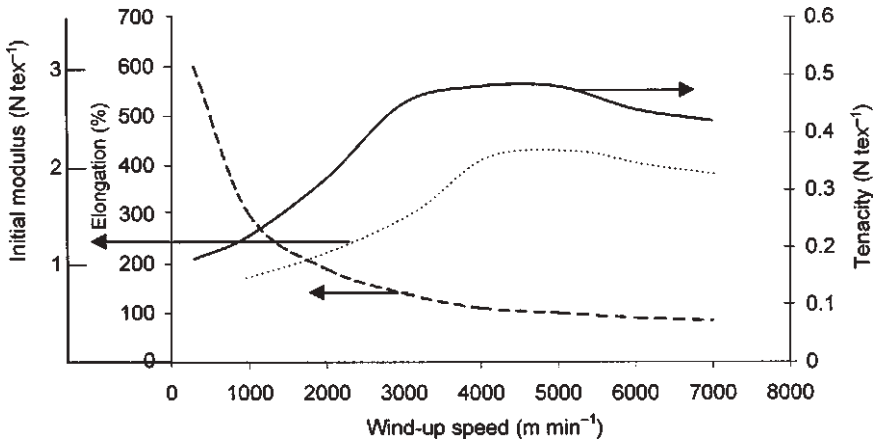
2.9 Effect of take-up speed on the tenacity (——), extension at break (– – –) and initial modulus (······) of nylon 6 fibres.

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 °C 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.
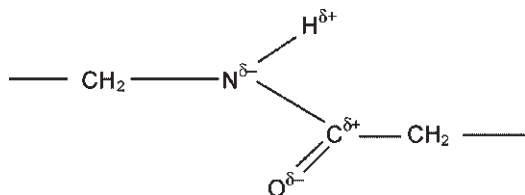
2.5.1   Fibre structure

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.

$$\text{---CH}_2\text{---N}^{\delta-}\begin{array}{c}\text{H}^{\delta+}\\ \\ \text{C}^{\delta+}\text{---CH}_2\text{---}\\ \parallel\\ \text{O}^{\delta-}\end{array}$$
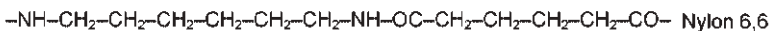
The polarity enables the carbonyl oxygen from an amide group in one molecule to attract and hydrogen bond with an amide hydrogen in another molecule. It also leads to an appreciable double bond character in the carbon–nitrogen bond and inflexibility in the group. Puffr explained this effect in terms 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.

$$-NH-CH_2-CH_2-CH_2-CH_2-CH_2-CO- \hspace{3cm} \text{Nylon 6}$$

$\longrightarrow$

$$-NH-CH_2-CH_2-CH_2-CH_2-CH_2-CH_2-NH-OC-CH_2-CH_2-CH_2-CH_2-CO- \hspace{0.3cm} \text{Nylon 6,6}$$

$\longleftrightarrow$

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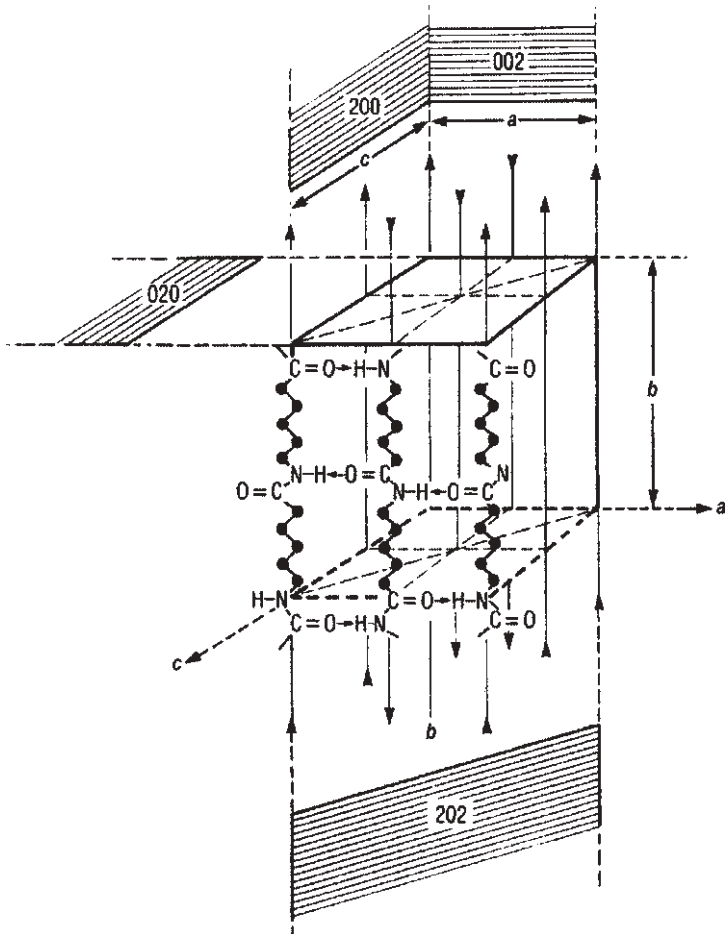
2.10 Unit cell of the α-form of nylon 6.

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
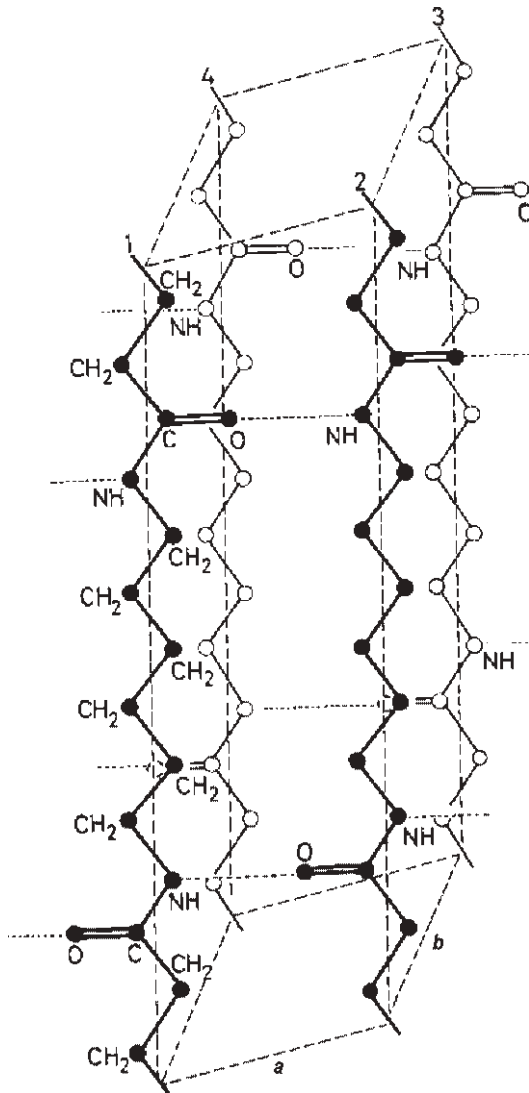
2.11 Unit cell of nylon 6,6.

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
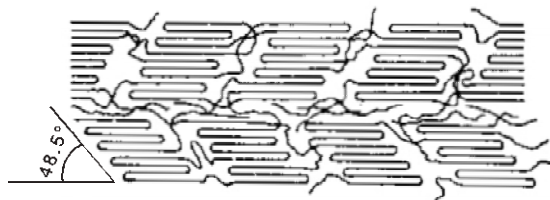
2.12 Modified fringed fibril structure with molecular folding for nylon.

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 °C 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.
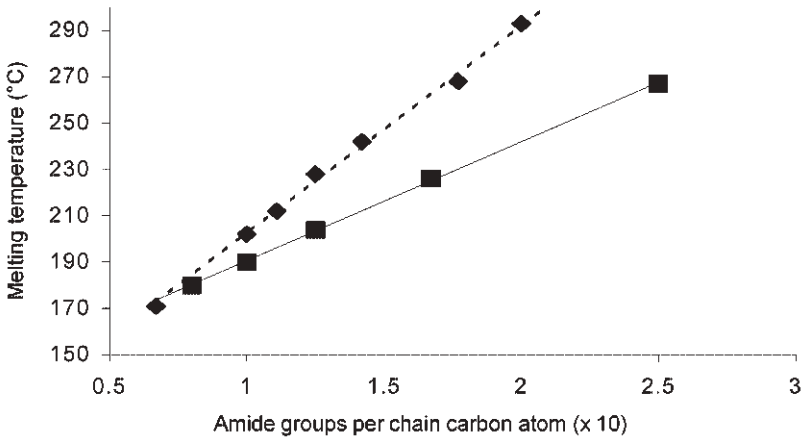
2.5.3   Thermal properties

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

Property	Temperature, °C	
	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
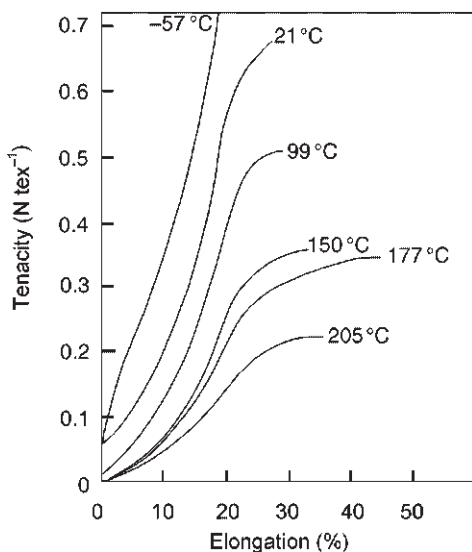
2.14 Effect of temperature on the tensile properties of nylon 6,6.

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 inter-chain 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 exten-sion is able to occur.[76]

The importance of the glass transition temperature in fibres is that the poly-mer 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 character-istics 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]

$$-CH_2-COOH + HOOC-CH_2- \longrightarrow -CH_2-CO-CH_2- + CO_2 + H_2O \qquad [2.24]$$

$$-CH_2-NH_2 + H_2N-CH_2- \longrightarrow -CH_2-NH-CH_2- + NH_3 \qquad [2.25]$$

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):

$$R-CONHCH_2CH_2-R' \longrightarrow R-CONH_2 + CH{=}CH-R'$$
$$\downarrow$$
$$RCN + H_2O \qquad [2.26]$$
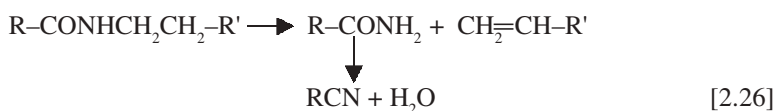
When nylon 6,6 is heated, considerable amounts of cyclopentanone are formed. This is a by-product of heating adipic acid end groups, which tend to cyclise and lose carbon dioxide and water (eq. 2.27). The formation of cyclopentanone is accompanied by an increase in the number of amine end groups owing 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]
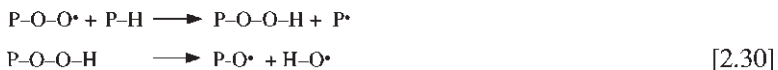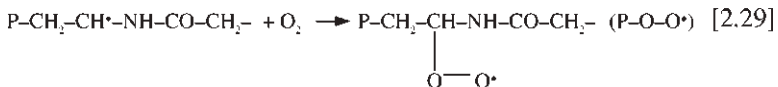

$$[2.27]$$
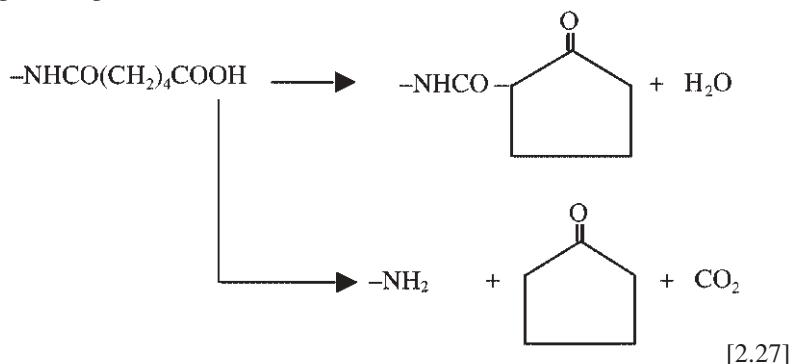
2.5.7.2   Oxidation

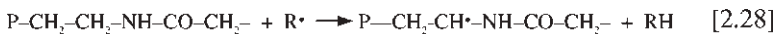Exposure of nylon 6,6 and 6 to air at temperatures above 100 °C results in a loss of both tenacity and breaking elongation. Figure 2.15 shows the effect of temperature and exposure time in air on the retained tenacity of nylon 6 and 6,6 yarns.[102] The changes are accompanied by discoloration and a reduction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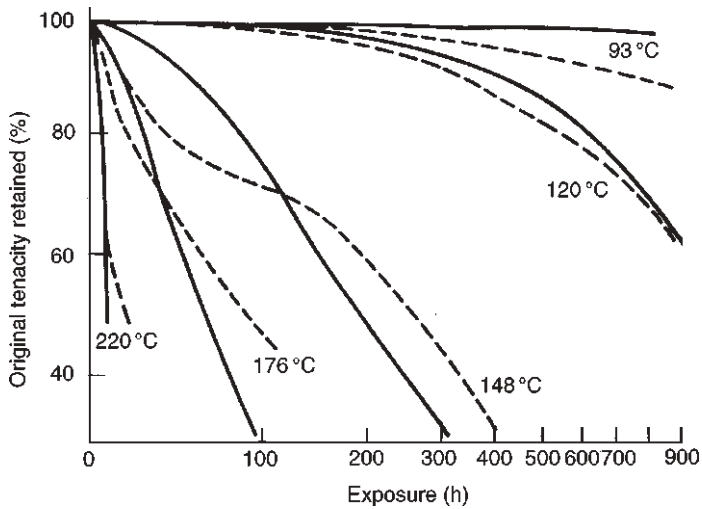
2.15 Effect of temperature and heating time in air on the retained tenacity of nylon 6 (——) and nylon 6,6 (– – –).

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):

$$P-CH_2-CH_2-NH-CO-CH_2- \; + \; R^\bullet \longrightarrow P-CH_2-CH^\bullet-NH-CO-CH_2- \; + \; RH \qquad [2.28]$$

$$P-CH_2-CH^\bullet-NH-CO-CH_2- \; + O_2 \longrightarrow P-CH_2-CH-NH-CO-CH_2- \; (P-O-O^\bullet) \quad [2.29]$$
$$\overset{|}{\underset{O-O^\bullet}{}}$$

$$P-O-O^\bullet + P-H \longrightarrow P-O-O-H + P^\bullet$$
$$P-O-O-H \longrightarrow P-O^\bullet + H-O^\bullet \qquad [2.30]$$

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 ultra-violet 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]

$$-CH_2-CH_2CHO + H_2N-CH_2- \longrightarrow -CH_2-CH=CH-CH=N-CH_2-CH_2- + H_2O$$

$$+ \text{by-products} \qquad [2.31]$$
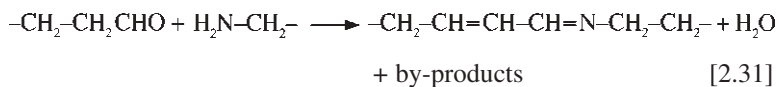
When nylon 6 or 6,6 is exposed to air at temperatures above the melting point, the fibre properties are no longer of interest, but the products of combustion have important implications for the use of nylons in applications (e.g. upholstery in vehicles and aircraft) where combustion in confined places 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]
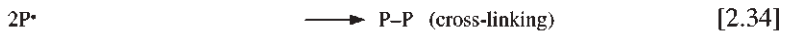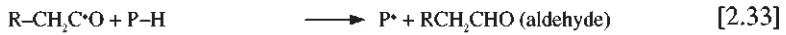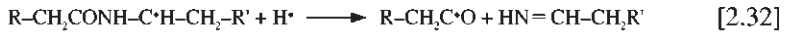
Considerable efforts have been made to increase the flame resistance of nylon by promotion of char formation and eliminating dripping polymer melt by means of copolymerisation, or the addition of flame retardants. Any additives used must be stable under the usual melt extrusion conditions and must

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:

$$R-CH_2CONH-C^•H-CH_2-R' + H^• \longrightarrow R-CH_2C^•O + HN=CH-CH_2R' \qquad [2.32]$$

$$R-CH_2C^•O + P-H \longrightarrow P^• + RCH_2CHO \text{ (aldehyde)} \qquad [2.33]$$

$$2P^• \longrightarrow P-P \text{ (cross-linking)} \qquad [2.34]$$

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
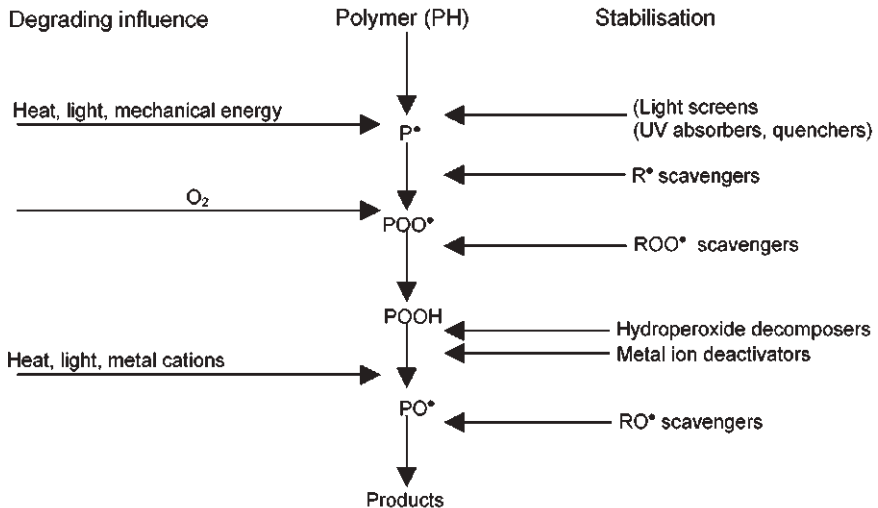
2.16 Scheme of degradation processes and stabiliser functions for nylon.

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, $R^•$ and $ROO^•$, 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:

$$POO^\bullet + Cu^+ \longrightarrow POO^- + Cu^{2+} \tag{2.35}$$

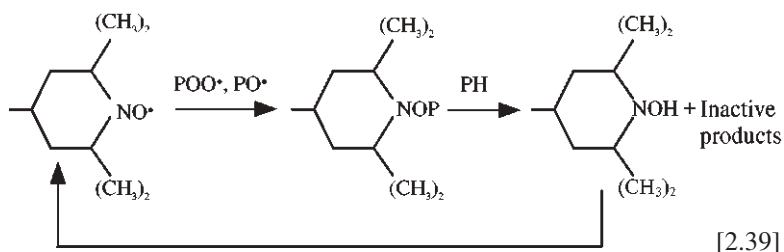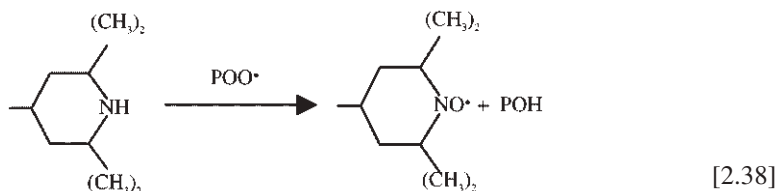$$P^\bullet + Cu^{2+} \longrightarrow P^+ + Cu^+ \tag{2.36}$$

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:

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

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:

$$(CH_3)_2 \quad \xrightarrow{POO^\bullet} \quad (CH_3)_2$$
NH $\quad\longrightarrow\quad$ NO$^\bullet$ + POH
$$(CH_3)_2 \qquad\qquad (CH_3)_2 \qquad\qquad [2.38]$$

$$(CH_3)_2 \xrightarrow{POO^\bullet,\ PO^\bullet} (CH_3)_2 \xrightarrow{PH} (CH_3)_2$$
NO$^\bullet$ $\quad\longrightarrow\quad$ NOP $\quad\longrightarrow\quad$ NOH + Inactive products
$$(CH_3)_2 \qquad\qquad (CH_3)_2 \qquad\qquad (CH_3)_2$$
$$[2.39]$$

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
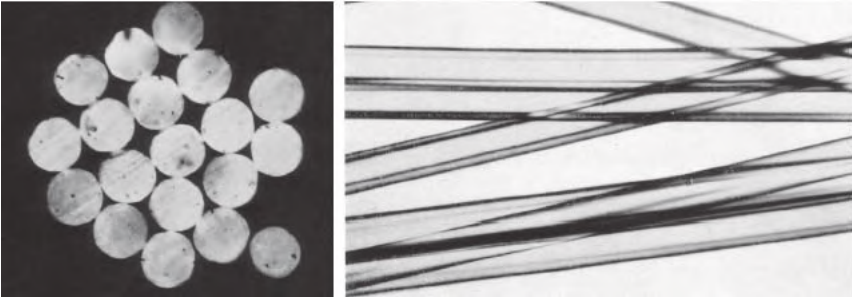
2.17 Transverse and longitudinal cross-sections of bright nylon 6,6 fibres.
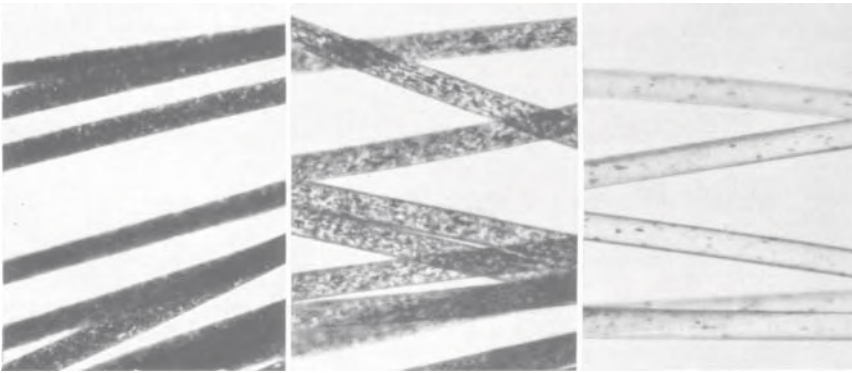
2.18 Nylon fibres with three levels of titanium dioxide: left, matt fibre 2% TiO_2; centre, semi-matt fibre, 0.3% TiO_2; right, bright fibre 0.03% TiO_2.

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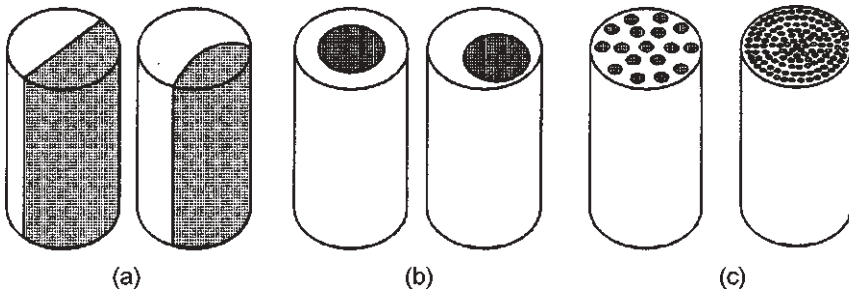
2.19 Bicomponent fibres: (a) side by side, (b) sheath–core, (c) islands in the sea.

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/poly-urethane 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 compo-
nents, 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 dimension-
ally 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:

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

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

Direct   Islands in the sea   Separation
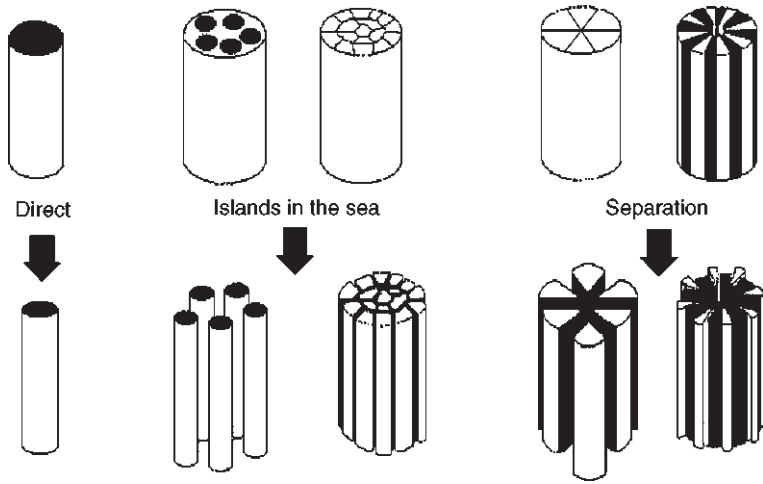
2.20 Methods of production of microfibres.

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 mono-sodium 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 pro-gramme, 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.

2.10   References

1. Mark H. and Whitby G.S., eds, Collected Papers of Wallace Hume Carothers on High Polymeric Substances, Vol I, Interscience Publishers, New York,1940.
2. Kaufman G.B., 'Nylon at 50', *Chem Tech*, 1988, **17**(12), 725.
3. Anton A., *Encyclopaedia of Chemical Technology*, Vol 19, 4th Edition, 1992, p. 520.
4. Thomas M., 'Happy birthday nylon!' *Text World*, 1988, **138**(3), 61.
5. Schlack P.A., 'Ein Leben für Forschung, Fortschitt und Lehre', *Chemifasern/ Textilindustrie*, 1967, **117**, 961.
6. Klare H., *Technologie und Chemie der Synthetischen Fasern aus Polyamiden*, Verlag Technik, Berlin, Germany, 1954, p. 13
7. Carothers W.H. (to E I du Pont de Nemours & Co., Inc.), Linear condensation polymers, US Patent Office, Pat No 2 071 250, February 1937.
8. Carothers W.H. (to E I du Pont de Nemours & Co., Inc.), Linear condensation polymers, US Patent Office, Pat No 2 071 253, February 1937.
9. Carothers W.H. (to E I du Pont de Nemours & Co., Inc.), Linear polyamides and their production, US Patent Office, Pat No 2 130 523, September 1938.

10. Carothers W.H. (to E I du Pont de Nemours & Co., Inc.), Synthetic fibers, US Patent Office, Pat No 2 130 948, September 1938.

11. International Rayon and Synthetic Fibres Committee (CIRFS) Annual Statistics 2000, http://www.cirfs.org/04–01.htm

12. Cubbon R., 'Synthetic polymer fibres', *Makromol Chem*, 1964, **80**, 44.

13. Rumsey J.S., 'The introduction of Qiana Nylon', *Modern Textiles*, 1970, **51**(2), 48.

14. Roerdink E.and Warnier J.M.M., 'Preparation and properties of high molar mass nylon 4,6', *Polymer*, 1985, **26**(10), 1582.

15. Rhodia product information, http://www.rhodia-filtec.com/en/products/industrial_ app. htm

16. DuPont Tynex product information, http://www.dupont.com/enggpolymers/filaments. html

17. Walczak Z.K., in *Formation of Synthetic Fibres*, Gordon and Breach, New York, 1977, p. 269.

18. Flory P.J., in *Principles of Polymer Chemistry*, Cornell UP, Ithica, NY, 1953, p. 122.

19. Hermans P.H., Heikens D. and van Welden P.F., 'Direct analytical test of the Flory– Schultz distribution in nylon 6 type equilibrium polymers', *J Polymer Sci*, 1955, **16**, 451.

20. Fukomoto O., *J Polym Sci*, 1956, **22**, 263.

21. Reimschuessel H.K., 'Nylon 6 polymerisation: chemistry and mechanism', *J Polym Sci Macromol Rev*, 1977, **12**, 65.

22. Gooding C.M., Neal R.H.and Valteich H.W. (to The Best Foods Inc.), Stabilisation of cheese, US Patent Office, Pat No 2 485 637, 1949.

23. Bergman K., 'Latest developments in polyamide 6 production technology and polymer modification', *Chem Fibres Int*, 2000, **50**, 536–539.

24. Winnick C.N. (to Halcon International Inc.), Oxidation of hydrocarbons by borate esters, US Patent Office, Pat No 2 243 449, 1966.

25. Russell J.L. (to Halcon International Inc), Cyclohexane oxidation, US Patent Office, Pat No 3 932 513, 1976.

26. BASF AG., Continuous production of alkane dicarboxylic acids, The Patent Office, London, Pat No 1 092 603, 1969.

27. Carus B. and Leyshon D.M., (to ICI), Hexamethylene diamine, The Patent Office, London, Pat No 1 123 683, 1968, also Neth. Patent No 6 515 869, 6 515 603.

28. Platz R., Kummer R., Schneider H.W. and Schwirten, K. (to BASF), Pent-3-enoic acid and its alkyl esters, Ger Pat No 2 630 086, 2 646 955, 1978.

29. Howk B.W. (to E I du Pont de Nemours & Co., Inc.), Catalytic hydrogenation of adipo- nitriles to produce hexamethylenediamines, US Patent Office, Pat No 2 166 151, 1937.

30. Anon., 'A glance at making adiponitrile electrolytically', *Chem Eng*, 1965, **72**, 80–82.

31 Drinkard W.C. (to E I du Pont de Nemours & Co., Inc.), Addition of hydrogen cyanide to butadiene, US Patent Office, Pat No 3 547 972, 1970.

32. Baird W.C. and Surridge J.H., 'Halogenation with copper(II) halides: synthesis of dihydroadiponitrile', *J Org Chem*, 1971, **36**, 2898.

33. Do Rooij A.H. (to Stamicarbon NV), Preparing solution containing hydroxylammonium salt, The Patent Office, London, Pat No 1 094 221.

34. Van der Linde S., 'How to solve the caprolactam dilemma', *Chem Fibres Int*, 2000, **50**, 328–330.

35. British Rubber and Plastics on line, http://www.polymer-age.co.uk/archive30, 2000.

36. Zimmerman J., in *Encyclopaedia of Polymer Science and Technology* Vol. 11; *Polyamides*, Interscience Publishers, New York, 1981, p. 331.

37. Reimschuessel H.K., in *Fiber Chemistry*, editors Lewin M. and Pearce E.M., Marcel Dekker, New York, 1996 p. 131.
38. Bergman K., 'Latest developments in polyamide 6 production technology and polymer modification, *Chem Fiber Int*, 2000, **50**, 536–539.
39. Stibal W. and Schmidt G., 'New cost effective PA6 production', *Chem Fibres Int*, 2000, **50**, 331–333.
40. Enka Tecnica, Product Information: Spinnerets and Spin Packs, 2002.
41. Borovskii V.R., Klochko N.F., Pankeev A.M. and Polovets L.M., *Khimicheskiye Volokna*, 1974, **3**, 23.
42. Rhodia Noval Opal product information, http://www.performance-fibres.rhodia.com/front-office.
43. Anton A., Johnson K.A. and Jansson P.A., 'Characterisation of fibre lustre via image analysis', *Text Res J*, 1978, **48**(5), 247.
44. Minetti S. and Staiano B., 'PA6/66 Fibres with modified cross-section', Paper to 39th International Man-made Fibres Congress, Dornbirn, 2000, http:// www.nylstar.com/all/news/f_mmf.
45. Kanebo Lightron product information, http://www.kanebotx.com/english/gohsen/index.htm.
46. Nystar Meryl® Nexten product information, http://www.nylstar.com/all/products/produ-next.html.
47. DuPont Antron® carpet yarn product information, http://antron.dupont.com/content/fiber/ant04_03_01.shtml.
48. Ziabicki A., *Fundamentals of Fibre Formation*, Wiley Interscience, London, 1976., pp. 184–186.
49. Bell J.P., 'The effect of temperature and rate of drawing on the properties of nylon 6,6 fibre', *Text Res J*, 1972, **42**, 292.
50. Shimizu J. *et al.*, *J Soc Fiber Sci Technol Jpn*, 1981, **37**(4), T143.
51. LVD Lummus International product information, http://www.lvdlummus.com/prod/towc.htm.
52. D.M. & E. Corporation product information, http://www.dmecutter.com/Equipment/Cutters/.
53. Wilson D.K. and Kollu T., 'The production of textured yarns by the false twist technique', *Textile Progress*, 1991, **21**(3).
54. Wilson D.K., Kollu T., 'Textured Yarns by Methods other than False Twist', *Textile Progress*, 1987, **16**(3).
55. Denton M.J., 'Synthetic fibre and yarn production; an ITMA perspective, Part 2: Texturising machines', *Textile Month*, 1984(2), 9.
56. Puffr R., in *Lactam-based Polyamides*, editors Puffr R. and Kubanek V., Vol. I, CRC Press, Boca Raton, Florida, 1991, p. 2.
57. Hearle J.W.S. and Morton W.E., in *Physical Properties of Textile Fibres*, Textile Institute, Manchester, 1993, pp. 61–62.
58. Reimschuessel H.K., in *Fiber Chemistry*, editors Lewin M. and Pearce E.M., Marcel Dekker, New York, 1998, p. 85.
59. Holmes D.R., Bunn C.W. and Smith D.J., 'Crystal structure of polycaproamide-nylon 6', *J Polym Sci*, 1955, **17**, 159.
60. Bunn C.W. and Garner E.V., 'Crystal structure of two polyamides', *Proc Royal Soc London*, 1947, **189A**, 39.
61. Heuvel H.M. and Huisman R., in *High Speed Fibre Spinning*, editors Ziabicki A. and Kawai H., Wiley Scientific, Chichester, 1985, pp. 295–332.

62. Hearle J.W.S. and Greer R., 'On the form of lamellar crystals in nylon fibres', *J Text Inst*, 1970, **61**, 243.

63. Reimschuessel H.K., in *Fiber Chemistry*, editors Lewin M. and Pearce E.M., Marcel Dekker, New York, 1998, p. 89.

64. Reimschuessel A.C. and Prevorsek D.C., 'Domain structure of nylon 6 fibres', *J Polym Sci*, 1976, **14**, 485.

65. Hearle J.W.S. and Morton W.E., in *Physical Properties of Textile Fibres*, Textile Institute, Manchester, 1993, p. 120.

66. Hearle J.W.S. and Morton W.E., in *Physical Properties of Textile Fibres*, Textile Institute, Manchester, 1993, p. 327.

67. Meredith R. and Pierce F.T., 'Effect of repeated extension on textile yarns', *J Text Inst,* 1948, **39**, T159.

68. Saunders J.H., in *Encyclopaedia of Polymer Science and Technology*, Vol. 11; *Polyamide Fibers*, Interscience Publishers, New York, 1981, p. 429.

69. Hearle J.W.S. and Morton W.E., in *Physical Properties of Textile Fibres*, Textile Institute, Manchester, 1993, p. 296.

70. Moncrieff R.W., 'You're safer with synthetics', *Man-made Text*, 1964, **41**(481), 136.

71. Hearle J.W.S., Sen Gupta P.K. and Mathews A., 'Changes in length and mechanical properties due to single and double heat treatment of nylon 6,6 yarn under tension', *Fibre Sci Technol*, 1971, **3**, 167.

72. Hearle J.W.S. and Morton W.E., in *Physical Properties of Textile Fibres*, Textile Institute, Manchester, 1993, pp. 594–595.

73. Greer R.E.S., 'Torsional and Heat Setting Characteristics of Viscoelastic Materials', PhD Thesis, Manchester, 1969.

74. Hearle J.W.S. and Greer R.E.S., 'Fibre structure', *Text Progress*, 1970, **2**, 4.

75. Buchanan D.R. and Walters J.P., 'Glass transition temperature of polyamide textile fibres', *Text Res J*, 1977, **47**, 398.

76. Hearle J.W.S. and Morton W.E., in *Physical Properties of Textile Fibres*, Textile Institute, Manchester, 1993, p. 600.

77. Puffr R. and Subenda J., 'Polymerisation of lactams', *J Polym Sci*, 1976, **C-16**, 79.

78. Papero, P.V., Kubu E. and Roldan L., 'Fundamental property considerations in tailoring a new fibre', *Text Res J*, 1967, **37**, 823.

79. Freitag J., 'The influence of moisture on polyamides', *Chemifasern/Textilindustrie, Man-made Fibre Year Book 1989*, p. 58.

80. Preston J.M. and Nimkar J.V., 'Measuring the transverse swelling of fibres', *J Text Inst*, 1949, **60**, 74.

81. Mark H.F., Atlas S.M. and Cernia E., *Man-made Fibres*, Vol. 2, John Wiley & Sons, New York, 1968, p. 280.

82. Holme I., McIntyre J.E. and Shen Z.J., 'Electrostatic charging of textiles', *Text Prog*, 1998, **28**, 1.

83. Mark H.F., Atlas S.M. and Cernia E., *Man-made Fibres*, Vol. 2, John Wiley & Sons, New York, 1968, p. 259.

84. Gur-Arieh Z. and Reuben B.J., 'Antistatic agents', in *Encyclopaedia of Chemical Technology*, 2nd ed, Vol. 3, Wiley Interscience, New York, 1980, p. 157.

85. Kratzsch E., 'Das elektrostatische Problem bei Polyamiden ist gelost', *Melliand Textilberichte*, 1973, **54**, 1260.

86 Alderson T. (to E I du Pont de Nemours & Co., Inc.), Antistatic polymer fibres, The Patent Office, London, Pat No 1 237 589, 1967.

87. Sano Y., Saegusa T. and Kimura Y., 'Antistatic modification of synthetic fibres by blend-

spinning of polymers containing zwitterionic antistatic modifiers and their copolymers', *Agnew Makromol Chem*, 1995, **224**, 153–166.

88. Pavlinec J., 'Bekinox Stahlfasern für antistatische Anwendung in der Textilindustrie', *Chemifasern/Textilindustrie*, 1986, **38/88**, T58–63.

89. Arsac A. (to Rhone Poulenc), Silvering Polyamides, The Patent Office, London, Pat No 1 445 772, 1976.

90. Nemoz G., 'Les Textiles Conducteurs et Métallisés', *L'Industrie Textile*, 1990, **10**, 56–63.

91. Anon, BASF plc., product information, 'Resistant Conductive Fibre', Leicester, UK, 1995.

92. Hull D.R. (to E I du Pont de Nemours & Co., Inc.), Synthetic Filament having Antistatic Properties, US Patent Office, Pat No 3 803 453, 1974; The Patent Office, London, Pat No 1 393 234, 1975 amended 1979.

93. Kanebo Gohsen Ltd, Belltron 931 and 961 product information, http://www.kanebotx .com/english/gohsen/index.htm.

94. Anon., 'Carbon leaks static', *High Performance Textiles*, 1987, **7**(9), 10–11.

95. Pickering T.P. and Streetman W.E. (to BASF Corp.), Electrically Conducting Filaments, European Patent No 0 341 554, 1989.

96. Ducarre M., 'New way to solve static problems in carpets', *Chemifasern/Textilindustrie*, 1978, **28/80**, 53–58.

97. Kanebo Gohsen Ltd, Kanebo Belltron Brochure, 1991 (also http://www.kanebotx.com/ english/gohsen/index.htm).

98. Achhamer B.G., Reinhardt F.W. and Kline G.M., 'Degradation of polyamides', *J Appl Chem*, 1951, **11**, 301.

99. Kamerbeck B., Kroes G.H. and Grolle W., 'Thermal degradation of polymers', *Soc Chem Ind Monograph*, 1961, **13**, 357.

100. East G.C., Kavan S.K., Lupton S.J., Truter E.V., 'Decomposition of nylons in the solid state', *Proc. Soc. Analyt. Chem.*, 1973, 10, 93.

101. Peebles L.H. and Huffman M.W., 'Thermal degradation of nylon 6,6', *J Polym Sci*, 1971, **A1, 9**, 1807.

102. Valko E.I. and Chiklis C.K., 'Effects of thermal exposure on the physicochemical properties of polyamides', *J Appl Polym Sci*, 1965, **9**, 2855.

103. Valk G., Kruessman H. and Diehl P., 'Photo and thermal degradation of fibre forming polymers', *Makromol Chem*, 1967, **107**, 158.

104. Gijsman P., Meijers G. and Vitarelli G., 'Light degradation of PA 6', *Polym Degrad Stab*, 1999, **65**, 433.

105. Karstens T. and Rossbach V., 'Thermo-oxidative degradation of nylon 6 and 6,6', *Makromol Chem*, 1990, **191**, 757.

106. Levchik S.V. and Weil E.D., 'Combustion and flame retardancy of aliphatic nylons', *Polym Int*, 2000, **49**, 1033–1073.

107. Vaidya A.A., Chattopadhyay S. and Raavishankar S., 'Flame retardancy in nylons', *Text Dyer Printer*, 1977, **110**(8), 37.

108. Bever P.M., Breiner U., Conzelmann G. and von Bernstorff B.S., 'Protection of polyamide against light', *Chem Fibres Int*, 2000, **50**, 176–178.

109. Lanska B., 'Degradation and stabilisation', in *Lactam based Polyamides*, editors Puffr R. and Kubanek V., Vol. I, CRC Press, Boca Raton, Florida, 1991, p. 284.

110. Reinert G. and Fuso F., 'Stabilisation of textile fibres against ageing', *Rev Prog Coloration*, 1997, **27**, 32–41.

111. Ciba Speciality Chemicals product information, http://www.cibasc.com/fibersandtex tiles/ebene1.asp?ID_bereich=4.

112. Lanska B., 'Degradation and stabilisation', in *Lactam-based Polyamides*, editors Puffr R. and Kubanek V., Vol. I, CRC Press, Boca Raton, Florida, 1991, pp. 285–286.

113. Ciba Speciality Chemicals product information, http://www.cibasc.com/fibersandtex tiles/ebene1.asp?ID_bereich=4.

114. Breiner U., Julius M., Weiss R., Wilms A. and Hu H.Y. (to BASF AG), Inherently heat and light stabilised polyamides with improved wet fastness, International Patent No WO9948949, 2002.

115. Breiner U. and Bever P.M., 'Lumaxx: a new polyamide with inherent light resistance', *Chem Fibres Int*, 2001, **511**, 413–416.

116. Richards A.F., 'Titanium dioxide in fibres', Paper to *TiO₂ '99 Conference*, Padova Italy, Intertech Conferences, 1999.

117. Anon., *Identification of Textile Materials*, 7th ed, Textile Institute, Manchester, 1975, p. 116.

118. Donat J., 'Delustering of man-made fibres', *Chemifasern/Textilindustrie*, 1985, **35/ 87**(9), 574–581.

119. Bever P.M., Breiner U., Conzelmann G. and von Bernstorff B.S., 'Protection of polyamide against light', *Chem Fibres Int*, 2000, **50**, 176–178.

120. Tippets E.A., 'Fibre engineering to meet end use requirements', *Text Res J*, 1967, **37**, 524.

121. DuPont Tactel® T-800 product information, http://www.dupont.com/tactel/business/ html/fabfxix.html.

122. Saunders J.H., 'Biconstituent fibres from segmented polyurethane and nylon 6', *J Appl Polym Sci*, 1975, **19**, 1387.

123. Kanebo Gohsen Ltd., Sideria product information, http://www.kanebotx.com/english/ gohsen/index.htm.

124. DuPont, Cambrelle product information, http://www.cambrelle.com.html.

125. Kanebo Gohsen Ltd, Masonic N product information, http://www.kanebotx.com/ english/gohsen/index.htm.

126. Toray Textiles Inc, Bodyshell product information, http://www.toray.co.jp/e/products/ seni/seni_15.html.

127. D.K. Consulting S.A., 'The European potential of microfibres', *Text Month*, 1992, **1**, 23–25.

128. Hearle J.W.S. and Morton W.E., in *Physical Properties of Textile Fibres*, Textile Institute, Manchester, 1993, p. 401.

129. Burkinshaw S.M., in *Chemical Principles of Synthetic Fibre Dyeing*, Blackie & Sons, London, 1995, p. 202.

130. Fiber Innovation Technology product information, http://www.fitfibers com/product.

131. Kanebo Gohsen Ltd, Glacem product information, http://www.kanebotx.com/english/ gohsen/index.htm.

132. Kanebo Gohsen Ltd, Bellima X product information, http://www.kanebotx.com/ english/gohsen/index.htm.

133. Toray, Ecsaine product information, http://www.toray.co.jp/e/products/seni/seni_4.html.

134. Dugan J., 'Critical factors in engineering segmented bicomponent fibers for specific end uses', http://www.fitfibers.com/product.htm.

135. Nylstar Meryl® Skinlife, http://www.nylstar.com/all/products/produ-skin.html.

136. Kanebo Livefresh®, http://www.kanebotx.com/english/gohsen/index.htm.

137. Ciba Speciality Chemicals, Irgaguard B5000 and B7000 product information, http:// www.cibasc.com/fibersandtextiles/.

138. Toray, Miracosmo® product information, http://www.toray.co.jp/e/products/seni/ seni_15.html.

139. Reimschuessel H.K., in *Fiber Chemistry*, editors Lewin M. and Pearce E.M., Marcel Dekker, New York, 1996, p. 151.
140. Nylstar, Meryl® UV Protection product information, http://www.nylstar.com/all/products/produ-uv.html
141. DuPont, Solarmax® product information, http://www.dupont.com/solarmax/index.html.
142. BASF AG, Carpet Fibre product information, http://www.basf.com/businesses/fibres/carpet/
143. DuPont, Antron® product information, http://antron.dupont.com/index.shtml
144. Greeson L.B. (to Monsanto), Varicoloured polyamide fabrics, US Patent Office, Pat No 3 375 651, 1968.
145. Magat E.E. (to E I du Pont de Nemours & Co., Inc.), Polyamides with improved dyeability, US Patent Office, Pat No 3 184 436, 1965.
146. Burkinshaw S.M., in *Chemical Principles of Synthetic Fibre Dyeing*, Blackie & Sons, London, 1995, p. 211.
147. *World-wide and Regional Trends in Man-made Fibre Production*, Technical Textiles Markets 2001 (2nd quarter), Textiles Intelligence Ltd, Wilmslow, p. 11.
148. DuPont Tactel® product information, http://www.dupont.com/tactel/business/.
149. Nylstar Meryl® product information, http://www.nylstar.com/all/products.
150. Booij M., 'DSM closes the Loop', Paper to *Polyamide 2000 World Congress*, Zurich, 2000; http://www.dsm.com/dfi/publications
151. DuPont, Antron® White Paper, 'Issues of Recycled Content Nylon Fiber in Carpet', 2001.
152. DuPont environmental initiatives, http://antron.dupont.com/pdf_files/literature/enviro_initiatives.pdf