4

Acrylic fibres

R . C O X
Acordis Acrylic Fibres

4.1   Introduction

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

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

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

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

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

Table 4.1 Polymer composition of acrylic fibres

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

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

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

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

4.2   Chemical intermediates

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

Table 4.2 Solvents used commercially for spinning acrylic fibres

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

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

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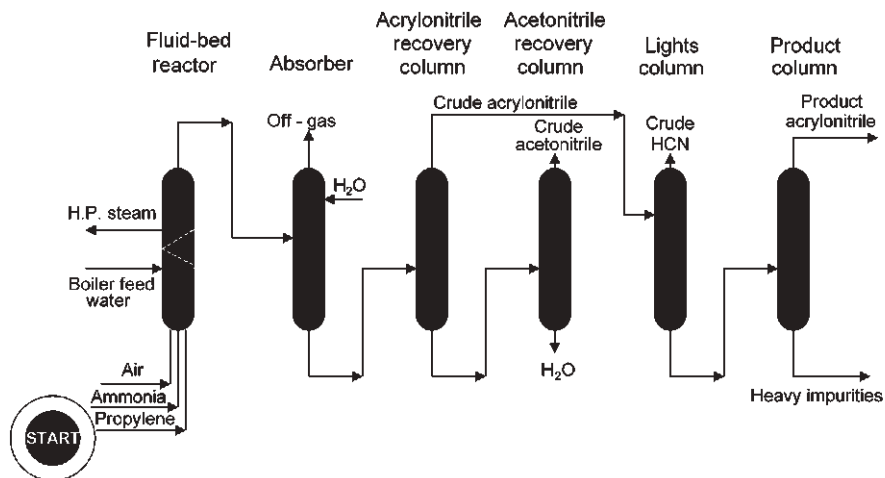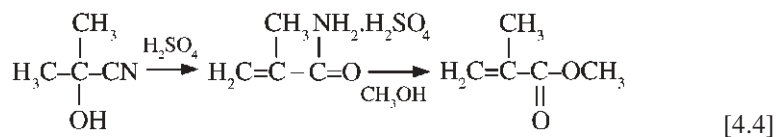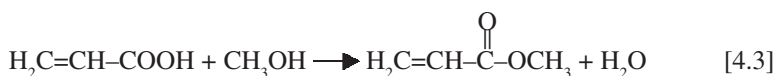

4.1 Process flow diagram of the commercial propylene ammoxidation process for acrylonitrile – Sohio process. Source: Jacqueline I. Kroschwitz, editor, *Encyclopedia of Chemical Technology*, Vol. 1, p. 357 ©1991 John Wiley & Sons, reprinted by permission of John Wiley & Sons Inc.

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

$$CH_2=CH-C\equiv N: \longleftrightarrow CH_2=CH-C^+=\bar{N}: \longleftrightarrow \overset{+}{C}H_2-CH=C=\bar{N}: \qquad [4.2]$$
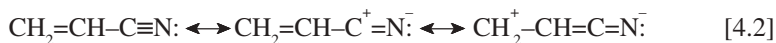
Acrylonitrile undergoes a wide range of reactions at its two chemically active sites, the nitrile group and the carbon–carbon double bond. Acrylonitrile must be stabilised with a hydroquinone inhibitor in order to prevent polymerisation, which occurs readily, particularly in the presence of light. Polymerisation is initiated by free radicals, redox catalysts or bases and can be carried out in the liquid, solid or gas phase. Homopolymers and copolymers are most easily produced using liquid phase polymerisation.

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

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

$$\underset{\overset{|}{OH}}{\overset{\overset{CH_3}{|}}{H_3C-C-CN}} \xrightarrow{H_2SO_4} \underset{\overset{|}{C=O}}{\overset{\overset{CH_3}{|}}{H_2C=C}} \overset{NH_2.H_2SO_4}{\underset{CH_3OH}{\longrightarrow}} \underset{\overset{\|}{O}}{\overset{\overset{CH_3}{|}}{H_2C=C-C-OCH_3}}$$

$$[4.4]$$

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

$$H_2C=CH-CN + H_2O \longrightarrow H_2C=CH-\overset{O}{\overset{\|}{C}}-NH_2 \qquad [4.5]$$
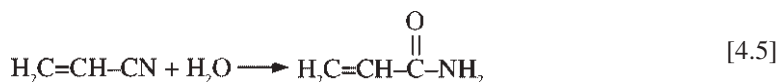
The main comonomer used in acrylic fibre manufacture today is undoubtedly vinyl acetate. This is a colourless liquid with a b.p. of 72.5 °C which has a pleasant, sweet odour. It was traditionally manufactured by the reaction of acetylene with

acetic acid, but this has been almost completely replaced by a more economical process in which a mixture of ethylene and acetic acid in the gaseous phase is oxidised over a palladium catalyst at a pressure of 0.5–1 MPa and a temperature of 150 °C –200 °C (eq. 4.6). The exit gases are quenched and vinyl acetate is separated by distillation.

$$H_2C{=}CH_2 + CH_3COOH + \tfrac{1}{2}O_2 \longrightarrow H_2C{=}CH{-}O{-}\overset{\displaystyle O}{\overset{\|}{C}}{-}CH_3 + H_2O \quad [4.6]$$
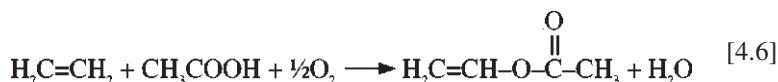
4.3   Polymerisation techniques

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

4.3.1   Properties required in acrylic polymers for fibre end-uses

4.3.1.1   Molecular weight

The molecular weight and the distribution of molecular weights are key polymer properties and are used by all manufacturers as key quality control measures. The molecular weight of the polymer must be low enough that the polymer is readily soluble in the spinning solvents, yet high enough to give a dope of moderately high viscosity. Typical commercial acrylic polymers for textile purposes have number

average molecular weights in the range 40 000–70 000. The weight average molecular weight is typically in the range 90 000–170 000, with a polydispersity index between 1.5 and 3.0. Higher molecular weight polymers are used for specific end-uses in which fibre strength and modulus need to be higher; for example, cement reinforcement and carbon fibre precursor.

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

4.3.1.2   Dyeability

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

4.3.1.3   Fibre whiteness

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

In terms of polymer control, high monomer concentration (low conversion)[8]

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

4.3.2   Polymerisation methods

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

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

4.3.2.1   *Bulk polymerisation*

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

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

4.3.2.2   Aqueous dispersion polymerisation

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

$$S_2O_8^{2-} + Fe^{2+} \longrightarrow Fe^{3+} + SO_4^{\bullet-}$$

$$HSO_3^- + Fe^{3+} \longrightarrow Fe^{2+} + HSO_3^{\bullet}$$

[4.7]

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

$$P_m\bullet + HSO_3^- \longrightarrow P_mH + SO_3^{-}\bullet$$

[4.8]

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

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

The resulting polymer is washed and separated by filtration prior to storage. Depending upon the polymer solvent to be used in fibre spinning, the polymer will

be dried for organic solvents but may be stored wet for aqueous salt solvents. Polymer blending may take place prior to the polymer dissolution stage in which a spinning dope is formed.

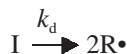### 4.3.2.3   Solution polymerisation

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

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

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

   The kinetics of solution polymerisation are fairly straightforward, as there is only a single phase to be considered. A typical reaction scheme would be:
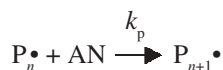
(a)   Radical formation (I = azo or peroxide initiator; R• = free radical):
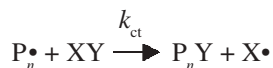
$$I \xrightarrow{k_d} 2R\bullet$$

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

$$R\bullet + AN \xrightarrow{k_i} P_1 \bullet$$

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

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

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

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

(e) Termination by radical recombination:

$$P_n^\bullet + P_m^\bullet \xrightarrow{k_{tr}} P_{n+m}$$
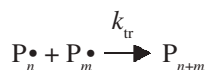
(f) Termination by radical disproportionation:

$$2 P_n CH_2 \overset{\bullet}{C}HCN \xrightarrow{k_{td}} P_n CH = CHCN + P_n CH_2 CH_2 CN$$
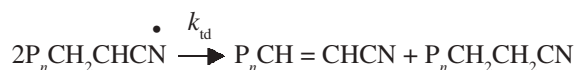
(g) Termination by metal ion (such as ferric):

$$P_n^\bullet + FeCl_3 \xrightarrow{k_{tm}} P_n Cl + FeCl_2$$
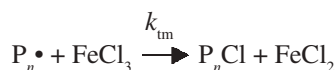
The rate of polymerisation, R_p, is

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

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

4.3.2.4   Emulsion polymerisation

The mechanism of this polymerisation technique has been fully studied by a number of researchers.[16–21] The technique involves stirring the monomers in water along with a suitable emulsifier and a radical initiator. It has been shown that the emulsifier disperses a small portion of the monomer in aggregates of 50–100 molecules. These micelles have a diameter of about 5 nm. The majority of the monomer, however, stays suspended in droplet form with a diameter of 1000 nm. Radical formation occurs in the aqueous phase as described in aqueous dispersion

polymerisation. These radicals are rapidly absorbed into the monomer micelles. Polymerisation proceeds rapidly, converting the micelle into a polymer particle nucleus. This particle nucleus continues to grow in size, being supplied with monomer by diffusion from the monomer droplets.

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

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

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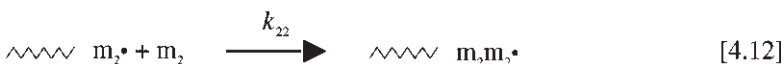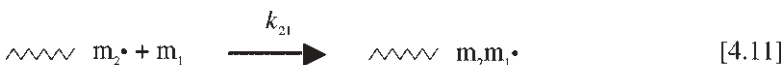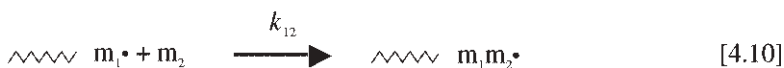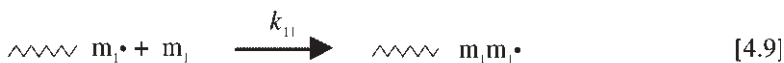
4.3.3   Copolymerisation kinetics

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

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

Table 4.3 Reactivity ratios for acrylonitrile copolymerisations

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

$$\text{\textasciitilde\textasciitilde\textasciitilde } m_1\bullet + m_1 \xrightarrow{\quad k_{11} \quad} \text{\textasciitilde\textasciitilde\textasciitilde } m_1m_1\bullet \qquad [4.9]$$

$$\text{\textasciitilde\textasciitilde\textasciitilde } m_1\bullet + m_2 \xrightarrow{\quad k_{12} \quad} \text{\textasciitilde\textasciitilde\textasciitilde } m_1m_2\bullet \qquad [4.10]$$

$$\text{\textasciitilde\textasciitilde\textasciitilde } m_2\bullet + m_1 \xrightarrow{\quad k_{21} \quad} \text{\textasciitilde\textasciitilde\textasciitilde } m_2m_1\bullet \qquad [4.11]$$

$$\text{\textasciitilde\textasciitilde\textasciitilde } m_2\bullet + m_2 \xrightarrow{\quad k_{22} \quad} \text{\textasciitilde\textasciitilde\textasciitilde } m_2m_2\bullet \qquad [4.12]$$

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

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

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

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

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

Some polymer systems are based upon more than two monomers. For example, *Courtelle* fibre manufactured by Acordis in Grimsby, UK, incorporates methyl acrylate at 6 or 8 % and the dye-site monomer sodium 2-methyl-2-acryl-amidopropane sulphonate (AMPS) at 1 %. Copolymer composition can be predicted for this system quite reliably by assuming that the component reactions involve only the terminal monomer units of the chain radical. A series of binary reactivity ratios can then be derived.
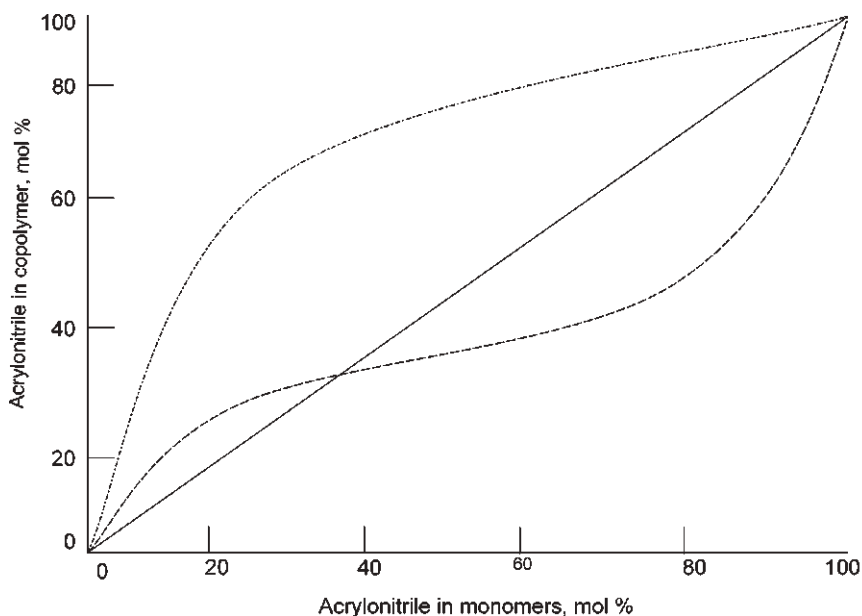
4.2 Three principal patterns of copolymer composition *vs.* monomer composition found in free-radical copolymerisation of acrylonitrile. Acrylonitrile is monomer 1; monomer 2 is vinyl acetate ($r_1/r_2 = 4.05/0.61$) (·–··–); methyl acrylate ($r_1/r_2 = 1.5/0.84$) (–––) and styrene ($r_1/r_2 = 0.04/0.37$) (——). Source: Jacqueline I. Kroschwitz, editor, *Encyclopedia of Chemical Technology*, 2nd edn, Vol. 1, p. 356 ©1985 John Wiley & Sons, reprinted by permission of John Wiley & Sons Inc.

4.3.4   Commercial processes

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

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

by changes to residence time in the reactors rather than the starting up and shutting down of reactors, as reactor start-ups can cause major polymer quality disruptions.
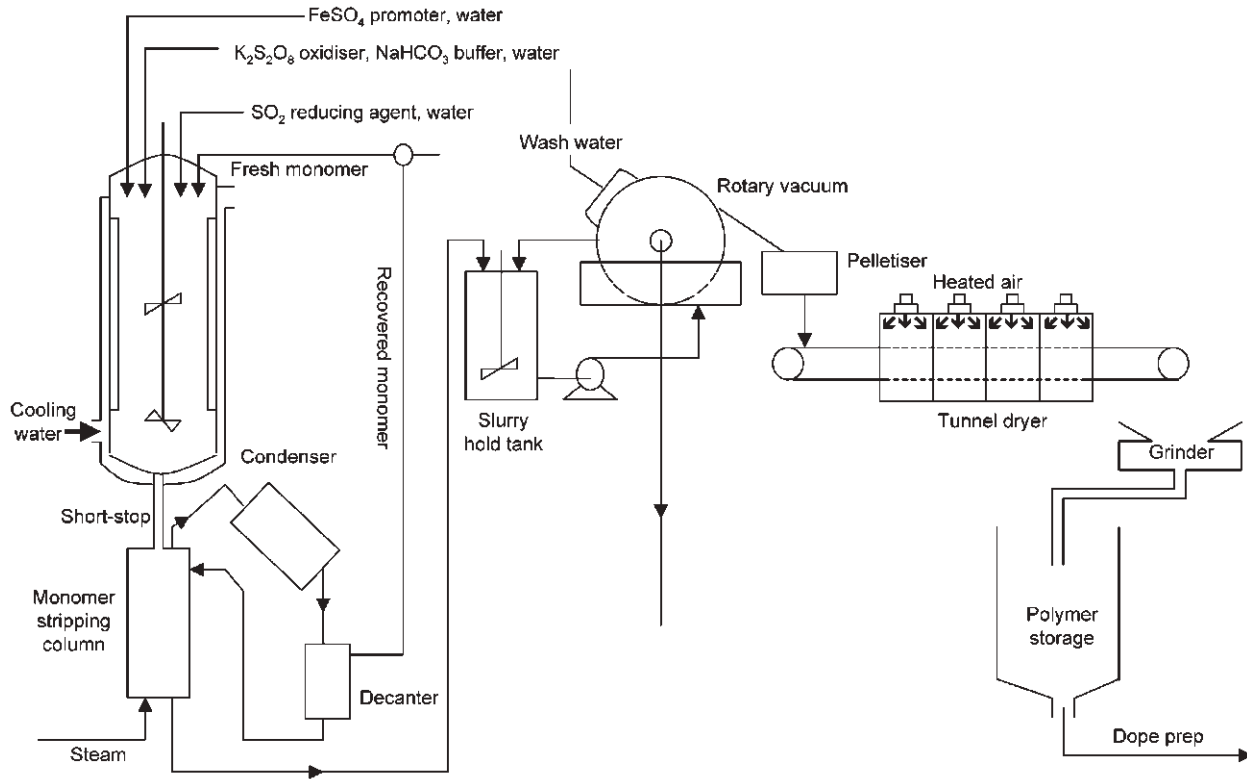
For aqueous dispersion reactions, the reactors tend to be manufactured from aluminium. This is to prevent the build-up of polymer on the walls of the reactor. The aluminium surface slowly dissolves because of the acidic nature of the reaction medium and it is necessary to determine the reactor wall thickness periodically in order to determine when new reactors are required. In solution polymerisation, the reactors need to be of specific grades of stainless steel in order to withstand the strong solvating properties of the solvents used.

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

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

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

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

FeSO$_4$ promoter, water

K$_2$S$_2$O$_8$ oxidiser, NaHCO$_3$ buffer, water

SO$_2$ reducing agent, water

Fresh monomer

Wash water

Rotary vacuum

Recovered monomer

Cooling water

Condenser

Short-stop

Monomer stripping column

Decanter

Steam

Slurry hold tank

Pelletiser

Heated air

Tunnel dryer

Grinder

Polymer storage

Dope prep

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

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

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

4.4   Fibre production techniques

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

We have seen from the description of the polymerisation techniques that the

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

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

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

Polymer dopes of an appropriate concentration (for the solvent used) and viscosity (for the spinning technique) are common to both wet and dry-spinning. For both processes it is very important that the polymer dope is filtered and de-aerated prior to fibre spinning. Filtration is commonly achieved by passage of the polymer dope through a series of filters, which start off quite coarse and become finer as the polymer dope nears the spinneret. De-aeration is a function of time/pressure and air-free dopes usually emerge from the filtration processes. Various polymer additives are often introduced at an appropriate point in the filtration process. Common examples are titanium dioxide, which acts as a delustrant, and carbon black, which acts as a pigment.
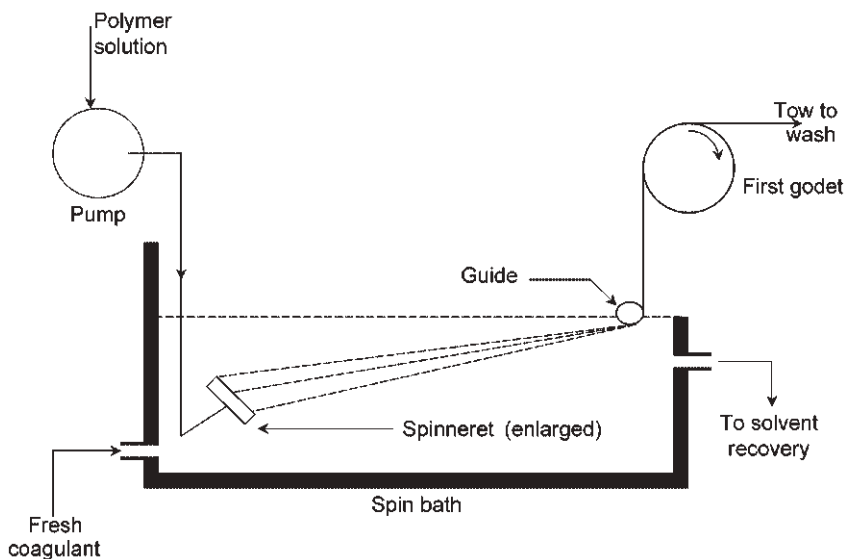
4.4 Simplistic schematic of an acrylic fibre wet-spinning bath. Source: J. C. Masson, *Acrylic Fiber Technology and Applications*, p.73, by courtesy of Marcel Dekker Inc.

4.4.1   Wet-spinning

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

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

designs also vary from simple circular jets containing a small number of holes but which tend to be used in large clusters (perhaps 20 jets in one bath) to the large strip jets pioneered by Courtaulds (Acordis), which contain as many as 360 000 holes.

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

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

The basic steps are common to all wet-spinning processes but the designs for each technology can be quite different. Figure 4.5 is a simple schematic, showing one of the many variants possible. The stretching operation can be done in hot water over a series of small nip rollers, each one with a progressively higher velocity, or it can be done in steam over a very short distance. The stretching operation may also be done early in the fibre-making sequence and significantly before the residual solvent has been washed out, or it may be done late in the process, after the majority of the residual solvent has been removed. These various options account for the subtle differences in the properties of the resulting fibre. For example, the way the fibre tensiles are built as a result of the tension under stretch will be influenced by the amount of residual solvent (which has a plasticis-ing effect) present during the stretching process. The overall stretch ratios commonly used are between 3 and 12 times and this process orients the polymer chains within
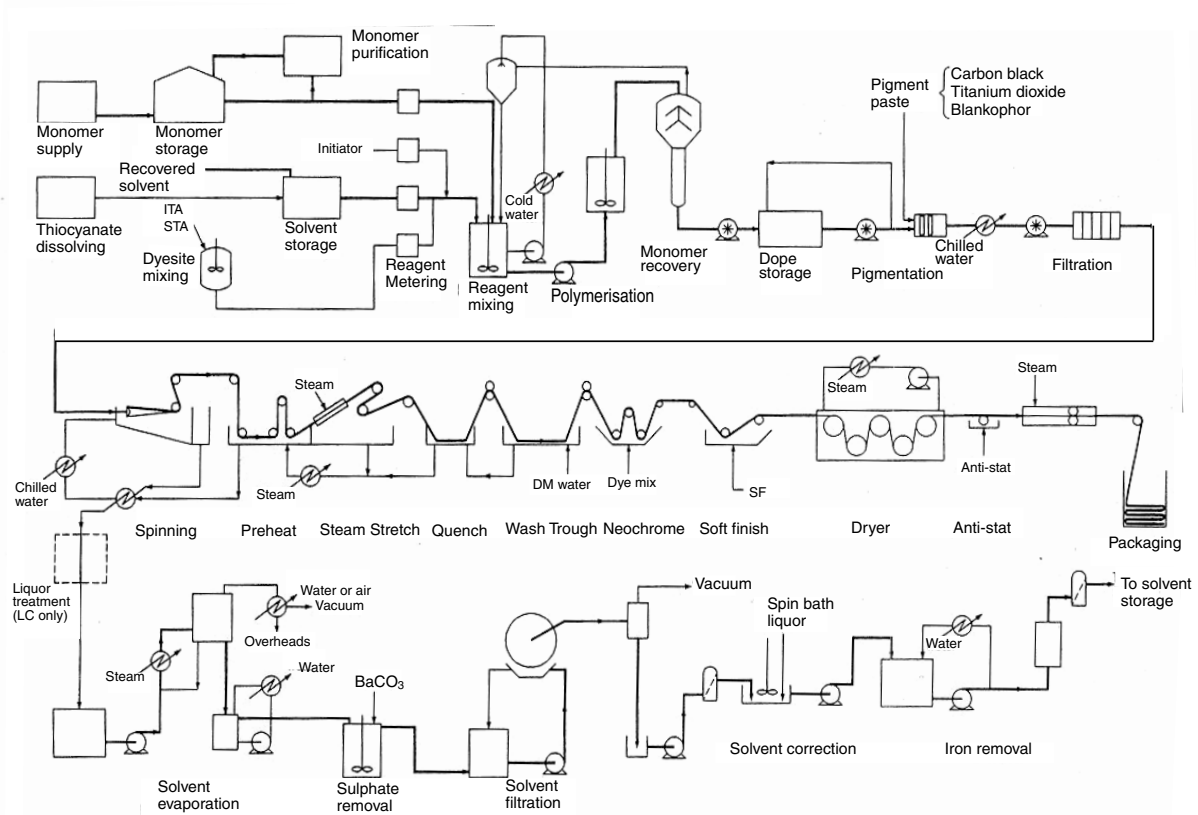
4.5 Schematic diagram illustrating solution polymerisation and fibre spinning. DM is demineralised water, ITA is itaconic acid, LC is Latent Crimp (a bicomponent fibre made by Acordis), SF is soft finish, STA is a polymerisation control agent. Source: Copyright Acordis UK Ltd.

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

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

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

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

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

4.4.1.1   *Fibre formation in detail*

The formation of acrylic fibre using wet-spinning technology has been studied in great detail by all of the companies involved in acrylic fibre production. A good understanding of the thermodynamics and kinetics of a phase-separating polymer

solution is important if product optimisation is to be achieved. The individual steps that need to be understood can be described by the terms diffusion and phase separation. These determine the structure of the resulting polymer.

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

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

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

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

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

The final factor that needs to be considered in this overview of diffusion is the rate at which fresh spin bath liquor is introduced. As fibre spinning progresses,

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

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

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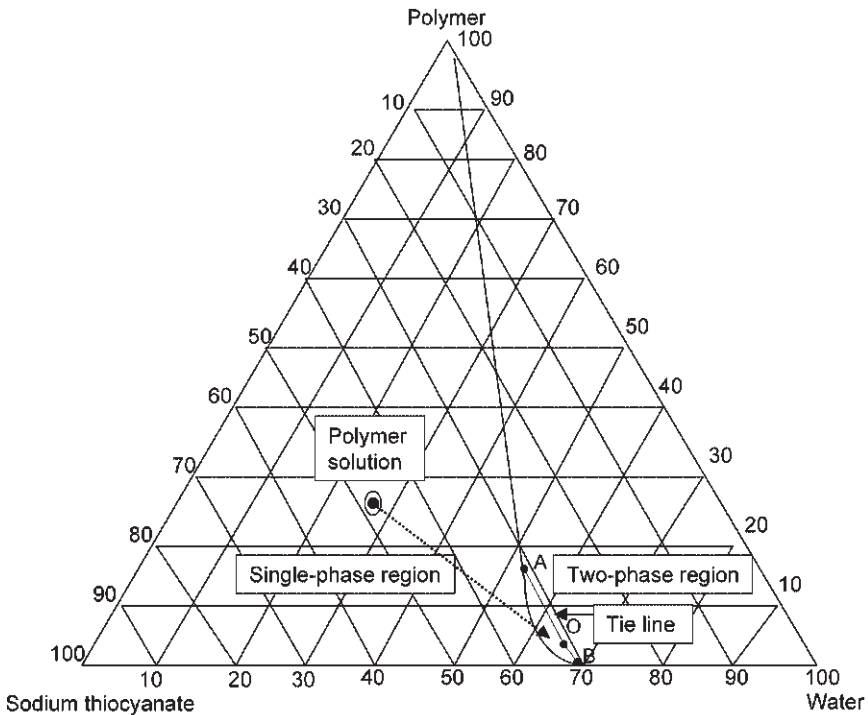
4.6 Phase diagram for the sodium thiocyanate/water/polymer three-component system. Source: Acordis UK Ltd.

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

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

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

$$\Delta G_m = G_{12} - (G_1 + G_2) \le O \qquad [4.13]$$

The term ΔG_m can be calculated from:

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

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

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

$$\Delta S_m = -R(n_1 \ln \Phi_1 - n_2 \ln \Phi_2) \qquad [4.15]$$

where R is a constant

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

Where minima approach each other, and eventually coincide, is the point where the first and second derivatives of ΔG with respect to volume fraction are zero. This is termed the critical point. Inside the spinodal curve, compositions are instantaneously unstable and phase separation is energetically favourable. This process is known as spinodal decomposition. Between the binodal and spinodal, solutions are metastable and a finite composition change is required (a nucleus) to begin phase separation. This is known as nucleation and growth.
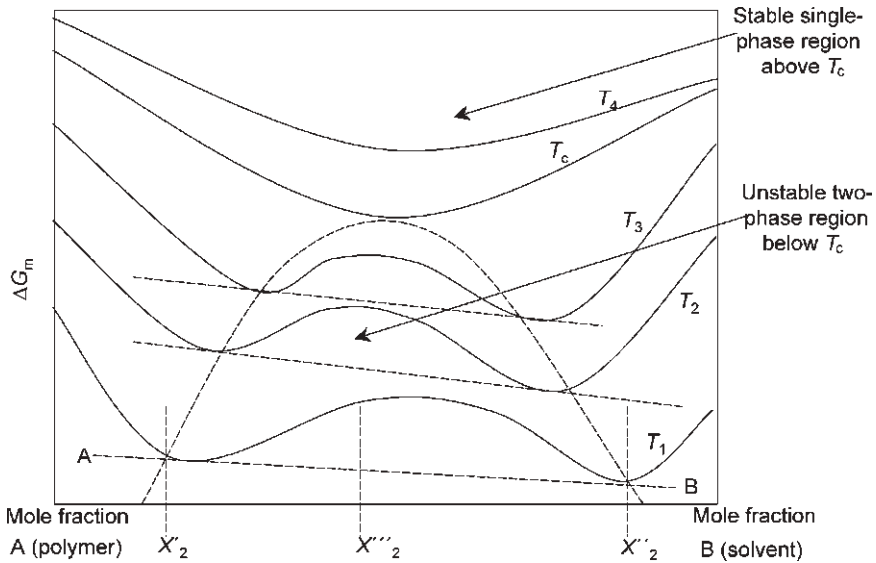
4.7 Schematic diagram of Gibbs free energy of mixing as a function of mole fraction of solute X_2 showing behaviour over a range of temperatures. Source: PhD Thesis, S. Law.[28]

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

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

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

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

4.4.2   Dry-spinning

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

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

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

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

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

Like wet-spinning in which the removal of the polymer solvent is the key step, the most important stage in the dry-spinning process is the evaporation of the solvent after spinning. Figure 4.8 shows a typical design for the spinning tube.
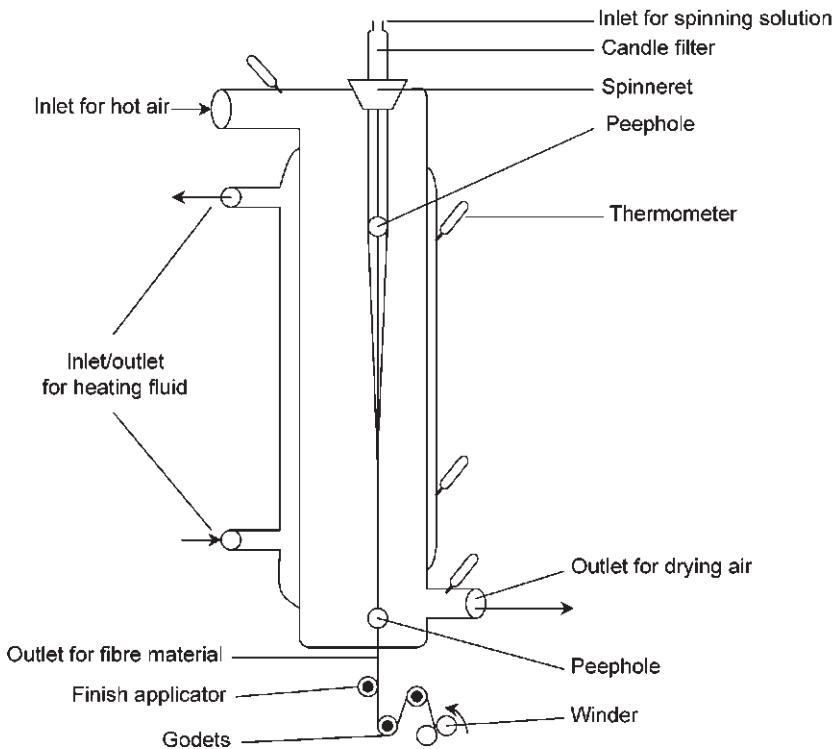
4.8 Spinning tube for dry-spinning process (length 6–10 m). Source: reprinted from J. C. Masson, *Acrylic Fiber Technology and Application*, p. 119 by courtesy of Marcel Dekker Inc.

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

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

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

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

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

The resulting fibre is taken up by a godet and finish is applied prior to the fibre being collected in spin cans. Some dry-spinning units will incorporate a water quench trough just after the take-up godet. For filament routes, an oil-based finish is applied to the filaments at the bottom of the spinning tube. They are then drawn off via godet rollers and wound at 200–500 m min^{-1}. For tow end-uses the fibres from each spinning cell on each half of the machine are combined together to form
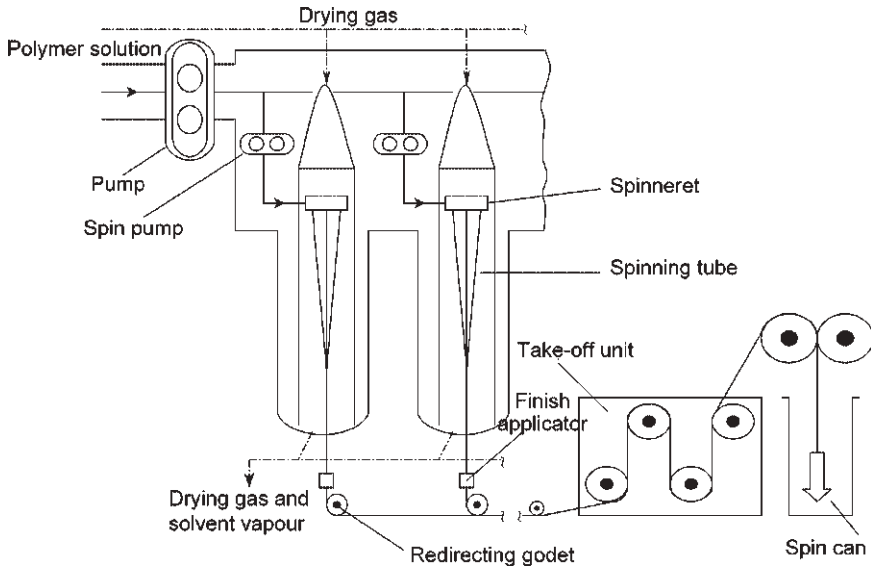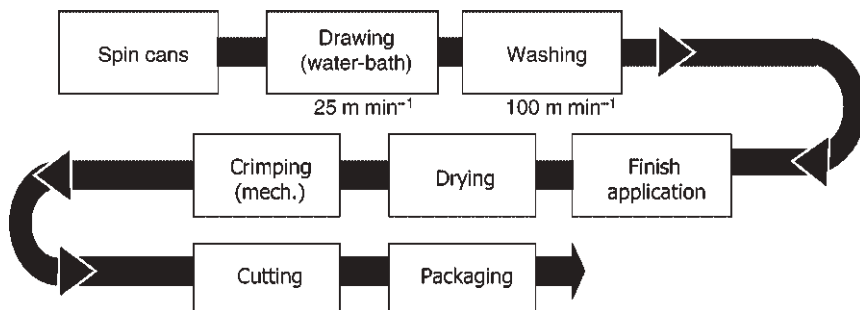
4.9 A typical dry-spinning unit for the production of staple fibres.
Source: Reprinted from J. C. Masson, *Acrylic Fiber Technology and Applications*, p. 121 by courtesy of Marcel Dekker Inc.

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

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

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

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

```
┌────────────┐   ┌──────────────┐   ┌────────────┐
│ Spin cans  │──▶│   Drawing    │──▶│  Washing   │──▶
│            │   │ (water-bath) │   │            │
└────────────┘   └──────────────┘   └────────────┘
                   25 m min⁻¹         100 m min⁻¹
        ┌──────────────┐   ┌────────────┐   ┌──────────────┐
     ◀──│   Crimping   │◀──│   Drying   │◀──│    Finish    │◀──
        │   (mech.)    │   │            │   │ application   │
        └──────────────┘   └────────────┘   └──────────────┘
        ┌──────────────┐   ┌────────────┐
     ──▶│   Cutting    │──▶│ Packaging  │──▶
        └──────────────┘   └────────────┘
```

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

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

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

Finally, the fibre is dried. The mode of drying is important, as this is the stage at which the final shrinkage potential of the fibre and the dye rate of the fibre are manipulated. The fibre tow is usually dried at temperatures of between 120 and 170 °C with throughput speeds of 100 to 150 m min⁻¹. The fibre entering the dryer has a shrinkage potential determined by the fibre drawing stage. Drying under tension, usually over heated drums, can retain this shrinkage potential. By altering

the tension on the drum dryers along with speed and temperature, the final shrinkage and dyeability can be determined. The drying process also sets the fibre to some extent. As this affects the ability of the fibre to be crimped, then the degree of setting becomes another control variable.

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

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

4.4.2.1   Fibre formation in detail

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

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

As the solvent is evaporated from the polymer solution, a number of changes take place up to the solidification point. These are summarised in Fig. 4.11. The fibre dtex drops constantly until the solidification point is reached. The velocity and tension of the forming fibre increase proportionately. The rate of solidification
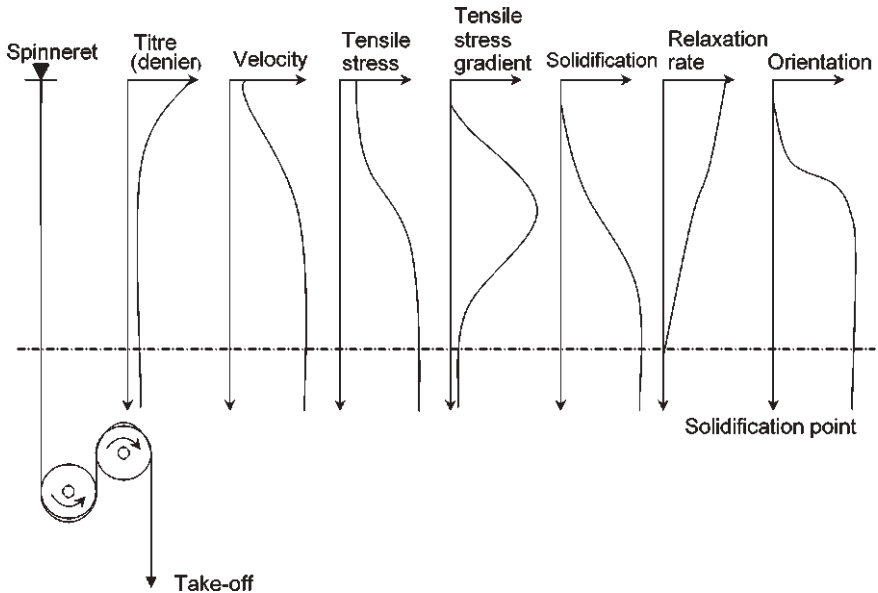
4.11 Processes occurring during dry-spinning. Source: Reprinted from J. C. Masson, *Acrylic Fiber Technology and Applications*, p. 115 by courtesy of Marcel Dekker, Inc.

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

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

One of the ways in which dry-spun fibres are easily differentiated from wet-spun fibres is by the cross-sectional shape. Dry-spun fibres are dog-bone or dumbbell shaped while wet-spun fibres are mainly round or kidney bean shaped. The reason for the dog-bone shape is easily explained; it is an artefact of the solvent diffusion and evaporation stages that lead to polymer solidification. As the solvent evaporates from the polymer solution, the outer part of the forming fibre solidifies before the inner sections. This causes radial inhomogeneity within each filament, which can be considered in simple terms as a core–sheath structure. Clearly, once the

outer section of the filament solidifies, further solvent vapour generated within the core of the filament has to pass through this newly formed solid polymer. As this solvent evaporates from the core of the filament, the mass of the core is reduced and this results in the outer sheath collapsing inwards. The faster the evaporation rate compared with the diffusion rate, the more likely the cross-section of the fibre is to change from circular through bean shaped to dog-bone. This phenomenon occurs to a much lesser extent in wet-spinning in which fibre is formed by a coagulation process. This is why only circular or kidney bean shaped fibres are formed in wet-spinning.

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

4.5   Physical properties and structure of fibres

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

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

$$-(CH_2-CH)_n- \atop \quad\ \ |\ \ CN$$

[4.16]

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

$$\cdots CH_2-CH(CN)-CH_2-CH(CN)\cdots$$

[4.17]

rather than the less favourable 'head to head' structure:

$$\cdots CH_2-CH(CN)-(CN)CH-CH_2\cdots$$

[4.18]
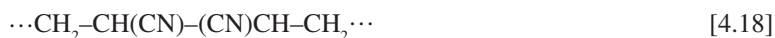
Acrylonitrile is an asymmetric monomer, and following polymerisation every tertiary C atom can be considered as a chiral centre, s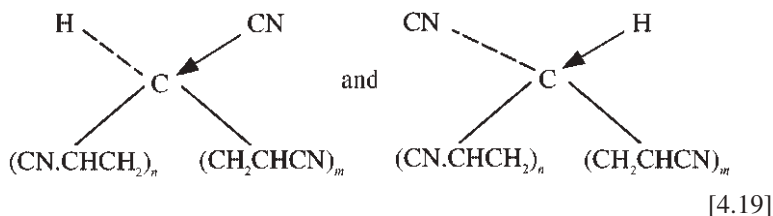ince adjacent chain fragments have different lengths. There are therefore two possible configurations represented by simply reversing the positions of the hydrogen and nitrile groups:

$$H \diagdown \qquad \diagup CN \qquad\qquad CN \diagdown \qquad \diagup H$$

$$C \qquad\qquad and \qquad\qquad C$$

$$(CN.CHCH_2)_n \quad (CH_2CHCN)_m \qquad (CN.CHCH_2)_n \quad (CH_2CHCN)_m$$

[4.19]

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

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

The protruding nitriles are also able to interact with nitriles on adjacent chains. Calculations suggest that the greatest energy can be gained when nitriles are in an antiparallel arrangement, and chains will modify their structure to approach this ideal position. Where chains are highly extended, as in the case of drawn fibres, groups of PAN tubes will approach closely enough to form larger groups, which give rise to the characteristic wide-angle X-ray diffraction pattern. The diffuse halo in the X-ray diffraction patterns normally associated with semicrystalline
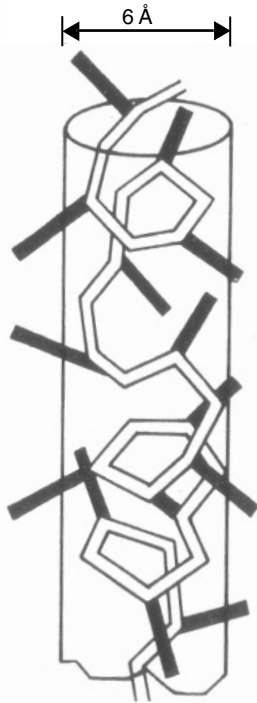
4.12 Diagrammatic representation of polyacrylonitrile molecule.
Source: Henrici-Olivé & Olivé.[32]

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

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

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

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

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

The structure was first comprehensively characterised by Craig and co-workers.[40] By a combination of transmission electron microscopy (TEM), mercury porosimetry, density and surface area measurements, the pore and matrix structures of a range of PAN fibres were described. The TEM photographs showed a continuous network of polymer rods connected by nodes, and a porous structure interspersed. A gradation in pore size was also noted, with smaller pores towards
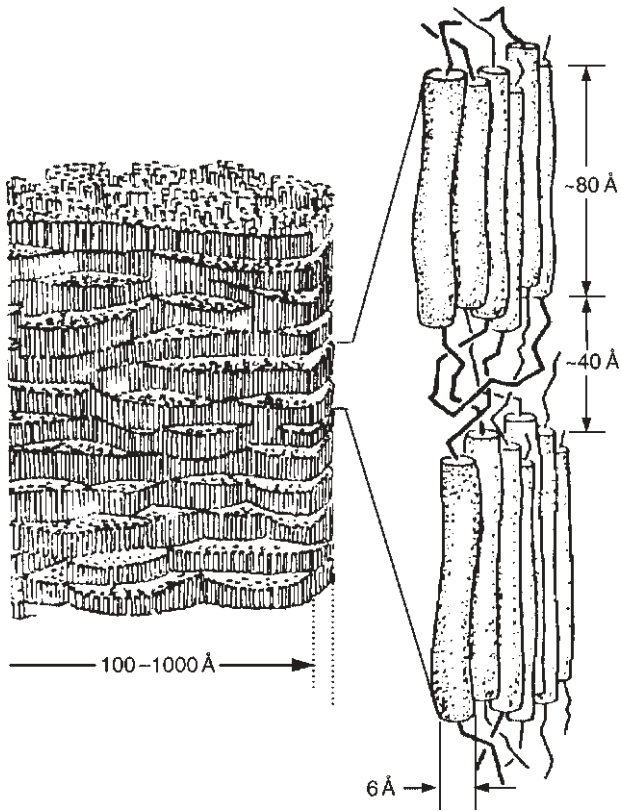
4.13 Diagrammatic representation of two-phase morphology of polyacrylonitrile. Source: Warner, Uhlmann and Peebles.[35]

the outside of the filament. In a later paper, Knudsen illustrated how the various coagulation variables affected the size of the pores, and that those conditions that favoured a slower precipitation led to a finer structure.[41] Work by the author using cationic dyes and disperse dyes of differing molecular size and volume on fibres prepared under differing conditions led to suggested pore sizes being postulated for the Acordis wet-spun fibre.[42] One of the drawbacks of the on-line dyeing of gel state fibres is that uneven dyeing across and down a continuous tow can occur. This is commonly referred to as 'streakiness'. Many factors can influence the degree of streakiness observed in a tow, and it is known that dyestuff selection is one of these factors. This work by the author suggested that the kinetics of the dyeing process were influenced by the pore gradation observed within wet-spun acrylics and that the molecular volume of the dyestuffs was a critical factor. The observed time constants for dyeing of individual dyes and then pairs of dyes changed as the pore size decreased and those dyes with a large molecular volume were the first to be affected. Figures 4.14 and 4.15 illustrate this structure.
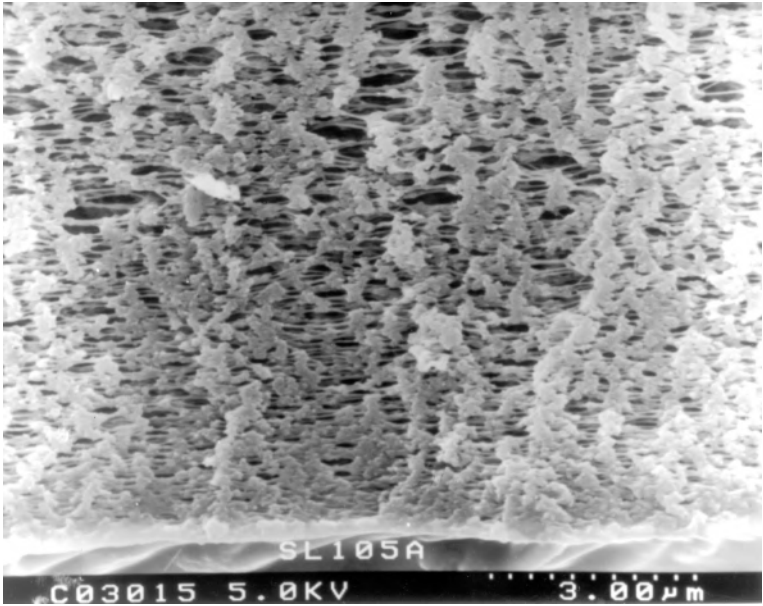
4.14 Pore structure within wet-spun acrylic fibre (1). Courtesy: Acordis UK Ltd.
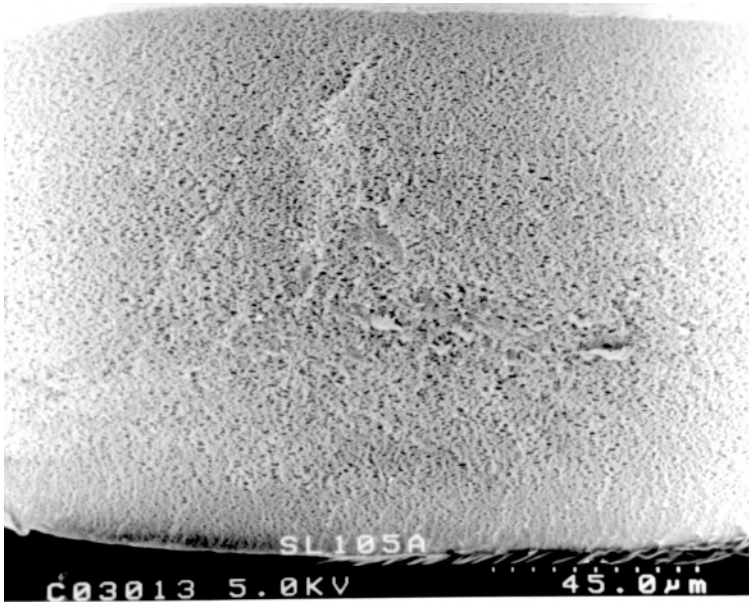
4.15 Pore structure within wet-spun acrylic fibre (2). Courtesy: Acordis UK Ltd.

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

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

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

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

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

Acrylic fibres do, however, undergo thermal transitions at lower temperatures. Various transitions have been reported at temperatures between 39 and 180 °C. However, it is generally acknowledged that acrylic fibres undergo two transitions in this range. The first one, identified as the glass transition temperature, occurs at 80–100 °C for typical acrylic fibres containing vinyl acetate or methyl acrylate comonomers. During this transition, the fibre goes from a glassy solid to a rubber-

like structure. The second transition occurs at around 140 °C but the precise cause of this transition is still under debate. Low molecular weight molecules with high dipole moments, of which water is a typical example, have been shown to interact strongly with nitrile groups. These interactions can result in a sharp reduction in the first observed thermal transition. A whole range of temperature reductions for different acrylic polymers has been recorded. Some of these reductions are as high as 50 °C. However, for conventional acrylic fibre polymers, reductions of around 15–20 °C are the norm.[47–49]

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

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

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

Table 4.4 Physical properties of acrylic and modacrylic fibres

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

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

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

Other notable physical characteristics are high electrical resistance, moderate flammability, excellent resistance to sunlight, chemical and microbiological attack and a moisture regain of 2–3%. These properties are thought to be due to the dipole effects between the nitrile groups within polymer chains and between
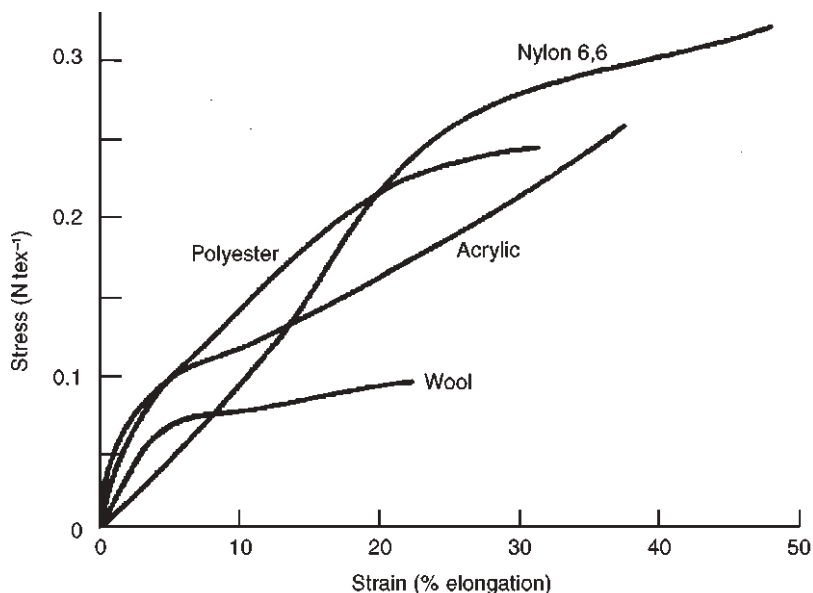
4.16 Typical stress–strain properties of acrylic and other fibres at 65% r.h. and 21 °C. Source: Jacqueline I. Kroschwitz, editor, *Encyclopedia of Chemical Technology*, 2nd edn, Vol. 1, p. 343, ©1985 John Wiley & Sons, reprinted by permission of John Wiley & Sons Inc.

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

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

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

Table 4.5 Chemical properties of fibres

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

4.6   Chemical variants

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

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

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

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

4.6.1   Copolymer variants

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

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

4.6.1.1   Asbestos replacement fibres

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

Table 4.6 The chemical resistance of Dolanit 10 fibre

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

Source: Acordis Kelheim Acrylics

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

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

Table 4.7 Flame-retardant fibres

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

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

4.6.1.2   Flame-retardant fibres

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

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

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

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

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

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

4.6.1.3   *Acid dyeable fibres*

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

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

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

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

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

4.6.1.4   Carbon fibre precursor

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

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

The ionic process is initiated by the incorporation of nucleophilic agents such as itaconic acid, methacrylic acid or vinyl bromide into the polymer. The Acordis carbon fibre precursor (CFP) business uses the itaconic acid route. This comonomer reduces the temperature at which the nitrile polymerisation starts and as such moderates the exotherm. This fibre also incorporates methyl acrylate (MA) as a comonomer and although this comonomer has been shown not to catalyse the exotherm, it is known to interrupt the nitrile polymerisation.[53] Maslewski and Urbanska[54] have shown that there is a relationship between the precursor fibre strength and modulus and the carbon fibre strength and modulus. It is therefore desirable to produce polymers with higher molecular weights and fibres with higher stretch ratios for this end-use.
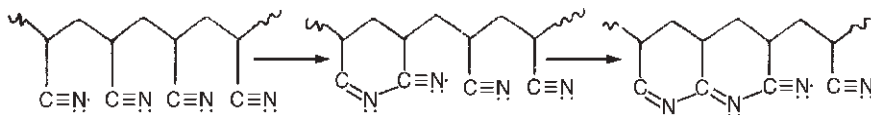
4.17 First stage carbon fibre–nitrile polymerisation. Source: Gupta, Paliwal and Bajaj, *Rev Macromol Chem Phys*, 1991, **C31**(1), 13.

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

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

4.6.1.5   *Bicomponent fibres*

DuPont first introduced bicomponent acrylic fibres to the market in 1958. The much-lamented type 21 fibre was made by dry-spinning a polyacrylonitrile homopolymer and a copolymer of acrylonitrile with sodium styrene sulphonate (SSS) through a bicomponent jet. The jet technology required to produce true bicomponent fibres is critical, with the two polymers needing to be kept separate to a late stage and delivered to each hole in the jet face side by side, thus forming side-by-side bicomponent filaments. Polymer rheologies are also very important, as flow characteristics also need to be matched. This type of technology is best suited to the small dry-spinning jets but pose huge design problems with the larger

wet-spinning jets. These jets contain much larger numbers of holes and it is extremely difficult to engineer true bicomponency in such jets. Monsanto claims such a jet is possible.[55] Acordis has experience of the *Kasen* bicomponent jet that contained up to 20 000 holes.

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

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

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

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

When these two polymers are brought together at the jet face and fibre formation
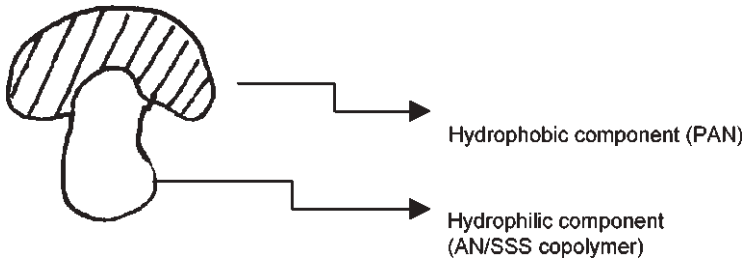
4.18 Cross-section of *Orlon 21* fibre. Source: Reprinted from J. C. Masson, *Acrylic Fiber Technology and Applications*, p. 172 by courtesy of Marcel Dekker, Inc.

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

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

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

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

4.6.2   Functional additives

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

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

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

98–100% polymer solution

0–2% stable dispersion

In line mixer   Spin jet   Fibre
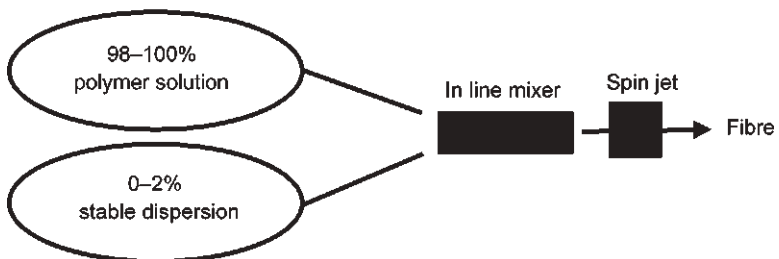
4.19 Late injection scheme. Source: Acordis UK Ltd.
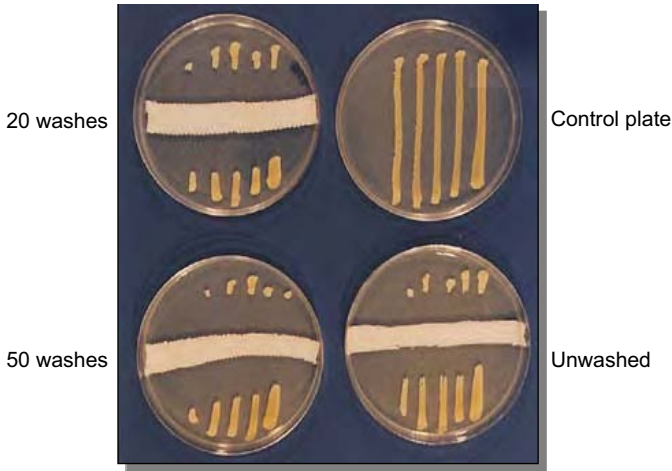
4.20 Antibacterial performance of a 70% cotton/35% *Amicor* fabric
using Swiss SNV195920 protocol. Source: Acordis UK Ltd.

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

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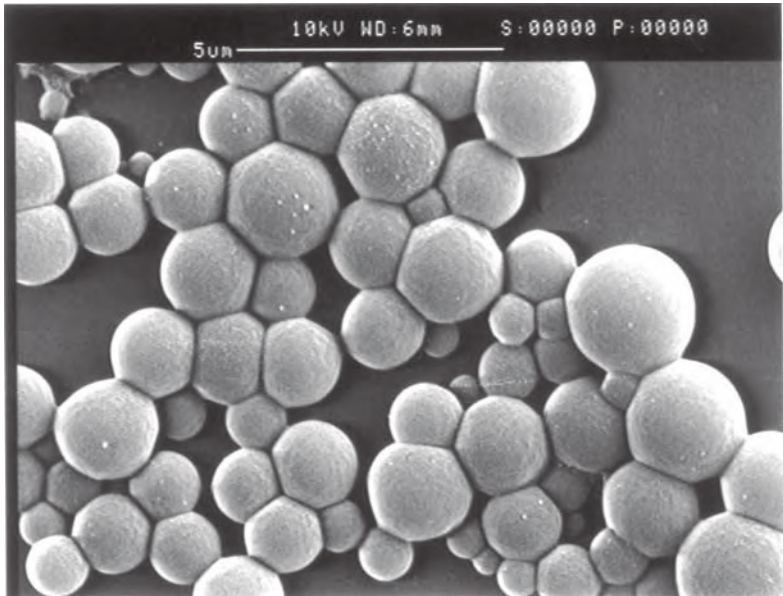
4.21 Microencapsulated phase change material used in *Outlast* fibre.
Source: Acordis UK Ltd.

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

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

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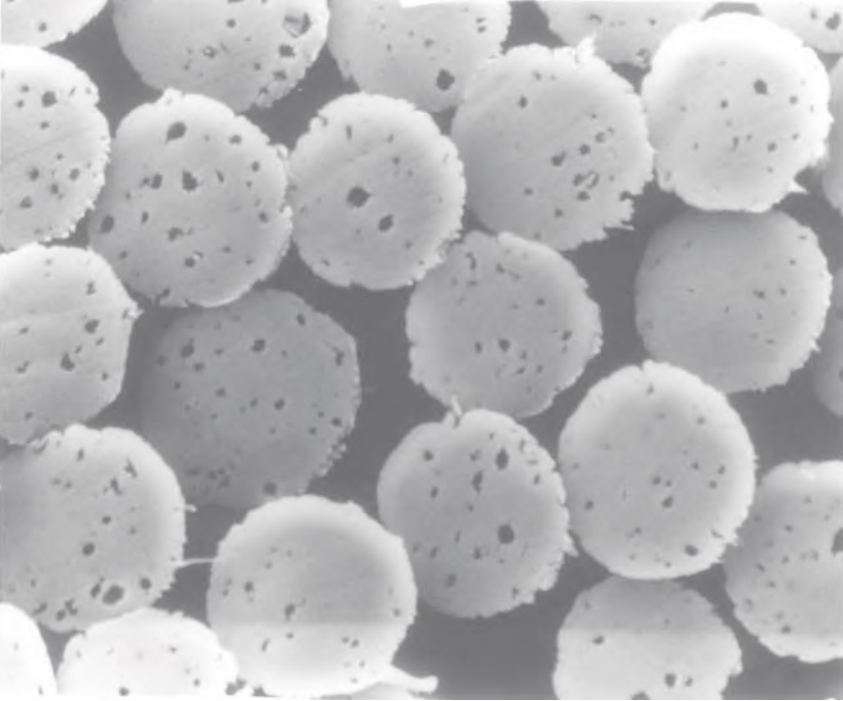
4.22 Cross-section of *Outlast* acrylic fibre. Source: Acordis UK Ltd.

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

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

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

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

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

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

4.7   Fibre variants

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

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

4.7.1   On-line coloration

A number of acrylic fibre variants can be made by manipulation to the fibre formation conditions and subsequent on-line processes. One of the most important

of these is the ability to producer dye (gel dye) the fibre on line. Three possibilities exist for on-line coloration: gel state dyeing, solution or dope dyeing and tow dyeing. Dope dyeing and pigmentation with coloured pigments is fairly routine and no further comment is offered in this chapter. Tow dyeing is a small speciality product for some manufacturers in which dried fibre tow is fed into a Serracant dyeing machine, which works on the pad/steam fix principle. By far the most significant coloration technique is the gel-dyeing process. Recent figures from one of the major dyestuff manufacturers in the world indicate that over 20% of all dyed acrylic fibres are gel-dyed and that this figure is increasing each year.
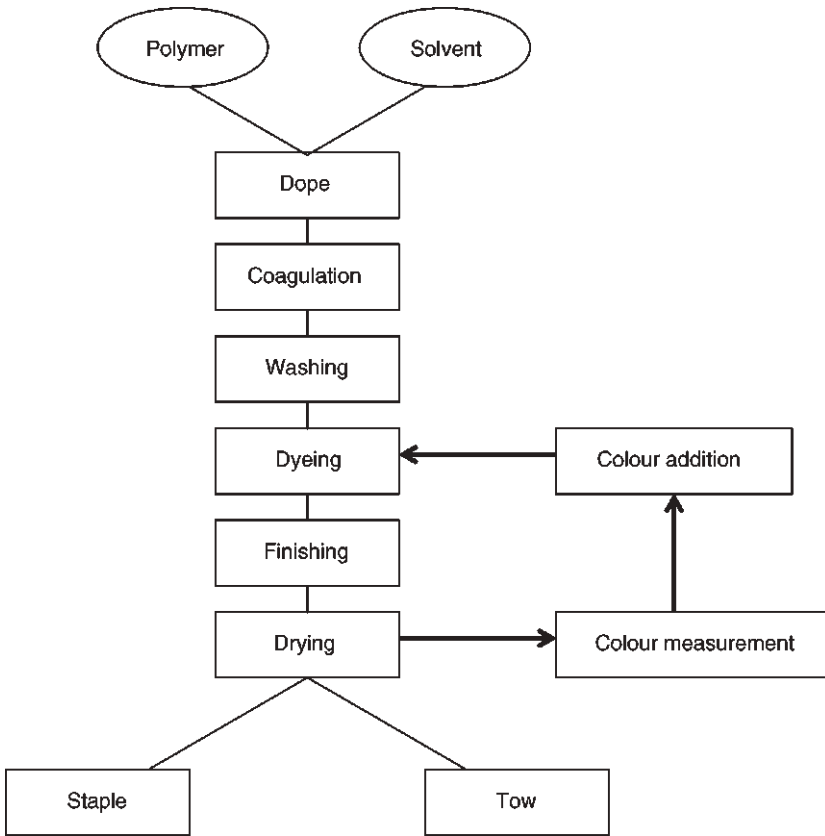
We have already seen that wet-spun fibres prior to drying have a porous structure which can be as much as 60% of the void structure. When the 'as formed fibre' is wet, this porous structure acts like a sponge. It is quite easy to exchange water within the fibre for dye/water from an external bath by using simple fluid mechanics principles. This exchange mechanism can occur within a few seconds and at ambient temperatures, although temperatures of between 50 and 100 °C are usually used.

Dye can be applied at almost any stage of the fibre formation process from the coagulation bath through washing and stretching and after stretching. It is, however, advantageous to have a washing stage after the dye application in order to remove any unfixed dyes before the fibre is dried and collapsed.

Liquid cationic dyestuffs, including optical whites and fluorescent dyes which were developed specifically for gel dyeing, are used in this process. Some companies offer coloured fibres from fixed shade cards and some companies produce coloured fibres to specific orders. Acordis in Grimsby has over 12 000 shades on record and offers minimum order quantities of only 1 tonne of fibre. This is achieved by having a very efficient on-line colour correction system in which it is possible to change colours within seconds. This rapid colour change is made possible by having two inline dyebaths fitted with dip rollers that can be raised out of the bath. As one colour run is coming to an end, the second bath is prepared with the new colour. The rollers are lifted on dyebath 1 as the rollers on dyebath 2 are lowered. This allows for a colour change to happen within about 2 minutes and for the new shade to be colour measured and corrected in about 10 minutes. Figure 4.23 is a simplistic diagram of the Courtelle process in Grimsby.

4.7.2   Low-pill fibres

One of the major criticisms aimed at apparel products made from acrylic fibres is the rather poor pilling performance. The mechanism of pill formation in textile fibres is well understood and documented. Pills will form when short lengths of fibre work their way free from the yarn structure and protrude from the fabric surface. Although they are held firmly at one end, the other free end is able to tangle with other free fibres and form small fuzz balls. These lie on the fabric surface and give the fabric a poor, worn appearance. The propensity of any fabric to pill is

```
  ( Polymer )        ( Solvent )
         \              /
          \            /
        +----------------+
        |      Dope      |
        +----------------+
        |  Coagulation   |
        +----------------+
        |    Washing     |
        +----------------+
        |    Dyeing      |  <---  +------------------+
        +----------------+       | Colour addition  |
        |   Finishing    |       +------------------+
        +----------------+                ^
        |    Drying      |  ----->  +---------------------+
        +----------------+          | Colour measurement  |
         /            \
        /              \
 +-----------+    +-----------+
 |  Staple   |    |    Tow    |
 +-----------+    +-----------+
```

4.23 Schematic of an on-line coloration process. Source: Acordis UK Ltd.

influenced by a number of factors – the staple length and decitex of the fibre, the yarn and fabric construction as well as the fibre tensile properties. As it is very difficult to stop short fibre lengths from freeing themselves from the yarn structure, the best way to minimise the problems of pilling is to ensure that the fuzz balls can break away from the fabric surface soon after they have formed.

The acknowledged way of doing this is to produce fibres with reduced knot tensiles (i.e. work to break). As tensile properties are developed in the fibre formation process and subsequent operations, then the skill is to reduce the knot properties without reducing the straight tensiles. The resulting yarns/fabrics will therefore perform in much the same way but as the pills form by entanglements, then the reduced knot tensiles allow the fibres to break at the points of stress within the loops.

Most acrylic fibre manufacturers have the ability to achieve this by a combination of stretch ratios and drying profiles. Regular acrylic fibres will give pill ratings of 3–4 using the European standard pill test. A fabric that does not pill will have a

rating of 5 using this technique. Low-pill fibres on offer today will have ratings of 4–5, which is excellent by any standards. There are many low-pill fibres on the market today. Some of the better known ones in Europe are *Dralon Low Pill* made by Bayer, the Montefibre fibre *Leacril NP* and *Courtelle Low Pill* from Acordis, while in the USA, Solutia's *HP* fibre has these properties.

4.7.3   Microfibres

Microfibres have become an important product in most companies' product ranges since 1995 and have allowed many new fabric developments to be brought to market. The reason for this is that fabrics made from microfibres have quite different aesthetics and moisture management properties. Microfibres are manufactured by attention to the fibre-formation parameters and the draw ratios used in the fibre stretching stages. It is usual practice to slow the rate of fibre formation by changes to the conditions used and to draw the fibre by as many as 20 times. The structure of the fibre surface in microfibres is therefore usually much smoother and, for dry-spun fibres, the cross-sectional shape remains circular rather than dog-bone.

The resulting yarns are much finer and contain more filaments per unit length. This influences the handle and drape of resulting fabrics, which tend to be very soft and with excellent drape. The closer packing of the filaments within the yarn structure can facilitate better wicking of water molecules by the resulting fabrics. This is claimed in some fibre types to be due to the dye site end groups in individual fibre filaments packing closely enough to allow for dipole interactions between the water and the negatively charged acid end groups. These performance claims have been substantiated by independent testing[60] of the fabrics, which have shown that acrylic fabrics made with microfibres perform as well as many of the functionalised moisture management polyester fabrics. These fabrics often use finish treatments such as *Intera* to achieve these effects. This licensed technology is described as a semipermanent hydrophilic coating.

4.8   End-use survey

The acrylic fibres business is now very mature, having been established for over 50 years and it can be described as being a truly global business. The business has gone through many periods of rationalisation and significant changes have been seen in the breakdown of global capacities. The world production of chemical fibres in 2001 was 30 112 000 tonnes. The breakdown by fibre type of this volume is given in Table 4.8.

Acrylic fibre production in 2001 was 2 574 000 tonnes, with Western Europe producing some 510 000 tonnes, the USA 240 000 tonnes, Asia (excluding Japan) some 990 000 tonnes and Japan 370 000 tonnes. Table 4.9 summarises the trends in acrylic fibre production from 1980 through to 2001 and gives projections through to the year 2010.

Table 4.8 World production (in thousands of tonnes) of chemical fibres

	1995	1997	1999	2001
Polyester				
Filament yarns	6 408	8 384	10 189	11 234
Staple fibres	5 540	6 783	7 696	8 148
Total	11 948	15 167	17 885	19 382
Polyamide				
Filament yarns	3 139	3 425	3 276	3 255
Staple fibres	601	558	528	428
Total	3 740	3 983	3 804	3 683
Acrylic				
Filament yarns	4	4	5	5
Staple fibres	2 442	2 724	2 516	2 569
Total	2 446	2 728	2 521	2 574
Olefin				
Filament yarns	1 678	1 800	2 543	2 891
Staple fibres	901	1 065	1 181	1 255
Total	2 579	2 865	3 724	4 146
Others				
Filament yarns	136	164	193	222
Staple fibres	111	110	101	105
Total	247	274	294	327
Grand total	20 960	25 017	28 228	30 112

Table 4.9 World production (in millions of tonnes) of acrylic fibres (1980–2001)

	1980	1985	1990	1995	2001	2010 (predicted)
North America	0.42	0.37	0.33	0.35	0.24	0.15
South America	0.05	0.06	0.06	0.05	0.07	0.07
Western Europe	0.69	0.84	0.67	0.62	0.51	0.33
Eastern Europe	0.20	0.25	0.25	0.15	0.09	0.00
ME/Africa	0.04	0.12	0.14	0.23	0.27	0.45
South & South East Asia	0.01	0.02	0.05	0.11	0.16	0.29
East Asia	0.25	0.37	0.44	0.58	0.83	1.33
Japan	0.35	0.38	0.36	0.37	0.37	0.36
World	2.01	2.41	2.31	2.47	2.55	2.98
Idle capacity	0.53	0.19	0.50	0.57	1.16	

Source: CIRFS.

The trends indicated in Table 4.9 suggest that the changes seen in the acrylic fibre production statistics since 1995 will continue and will result in dramatic changes by the year 2010. Production output in North America has fallen from 420 000 tonnes in 1980 to 240 000 tonnes in 2001 and is projected to fall to 150 000 tonnes by 2010. In Western Europe production has fallen from a peak of 840 000

tonnes in 1985 to 510 000 tonnes in 2001 and is projected to fall to 330 000 tonnes by 2010. However, the world production of acrylic fibres has increased steadily from 2.01 million tonnes in 1980 up to 2.55 million tonnes in 2001 and is predicted to rise to 2.98 million tonnes by the year 2010. Obviously, we are witnessing a significant change in the global business with the development of new capacity in East Asia and with significant new capacity projected for South East Asia and the Middle East/Africa regions by the year 2010. It is clear therefore that for the economically developed nations, the growth in acrylic fibre consumption has stopped and in many cases reversed, while in the developing nations it is expanding.

Despite these changes in production statistics, the end-uses for acrylic fibres are well established. These applications fit in very well with the unique properties that acrylic fibres display and which are fully exploited by the fibre conversion routes available. Acrylic fibre demand remains strong because it has a number of major differences from other fibres, which give it a strong differentiation. It has a low specific gravity of 1.18 (cotton is 1.58), which gives bulk and warmth at reduced weight and hence good value. Yarns and fabrics have soft, wool-like aesthetics, and can be dyed at atmospheric pressure with well-developed and very cost-effective dyestuffs. A full shade range is easily achieved with colours being bright and with an excellent colour yield. Yarns and fabrics resist UV fading and biodegradation. The moisture regain level of 2–3% is useful, while allowing rapid drying and good wicking, and fabrics retain their shape after machine washing. The major end-uses for acrylic fibres are knitwear, socks, fleece-wear, handknitting or craft yarns, blankets, upholstery and a number of industrial fields of application.

In terms of fibre conversion routes, acrylic fibres process with high yields through all of the known conversion routes. Three forms of acrylic fibre are sold into the market for conversion into yarns and fabrics: tow, short staple and long staple. The tow to top route using stretch-breaking equipment is particularly cost effective with acrylic fibres and when combined with some of the shorter fibre spinning routes such as Repco spinning, the yarn-making costs are extremely competitive. Short staple fibre is converted through conventional cotton spinning equipment with ring spinning, open-end spinning and air jet spinning being used to manufacture yarns. Long staple spinning produces yarns through the woollen system. As one of the key advantages of acrylic fibres is the cost effectiveness of the on-line coloration process, the processing of coloured fibres is very common for acrylics. This puts some demands on conventional ecru mills in that segregation of coloured fibres from ecru fibres is essential and the sequential production planning of colours is important. Effective cross-blending is also very important, particularly for the shorter routes. Although on-line coloration of acrylic fibres is a great benefit, colour variation down a continuous tow and from tow to tow does mean that cross-blending is essential for good colour continuity. Staple end-uses take care of this cross-blending quite efficiently but in the tow to top conversion route it is very important that measures are put in place to ensure good cross-

blending. In tow to top conversion it is usual practice for two tow bales to be fed into one stretch breaker. The resulting broken fibres are collected in cans and these are stored in columns until there is sufficient stock to feed into the subsequent drawing operation. The cans are taken from across the columns as they are fed into the drawing operation, thereby ensuring good cross-blending.

Tables 4.10 and 4.11 summarise the latest data from CIRFS on the end-uses into which acrylic fibres are utilised. These tables cover declared figures for sales of acrylic fibres into staple, tow and tops for Western Europe, Central and Eastern Europe and Turkey for the year 2000. The data are split into spun yarn and non-spun end-uses and it is concluded that these countries shipped 524 905 tonnes of acrylic fibre in the year 2000.

It is clear from these figures that acrylic fibres have made little impact in non-spun areas, with only 13 959 tonnes (2.3%) being used. Of this volume, the most significant is the Wildman process that produces fleece type fabrics for apparel end-uses. This product accounts for 7 715 tonnes of this total, which leaves only just over 6 200 tonnes for other non-spun applications. The reason for the low consumption of fibre into these non-spun end-uses is that, generally speaking, acrylic fibres do not provide any specific properties, including fibre price, that cannot be bettered by other fibres. Clearly, there are some niche end-uses into which acrylics do offer real benefits, but these are low volume areas such as concrete and bitumen reinforcement and hot gas filtration.

For spun yarns, it is clear that acrylic yarns have wide appeal in terms of application; however, with only 79 114 tonnes (18.3%) going into woven end-uses, it is the knitted area that dominates. Of these knitted end-uses there are two

Table 4.10 Acrylic fibre deliveries (in tonnes) for Western Europe, Central and East European countries (CEEC) and Turkey (2000)

Process	Western Europe	CEEC + Turkey
Spun yarn		
Cotton, Schappe & flax spinning	113 256	40 619
Woollen & semi-worsted spinning	21 519	41 754
Worsted spinning	134 803	143 071
Total of spun yarns	269 578	225 444
Of which open-end	33 598	2 763
Unspun yarn		
Filling & wadding applications	2 881	68
Needlepunch carpets	175	
Non-wovens	823	30
Wildman	7 514	201
Other processes	1 778	489
Total unspun	13 171	788
Traders & jobbers	15 026	898
Total	297 775	227 130

Table 4.11 End-use breakdown (in tonnes) for acrylic fibre deliveries to Western Europe, Central and East European countries (CEEC) and Turkey (2000)

End-uses	Western Europe	CEEC + Turkey
Spun yarn		
1 *Weaving*	37 630	41 484
Apparel fabrics	4 802	12 050
Cotton-type fabrics	3 794	3 200
Wool type fabrics	1 008	8 850
Furnishing and household fabrics	28 567	29 434
Blankets	15 387	16 405
Bedding and household fabrics	2 822	3 504
Net curtains and transp. voile	1 270	1 645
Other furnishing fabrics	9 088	7 880
Industrial fabrics	4 261	
2 *Textile narrow fabrics*		
3 *Knitting*	220 266	132 351
Warp, Raschel and Leaver knit	82 505	41 314
Apparel fabrics	79 806	40 141
Net curtains and transp. voile	80	74
Furnishing, household and Industrial	2 619	1 099
Other knittings	137 761	91 037
Hosiery–footwear	7 158	12 665
Underwear	7 928	8 000
Outerwear	120 857	58 297
Furnishing and household	1 639	1 2023
Industrial applications	179	52
4 *Carpets*	5 916	37 090
Backing	Not used	Not used
Pile: tufted	4 969	4 690
Pile: others	947	32 400
5 *Others*	5 766	14 519
Hand knitting	4730	14519
Other processes	1 036	
Total spun yarns (1 + 2 + 3 + 4)	269 578	225 444
Unspun yarn		
For apparel	7 609	234
For furnishing and household	3 527	34
For industrial uses	2 035	520
Total unspun	13 171	788

Source: CIRFS.

that consume the bulk of the volume – apparel fabrics produced by warp and Raschel knitting, and outerwear, produced by flat bed or circular knitting. Other end-uses, which make very worthwhile contributions to volumes, are blankets, furnishing fabrics, hosiery, carpets and hand-knitting or craft yarns.

Of these spun yarns, worsted or tow to top spinning accounts for over 56%, with

cotton ring spinning accounting for a further 23.4%. These statistics tie in quite nicely with the major attributes of the acrylic fibre technologies. We have already seen that acrylic fibres have a low specific gravity that allows yarns and fabrics to be made which have a high bulk to weight ratio. If we combine with this the simple and effective on-line coloration capability of the acrylic fibre technology then we have all the makings of a very cost-effective route to market. It is these attributes that have contributed more than any others to the development of the worsted-spinning route. The worsted route is designed to produce yarns with high shrinkage and hence bulk potential as well as fully relaxed yarns. It is also ideally suited for processing of coloured fibres with changeovers from one colour to another quite easy.

We have therefore a whole sequence of technologies that allow finished fabrics and garments to be produced without any need for wet processing. The fibre manufacturer produces coloured fibres and these are converted into high bulk or fully relaxed coloured yarns through worsted spinning. These are, in turn, used in knitted socks or outerwear, or in craft yarns. This is an extremely cost-competitive route to market and is one of the major reasons for the success of acrylic fibres. It also clearly accounts for the split of end-uses. Acrylic fibre manufacturers have also tried to maximise these attributes over the years with fibre variants such as the bicomponent fibres playing to these strengths.

While on-line coloration and knitted end-uses are key to the acrylic business, they are best suited to the wet-spun technologies. However, dry-spun fibres also have physical properties, that allow them to provide desirable fabric properties in certain end-uses. One of the important differences in the physical properties between dry-spun and wet-spun acrylics is the little-discussed property known as flexural rigidity. This is a measure of the ability of a fibre or group of fibres to recover from deformation. It is an important property in short pile fabrics that are used in situations where deformation occurs frequently. Good examples are upholstery and carpets, in which the short tufts or piles can be deformed by people sitting or walking on them. In order for the fabric or carpet to remain aesthetically pleasing it is important that these tufts or piles recover from the deformation quickly and repeatedly. Dry-spun acrylic fibres have this ability and so they find quite extensive use in this type of end-use. The name *Dralon* is not only the name given to the dry-spun acrylic fibre manufactured by Bayer; as already noted it is almost synonymous with acrylic upholstery fabrics.

Other properties associated with acrylic fibres in upholstery end-uses are their ability to be dyed to brilliant shades, excellent light fastness, good abrasion resistance, high resistance to staining and good cleanability. The use of acrylic fibres in carpet yarns has declined significantly since the 1980s as polyamide and polypropylene yarns have become more dominant. However, acrylic fibres are still important in carpet yarns, particularly in certain types of high-quality products such as rugs.

There will be some subtle differences in these statistics for Europe when

compared with the USA and the Far East, but the general patterns are consistent. Two notable differences between the USA statistics and Europe will be the consumption of acrylic fibres in the USA into hosiery end-uses and craft yarns. The acrylics council set up in the USA in the 1980s to promote acrylic fibre has worked very hard and with some notable success on the use of acrylics in hosiery end-uses. Acrylic fibres offer a number of performance benefits in hosiery over cotton and wool. They transport moisture away from the skin more efficiently than cotton or wool and they hold less water. These combine to provide wearer comfort and reduce the risk of blisters during high-stress conditions. Within Europe, the use of craft yarns for hand knitting and crocheting has declined significantly since the 1980s. This is due to lifestyle changes within European society. However, in the USA this industry is still very strong and although some decline has been seen, the percentage of fibres consumed in this area is much larger than in Europe or the Far East.

Finally, it is worth noting that acrylic fibres do have some unique properties that allow them to find uses in some industrial products. The outstanding resistance of acrylic fibres to chemicals and their non-melting properties advocate their use in cement and bitumen reinforcement. Fibres used in these areas tend to be nominally PAN homopolymers with high molecular weights although there are notable exceptions to this general rule. This gives them excellent resistance to the highly alkaline wet conditions in cement and the high temperatures found in bitumen end-uses. Similar properties account for the use of certain acrylic fibres in battery plate reinforcement. It is the excellent resistance to hydrolysis by sulphuric acid that is the major attribute of acrylics in this end-use.

The outstanding ultraviolet stability of certain acrylic fibres combined with the dimensional stability of the woven acrylic fabrics allows them to find a niche end-use in awnings, boat covers, outdoor furniture, car convertible roof fabrics and sandbags. The final end-use of note is that of certain acrylic fibres in hot gas filtration. These fibres tend to be PAN homopolymers and they offer excellent resistance to these aggressive environments. A typical example of such an end-use is in power stations that burn fossil fuels.

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