
R. R. MATHER
Heriot-Watt University, UK

5.1 Introduction

Polyolefin fibres comprise those fibres whose polymer chains are essentially high molar mass, saturated, aliphatic hydrocarbons. The United States Federal Trade Commission approves two names, 'olefin fibres' and 'polyolefin fibres' to describe manufactured fibres in which the synthetic polymer is composed of at least 85% by mass of polyolefin units.^{1,2} Chief among polyolefins in commercial importance are polypropylene (PP) fibres and, to a lesser extent, polyethylene (PE) fibres. Both types of fibre are recognised as generic names defined in ISO2076.¹ Their structures are given in Table 5.1. The correct chemical names of PP and PE are, in fact, poly(propene) and poly(ethene) respectively, propene and ethene being the chemical names for propylene and ethylene.

Other polyolefin fibres that have been produced with commercial application in mind are poly(4-methyl-1-pentene), poly(1-butene) and poly(3-methyl-1-butene), although commercial interest in these types of fibre is only marginal.² The outline structures of these polyolefins are also shown in Table 5.1, apart from PE, polyolefins are in practice polymers of α -olefins of general formula, $\text{CH}_2=\text{CHX}$, where X represents an alkyl chain. In addition, copolymeric polyolefins, such as ethene-propene and ethene-octene copolymers, have some commercial significance. Blends of different polyolefins are also produced commercially: for example, bicomponent multifilaments, with each filament containing a PP core and a PE sheath. If the fibres are heated, the PE sheath can melt and so bond the multifilaments into resilient monofilament yarns. These bicomponent fibres also find use in non-woven fabrics. Fibres from blends of PP with other polymers, such as nylon and polyester, are also available.

The first polyolefin fibres, from low-density polyethylene (LDPE), were extruded as long ago as the 1930s,² but their commercial impact was very limited. Fibres melt-extruded from high-density polyethylene (HDPE), which became available in the late 1950s, were found to possess considerably superior mechanical properties. The processing technology by which Ward *et al.* in the 1970s developed high-modulus PE fibres³ was licensed commercially to produce

Table 5.1 Structures of some polyolefins

Polymer	Repeat unit
Polyethylene	$-(\text{CH}_2 - \text{CH}_2)-$
Polypropylene	$-(\text{CH}_2 - \underset{\text{CH}_3}{\text{CH}})-$
Poly(4-methyl-1-pentene)	$-(\text{CH}_2 - \underset{\begin{array}{c} \text{CH}_2 \\ \\ \text{CH} \\ / \quad \backslash \\ \text{CH}_3 \quad \text{CH}_3 \end{array}}{\text{CH}})-$
Poly(1-butene)	$-(\text{CH}_2 - \underset{\begin{array}{c} \text{CH}_2 \\ \\ \text{CH}_3 \end{array}}{\text{CH}})-$
Poly(3-methyl-1-butene)	$-(\text{CH}_2 - \underset{\begin{array}{c} \text{CH} \\ / \quad \backslash \\ \text{CH}_3 \quad \text{CH}_3 \end{array}}{\text{CH}})-$

*Tenfor*TM and *Certran*TM fibres.^{4,5} However, the commercial success of these fibres appeared only limited and their production eventually ceased. Commercial interest in PE fibres increased again when gel-spun PE fibres came onto the market in the early 1990s.

By contrast to PE fibre, PP fibre enjoys a massive acceptance in the marketplace. Its commercial impact started in the 1960s when it began to replace jute fibre in carpet backings and bast fibre in ropes and cords. Since then, PP fibre and tape have been developed for a huge variety of end-uses, including carpet face yarns, geotextiles, textiles for horticulture, filters, sports surfaces, packaging and strapping. During the 1990s, for example, the growth world-wide in PP fibre consumption was at least 6% in any one year. By the year 2000 the total world production of PP in textiles had risen to nearly 6.0 million tonnes^{6,7} and accounted for 96% of overall polyolefin fibre production. The equivalent amounts in 2000 for polyester (PET) fibre and nylon fibre were 18.9 and 4.1 million tonnes, respectively.⁷ More recently, there has been a spectacular rise of PP fibre use in the non-wovens sector, especially in medical and hygiene applications. Many observers believe that there are still further commercial applications to be explored, principally because some end-users are still unaware of the scope offered by PP fibres.⁸ The most tantalising

challenge is, arguably, the apparel industry, where the use of PP fibres is quite limited, except in a few specialist sectors such as protective clothing and some military uses.⁹ The emphasis in this chapter will be on PP fibres, since they account for by far the greatest market among polyolefin fibres.

It is apparent, then, that each of the many different end-uses of PP fibres demands a different set of technical specifications to be met. The different mechanical properties required will result from the different fibre structures produced by different processing conditions. Thus, to maximise the commercial potential of PP fibres, the importance of the relationship between processing, structure and fibre performance has to be recognised.

The considerable commercial market pull has been complemented in recent years by a significant technological push, arising from improvements in fibre technology, the ability to produce grades of PP using metallocene catalysts, and developments in additives. In future, there will be considerable benefits too from the application of plasma treatment, to alter the surface properties of PP fibres without affecting their bulk properties. Fibres treated in this way are likely, for example, to be used in protective clothing and biomedical applications.

5.1.1 Commercial advantages and disadvantages

The commercial advantages are summarised in Table 5.2. The low densities of PE and PP (both are lighter than water) confer on them very high covering power in comparison with other textile fibres. Moreover, both types of fibre can be produced by melt extrusion, the simplest of all synthetic fibre extrusion technologies and one that is perceived as clean. In addition, there is currently a high performance/cost ratio, notably with PP fibres.¹⁰ Nowadays, however, PE fibre produced by gel spinning accounts for much of PE fibre usage.¹¹ There is also some interest in PE fibres produced by solid-state extrusion.¹² Detailed accounts of high-performance PE fibres have been published in a sister volume.^{11,12}

However, PE and PP fibres do possess some serious inherent disadvantages, which are also summarised in Table 5.2. The low melting points of PE and PP, although they do facilitate fibre processing by melt extrusion, prevent their use in environments with elevated temperatures. PE and PP fibre types produced for outdoor use have to be protected from ultraviolet radiation. The inherent inability of PE and PP fibres to be successfully dyed, unless they contain suitable additives or comonomers to which certain types of dye are substantive, considerably restricts their use for clothing. Because of their high flammability, PE and PP fibres have to be treated with fire-resistant additives for many applications.

Despite many similarities in structure and properties between PE and PP fibres, the commercial production of PP far outstrips that of PE fibres.⁶ A number of reasons may be cited. For the majority of textile applications, fibres must be dimensionally stable up to at least 100 °C.¹³ This requirement limits the use of melt-extruded PE fibres. PP fibres possess better resilience, with tenacity and

Table 5.2 Commercial advantages and disadvantages of PE and PP fibres

Advantages	Disadvantages
Low density (0.90–0.96 g cm ⁻³)	Low melting point (120–125 °C for PE; 160–165 °C for PP)
Good tensile properties	Prone to photolytic degradation
Good abrasion resistance	Inferior shrink resistance above 100 °C
Excellent resistance to chemicals	Poor dyeability
Excellent resistance to mildew, micro-organisms and insects	High flammability
Almost negligible moisture regain	Inferior resilience
Good wicking action	Creep
High insulation	
Comfortable to the skin	

abrasion resistance equal to those of PE fibres.² PP fibres also possess better resistance to creep,¹³ although it has been pointed out that a considerable improvement in the resistance to creep in PE fibres can be obtained by radiation cross-linking.³

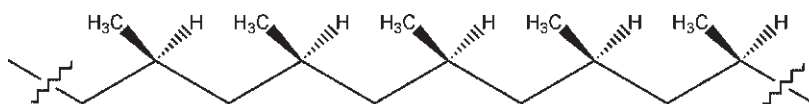
5.2 Molecular configuration

PE chains, which contain no asymmetric carbon atoms, tend to adopt a zigzag form. For PP and other α -olefin polymers, every other carbon atom along the chain backbone is asymmetric. The polymer chain can adopt a variety of configurations. As an example, the three different stereoisomeric forms that PP chains may assume are shown schematically in Fig. 5.1 in fully extended planar projections. In planar projections of isotactic PP chains, all the methyl side groups are situated uniformly on the same side of each chain. In practice, the chains normally adopt a three-dimensional helical configuration, as illustrated in Fig. 5.2. This highly regular structure favours the formation of PP fibres with superior mechanical properties. In syndiotactic PP chains, the methyl groups alternate in a regular fashion between the two sides of each chain. Syndiotactic PP chains can also adopt a helical configuration. In atactic PP chains, the methyl groups are arranged randomly on the two sides of the chain.

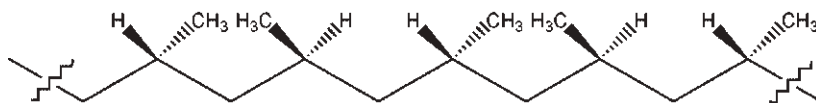
5.3 Production of polyolefins

5.3.1 Ziegler–Natta catalysis

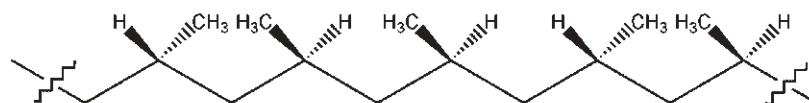
The structures and properties of polyolefin fibres are significantly influenced by the properties of their constituent polymer chains. In turn, these properties reflect the method of synthesis of the chains. In 1953, Karl Ziegler discovered catalysts that promote the polymerisation of ethene molecules to form PE macromolecules



Isotactic – methyl groups same side



Syndiotactic – methyl groups alternate



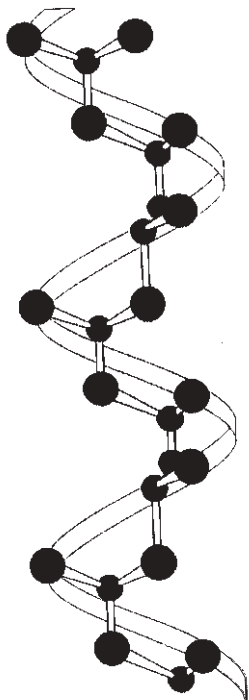
Atactic – methyl groups randomly arranged

5.1 Stereoisomeric structures of polypropylene.

even at low pressure. A year later, Giulio Natta synthesised isotactic PP macromolecules in the same way, and in the same year PP monofilament yarns were also extruded from the melt.¹⁴

Ziegler found that, in the presence of a catalyst containing an aluminium alkyl compound and a transition metal halide, ethene could be polymerised at atmospheric pressure and ambient temperatures. Natta, using similar types of catalyst, was able to polymerise a variety of α -olefins, including PP. These polyolefins possessed a high degree of stereoregularity in their polymer chains. Since the 1950s, a wide variety of Ziegler–Natta catalysts has been prepared, in which a Group I, II or III metal alkyl is combined with the halide of a transition metal, very often a titanium halide. Indeed, the nature of the solid catalyst is highly influential in determining the degree of stereoregularity in the polyolefin product.¹⁵ Thus, high stereoregularity is generally favoured by large catalyst particles. The formation of isotactic PP is, furthermore, favoured by the α -form of titanium trichloride rather than the β -form, by the presence of Ti^{3+} ions rather than Ti^{4+} ions, and by shorter alkyl groups in the metal alkyl.¹⁵

It is considered that, before it has been incorporated into the growing polyolefin chain, each α -olefin molecule undergoes complexation at a transition metal centre. Although various mechanisms for Ziegler–Natta-catalysed polymerisations have

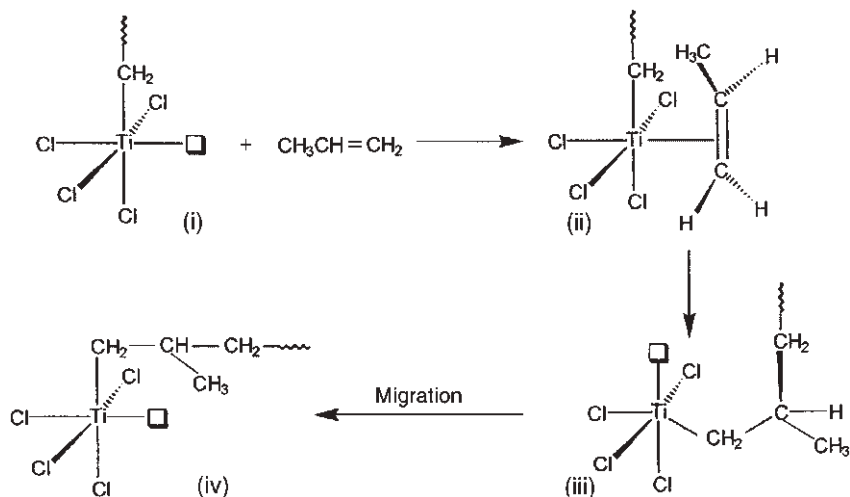


5.2 Helical configuration of an isotactic PP polymer chain.

been proposed, the so-called monometallic mechanism is now the most favoured.¹⁵⁻¹⁷ This mechanism can be conveniently outlined here for PP synthesis with a catalyst containing α -TiCl₃ and an aluminium alkyl.^{16,18} It is proposed that the Ti³⁺ ion is alkylated after chemisorption of the aluminium alkyl to the TiCl₃ crystal surface (Fig. 5.3 (i)). The complex so formed is, therefore, at the catalyst surface. However, at the catalyst surface, each Ti³⁺ is only 5-coordinated, so that a vacant *d*-orbital is present.

An incoming propene molecule can form a π -complex with the titanium through the vacant *d*-orbital (Fig. 5.3 (ii)). The propene molecule then becomes inserted between the titanium and the alkyl chain (Fig. 5.3 (iii)), whereupon the polymer that is formed returns to its original position (Fig. 5.3 (iv)). Further propene molecules can now in turn be incorporated in a similar fashion. Thus, the growing polyolefin chain is always attached to the transition metal.

For an isotactic polyolefin to be formed, each α -olefin molecule must approach the catalyst surface with the same orientation. Thus, it can be shown that a propene molecule can be accommodated in only one way at the catalyst surface, for it to be sufficiently close to the Ti³⁺ ion in complex (ii). Moreover, the formation of



5.3 Monometallic mechanism for Ziegler–Natta catalysis. The square boxes represent empty coordination sites.

isotactic polyolefin depends on the migration of the vacant *d*-orbital in the titanium back to its original position before another α -olefin molecule is incorporated. Without this migration, a syndiotactic polyolefin would be formed.

The dispersities of HDPE grades produced using Ziegler–Natta catalysts normally range between 5 and 20. Dispersity refers to the ratio of the weight-average molar mass, M_w , of a polymer to the number-average molar mass, M_n . M_w can be as high as 1 000 000 g mol⁻¹ but fibres can be produced from grades of such high molar mass only by gel spinning.^{3,11} For HPDE grades that can be melt-spun, the highest value of M_w is about 200 000 g mol⁻¹.³

The dispersities of PP grades normally range between 4 and 8. Thermal cracking of these grades results in a reduction in molar mass and a lower range of dispersities, 3–6, due primarily to the elimination of the high molar mass ‘tail’ in the molar mass distribution. These modified PP grades, often called controlled-rheology (CR) grades, are especially suitable for forming fibres. For most fibre applications, M_w is in the range 200 000–350 000 g mol⁻¹. However, for the production of monofilaments, M_w may be as high as 600 000 g mol⁻¹, and for the production of melt-blown non-wovens, as low as 150 000 g mol⁻¹.

5.3.2 Melt flow index

Polyolefin grades are normally supplied as granules. An important specification of these grades is the melt flow index, MFI. The MFI is the mass of polymer in grams extruded in 10 minutes at 230 °C under an applied load of 2.16 kg through a standard cylindrical dye in a flat entry extrusion rheometer.¹⁹ Equipment is

Table 5.3 MFI values for different grades of PP

Product	MFI
Monofilaments and tapes	1–11
Staple fibres	9–16
Bulk continuous fibres (BCF)	11–24
Spun-bond PP	20–40
Melt-blown PP	100–1500

Table 5.4 Dispersities of two samples of isotactic PP of MFI 12 g/10 min

M_n (number-average molar mass)	M_w (weight-average molar mass)	M_w/M_n (dispersity)
34 000	261 000	7.7
42 000	211 000	5.0

commercially available for the determination of MFI values. Table 5.3 shows some typical MFI values for PP grades of different products.

There is an inverse relation between MFI and the apparent melt viscosity under constant shear stress. Therefore, an increase in M_w results in a reduction in MFI. However, there is no simple relation between MFI and M_w . As an example,²⁰ two samples of isotactic PP, for both of which MFI is 12 g/10 min, are compared in Table 5.4.

5.3.3 Metallocene catalysis

In the 1980s, interest was kindled in a new range of catalysts, the metallocenes, following the discovery by Sinn and Kaminsky²¹ of a new catalyst system which was highly active in the polymerisation of ethene. Subsequently, Kaminsky and co-workers²² discovered a similar catalyst system for the synthesis of isotactic PP. These catalysts are soluble. (Although soluble Ziegler–Natta catalysts had been prepared, they were found largely to catalyse the production of atactic polyolefins.)

Metallocenes are organometallic compounds based on Group IV transition metals, such as titanium, zirconium and hafnium. Of these, zirconium is the most active, while titanocenes tend to be deactivated at higher temperatures. Metallocenes react with methylalumoxane (MAO), a co-catalyst, to form an active catalytic complex. MAO consists of oligomers, whose structure approximates to:



where $n = 10\text{--}30$.

The mechanism underlying catalysis by metallocenes has been discussed by Brintzinger *et al.*²³ The metal in the metallocene molecule is the active centre for polymerisation and is sandwiched between two η^5 -cyclopentadienyl (CP) ligands (the symbol η^5 signifies that all five carbon atoms in the CP ring are bonded to the metal atom). In addition, two σ -ligands, usually chlorine atoms, are also coordinated to the metal atom. However, molecules of simple metallocenes are too flexible to confer sufficient rigidity to the catalytic complex, and catalytic activity is consequently low. The two CP rings are, therefore, also bridged through one or more carbon atoms or a silicon atom, to provide the rigidity required. The structure of a zirconocene can be represented as:



It should be noted that the two CP rings are not situated directly opposite one another.

The CP rings remain attached to the metal atom during polymerisation, but the chlorine atoms leave the complex during formation of the active catalyst. Alkyl or aryl substituents may be present on the CP rings. Different substituents and different bridging entities alter the structural character of the CP ligand, the metal–CP distance and the CP–metal–CP angle. There is thus considerable electronic and structural versatility in metallocene catalysts.

The activity of the catalyst system is strongly influenced by the CP–metal–CP angle. A short bridge between the two rings reduces this angle, and catalytic activity is increased in consequence. A smaller angle is particularly important for propene polymerisation, although ethene polymerisation can be catalysed where the bridge is much longer.¹⁵ The ratio of MAO to metallocene concentrations is also important: the ratio required for maximum catalytic activity varies among different metallocenes. In addition, the molar mass of the polymer produced is

dependent on the structure of the CP ligands. A methyl substituent in the 2-position of each CP ligand, for example, gives rise to polypropylene of much higher molar mass. As with Ziegler–Natta catalysis, the true catalyst site is the metal, with the growing polyolefin chain as a ligand, and there is a vacancy at the metal atom to allow co-ordination of the incoming monomer.

Metallocene catalyst systems are becoming increasingly important for the production of PP. They are more specific and more active than Ziegler–Natta catalysts and can be designed so that only chains of isotactic PP are produced. By contrast, isotactic grades of PP made using Ziegler–Natta catalysts contain small proportions of atactic PP, typically up to 5%. Moreover, metallocene grades of PP possess a narrower molar mass distribution, of dispersity *ca.* 2.5. However, owing to small regio-irregularities in the polymer chains, where individual propene monomers have been inserted in a reverse manner, the melting points of commercial metallocene grades of PP are often about 15 °C lower than PP grades produced using conventional Ziegler–Natta catalysts.¹⁸

Fibres based on metallocene PP grades possess a number of advantages.¹⁸ The more uniform distribution of PP chain length results in a rheology more favourable for melt processing. Thus, finer fibres may be extruded to create spun-bonded non-woven fabrics with more cloth-like qualities.^{24,25} The greater control of fibre processing also leads ultimately to fibres of improved tensile strength. In addition, metallocene catalysts allow the incorporation of special comonomers into PP chains, thus permitting the modification of the structure and properties of PP fibres. These comonomers include flame-retardant units, chromophores, and compounds that, by increasing intermolecular attraction between the PP chains, can improve fibre resilience.^{25,26} More recently, an iron-based catalyst has been synthesised whose efficiency in catalysing the polymerisation of ethene matches those of the most active metallocene catalysts.²⁷

Polymers of low dispersity can, in principle, be synthesised by ‘living’ polymerisation,²⁸ in which there is virtually no chain termination or transfer. A living polymerisation of propene has recently been reported,²⁹ giving rise to PP of dispersities as low as 1.2 ($M_w \sim 42\,000\text{ g mol}^{-1}$).

5.4 Polyolefin structures

5.4.1 Arrangements of polymer chains

The simplest approach to the structures of polyolefin fibres is to consider that they consist solely of crystalline regions and amorphous regions. In the crystalline regions, segments of the polymer chains exist in well-defined lattice structures, such that they can be identified by X-ray diffraction. In the amorphous regions, an assembly of random interpenetrating chains may be considered. Degrees of crystallinity in fibres can be estimated by a variety of techniques, including X-ray

diffraction, fibre density measurements and heats of fusion.^{16,30} A method using Raman spectroscopy has also been recently reported.³¹

However, more recent developments have given rise to the concept of a spectrum of order/disorder, which is constructed around various degrees of organisation both within polymer chains and between them.³² At one extreme of the spectrum is the truly amorphous structure. If the random assembly of polymer chains which it contains is altered to a more extended conformation, accompanied by a parallel arrangement of chain segments, an amorphous structure with correlation results.³³ This arrangement can exist, however, only below the glass transition temperature, T_g , so will, in practice, not apply to PE and PP fibre technology. Further ordering now gives rise to regular chain conformations, whereby the chains are parallel but displaced along their axes, yet the chains' lateral packing remains irregular. Still further order appears if the axial displacement is lost and there is more efficient lateral packing. This degree of ordering is represented by the paracrystalline structure, which has particular importance in polyolefin fibre technology. As an alternative, conformationally disordered, or 'condis' crystals may result, in which there is regular packing of chains with some degree of conformational disorder.³⁴ Further ordering gives a crystalline structure with defects, and then finally an ideal crystalline structure.

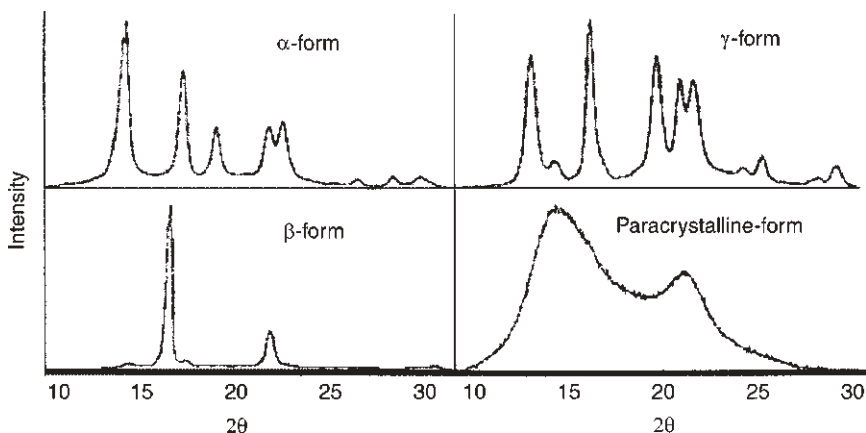
To understand the physical structure of a fibre more fully, further factors have to be taken into account. Thus, the locations of regions comprising the various degrees of order and disorder should be considered.³² Another factor is the degree of orientation of the polymer chains and even of the bonds and segments that constitute them. To resolve all these aspects is an ambitious task, but considerable progress may be possible using molecular and microstructural modelling techniques.³²

5.4.2 Crystalline structures

For PP, three different crystalline forms have been identified: α -monoclinic, β -hexagonal and γ -orthorhombic. A common feature of all three forms is the helical conformation of the constituent PP chains. The forms display narrow, sharp peaks in wide-angle X-ray scattering (WAXS) patterns (Fig. 5.4). However, they also display some features that are highly unusual in polymer crystallography.

The α -form is the most stable and also the most important in the context of PP fibres. Its monoclinic lattice has unit cell dimensions $a = 0.665$ nm, $b = 0.2096$ nm, $c = 0.650$ nm, $\alpha = \gamma = 90^\circ$ and $\beta = 99.3^\circ$. The PP chains lie in the direction of the c axis. Isotactic α -PP also exhibits a lamellar branching, which appears to be unique in polymer crystallography.³⁵ Evidence has been adduced that this lamellar branching is an intrinsic property of isotactic α -PP. In PP fibre extrusion, for example, an additional component whose chain axis is approximately at right angles to the fibre direction may develop at slower fibre take-up speeds.³⁵

Crystals of the β -form can be obtained with the use of special nucleating agents.



5.4 WAXS patterns of α , β , γ and paracrystalline polypropylene.

The unit cell dimensions of the trigonal lattice are $a = b = 0.1101$ nm and $c = 0.650$ nm. An unexpected feature of the β -structure is that it is frustrated:³⁵ the structure does not follow the normal crystallographic convention of structural equivalency.

The orthorhombic γ -form can be obtained by crystallisation of PP at high pressure or of PP with a small proportion of comonomer at low pressure. The γ -form may also be observed in WAXS patterns of isotactic PP with shorter chain lengths. It is hence of interest too in connection with metallocene PP, in which there are shorter isotactic chain lengths on account of occasional regio-irregularities in the chains.¹⁸ The unit cell dimensions of the orthorhombic γ -form are large: $a = 0.854$ nm, $b = 0.993$ nm and $c = 4.241$ nm.³⁵ A strange feature of the γ -form structure is that it consists of a series of bilayers of chains in a crossed pattern. The chains are tilted at 80° or 100° to one another.³⁵

A paracrystalline, or 'smectic', form has also been identified, whose WAXS peaks are broad and more poorly defined, and only of moderate intensity (Fig. 5.4). The PP chains within the paracrystalline structure also adopt a helical conformation.³⁶ A liquid crystalline model for the paracrystalline structure has recently been put forward, proposing a 'liquid-like' lateral packing of parallel PP helical chains, together with a high degree of registry in the direction of the chains.³⁷

PE generally assumes an orthorhombic crystalline structure, although on stretching in the formation of tape, for example, a monoclinic form may begin to emerge. The unit cell dimensions of the orthorhombic form are $a = 0.741$ nm, $b = 0.494$ nm and $c = 0.255$ nm. The PE chains lie in a planar zigzag fashion in the direction of the c axis. The a and b dimensions, therefore, characterise the side-by-side packing of the chains.³⁸

5.4.3 Crystal morphology

The crystallinity in freestanding PE and PP arises from the presence of crystallites, generally of dimension less than 100 nm. The crystallites are made up of thin lamellae, and the direction of the polymer chains lies across the thickness of each lamella. Thus, the chains within each crystallite are folded many times in order that it can accommodate them. The lamellae, in turn, are arranged into spherulitic structures, whose diameter can be as high as a few μm . Each spherulite grows in a radial manner from a nucleus. The arrangement of the polymer chains will be denser and more regular within the spherulites than in the regions between them, so that clearly defined boundaries are observable.

When undergoing elongational strain, as in fibre formation, the spherulites stretch out into ellipsoids. This deformation process is maintained until the lamellae within the spherulites can no longer accommodate the stress imposed on them. They then begin to fragment. The lamellae slide and rotate, and the regularly folded polymer chains within them slip, twist and even unfold.³⁹ The detailed nature of these changes depends on the orientation of each lamella with respect to the direction of stretch. The deformation of the spherulites eventually results in the formation of small fibrils,⁴⁰ which can consist of a hierarchy of structures at different scales from tens of nanometres to micrometres.^{41,42} During this transformation, the lamellae break into small fragments, and these fragments commonly form fresh crystalline domains in the new fibrils. Those polymer chains that were originally in the less dense regions outside the spherulites become much more stretched along the fibre axis and, in consequence, are aligned close to one another. Strain-induced crystallisation can then occur, and further crystalline domains are formed.

It is interesting to note that in the formation of PP fibrils, the appearance of 'shish-kebab' structures has been reported,^{41,42} in which a central core consisting of extended PP chains (shish) is surrounded by sections with folded chain crystals (kebab). Shish-kebab PE structures have also been reported.¹²

Further deformation is considered to occur through the sliding of fibrils past one another. There is also the stretching of tie molecules, which link the fibrils, and the unfolding of sections of polymer chains by which tie molecules are anchored in the crystal blocks of neighbouring fibrils.¹⁹ Eventually, the deformation stress is too great for the fibre to support, and the sample breaks.

5.5 Fibre production

5.5.1 Introduction

Polyolefin fibres can be produced by melt extrusion processes, which are followed by drawing and other after-treatments such as texturing and entanglement. While this technology is practised on a commercial scale for PP fibre production, PE

fibres are now very largely produced using gel-spinning and solid-state extrusion technologies. Since these are already described in a companion book,^{11,12} attention in this section is largely concentrated on PP fibre production.

Although the commercial production of PP fibre involves melt extrusion, a number of different melt extrusion processes are used. The choice depends on the type of fibre to be produced and the use for which it is destined. Different processes can be identified for the production of multifilament yarns, monofilaments, staple, tapes and non-wovens. Each of these is now discussed in turn.

5.5.2 Multifilament yarns

Multifilament yarns are produced as partially oriented yarns (POY), fully oriented yarns (FOY) or bulked continuous filament (BCF). The POY process is low cost and allows for greater flexibility in subsequent processing, such as drawing, or more complex processing as in draw-twisting and draw-texturing. POY can be produced in counts ranging from about 40 to 200 dtex, with 0.5–4.0 dtex per filament. An important feature of the POY process is the long length of the quench unit, which can be up to 10 m. Such a long unit is needed to ensure that at the high production speeds used, the filaments are cooled sufficiently before being wound. The filaments are taken off onto winders at speeds of 2000–3000 m min⁻¹.

The POY yarns are then further processed. Drawing is always a part of subsequent processing and, because of the high processing speeds involved, PP grades of sufficiently narrow molar mass distribution are desirable,¹⁸ in order to avoid an excessive number of filament breaks. However, where the molar mass distribution is narrower, the maximum draw ratio achievable is reduced.¹⁹ The processed POY yarns are used for such applications as upholstery cover fabrics, sportswear and socks.

Multifilament yarns may alternatively be produced as FOY yarn. Here the spinning and drawing form consecutive parts of a continuous process. Final winding speeds can be as high as 5000 m min⁻¹. The process is highly versatile, and a large variety of polymer grades can be used to produce yarns with different mechanical properties, depending on the control settings used. For example, high-tenacity yarns destined for technical fabrics, as well as standard yarns for more traditional applications, can be produced by the FOY process.

One difference between the production lines resides in differences in the fineness of the filaments produced: 1–2 dtex for standard yarns but 5–10 dtex for high-tenacity yarns. Another key difference is reflected in the fibre drawing and relaxation conditions, which will exert an important influence on the mechanical properties of the final yarn. Thus, standard yarns possess tenacities of 0.3–0.5 N tex⁻¹, whereas for high-tenacity yarns, values of 0.5–0.7 N tex⁻¹ are achieved, and in some instances, even higher. These values exceed those for multifilaments produced by the POY process, even after drawing has been applied (0.2–0.3 N tex⁻¹).

The BCF process combines high-speed spinning, drawing and texturing into one continuous process. The speed of filament production is generally 1500–4000 m min⁻¹. The process is quite similar to the FOY process, except that after drawing, the filaments are textured. The most prominent method of texturing is the stuffer box crimp process. After partial relaxation, the filaments are bulked by overfeeding in steam or hot air into a stuffer box, in which a three-dimensional crimp is induced. The crimped yarn is then ejected onto a cooling drum, from which it passes through an intermingling unit before the final winding stage. The level of crimp achieved depends on such factors as the temperature of the filaments on entering the texturing unit, the duration of the texturing process and the size and shape of the texturing unit.

5.5.3 Monofilaments

Monofilaments, being in excess of 100 dtex, are much coarser than multifilaments. In principle, however, monofilaments can still be produced by broadly the same methods as those used for the production of multifilaments, but monofilaments produced in this way tend to curl.¹⁹ This property renders them unsuitable for many applications. To avoid this problem, monofilaments are often formed at reduced speeds and extruded into water, because the cooling is much more efficient. After travelling a short distance (≤ 5 cm) in air from the spinneret, the filaments enter a bath of water. The subsequent drawing process may involve as many as three stages, often in a hot water bath or hot air ducts. The most important property required of monofilaments is high tensile strength.⁴³ Hence, they are produced for technical textile applications, such as belts, ropes and hawsers.

5.5.4 Staple fibres

Staple fibres can be produced by two methods: a two-stage discontinuous process or a single-stage compact continuous process. The two-stage process is generally utilised for high-quality, very fine staple fibre (0.5 dtex per fibre) and also in plants where the throughput is large (>20 000 tonnes per annum). The spinning speed is usually about 2000 m min⁻¹, 10–20 times greater than in the compact process. Spun tow is produced from the first stage. The second stage consists of drawing, crimping and cutting into staple. In the cutting stage, the tow is cut into staple fibres of the required length, whereupon the fibres are packed into bales. An alternative to cutting is converting, in which a sliver of parallel fibres is formed (this is called converter tow); such slivers are then used for worsted spinning. A major drawback to the two-stage process is that a lot of space is taken up for all the equipment required. In particular, the length of the quenching zone is approximately 10 times that used in the compact process.¹⁸ However, a great advantage of the two-stage process is considered to be that each stage can be operated independently under its own optimum conditions.

The single-stage compact process combines all the production stages and is becoming more important economically. Although the spinning speeds are much lower ($100\text{--}300\text{ m min}^{-1}$) than those used in the two-stage process, productivity is gained by using spinnerets with a very large number of holes – up to 100 000, arranged in a grid structure. The spinning speeds are sufficiently low that the tow can be continuously fed to a drawing unit.⁴⁴ The fibres produced possess a minimum count of 1–3 dtex and so are normally used for carpet yarns and non-woven products. The fineness limit and production speeds of the spun filament are governed by its cooling and the maximum level of drawing that can occur. The single-stage process is economic even for the production of only small quantities of staple and is highly flexible where colour changes are required.

5.5.5 Non-wovens

PP non-wovens can be produced by a multistage process that incorporates the production of staple fibre, described in the previous section. Alternatively, a single-stage operation can be utilised which integrates filament production and the formation of a non-woven fabric. The preferred method of holding the web together is thermal bonding, because of the low melting points of polyolefin fibres. Adhesives often adhere only poorly to polyolefin fibre surfaces because of their low surface energies. Also, much of the adhesive tends to be located away from the contact points between individual fibres and is, therefore, wasted.

There are two important versions of the single-stage process: the spun-bond process and the melt-blown process.⁴⁵ In the spun-bond process, bundles of individual filaments or a flat filament curtain are melt-extruded, cooled and stretched, either mechanically or by a current of air. The filaments are then laid down in a random fashion on a conveyor belt and the resulting web is passed through a hot calender, where it is thermally bonded. The method using filament bundles offers greater flexibility of production, but the method using filament curtains offers higher productivity. The PP grades used possess MFIs in the range $20\text{--}40\text{ g}/10\text{ min}$, and the density of the spunbond web ranges from 5 g m^{-2} to several kg m^{-2} . Spun-bond webs are noted for their strength.

The melt-blown process is used not only for PP but also for many forms of PE. In the process, polyolefin is extruded through numerous small spinneret holes, located close together. Just below the spinneret holes, a stream of molten polymer is caught in a current of hot air moving at high speed. The molten stream of polymer is thus broken up into an integrated network of very fine (microfibre range) entangled fibres of varying lengths, which are immediately deposited onto a rotating screen. Successful processing depends very much on the correct combination of extrusion conditions and the speed and temperature of the air current. The individual fibres which result from the fragmentation of the molten polymer will possess a fineness in the range $0.01\text{--}0.2\text{ dtex}$. Thus, the melt-blown fabrics, which possess densities in the range $10\text{--}500\text{ g m}^{-2}$, are lighter than spun-

bonded fabrics and have lower strength. Their texture, however, renders them excellent for use in filtration and absorption applications such as for industrial wipes, surgeons' masks and gowns, and oil clean-up products.

Production lines combining both processes are now being increasingly used for the formation of SMS (spun-bonded–melt-blown–spun-bonded) multilayer fabrics. These fabrics bring together the desirable properties of spun-bonded and melt-blown materials. The external spun-bonded layers provide good mechanical properties, while the internal melt-blown web provides good filtration and absorption properties. The layers are bonded either thermally or mechanically, depending on the weight and desired application of the SMS product. Thinner webs are bonded by means of heated calender rollers, whereas thicker webs are mechanically needled.

It should be noted that, apart from spun-bonded and melt-blown non-wovens, other types of PP non-wovens are produced. For example, needlepunched PP non-wovens are quite prominent, produced by mechanical interlocking of the loose fibres in a web through the use of arrays of barbed needles repeatedly passing into and out of the web. Hydroentanglement (spun-lacing) technology is also applied, in which the web of loose fibres is entangled by subjecting them to multiple rows of fine, high-pressure jets of water.

5.5.6 Tapes

Tapes can be produced by two methods.¹⁸ In the more common method, a film of polyolefin is extruded and cooled on rollers or in a water bath. The film is then stretched uniaxially, about ten-fold, when it begins to fibrillate. As it fibrillates, it is cut with knives into tapes. Alternatively, the actual fibrillation process may produce tapes of the desired dimensions. The tapes produced possess high tenacities, e.g. up to 6–7 N tex⁻¹ for PP tapes, and are used in carpet backings, sacks and bags. In the second method, each tape is extruded separately through an individual slit-shaped orifice. This process is much more expensive and is generally confined to specialist uses, such as dental and medical applications.

5.5.7 Spin finishes

The use of spin finishes to protect polyolefin filaments from wear is an important factor in their processing. A spin finish has several functions. For example, it acts as a lubricant to protect the filament surfaces, it provides good cohesion between individual filaments in a multifilament assembly, and it dissipates any static electricity that may be generated during processing. Static electricity can cause ballooning in multifilament yarns because of electrostatic repulsion between the individual filaments. Static may also distort or even rupture the yarn during processing and cause electric shocks when the processing equipment is touched. Spin finishes also normally contain biocides.

Table 5.5 Surface energies of some synthetic fibres

Fibre	Surface energy (mJ m ⁻²)
PP	31
Polyester	43
Polyacrylonitrile	45
Nylon	46

In order to accommodate all these requirements, commercial spin finishes consist of a complex mixture of chemical components, and so spin finishes are generally applied as emulsions. Good accounts of the compositions of spin finishes can be found elsewhere.^{19,46}

Different types of fibre, however, possess different individual properties. Moreover, different types of equipment will produce different patterns of wear on a fibre. The spin finish, therefore, must be formulated according to the properties of the fibre processing equipment. Thus, for polyolefins, their low surface energies, as manifest by their hydrophobicity, and low melting points have to be taken into account. Furthermore, different types of spin finish may be preferable at different processing stages.

Even among conventional synthetic fibres, polyolefin fibres possess very low surface energies, which render their complete coverage by emulsified spin finishes particularly demanding. Some values estimated for the surface energies of common fibres are given in Table 5.5, from which it may be noted that the surface energy of PP fibres is markedly lower than those of other common synthetic fibres. For initial wetting of polyolefin fibres, therefore, a spin finish of very low surface tension has to be applied. Yet water, which is one of the components in emulsified spin finishes, possesses a surface tension as high as 72 mN m⁻² at 20 °C. Thus, special wetting agents have to be included in spin-finish formulations for polyolefin fibres. Moreover, if all the water in the finish evaporates, the degree of coverage of the filaments may be substantially altered.

For multifilament yarns, there is an additional consideration. The spin finish must also penetrate the filament bundles in as short a time as possible. A spin finish of low viscosity is, therefore, required.

Polyolefins exhibit the highest friction among common synthetic fibres, and indeed the heat generated by friction during fibre processing can cause softening, or even melting of the fibres. Thus, an important role of spin finishes in polyolefin fibre processing is the reduction of friction, a role that is assuming increasing importance with the ever-increasing fibre production speeds.

It is not surprising, then, that there is still extensive effort in devising new ranges of spin finishes for the variety of processing routes from which polyolefin fibres are formed. Furthermore, the types of lubricants commonly used in the processing of other synthetic fibres, such as mineral oils and fatty esters of low viscosity,

Table 5.6 Examples of additives for synthetic fibres

Processing additives	Heat stabilisers HCl scavengers
Functional additives	UV stabilisers Flame retardants Colourants Antistatic agents Antimicrobial agents Agents against creep Agents against abrasion

cannot be applied to polyolefin fibres. Although such finishes wet polyolefin fibres well, they also migrate into the bulk of the fibres and swell them. Examples of lubricants currently used for PP fibres are alkoxyated long chain alcohols, alkoxyated triglycerides and fatty acid polyglycol esters.

5.6 Additives

5.6.1 Introduction

Additives are employed to assist the processing of polyolefin fibres and to achieve the fibre properties required. They are either present in the polymer grades supplied to the fibre manufacturer or are incorporated into the polymer melt prior to extrusion. Additives are conveniently classified into two main groups, and examples are shown in Table 5.6. It is clear that additives have a number of roles, and indeed commercially produced polyolefin fibres contain a variety of additives. Care has to be taken, therefore, that the effectiveness of an individual additive is not impaired by any of the other additives present. In some cases, though, there may be synergistic effects. Moreover, all the additives incorporated must withstand the fibre processing conditions used, the subsequent conversion of fibre to the finished article and the end use of the article during its lifetime. Some of the additives listed in Table 5.6 are discussed more fully below. The coloration of polyolefin fibres is discussed in Section 5.7.

Many of the additives listed in Table 5.6 are incorporated to counter the oxidation of the polyolefin chains. Unless these additives are present, polyolefin fibres are highly prone to both thermal and photochemical oxidation. In particular, oxidation is considered to be a major problem in the processing and handling of PP fibres, given the very high fraction of the polyolefin fibre market that they occupy. Oxidation leads to reduced mechanical properties and even undesirable discolorations. It may be accelerated too in the presence of some metals, though the use of chelating agents can often prevent the action of these metals. The

mechanisms underlying the oxidation process are complex, so only an outline is provided here. Detailed schemes are given elsewhere.^{19,47,48}

The thermal oxidation and resulting degradation of polyolefins occur through chain reactions involving free radicals. The process can be considered in terms of initiation, propagation, branching and termination steps.⁴⁷ Initiation occurs through abstraction of hydrogen atoms in the polyolefin chains by excited singlet oxygen molecules:



Hydrogen atoms linked to tertiary carbon atoms are the most readily abstracted. The products arising from the abstraction reaction may also combine to form a hydroperoxide:

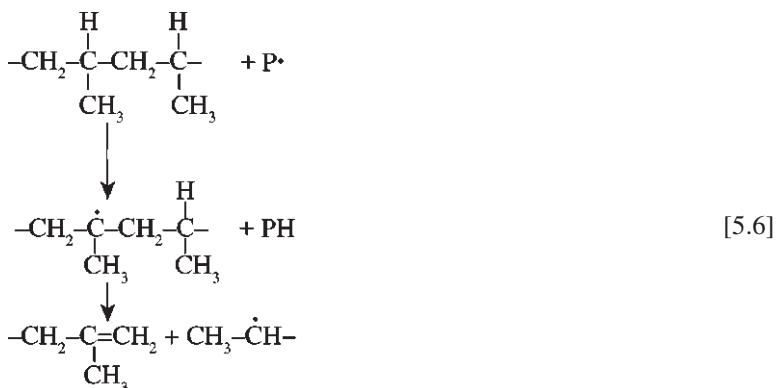


Initiation is followed by a complex series of propagation reactions, from which further hydroperoxides are formed. The number of free radicals in these reactions remains constant. However, the hydroperoxide may be split in a branching reaction, so that the number of free radicals increases:



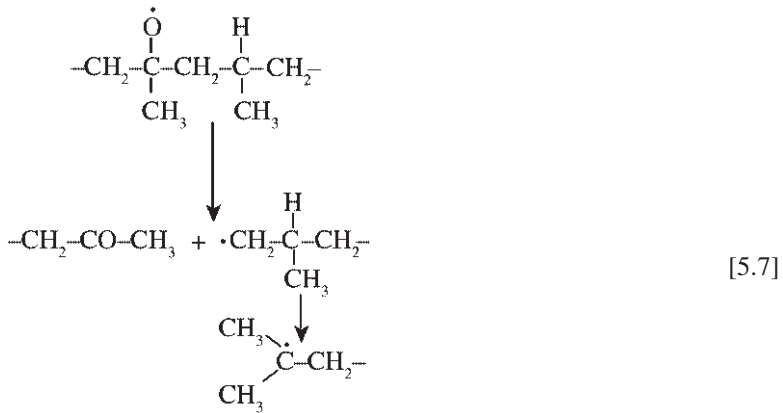
Termination of the overall process is through several reactions, in which the free radicals combine to form a variety of non-radical products.

None of the above reaction stages, however, leads to the degradation of the polyolefin chains. Indeed, an increase in molar mass results. Nevertheless, it is well established that polyolefins are susceptible to degradation as a result of oxidation. Clearly, scission of the chains must also occur. The scission of PP chains can be taken as an example:



An olefin and a new free radical are, consequently, formed. The olefin is even more prone to oxidation than a saturated hydrocarbon, and the new free radical can take part in further oxidation steps.⁴⁷

The alkoxy radical, $\text{PO}\cdot$, can also be degraded. The degradation of PP chains illustrates the process:



Polyolefin fibres are also degraded by weathering at ambient temperatures. Absorption of ultraviolet radiation in the range 300–400 nm triggers photochemical oxidation of the polyolefin chains. Photodegradation is initiated mainly by entities formed during manufacture of the polymer, its storage and subsequent fibre processing. These entities include catalyst residues, alkyl hydroperoxides and ketones.¹⁹ Thus, UV radiation can trigger the breakdown of hydroperoxides into free radicals:



The breakdown of ketones is more complex.¹⁹ In the case of PP, it has been proposed that an additional means of initiating photochemical oxidation is through the formation of excited charge transfer complexes between PP and oxygen.⁴⁹

5.6.2 Processing additives

5.6.2.1 Heat stabilisers

Resistance to thermal oxidation is conferred by the addition of antioxidants to the polymer. These antioxidants are oxidised themselves, in preference to the polymer chains. Thus, antioxidants generally remain effective until they have been consumed. Research into the development of more effective stabilisers is currently very active.

An antioxidant may be a primary stabiliser, which scavenges free radicals, or a secondary stabiliser, which decomposes hydroperoxides. Primary stabilisers can terminate the oxidation process by forming free radicals that are not reactive enough towards oxygen molecules to continue the chain reactions. These stabilisers are usually aromatic amines or hindered phenols, though a number of the phenolic stabilisers possess the drawback of assisting fading by gas fumes, such as nitric oxide. Indeed, many polyolefin fibre producers now demand that the polymer grades with which they are supplied are free of phenolic antioxidants.

Secondary stabilisers remove hydroperoxide radicals and prevent the start of new oxidation cycles. They are termed secondary stabilisers because they perform best when primary stabilisers are present.⁴⁷ There is a strong synergistic effect between a primary and secondary stabiliser, if the correct combination is made. Secondary stabilisers are drawn from a variety of compounds, containing sulphur or phosphorus: disulphides, thioesters, thioethers and tertiary phosphites and phosphonates.

5.6.2.2 *HCl scavengers*

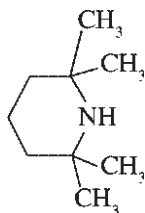
The residues of Ziegler–Natta catalysts in polyolefin fibres can compromise the efficiency of antioxidants present. The catalyst residues can react with phenolic oxidants to produce hydrochloric acid, which may corrode parts of the extrusion machinery. Formation of hydrochloric acid is prevented by the presence of epoxy compounds, dibutyl tin compounds, and calcium and zinc laurates, stearates and benzoates.

5.6.3 Functional additives

5.6.3.1 *UV stabilisers*

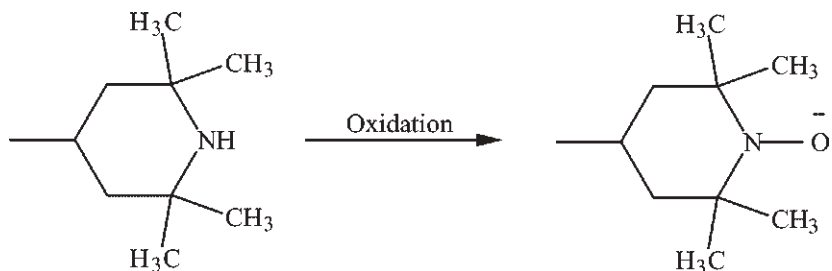
As noted in Section 5.6.1, polyolefins can also readily undergo photochemical oxidation, initiated by UV radiation. In fibrous form, polyolefins possess a very high ratio of surface area to volume; hence polyolefin fibres are especially susceptible to UV light. Moreover, photochemical oxidation is accelerated at higher temperatures. Therefore, without UV stabilisers to prevent photochemical oxidation, the application of polyolefin fibres, and particularly PP fibres, would be severely restricted.

Many factors combine to govern UV stability: fibre processing, the type of UV stabiliser and its concentration within the fibres, fibre count and treatments given to the fibres during subsequent processing. By far the most important class of UV stabilisers in PP fibres are the hindered amine light stabilisers, known as HALS. Many of these stabilisers contain 2,2,6,6-tetramethyl piperidyl groups:



[5.9]

The mechanism of action of HALS stabilisers has recently been reviewed.⁵⁰ Essentially, they function as free radical scavengers, though the active functional groups are nitroxyl radicals, formed by oxidation of the amine groups:



[5.10]

During scavenging, the nitroxyl groups are largely regenerated, but the regeneration process eventually ceases: in each regenerative cycle, some of the HALS is lost, and some inefficient radical scavengers are generated as well.⁴⁷ However, it has been shown that the addition of hydroperoxides or ketones to PE exerts only a small effect on its rate of photodegradation. It has been proposed that HALS stabilisers can also act by quenching excited polyolefin–oxygen charge transfer complexes which would otherwise initiate photodegradation.⁵⁰

The choice of HALS rests on a number of factors. A HALS with a low molar mass migrates readily from the bulk of the fibre to its surface, especially if the chemical structure of the HALS has little compatibility with that of PP. Not only does migration of the HALS give the fibres a chalky or metallic appearance, but the stabilisation of the fibres against UV radiation also suffers. A HALS of much higher molar mass, although possessing little propensity for migration, may in consequence have limited ability to scavenge radicals. Such a HALS may also have little compatibility with PP. Thus, a HALS with optimal properties will be sufficiently mobile to be effective as a radical scavenger, yet not so mobile that it escapes to the fibre surfaces.

A HALS of high molar mass is arguably the preferred option for fibres, in view of their high specific surface area and the elevated temperatures at which they are extruded and even may be drawn. In practice, combinations of types of HALS with

low and high molar mass are often employed, since quite often a synergistic effect results between the two types. Indeed, synergistic combinations of HALS are gaining increasing commercial importance.⁵¹ More recently, a new type of HALS has been launched from Clariant, *Sanduvor PR-31*, which can be grafted to the polyolefin chains under the action of light.

5.6.3.2 *Flame-retardant additives*

The incorporation of effective flame-retardant additives into PP fibres is crucial for many applications, including automotive, aerospace applications and in floor coverings. Indeed, PE and PP undergo combustion more readily than any other common synthetic fibres.² However, for effective protection against ignition to be conferred, the levels of flame-retardant additives can be so high that fibre processing is rendered more difficult, and the physical and mechanical properties of the fibres are impaired. In addition, the effectiveness of UV stabilisers can be reduced by flame-retardant systems, especially those containing halogen atoms, such as decabromodiphenyl oxide and hexabromocyclododecane. Furthermore, there is a risk of the generation of significant quantities of hydrogen chloride or hydrogen bromide from halogenated flame-retardant additives. For these reasons, other flame-retardant additives are now being exploited. These include additives based on phosphorus,¹⁸ aluminium trihydrate and magnesium hydroxide, although to be effective the levels of the metal-based additives have to be especially high.⁵² A number of intumescent flame retardants, which function by generating char, have also been evaluated for use with PP, notably ammonium polyphosphate and polytriazinylpiperazine.⁵²

A new *N*-alkoxy hindered amine flame-retardant system has been recently launched by Ciba. The product, *Flamestab*® *NOR*TM-116, is designed to act both as a flame-retardant chemical and as a UV stabiliser in polyolefin applications. It is claimed to be effective at levels as low as 1%. The impact on fibre physical and mechanical properties is, therefore, low.

5.6.3.3 *Antistatic additives*

The importance of spin finishes in reducing static effects during polyolefin fibre processing has already been noted. However, treatments with spin finishes are generally not effective during the subsequent use of the fibres. To extend antistatic properties into fibre use, antistatic agents may be added to the polymer granules before they are melt extruded. These agents must, therefore, be resistant to the elevated temperatures encountered during extrusion, drawing and texturing and must have no deleterious effects on the properties of other additives or on the polyolefin fibre itself. Indeed, they should possess a degree of compatibility with the polyolefin chains. However, antistatic products normally contain hydrophilic groups, which can attract water vapour and consequently lower static charge. The

presence of these hydrophilic groups, on the other hand, tends to compromise the compatibility of the antistatic additive with the polymer chains. This is a particular problem with polyolefin fibres, whose chains contain no polar groups.

Antistatic additives are often nitrogen-containing compounds, such as long chain amines, amides and quaternary ammonium salts. Other types of antistatic additive include derivatives of poly(ethylene glycol) and polyhydric alcohols. Whatever their chemical nature, they function by migrating to the fibre surface. The hydrophilic part of the antistatic agent is excluded from the fibre matrix. When enough antistatic agent is present at the surface, electrically conducting paths are formed through the absorption of moisture from the air. If the air itself is dry, the performance of these additives is impaired.

An alternative approach to reducing static charge is to blend the polyolefin fibre with an antistatic fibre, for example, by bicomponent filament extrusion. More recently, however, an antistatic agent has been launched from Ciba, *Irgastat P 22*,⁵³ which forms a conductive network throughout the fibre and is, consequently, still effective at low levels of humidity in the atmosphere.

Other approaches to dissipating static charge on polyolefin fibres have also been reported.⁵⁴ Thus, melt-blown PP fabrics for medical use are treated with conductive agents in order to lower the risk of sparking. Special grades of carbon are also incorporated into polyolefins: the products do not develop any static charge by friction and they conduct charge away to earth without spark formation. To be effective, however, a 15–20% loading of carbon is normally required, and the conductivity is influenced by the degree of crystallinity of the polyolefin fibre host.

5.6.3.4 Antimicrobial agents

Antimicrobial agents are designed to repel, inhibit or kill micro-organisms. Although polyolefin fibres exhibit excellent resistance to micro-organisms, it is still often desirable to incorporate antimicrobial agents into the fibres. The use of antimicrobial agents is particularly important in sportswear, floor coverings and bedding material. Thus, the growth of bacteria on carpets, for example, can present a real danger in hospitals, schools and homes for the elderly. The presence of dust mites in bedding poses a serious problem to those suffering from asthma. Although antimicrobial treatments can be sprayed onto carpets and bedding, their effectiveness is transient. Instead, effort is now concentrated on adding antimicrobial agents to polyolefin granules prior to melt-spinning. However, as with antistatic agents, antimicrobial agents have to be resistant to all the fibre processing stages they encounter, they must not impair fibre performance during use, nor must they reduce the effectiveness of other additives.

Many different antimicrobial agents are available on the market. They generally enter the cell membrane of each micro-organism and disrupt its metabolism, so that its ability to grow and reproduce is impaired. One antimicrobial agent that has been developed for use in polyolefin fibres is a silicon-based polymer containing

quaternary ammonium groups, to which are attached long aliphatic hydrocarbon chains.⁵⁵ The positive quaternary groups form complexes with the anionic lipoproteins in the cell membranes of the micro-organisms, and they are inactivated.

Antibacterial behaviour is also triggered by the presence of silver in the fibres,⁵⁶ and the use of silver for antibacterial treatments is becoming more widespread. Silver ions, in common with a number of other heavy metal ions, are reactive towards proteins. When silver ions are absorbed within the cell structures of bacteria, therefore, they are attracted to groups in the enzymes present in each cell. It is considered that silver ions are particularly reactive towards thiol groups.⁵⁶ The enzymes are consequently denatured, the metabolism of the bacterial cells is inhibited and the bacteria are rendered inactive.

5.7 Coloration of polyolefin fibres

In contrast to other types of conventional synthetic fibre, polyolefins cannot be dyed effectively, unless they have been specially modified. Access of dye to the interior of the fibres is limited, there is poor retention of the dye in the fibres, and the evenness of the dyeing is also often poor. The principal factor preventing effective dyeing is the high degree of crystallinity of polyolefin fibres. Another factor is the low affinity between dye and fibre, owing to the weak attraction between the hydrocarbon chains making up polyolefins and the functional groups in the dyes applied.

To overcome these problems, a number of approaches have been tried. Examples are the addition of nickel compounds to enable dyeing with ligand-forming dyes and the inclusion of suitable polymers to allow effective application of disperse dyes or acid dyes.¹⁹ The application of dyes with long alkyl chains has also been attempted. So too has the inclusion into PP fibres of suitable dendrimers and hyperbranched polymers, to act as dyeing promoters.⁵⁷ Indeed, it has been reported that the disperse dye, C.I. Disperse Blue 56, exhibits good wet-fastness in PP fibres containing 3% of a stearate-modified hyperbranched polymer, although the light-fastness of the absorbed dye is poor.⁵⁷

Nevertheless, dyeing of polyolefin fibres is still far from being commercially viable. For this reason, polyolefin fibres have to be coloured by pigments, which ideally are uniformly dispersed as tiny coloured crystals throughout the polyolefin fibre matrix. However, polyolefins are far from chemically aggressive, and so there is a wide selection of pigments for numerous shades.⁵⁸ The pigments applied must not be thermally degraded during processing of the polyolefin fibres and they must be compatible with other additives present, particularly UV stabilisers. In addition, they should not significantly reduce the mechanical performance of the fibres. Some pigments are known to promote the thermal and photodecomposition of polyolefins; yet other pigments exert a retarding effect.¹⁹

Many of the pigments applied are organic, in view of their bright shades and

greater compatibility with polyolefins. Nevertheless, the white pigment titanium dioxide, especially in its rutile form, is important as a delustring agent, and carbon black, being electrically conductive, confers antistatic properties. Some types of carbon black also possess a degree of antioxidant character.⁵⁹ Some brown iron oxide pigments are also used, as they are inexpensive relative to organic pigments.⁵⁸

Pigments consist of tiny crystals, whose cross-section in the case of organic pigments can be as low as 0.05 μm . Such small crystals have an innate tendency to aggregate. Pigment crystal aggregation is highly undesirable in that it reduces overall tinctorial strength and impairs the brightness and clarity of the colour. In synthetic fibre technology, crystal aggregates can cause problems in processing by upsetting the rheology of the molten polymer, clogging the filter pack in the spinneret and hindering fibre drawing. Crystal aggregates also reduce the mechanical performance of the final fibres. It is, therefore, essential to prevent, or at least severely restrict, pigment crystal aggregation in the pigmentation of polyolefin fibres. One approach is the treatment of the pigment crystals by the manufacturer with additives that render the crystal surfaces more compatible with polyolefins. However, the size and shape of the pigment crystals can also be important in reducing crystal aggregation. The problems of pigment crystal aggregation and means of overcoming them are more fully discussed elsewhere.^{60,61}

In view of the propensity of organic pigment crystals to aggregate and of the viscous nature of molten polyolefins, uniform dispersions of the tiny pigment crystals are difficult to achieve. As a result, the conditions giving rise to optimum mixing of pigment and polymer tend to be quite different from those required for fibre processing. The achievement of the pigment dispersion, therefore, is often separate from the fibre-forming process. The pigment is first dispersed in a binder, and the coloured predispersion is supplied to the fibre processor.

Predispersions can be supplied in several different forms. The most usual is the master-batch, in which the pigment is predispersed at high concentration (up to 50% or more) in a binder and processed into granular form. The master-batch is then mixed with sufficient uncoloured polyolefin granules to achieve the desired tinctorial strength in the fibre after processing. Traditionally, the binder has been low-density PE, but for the coloration of PP fibres, PP has now become the predominant binder. Moreover, to promote the dispersion of pigment in the binder, low-viscosity synthetic waxes may be incorporated.⁶² Occasionally, a predispersion is supplied as a 'compound', which is a composition in granular form ready for processing without further addition of polyolefin granules.

5.8 Properties of PP and PE fibres

As with other synthetic fibres, the technological properties of polyolefin fibres are influenced by the grade of polymer, the fibre processing conditions used and the

Table 5.7 Properties of common synthetic fibres

	Tenacity (N tex ⁻¹)	Initial modulus (N tex ⁻¹)	Elongation to break (%)	Density (g cm ⁻³)	Moisture regain* (%)	Glass transition temperature (°C)	Melt temperature (°C)
HDPE	0.3–0.6	2–5	10–45	0.95	0	–85	120–125
PP	0.3–0.8	2–9	15–35	0.90	0.04	–5	160–165
PET	0.3–0.8	6–12	15–55	1.34–1.38	0.4	70–80	265
Nylon 6.6 (dry)	0.2–0.6	2–5	15–65	1.14	4–5	60–70	265
Acrylic (dry)	0.2–0.3	6–7	20–50	1.16	1.5	95–100	–

*Values of moisture regain at 20°C and 65% relative humidity.

additives present in the fibre. However, the extent to which each of these factors exerts its influence depends on the property of interest. In some examples, such as moisture regain, the chemical structure of the polymer is by far the dominant factor. In other examples, especially fibre mechanical properties, fibre processing conditions are highly influential.

There are two particularly striking differences between the properties of PE and PP fibres and those of other synthetic fibres. There is an almost complete lack of water absorption by polyolefin fibres, and they possess densities lower than that of water, as already noted in Section 5.1. The glass transition temperatures and melt temperatures of PP and PE fibres are appreciably lower than those of other common synthetic fibres. In addition (Table 5.2), PE and PP are very resistant to chemical attack, though, as noted above, they are sensitive to oxidising agents.

Some properties of PE and PP fibres are listed in Table 5.7. Many of these properties are highly influenced by processing conditions, and so the values for them in Table 5.7 are subject to considerable variation.

5.9 Hard-elastic fibres

A number of polyolefins can be processed into fibres with elastic properties, so-called hard-elastic fibres. These polyolefins include PE, PP, poly(4-methyl-1-pentene), poly(1-butene) and poly(3-methyl-1-butene).^{2,20} The fibres are capable of high recovery from large extensions, e.g. more than 90% recovery from at least 50% elongation.² They are produced by melt-spinning at high levels of spinline stress and little (if any) subsequent drawing, followed by annealing treatments, which may be severe. If the spinline stress is too high, however, structures result with reduced elasticity but increased tensile properties.

The elastic nature of the fibres cannot originate from flexible chain segments, as is the case with true elastic fibres. Instead, the high spinline stress during

melt-spinning gives rise to a row-nucleated morphology aligned at right angles to the fibre axis. Annealing produces further ordering into stacked crystalline structures.⁶³ These lamellae are connected to one another by short tie molecules, which can transfer stress between the lamellae. A detailed review of the structure in hard-elastic fibres has been written by Cannon *et al.*⁶⁴

As the fibre is stretched, so the lamellae splay apart, with the development of a large number of microvoids. The overall density of the fibre is hence considerably reduced by stretching.¹⁹ By contrast, the density of a true elastomeric fibre scarcely changes on stretching. In addition, the elastic behaviour of hard-elastic polyolefin fibres is observed only in the direction of the fibre axis. The mechanism of elastic recovery in these fibres is principally, though not totally, energetic, in contrast to the recovery in elastomeric fibres, which is largely entropic.²

A number of applications have been considered for hard-elastic polyolefin fibres, although none appears to have been extensively commercialised. These applications include stretchable sewing threads, stretchable non-woven fabrics and cardiovascular prosthetic devices.² One practical problem is the construction of fabric from hard-elastic fibres such that their elastic behaviour can still be utilised in a number of directions.

5.10 Processing–structure–property relationships

5.10.1 Introduction

The extensive commercial interest in melt-spun polyolefin fibres, and especially PP fibres, stems from their mechanical properties. As with other synthetic fibres, there is particular emphasis in this regard on fibre strength, as indicated by tenacity, and fibre stiffness, as indicated normally by initial modulus.⁶⁵ Elongation to break is also an important technological property. All these parameters are evaluated from curves relating specific stress to strain, measured at moderate strain rates. They may not, however, always be reliable indicators of practical mechanical performance over very short or very long durations, as experienced respectively by the fibres under impact or under continuous loading. Nevertheless, strength, stiffness and elongation to break are helpful guides towards assessing the mechanical performance of fibres.

It is, therefore, useful to estimate the maximum theoretical values of fibre tenacity and modulus. Maximisation of initial modulus requires a high value of modulus for the constituent polymer chains, a high degree of chain orientation and strong intermolecular forces between adjacent chains.⁶⁶ In addition, a high molar mass is desirable to allow greater continuity of the chains along the fibre, and also a narrow molar mass distribution. Chain modulus is higher for those polymer chains whose extension is a result of bond angle opening and bond stretching. The presence of side groups, especially large ones, reduces the strength of intermolecular attraction between chains and is, therefore, undesirable.

The modulus achievable for PE should, then, be higher than that for PP. PE consists of zigzag chains which contain no side chains. On the other hand, PP consists of helical chains which are more readily stretched. Moreover, the methyl side groups reduce the attraction between adjacent chains, by increasing the overall cross-sectional area of each chain. The chain modulus calculated for PE chains is about 300 GPa, whereas for PP chains the value is only around 40 GPa.⁶⁵ Nevertheless, for melt-spun PE fibres,³ the maximum value which has been achieved in practice is about 60 GPa. For PP fibres, values up to 6 GPa are obtained for commercial samples, although it has been shown that PP fibres with a modulus of *ca.* 11 GPa can be produced by melt-spinning.⁶⁵ However, this value is still less than 30% of the theoretical maximum value. The modulus of gel-spun PE fibres is over 100 GPa.¹¹

Estimation of the maximum fibre tenacity achievable is more difficult, although one approach suggests that the value should be around 10% of the modulus.⁶⁵ On this basis, the theoretical maximum strengths of PE and PP will be *ca.* 30 and 4 GPa, respectively. However, a value as high as 18 GPa has also been suggested for PP fibres.¹¹ For melt-spun PE, fibre tenacities of 1.3 GPa have been achieved, and the tenacity of gel-spun PE fibres is over 3 GPa.¹¹ For PP fibres, values up to 0.8 GPa can be obtained commercially, although values as high as 1.1 GPa have been reported.⁶⁵ As with the modulus values, these values are far below the theoretical maximum.

The theoretical achievable values for fibre tenacity and modulus are calculated for extended polyolefin chains, aligned in perfect orientation in the direction of the fibre axis. The shortfall of the values obtained in practice can be attributed to the extensive folding of the chains in drawn fibres and, in consequence, the load borne by the small fraction of tie molecules. The achievement of higher values for tensile strength and modulus depends, therefore, on reduction in chain folding. It should be noted that for gel-spun PE fibres, where the chains are better oriented along the fibre axis, the values of fibre tenacity and modulus are indeed higher.¹¹

However, it is not clear that the alignment of polyolefin chains can be significantly improved in fibres produced by melt-spinning and subsequent drawing, because of the chain entanglements occurring in the molten state, which are then retained in the solid fibres. In addition, polyolefins crystallise readily from the melt during the extrusion process, yet it is beneficial if an extensive crystalline structure is formed only after the drawing stage, to allow a high draw ratio to be achieved. However, it has been demonstrated for PP that the production of fibres in the paracrystalline state does assist the drawing stage.^{67,68}

It is evident then that to achieve improved mechanical performance, attention has to be focused not only on the properties of the polymer grade used, notably its molar mass and dispersity, but also on fibre processing itself. The control parameters involved in melt-spinning which determine the successful formation of fibres (good spinnability) and the resultant fibre properties have been extensively discussed by Ziabicki,⁶⁹ who subdivides melt-spinning variables into three groups.

The independent, or primary variables, uniquely determining the course of the spinning process and the resultant fibre structure and properties, include the grade of polymer material, spinning temperature, the number of holes in the spinneret and their dimensions, the mass output rate of each filament, spinning path length, take-up velocity and cooling conditions. Ziabicki also identifies secondary variables, which are related to the primary variables and govern spinning conditions. Examples of secondary variables are filament tex and draw-down ratio. The third group comprises resulting variables, including filament structure, tensile stress at take-up godet and the temperature of the filaments at a given distance from the spinneret.

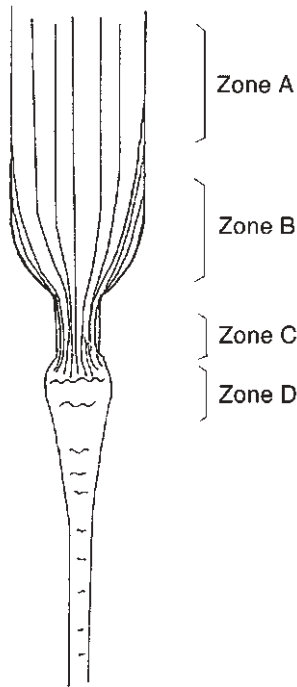
For discussion in this chapter of processing–structure–property relationships, the fibre processing stages may be conveniently considered as follows: the processing of the melt, the solidification of the melt and draw-down of the filaments formed, and the subsequent drawing process. Each of these is discussed in turn.

5.10.2 The polyolefin melt

Once fed into the extruder, the polyolefin granules become molten. By virtue of a screw (or in bench-top equipment perhaps a ram), the melt moves through the barrel of the extruder to the spinneret. The flow of the melt in the spinneret is controlled by a metering pump. During this stage, intimate mixing and a high level of dispersion of the additives has to be achieved. In addition, the polyolefin melt is prone to oxidation, although resistance to oxidation is increased in the presence of suitable antioxidants (as discussed in Section 5.6.2.1). Nevertheless, one study has shown that degradation of PP within the extruder is apparent at 260 °C and above.⁶⁷

It is evident that the flow of the melt through the barrel of the extruder will be influenced by the melt's rheological properties. These properties are particularly important during passage of the melt through each hole in the spinneret and in its egress from these holes. The pattern of flow immediately above each hole, through it and out of it has a major influence on the settings of the melt extrusion equipment.

The passage of the polymer melt is illustrated schematically in Fig. 5.5. The pipe leading to each spinneret hole (zone A) is considerably wider than the hole itself. The melt has a relatively high viscosity and the shear rate it experiences is small. In zone B, immediately above the entrance to the spinneret hole, there is usually tapering of the pipe from its diameter in zone A to that in zone C. The tapering serves to counteract prolonged stagnation of the melt and hence avoid its consequent thermal degradation in the corners of the entry zone. In zone B, the flow pattern is complex and is characterised by a progressive rise of stress, a rapidly decreasing viscosity and a build-up of recoverable viscoelastic strain.¹⁹ The rheological behaviour is predominantly governed by the molar mass and dispersity of the polymer, and the nature and concentration of the additives present. Hence, different grades of polyolefin possess different flow behaviour in zone B. The



5.5 Passage of polymer melt through a spinneret hole.

rheological behaviour of the melt largely determines the angle at which the pipe should be tapered towards the spinneret hole. A taper of 60° to 90° is commonly used commercially for PP.¹⁹

In zone C, the shear rate is almost constant. The shear stress decreases in the initial section of the zone but then remains virtually constant. There is, too, a reduction in recoverable strain, because of the reduction in stress and relaxation of the polymer melt. The volume output of the melt is governed by the drop in pressure along the length of the spinneret hole, and in turn this drop in pressure is determined by the dimensions of the hole. In common with many other polymer melts, the viscosities of fibre-forming polyolefins decrease markedly with increasing shear. Thus, the flow of melt through the spinneret hole is greater than that expected if the viscosity had remained constant. The dimensions of the spinneret hole are important factors in melt extrusion, and indeed it is common practice to characterise the hole by the ratio L/D , its length to its diameter, which for polyolefins is normally in the range 1–4.

The egress of the melt from the spinneret hole (zone D) sees a rapid change from shear flow to elongational flow. The melt is no longer constrained by the walls of

a narrow spinneret hole. The melt also begins to cool. There are sharp reductions in shear rate and shear stress, and an increase in viscosity. The release of elastic energy on emergence of the melt from the spinneret gives rise to die-swell (or Barus effect), which is manifest by a dilation of the extruded filament at the exit from the spinneret. It is particularly evident, for example, in PP melts, where the increase in diameter can be two- to three-fold. It thus has a pronounced effect on the speed of spinning, and indeed distortions in the shape of the fibre cross-section may occur. For PP fibre melts, it has been observed that die-swell is reduced for spinneret holes of increased L/D values, increased values of D , and lower flow rates through the melt.^{19,70} A theoretical analysis of the die-swell in extruded PP filaments has been published.⁷¹

The dimensions of the spinneret hole also govern the conditions for the onset of melt fracture, which refers to the distortion of the surface of the extruded melt. Severe distortions may be in the form of helical indentations, and extruded PP melts are susceptible to this phenomenon. Melt fracture is intensified by higher flow rates through the spinneret hole, a low angle of taper on entry to the spinneret hole (zone B), a decrease in L/D , reduced temperature of the melt and increased molar mass.¹⁹

Molar mass distribution also exerts a pronounced effect on susceptibility to melt fracture in extruded PP melts.⁴⁸ Molar mass distribution has been shown also to have a significant influence on the elongational flow of high-density PE.⁷⁰ When the apparent elongational viscosity, λ , of a PE grade of broad molecular distribution is plotted as a function of distance from the spinneret exit, a minimum is observed. For a PE melt of narrower molar mass distribution, no such minimum is apparent. The same contrast was also noted in plots of λ against the reciprocal of spinning temperature. It was concluded that the unexpected minimum in elongational viscosity in highly disperse PE melts may arise from the wide variation in strain rates in PE chains of such considerably different lengths. Alternatively, the minimum may arise from the formation of liquid crystals.⁷⁰

Another source of instability in the filament melt emerging from the spinneret is draw resonance. This term refers to periodic fluctuations in diameter in the filament melt. Whereas melt fracture appears to commence at a particular value of throughput rate, draw resonance will occur only when the filament is being stretched.⁷² The onset of draw resonance occurs, therefore, at a critical draw-down ratio. Both PP and high-density PE are prone to draw resonance, but it appears to be less of a problem with low-density PE. The intensity of draw resonance is influenced by the molar mass distribution of the polyolefin and also by the shear deformation of the melt in the spinneret holes. The presence of additives, such as pigments and stabilisers, can also promote draw resonance. Moreover, additives that exist in solid particulate form during fibre extrusion may cause knots (short irregular sections) in as-spun fibres.

5.10.3 Solidification of the melt and draw-down of the filaments

5.10.3.1 Crystallinity

After the polymer melt has emerged in the form of filaments from the spinneret holes, it rapidly cools. At the same time, the extruded filaments are attenuated because of the extensional force applied to them. On solidification, the rate of crystallisation of polyolefins is innately high and is even further increased by the chain orientation effects occurring during draw-down of the filaments. However, to achieve maximum extension during the subsequent drawing stage (discussed in Section 5.10.4), it is desirable to suppress crystallisation. In the case of PP fibres, however, it has been amply demonstrated that as-spun fibres can be successfully drawn, provided they are in a paracrystalline state, rather than in a true crystalline state.^{67,68,73} Paracrystalline PP fibres can be readily obtained by rapid cooling of the melt into a water bath,^{74,75} whereas quenching by air often produces PP fibres in the α -monoclinic state. However, under carefully controlled conditions, paracrystalline fibres can also be obtained by air quenching.^{67,76} As-spun PE fibres are formed with a well-defined orthorhombic crystalline structure, irrespective of spinning conditions.⁷⁵ Poly(1-butene) fibres are formed with a well-defined hexagonal structure in air, but rapid quenching gives instead a tetragonal structure, which then ages to the more stable hexagonal form.⁷⁵ As-spun poly(4-methyl-1-pentene) fibres possess a well-defined tetragonal structure.⁷⁵

The rate of crystallisation and the extent of crystallinity in as-spun fibres depend both on the grade of polymer extruded and the extrusion processing conditions.^{67,76} The magnitude of the spinline stress has been noted as particularly important in this respect.^{67,77,78} It has been observed that an increase in spinline stress increases the crystallisation rate and the overall crystallinity of the as-spun fibres produced. In turn, spinline stress can be increased by raising cooling rate and winding speed and by lowering metering pump speed and spinning temperature. In contrast to this observation, however, some recent work on the extrusion of PP monofilament has revealed that crystallinity can decrease with increase in winding speed.⁴² It therefore appears that filament thickness also has a bearing on the crystallinity of the as-spun fibre produced.

The factors governing the rate of crystallisation in the formation of as-spun fibres are complex and are markedly influenced by the rate of cooling of the filaments and the tensile stress at crystallisation. Studies of the onset of crystallisation in the spinline have been reported for PE and PP fibres.^{77,78} For example, it has been shown that the crystallisation temperature of PP under melt-spinning conditions is much higher than under quiescent conditions. Moreover, the temperature of the onset of crystallisation is higher with increased spinline stress. Thus, the higher chain orientation arising from elongational flow, together with the draw-down tension in the filament, increase crystallisation rate appreciably.

Spinning temperature also has a part to play. Low spinning temperatures favour the onset of crystallisation but reduce the mobility of the polymer chains. There is a temperature range over which the rate of crystallisation reaches a maximum. For PP, this maximum is generally between 100 and 110 °C, though in the presence of nucleating agents the temperature may be as high as 140 °C.¹⁹

The influence of molar mass on the rate of crystallisation remains unclear. It is known that PP grades of higher molar mass lead to increased spinline stress,⁷⁸ and this increase would be expected to enhance crystallisation rate. Although evidence has been presented to support this argument,⁷⁹ other evidence favours the opposite.¹⁹ This conflict may arise from an interaction between molar mass and spinning temperature.

However, it is generally accepted that the degree of crystallinity increases with increasing molar mass. Moreover, the molar mass distribution is also an important factor. A greater proportion of longer chains in PP fibres, for example, promotes the formation of α -monoclinic crystals and raises the degree of crystallinity.

It is noteworthy too that the presence of pigment particles can affect the crystalline structures of synthetic fibres.⁸⁰ Thus, as-spun PP fibres coloured with a phthalocyanine pigment have been observed to be in the α -monoclinic form, even when extruded under conditions where the uncoloured fibres are in a paracrystalline state. As-spun PP fibres coloured with a quinacridone pigment can contain both α - and β -forms, though on heating of the fibres, the β -form transforms to the α -form.

5.10.3.2 Orientation

The overall orientation of the polyolefin chains in as-spun fibres is largely determined by the degree of stretching during draw-down (the draw-down ratio). Kitao *et al.* have reported that, at lower draw-down ratios, the chain orientation in as-spun polyolefin fibres increases with increasing draw-down ratio.⁸¹ At draw-down ratios between 8 and 80, however, they report no further increase in chain orientation in PE and PP fibres, although there is an increase in poly(1-butene) fibres. They also concluded that crystalline regions contribute more to overall orientation than non-crystalline regions. Moreover, in addition to the orientation of crystals along the fibre axis, orientation at right-angles to the fibre axis may occur at draw-down ratios of <50. These conclusions have been largely confirmed by Choi and White,⁷⁵ who have also reported that crystal orientation is correlated better with spinline stress than with draw-down ratio. They report that at a given spinline stress, the ranking of the crystal orientation is: poly(4-methyl-1-pentene)>poly(1-butene)>PP>PE.

5.10.3.3 Skin-core effect

The as-spun fibres may exhibit a skin-core effect, which tends to be more pronounced the thicker the filament. The outer filament of the skin is composed of

polymer chains of higher orientation than those in the core of the filament.⁸² The principal factor giving rise to the skin–core effect is the transfer of heat from the surface of a filament, which in turn leads to a temperature gradient across the filament. In consequence, variations in polymer viscosity, along with variations in stress, may occur through the filament cross-section.

The processing of the fibre may be impaired if the skin does not have uniform thickness around the core. Such non-uniformity can arise where fibre extrusion involves polymer of high molar mass, low spinning temperatures, high rate of cooling and high speed of winding of the solidified filaments.¹⁹ The filaments, on relaxation, tend to curl, a tendency that may be further enhanced during subsequent drawing. However, a pronounced skin–core structure can be deliberately encouraged, to produce ‘self-crimping’ fibres.

5.10.4 Fibre drawing

As-spun polyolefin fibres possess mechanical properties that are much too inferior for practical application. The tenacity and initial modulus of the fibres are too low, and there is also a high, irreversible elongation. However, as with other synthetic fibres, drawing under carefully controlled conditions can markedly improve fibre mechanical performance in polyolefins. Generally, the higher the draw ratio, the higher the tensile strength and modulus of the drawn fibres and the lower the elongation to break. The process can directly follow the melt-spinning operation, as in the production of FOY and BCF, or it can be a separate operation using as-spun filaments wound onto bobbins, as in the production of POY and in the two-stage process for producing staple fibres (Section 5.5.4). Thus, the structure and mechanical properties of drawn fibres are markedly influenced by the structure of the precursor as-spun fibres and the drawing conditions employed.^{68,73} Important control parameters for fibre drawing are draw ratio, draw temperatures, draw speeds and the number of draw stages.

Polyolefin fibres can deform in a draw stage either inhomogeneously, where there is a marked necking effect, or homogeneously, without any necking. The type of deformation depends on the structure of the as-spun fibre and the drawing conditions.¹⁹ For example, neck formation in PP fibres is favoured by lower temperatures and increased draw speeds. It is also favoured by higher orientation of the polymer chains and the presence of monoclinic crystals in the as-spun fibre. Drawing of fibres with larger cross-sections is also more likely to involve necking.

Neck formation arises from variation in the distribution of stress along a filament, as a result of tensile deformation during drawing. Such stress variation may arise from small variations in cross-sectional area or from other inhomogeneities along the length of the filament. Once a neck has formed, however, it is essential that the thin portion maintains a constant cross-section, through strain hardening. Strain hardening will occur if there is increased orientation of the polyolefin molecules in the direction of the fibre axis. The angle of the neck is

likely to be important in this respect. If there is a sharp neck angle, leading to a more pronounced necking effect, there will be a higher degree of overall chain orientation. However, the draw process may also become unstable.

The drawability of an as-spun fibre is usually considered in terms of the maximum draw ratio to which it can be drawn. Certainly, draw ratio profoundly affects the character of drawn fibres, and several empirical relations have been proposed to relate draw ratio to overall chain orientation.^{83,84} Changes in structure as a result of deformation forces of the type that occur during fibre drawing have already been discussed in Section 5.4.3.

Draw temperature is also an important factor, because temperature influences the mobility of the structural units during deformation. Drawing at ambient temperatures, for example, converts as-spun PP fibres with α -monoclinic crystalline structures into more oriented, yet less ordered structures with reduced crystallite size, increased lattice strains and defects that are similar to the paracrystalline form.⁸⁵ Subsequent annealing, however, transforms this disordered structure into a highly ordered α -monoclinic structure, with a high overall chain orientation.

Drawing at low temperature can induce the formation of microvoids, which elongate in the direction of the fibre axis as a result of the tensile force applied.⁸⁶ The formation of these microvoids occurs in the interspherulitic regions, and their presence lowers the modulus of the fibres.⁸⁷ The number of microvoids can be considerably reduced by annealing, with a resultant increase in the fibre modulus.

Drawing at more elevated temperatures can be considered to be similar to a combination of cold drawing followed by annealing.⁸⁵ Fibres with highly ordered and highly oriented structures are formed. In contrast to cold drawing, there is no formation of necks and a steady reduction in filament cross-section is observed. The structural changes occurring during drawing at higher temperatures include healing of crystal defects, a reduction in the number of tie molecules, relaxation of the non-crystalline material in each fibre and increased mobility of the polymer chains throughout the fibre.³⁹

To explain the effects of temperature on fibre drawing, the concept of crystal mobility temperatures, CMT, has been applied. CMT is the critical temperature above which crystalline lamellae become mobile enough to be oriented. For instance, it has been shown that deformation of as-spun fibres with a spherulitic structure at 90 °C is largely influenced by non-crystalline polymer chains.⁸⁷ The CMT is 110 °C and so the crystalline lamellae resist orientation. When the drawn fibres are annealed under tension at 140 °C, however, the lamellae are able to slip and rotate, so that their chain axes are oriented along the fibre axis, and the transformation from spherulitic structure to fibrillar structure is completed.

Speed of drawing (draw rate) is a further factor affecting structural changes to polyolefin fibres. A concept that is often used is 'ease of drawing', which determines the speed of drawing without an excessive number of filament breaks.¹⁹ This consideration is especially important to commercial fibre manufacture, where draw speeds may be higher than 4000 m min⁻¹.¹⁸ Polymers with narrower molar

mass distribution are generally easier to draw without filament breaks, although the maximum draw ratio achievable may be low. The inclusion of additives such as stearates, paraffin waxes and silicon-based additives, promotes ease of fibre drawing. Higher draw speeds can be obtained, the maximum draw ratio is increased and the formation of microvoids is reduced.

More than one drawing stage is often needed to achieve the desirable mechanical properties in the final fibre, despite the added complexity in terms of processing. For the drawing of PP fibres, it has been shown that two-stage drawing can provide a route to filaments of high tenacity, where the first stage utilises a high draw ratio at low temperature (≤ 60 °C) and the second stage utilises a low draw ratio at high temperature (*ca.* 140 °C).^{67,68} The as-spun fibre should be in the paracrystalline state. With this two-stage approach, a high orientation of the PP chains could be obtained in the first stage before transformation from the paracrystalline to the α -monoclinic form in the second stage. PP fibres of count < 0.6 tex could be obtained with a tenacity as high as 0.85 N tex⁻¹, although the draw speeds in both stages were limited to 200 m min⁻¹. It was suggested, however, that this problem could be eased by integration of spinning with the first draw stage, using an optimised design for this draw stage. The second draw stage could be designed to provide a compromise between achievable mechanical performance and commercially acceptable production speeds, with the possibility of integrating this draw stage with further processing downstream. The advantages of multistage drawing have also been demonstrated by other workers,^{88,89} and indeed multistage drawing is widely practised on a commercial scale.

The development of flaws and defects during the drawing of polyolefins, particularly to high draw ratio, has been the subject of recent research, notably by Bassett and Ward and their co-workers. In the drawing of paracrystalline PP fibres at 60 °C, the development of longitudinal defects, often several μ m long, has been demonstrated.⁸⁶ Moreover, at higher draw ratios (≥ 7), the drawn fibres were observed to contain transverse bands of defects, which alternated with homogeneous sections along the length of each fibre. As the draw ratio increased, the defect bands increased in length and proportion until they occupied very nearly all of the fibre. The defects have been identified as regions of reduced density.

A similar distinct longitudinal morphology has also been observed in some highly drawn polyethylenes.^{90,91} In this case dumbbell specimens were cut from sheets and drawn at 75 °C in tensile testing equipment. A regular morphology of alternating transverse bands and rows of etched pockets was observed, termed Pisa structure by the authors because of their resemblance to the façade of the Leaning Tower. In addition, transverse sections of the highly drawn fibres revealed large voids and some featureless patches – a morphology termed by the authors as mesa structure, in view of its resemblance to features of the North American desert.

Understanding of the formation of these structures is still quite limited. However, a new model of the underlying structure of polyolefin fibres has recently been

put forward.⁹² The structure, it is proposed, develops as a consequence of the nucleation of an extended network of entangled polyolefin chains throughout the fibres. Subsequent growth into spaces in the network will encounter stresses because of contraction on crystallisation giving rise to density-deficient regions within the fibres.

5.11 Applications

5.11.1 Introduction

By far the most important type of polyolefin fibre in a commercial sense is PP fibre. Although there are specific markets for PE fibres, the PE fibres for these markets are generally produced by gel spinning.¹¹ Attention, therefore, is devoted primarily in this section to PP fibres.

PP fibres enjoy a wide range of end-uses, and these uses are expected to increase over the coming years.¹⁰ There are several reasons to account for the swing towards PP fibres. Propene is perceived to be a secure raw material for the production of PP, and the ratio of technical performance to cost of fibre is high. PP fibre is uncomplicated to process, is a good substitute for numerous other materials, is quite readily recycled and is considered to have little adverse environmental impact. PP fibres are to be found, for example, in carpets and other household textiles, motor vehicles, geotextiles, healthcare and hygiene products, filters, sacks and bags, cables, ropes, netting and agricultural and horticultural products. Some selected examples of the many applications of PP fibres are now given.

5.11.2 Carpets

PP fibres have very largely replaced jute as the material for carpet backings. Primary carpet backing, the backbone of the carpet, must be able to withstand a number of harsh processing treatments, such as tufting, dyeing and steaming, without loss of strength or undue change in dimension. PP fibres are, therefore, well suited. For the secondary carpet backing, the base of the carpet, PP fibres are again well suited in view of their resistance to moisture. There is no swelling of the fibres that would result from the absorption of moisture, and there is little growth of moulds. Carpet backings normally consist of PP fibres produced by the FOY process, or PP tapes. Both forms provide the high strength required.

PP fibres are finding increasing application too in carpet pile yarns, owing extensively to the texturing processes now available for BCF yarns. The excellent stain resistance of coloured PP fibres is also important, a feature due to the inherent properties of PP and to the presence of the colour in the form of pigmentary particles. Carpet pile can be subjected to many different kinds of spillages, whether in the home, the office, in shops or in transportation, yet the inertness of PP renders the fibres resistant to most types of chemical spillage. The colouristic properties

are also largely unaffected by such spillages, and moreover the fibres resist fading by light.

There is still considerable effort, however, in improving the resilience of PP pile yarns and their resistance to continuous wear. Some of this effort is centred around the design of suitable profiles for spinneret holes in melt extrusion and the consequent shape of the fibre cross-section (Section 5.13.2).

5.11.3 Household furnishings

PP fibres are applied in a wide range of home furnishings. For example, PP fibres are being used more and more for upholstery cover fabrics in view of their high abrasion resistance. These fibres are produced in POY form or as staple fibre yarns. In addition, mattress duck, made from PP fibres that can be given long-term antimicrobial treatments, can help to alleviate the problems suffered by those especially susceptible to allergies, as with asthma and eczema. Other PP household textiles include bed linen, bedspreads, cleaning cloths, net curtains and bath mats.

5.11.4 Geotextiles

Geotextiles have a wide variety of uses. They can provide reinforcement in roads and stabilisation in embankments, by absorbing forces from which other components in a construction must be protected. They can also provide filtration and drainage of water in foundations and keep materials separate, to prevent intermixing of layers of these materials.

Geotextiles are manufactured from woven and non-woven fabrics, the choice of fabric depending on the function required. Thus, woven fabrics, often from slit tapes, are used where strength and stability are important, but non-wovens are used where filtration, drainage and cushioning are among the principal requirements.

The chemical inertness, high strength, low density and low cost of PP fibre render it an attractive option for many geotextile applications. In addition, for those geotextile applications where the PP fibres are below ground level, their susceptibility to photodegradation is a less serious factor. Nevertheless, there are some problems associated with the use of PP fibre in geotextile applications, one of these being poor creep resistance. Thus, during use, many geotextiles constructed from PP fibres are readily deformable and should, therefore, be used in roles where the stress to them is limited.

A further problem is sensitisation under stress to oxidative degradation. Evidence has been obtained that stress increases the rate of oxidative attack through the promotion of PP chain scission.⁹³ Furthermore, it has been pointed out that this observation has implications for durability tests and predictions of the lifetimes of PP textiles not only in geotextile applications but in any application where a PP textile is continuously under stress. Indeed, it has been suggested that creep tendency and stress sensitivity to oxidation are related via a common

mechanism. Thus, strategies for reducing creep may also reduce stress sensitivity to oxidative degradation, with consequent improvement in durability. The presence of some grades of carbon black in PP fibres appears to be beneficial in this respect.⁹⁴

5.11.5 Motor vehicles

Textile components in a standard car account for 2–4% of its total mass. Some of these textile components are readily seen: for example, carpets, interior trim and boot liners. Many textile components, however, such as tyre cord and airbags, are hidden from view. Components such as seat belts and airbags play a vital role in protecting drivers and passengers in the event of a vehicle accident.

The application of PP textiles in the automotive sector is steadily increasing, owing to the low density and ready recycling of PP. In addition, as already noted, PP textiles generally possess better colour stability than other synthetic fibres and have good resistance to chemicals and staining.

PP textiles, then, are to be found in many parts of a vehicle. Needle-punched, non-woven PP fabrics are used in parcel shelves, boot liners and bonnet liners, door panels and the top decorative layers of floorcoverings.^{95,96} Woven and knitted PP textiles are used in door linings. The use of PP textiles in car seats is limited, as the abrasion resistance is considered too low compared with polyester. However, PP fabrics are occasionally used in the side linings of seats. It is expected that the increasing legislation requiring greater emphasis on the recovery and recycling of waste material will promote the growing application of PP fibres in automotive textiles.

5.11.6 Healthcare and medical applications

Polyolefin fibres have found a wide variety of applications in the hygiene and medical sector. Moreover, their uses continue to expand, especially for PP non-wovens. Textiles for healthcare and medical applications are conveniently categorised into four groups:⁹⁷

1. non-implantable materials, e.g. plasters, bandages and gauzes;
2. extracorporeal devices, e.g. artificial lungs, kidneys and livers;
3. implantable materials, e.g. sutures, vascular grafts and artificial ligaments;
4. healthcare/hygiene products, e.g. surgical gowns, cloths, wipes and bedding.

Polyolefin fibres find application in all four groups. They are highly inert in living tissues and may retain their tensile properties over several months or even years *in vivo*. Thus, PP fibres are commonly used in woven and non-woven orthopaedic cushion bandages, applied under plaster casts or compression bandages to prevent discomfort to the patient. PP fibres are also used in plasters and gauzes.

The commonest application of polyolefin fibres in extracorporeal devices is as

hollow fibres in mechanical lungs. The porous construction is such that the lung possesses high permeability to gases but low permeability to liquids. Thus, carbon dioxide can be removed from the patient's blood and oxygen can be supplied to it, yet leakage of blood plasma is prevented.

PP fibres are also used in sutures for wound closures. There is minimal tissue reaction, an important factor in contaminated and infected wounds. Moreover, PP sutures retain knots better than do most other synthetic materials, yet because they do not adhere to tissue, they are readily pulled out when the wound has healed. Meshes fabricated from PP fibres may be used to replace abdominal walls and replace hernias, when the suture experiences extensive stress during healing of the wound. PP sutures are generally suitable for repairing blood vessels, such as coronary arteries, where excessive tissue reaction to the suture could lead to reduced cross-section of the blood vessel or the formation of a thrombus within it. Skin sutures usually consist of PP monofilaments.

Textile materials are particularly suitable as soft-tissue implants, in view of their strength and flexibility. Woven or braided porous meshes of PE fibre surrounded by a silicone sheath are often used for fabricating artificial tendons. Non-woven low-density PE is often used for artificial cartilage in the face, ear, nose and throat, as it is considered to resemble natural cartilage quite closely.

Polyolefin fibres are used extensively in healthcare and hygiene products. Thus, woven and non-woven PP is used in surgical gowns. In isolation wards and intensive care units, non-woven PP is used in disposable, protective clothing, worn to minimise cross-infection. Woven and non-woven PE is commonly used in surgical drapes and cover cloths in an operating theatre. The drapes are designed to cover the patient, and the cover cloths to cover the area around the patient. Both types of polyolefin are used in incontinence products, such as nappies. Spunbonded, non-woven PP often forms the inner covering layer, while the outer layer may consist of non-woven PE. Bicomponent fibres, consisting of a PE sheath and PP core, are used for sanitary towels, tampons and incontinence products.

5.11.7 Filters

PP fibres are used extensively in filters, both for solid–gas and solid–liquid filtration systems. Although filtration products used to be typically manufactured from woven fabrics, non-woven fabrics are now being increasingly utilised. Non-wovens are considered to possess greater versatility, in that they can often be readily used on their own or in conjunction with some other material. Moreover, in dry filtration, non-wovens permit greater flow of gas without reduction in filtration efficiency.

Improvements in filtration systems are being driven by the need for higher rates of filtration, improved efficiency of filtration and stricter environmental legislation. These factors have led to the increasing use of PP textiles, with additional factors being their superior chemical and abrasion resistance and low cost of

manufacture. In wet filtration applications, woven and non-woven PP textiles are used more than any other types of textile. The rapidly increasing application of melt-blown nonwovens for dry filtration has also promoted the use of PP fibres.

5.11.8 Slit tape products

The commercial importance of PP fibres in carpet backings has already been discussed (Section 5.11.2), but there are also many other outlets for fabrics woven from PP tapes. These outlets include sacks, bags, flexible intermediate bulk containers (FIBCs) and tarpaulins. The same properties which are important for carpet backings are important too for these other products, notably low density, low cost of manufacture and high tensile strength. Many of these products are used in exterior applications; hence effective stabilisers in the fibres against photo-chemical degradation are vital.

5.11.9 Ropes and netting

PP ropes have extensive maritime use. Because the density of PP is less than that of water, ships' ropes made from PP float on water and can consequently be in constant view. Moreover, PP ropes cannot become waterlogged, as the moisture regain of PP is tiny (Table 5.2). PP lines are evident too in water sports: they connect waterskiers to the boats towing them and are used to separate swimmers in races.

PP netting has a wide range of applications. These applications include safety fences such as those used around building sites and in downhill runs to protect skiers. PP netting is also used in horticulture to control the intensity of light incident on plants and to protect them from insects. It is utilised too as a base in road construction and as a grid to limit the movement of fill materials in construction work.

5.11.10 Sports surfaces

The replacement of grass by artificial sports surfaces is becoming increasingly widespread. In winter, natural grass is prone to severe erosion if used for more than a few hours per week. The erosion can be all too obvious around goalmouths during a football match on a wet day! Even in summer, heavy use of sports surfaces, as in lawn tennis courts, can wear grass away.

Polyolefin fibres are now being increasingly used as artificial grass. While PP fibres have been historically used, the more sophisticated present-day systems often employ PE-based fibres, in order to achieve the required flexibility and performance. Polyolefin fibres are almost completely unaffected by ambient temperature and humidity, in that they retain their dimensions, strength and abrasion resistance. However, the presence of HALS compounds, particularly in

PP fibres, is essential, given the susceptibility of polyolefins to photodegradation. The green colour is provided by pigments dispersed within the fibres, such as chlorinated copper phthalocyanine pigments. The pigment too must be resistant to temperature, humidity and light.

5.11.11 Apparel

PP fibres have had very limited application in the fashion industry. One major drawback is the difficulty in dyeing PP textiles, especially for an industry so heavily involved with trends in fashionable colours. Nevertheless, PP textiles are used in some types of apparel. For example, PP textile garments are often worn next to the skin, because they adsorb little water. Consequently, perspiration can pass from the skin through the PP garment to an absorbent outer layer. The good wicking and low thermal conductivity of PP fibres thus keep the wearer warm and dry. PP fibres are, therefore, used in some types of underwear and socks. They are finding increasing application in sports and leisure wear, such as lightweight outerwear for climbers, walking socks, cycle shorts, swimwear and garments for divers.

5.12 Recycling

The increasing concern about the environment and the consequent legislation passed to protect it are changing the emphasis in the commercial arena from waste disposal to waste management. Thus, there is great interest in renewable materials, recyclable materials and the conversion of waste to energy, as in incineration. For polyolefins, recycling is the most feasible approach: new polyolefin textiles can be fabricated from used or waste polyolefin products. Such products are generated during production of a polyolefin textile and after use by a consumer.

In polymer production, considerable quantities of waste material may accumulate if the product fails to reach a required range of specifications. This waste normally requires no extensive cleaning, nor does it attract substantial costs for its collection. There could, therefore, be real economic benefits to the producer if the waste could be used as a partial replacement for virgin polyolefin. However, in order that it can be accepted by the extruder, the polyolefin fibre waste has to be converted into material of much higher bulk density, through repelletising (densification). Moreover, as little stress as possible must be exerted on the polyolefin material, to prevent any significant changes to its properties. Any pigment in the fibres also has to be segregated, unless the recycled material is destined for applications where the colour is unimportant.

During fabric manufacture, trimmings from the edges of a fabric can be produced, as for example with spunbonded PP. With suitable fibre extrusion equipment, the trimmings may be fed back to the extruder without the need for repelletising. The trimmings have the same additives and colorants as the virgin polyolefin, and

the melt flow index is likely to be only slightly higher. The trim should comprise a maximum of no more than 10% of the total throughput rate of the polymer in the extruder, so that the slightly higher MFI will only marginally affect the processing of the polymer blend and the properties of the textile produced.

Recycling of used product, once the consumer has thrown it away, is far more complex. It involves collection of the used product and then segregation of polyolefin fibres from all the other components. Segregation includes size reduction, sorting, separation, cleaning and drying.

The polyolefin eventually isolated may still be contaminated, so that its range of end-uses becomes limited. Fabrics containing recycled polyolefins are, for example, likely to be barred from biomedical, agricultural and even industrial applications, because of concerns about residual contamination. Moreover, especially after prolonged use, the polyolefin may have been partially degraded by heat, light, oxidising chemicals and other agents. The MFI may, consequently, be substantially raised. Indeed, re-extrusion of the polyolefin may also raise the MFI, by reducing the molar mass and narrowing the molar mass distribution.

It is evident, then, that for the successful recycling of polyolefin fibre waste into high-quality repelletised material, factors such as residual contamination, colour and MFI are important. Nevertheless, the increasing demands of environmental legislation are forcing many polypropylene fibre producers to try to increase the proportion of recycled polyolefin in their products. Horrocks and co-workers have investigated the inclusion of recycled waste PP on the performance of geotextile tapes.^{98,99} They have noted a significant loss in the strength of PP tape when recycled PP is added, owing to thermo-oxidative degradation. However, if suitable antioxidants are also introduced along with the recycled PP, tapes with acceptable tensile properties can be produced. Christiani *et al.* have carried out rheological analysis of PP melts, to predict the state and level of degradation of PP fibrous waste material, and hence its spinnability.¹⁰⁰ They concluded that a melt-spinning grade of PP could be recycled five times before the properties of the fibre became significantly impaired. After five cycles, spinnability was lost because of marked reduction in molar mass and melt viscosity.

5.13 Future trends

5.13.1 Challenges

What are the future prospects of polyolefin fibres? It seems almost certain that PP fibres will continue to play an important role in textiles, provided that supplies of propene, the source of PP, remain secure and that recycling of PP can be managed economically. There is a possibility too of a resurgence of interest in PE fibres produced by melt-spinning. There are signs of this renewed interest in biomedical applications (Section 5.11.6).

As made evident in Section 5.11, the uses of polyolefin fibres, and in particular

of PP fibres, are highly diverse. Yet, despite the obvious advantages enjoyed by polyolefins, there are a number of inherent drawbacks (Table 5.2). Although some of these drawbacks can, in practical terms, be largely overcome (e.g. resistance to photodegradation, through the incorporation of HALS compounds), several still remain. Perhaps, the most prominent is the inability to dye polyolefin fibres successfully.

There is still, therefore, a clear need for further technical improvements in polyolefin fibres. These improvements can arise from superior grades of polymer and advances in processing technology. The impact of metallocene catalysts on the production of polyolefin grades has already been discussed (Section 5.3.3), and indeed catalysts of even greater promise are already being investigated.²⁷

The quest to advance processing technology, particularly in the case of PP fibres, to meet such a wide variety of end-uses, continues. Efforts to produce polyolefin fibres that can be readily dyed have been discussed in Section 5.7. There is also considerable activity in the production of PP fibres of greater resilience and even interest in 'smart' PP fibres. The use of systems such as neural networks as a forecasting tool and modelling technique is also attracting interest.¹⁰¹ From a production viewpoint, a model should quickly be able to predict whether a desired range of fibre specifications is in fact achievable. If the specifications can be met, then the model will enable a production manager to set up the necessary processing conditions rapidly.

The following sections highlight some of these challenges, with particular emphasis on PP fibres.

5.13.2 Improvements in fibre resilience

A major drawback with PP fibres is their poor resilience, and this problem has limited the use of PP fibres as carpet face yarns. In most carpet pile constructions, PP fibres are markedly inferior to nylon fibres in crush resistance and appearance retention. However, a number of approaches are being adopted to overcome the problem.²⁵ These approaches make use of inhomogeneities deliberately introduced into the fibre during processing or the effects of fibre cross-sections other than circular.

One method is the differential cooling of individual filaments in the quench chamber after they have emerged from the spinneret. By passing cold air at speed in a direction perpendicular to the path of the filaments, a differential filament structure results. The side of each filament facing the air is cooled more quickly than the opposite side, and hence the structures of the two sides differ. This difference can be enhanced on subsequent drawing.

The use of twin extruders also offers a range of possibilities. For example, PP resins of different grades can be extruded through separate metering pumps into a bicomponent spinning manifold. Alternatively, different degrees of crystallinity may be induced through the addition of a small amount of nucleating agent in one

PP melt stream, or the two streams of PP melt can be at different temperatures when they meet.

Another approach is to tailor the cross-section of the PP fibre. Cross-section has a significant impact on the mechanical performance of a synthetic fibre, and indeed on its aesthetic qualities. Both the shape and size of the cross-section are important in this respect. Spinneret holes in extrusion equipment are normally circular. Holes of different shapes will give rise to fibres with profiled, 'exotic' cross-sections. Many of these fibres produced on a commercial scale possess triangular or trilobal profiles, and in both cases fibre resilience is improved.

Yet another approach is to produce PP fibres of helical geometry. During extrusion, turbulence is generated in the PP before the filaments leave the spinneret plate. The molten filaments are then quickly cooled to induce rapid solidification. After drawing and subsequent relaxation, the fibre adopts a helical structure. The structure is composed of sections of helices in clockwise and anticlockwise directions alternately.

5.13.3 Control of fibre processing

It has become increasingly apparent in the PP fibre processing industry that better control of processing is needed. Often a traditional 'one factor at a time' approach is followed: only one process control parameter is varied at a time, while all the rest are kept constant. However, this approach has several drawbacks. Large numbers of experimental trials are needed, and the acquisition of all the data required can take a long time. Furthermore, any significant interactions existing between control parameters may well not be identified.

It has been proposed that a more soundly based alternative is an integrated approach,^{76,89} comprising factorial experimental design^{102,103} and comprehensive statistical analysis of the results. This approach is well established, having been first formulated by Sir Ronald Fisher many decades ago.¹⁰⁴ Using this approach, we may reliably estimate the level of significance of each of the processing control parameters and identify any significant interactions between them.

5.13.4 Copolymers

Optimised processing, while highly valuable, cannot remove those limitations inherent in the very nature of a polyolefin macromolecule. The limitations can, however, be tackled by adding small proportions of other materials. Additions may be made on a molecular level to produce copolymers, or on a larger scale through blending.

A number of polyolefin copolymers have been available commercially for some time. The introduction of ethene comonomer into a PP chain reduces the degree of crystallinity, and indeed the degree of crystallinity is generally lowest in copolymers containing equal proportions of ethene and propene.¹⁰⁵ Moreover, ethene-rich

copolymers exhibit the orthorhombic form of PE and propene-rich copolymers exhibit the α -monoclinic form of PP.¹⁰⁵ The two types of crystal do not exist together in any PE/PP copolymer. The presence of ethene comonomers also broadens the melt temperature range, an effect useful in the production of spun-bonded non-wovens. PE/PP copolymers have also been developed for BCF yarns, and these yarns generally reveal improved resilience over standard PP yarns. Terpolymers are also available, containing propene, ethene and butene. The effects of copolymers in metallocene PP fibres have already been highlighted in Section 5.3.3.

5.13.5 Fibre blends

Although the production of polyolefin copolymers could clearly serve to overcome some of the disadvantages of polyolefin fibres, the approach may not always be viable commercially, unless one or two comonomers are identified that can confer many of the wide range of fibre properties required. An alternative approach is to incorporate other materials into the fibres to produce these properties, and indeed the incorporation of a variety of additives (Section 5.6) and of pigments (Section 5.7) has already been highlighted. In PP fibre technology, however, there is also considerable interest in utilising blending to produce fibres of enhanced mechanical performance. Thus, improvements can be achieved by the presence of fillers, such as glass or carbon fibres, but there are difficulties associated with processing. Blending with filler fibres can create a melt of increased viscosity, and it is consequently more difficult to obtain a uniform distribution of the filler in the PP fibre matrix. The extrusion equipment tends to be subjected to greater wear and tear, and the filler fibres are prone to fragmentation during processing. In addition, the reinforcing effect of the filler fibres will not be transferred to the PP fibre matrix unless there is good interfacial adhesion between the filler and PP phases.

Some of these difficulties may be less pronounced if fillers containing particles or fibres of nanometre dimensions are used. For example, the incorporation of nano carbon fibres as a minor component has been shown to provide PP fibres with some improved mechanical properties.¹⁰⁶ However, whatever property they confer, the blending of nano-materials into a polyolefin requires care: where significant pressure is experienced by the nano-material, its particles are liable to compact into aggregates, and the nano-scale benefits are lost. Nevertheless, there is currently considerable research activity in the application of nano-materials that will enhance specified fibre properties without impairing other properties, and it is likely that developments on a commercial scale will result.

An alternative approach is to blend polyolefin fibres with a small proportion of a thermotropic liquid crystalline polymer (TLCP), which exhibits liquid crystalline properties in the desired melt temperature range. This strategy has been discussed for PP fibres.⁸⁸ As with PP, a TLCP can be melt extruded. These TLCPs

generally possess chains containing rigid rod-like structures, which can be readily aligned in the direction of flow during melt extrusion. Thus, TLCPs exhibit surprisingly low viscosities when in the liquid crystalline state, a property that would facilitate PP fibre extrusion. Not only can improvement of PP fibre mechanical performance be provided, but also less energy is likely to be used during melt extrusion, owing to the reduced viscosity of the melt that the TLCP component confers. The PP blend fibre can also have lower thermal shrinkage¹⁰⁷ and better resistance to creep. However, care has to be taken to prevent fragmentation of the TLCP component during the drawing stage.

In these blends, the TLCP component exists as tiny fibrils inside the PP matrix. Other matrix/fibril bicomponent fibres, in which the PP component forms the matrix, are also attracting interest. Among these are PP/PE fibres designed to improve fibre handle, and blends of PP and polyester to enable dyeing. Skin-core bicomponent fibres have also been developed. One example is a fibre with a PP core and a PE sheath, which has application in spun-bonding technology. The lower melt temperature of the PE sheath, compared with the PP core, allows bonding of the web at a lower temperature without affecting the mechanical properties of the core PP.

5.13.6 Auxetic PP fibres

Auxetic materials possess a negative Poisson's ratio, ν : in contrast to most materials, they become thicker when stretched, with an increase in void volume. This behaviour contrasts with that of hard-elastic fibres (Section 5.9), whose diameter remains constant on fibre stretching, before decreasing.²⁰ A wide variety of auxetic materials have now been produced since the successful synthesis of auxetic polymeric foams in 1987.¹⁰⁸ Among these materials are auxetic versions of PP,¹⁰⁹ ultra-high molecular weight PE¹¹⁰ and, recently, PP fibres.¹¹¹

It has been demonstrated that auxetic fibres can be processed by melt-spinning with some novel modifications. In particular, a low processing temperature seems to be required throughout the extrusion equipment. Indeed, it has been reported that a temperature as low as 159 °C can achieve the formation of auxetic PP fibres.¹¹¹ The fibres were not subsequently drawn. The Poisson's ratio obtained for these fibres was -0.60 ± 0.05 . The auxetic behaviour of these PP fibres was, therefore, found to be more pronounced than that of PP rods, reported previously,¹⁰⁹ for which $\nu = -0.22$. Characterisation by scanning electron microscopy revealed that the PP fibres possessed a modified version of the typical auxetic polymeric microstructure of nodules connected to one another by fibrils.

While it is clear that considerable development of auxetic PP fibres is yet required, applications for them can already be envisaged. Auxetic PP fibres may find application in composite materials, owing to enhancements in fibre fracture toughness, increased energy absorption capabilities and reduced fibre pull-out.¹¹² A further application may be for drug release materials, where the auxetic fibres

contain wound-healing particles trapped within the pores of the fibre structure. If a wound, covered by a bandage containing these fibres, swells as a result of infection, the stretching of the fibres will be accompanied by an increase in their width. This auxetic effect will enlarge the pores in the fibres and enable the release of a wound-healing agent.

5.13.7 Plasma treatments

The application of plasma treatments offers exciting technological developments for the future, especially as equipment on a commercial scale is becoming increasingly available. With this technique, fibre surfaces can be modified, while the fibre bulk remains unaffected.

Plasma is an electric glow-discharge of a gas. There are many everyday examples of plasmas, such as fluorescent lighting and neon signs. In these cases, the objective is to produce light, but plasma can equally be utilised for modifying solid surfaces. The plasma atmosphere comprises a mixture of ions, free radicals, electrons and UV radiation. The interactions of all these species with one another and with a solid surface, therefore, constitute a complex process.

A variety of different gases may be used for plasma treatments, and even mixtures of gases have been tried. Depending on the nature of the gas and the conditions under which the plasma is generated, different effects may be experienced by the solid surface. In the case of synthetic fibres, a number of possible effects can be identified. Thus, plasma treatment with a noble gas such as helium or argon may alter the detailed topography of the surface, to generate roughness on a micro-scale and increased surface porosity. Plasma treatment may, additionally, alter the chemical nature of the surface through the introduction of various functional groups within the polymer chains at the fibre surface. Gases such as oxygen, nitrogen and ammonia may give this effect. Plasma treatment may cause the deposition of a very thin polymeric coating on the fibre surface. This polymeric coating has a highly crosslinked structure. Hydrocarbons and fluorocarbons can, for example, bring about plasma polymerisation.

Plasma treatments may be given under atmospheric or vacuum conditions. In processing terms, plasma equipment operating under atmospheric conditions can be incorporated in a production line,¹¹³ but modification of the fibre surface is often less stable and less reproducible. Vacuum plasma treatments, on the other hand, require more sophisticated equipment but provide stronger, more stable fibre surface modifications.¹¹⁴

There are a number of attractions in the application of plasma treatments to polyolefin fibres. Coating techniques traditionally provide means of adapting fabric surfaces to confer particular desired properties, but polyolefin textile surfaces are more difficult to coat successfully than many other synthetic fibre surfaces. Thus, plasma treatment offers an alternative approach, which is also, importantly, a 'clean' technology in an environmental sense.

For any application of polyolefin fibres which requires good interaction with more polar environments, notably aqueous environments, the hydrophobicity of the fibre surface becomes a disadvantage. With the aid of suitable plasma treatments, such as oxygen plasma treatments, the fibre surfaces become more hydrophilic owing to the introduction of polar groups at the surface. This modification confers, for example, greater biocompatibility, given that the majority of fluids in the body are aqueous based. Greater hydrophilicity is, therefore, advantageous for such applications as scaffolds, wound dressings and blood filters.

The mechanisms by which oxygen and other gases confer increased hydrophilicity on polyolefin fibre surfaces are far from completely resolved. It has, however, been demonstrated that, when PP is treated with oxygen plasma, there is negligible insertion of oxygen as a result of reaction with active sites on the polymer.^{115,116} It appears, instead, that there is formation of a surface layer of a random copolymer consisting of oxidised and unaltered segments. The layer, once formed, then rearranges itself over time, to lower the free energy at the fibre surface.

Polyolefin fibre surfaces may also be made more oleophobic. This increased resistance to oils can be useful in some filtration systems. Increased hydrophobicity can be conferred by plasma treatment with a fluorocarbon, such as tetrafluoromethane or hexafluoroethane. Although these gases are expensive, very little is required for surface modification. Fluorocarbon plasma treatments cause the deposition of fluorinated plasma polymers. One report has shown that a variety of fluorinated functional groups are present at the fibre surface.¹¹⁷ These groups include $-\text{CHF}$, $-\text{CF}_2-$, $-\text{CF}_3$ and even $-\text{CH}_2-\text{CF}_2-$.

An important technological aspect is the durability of plasma treatments. It is known, for example, that the wettability of PP films treated with ammonia plasma gas decreases over a period of time. However, durability can often be enhanced through pretreatment with helium or argon gas plasma, which increases the mechanical resistance of a fibre surface through cross-linking of the polymer chains at the surface.³

Another important result of plasma treatment is manifest as changes in the topographical nature of the fibre surface. Different changes of the surface topography can be effected by different plasma gases and varying conditions of exposure. It has been shown, for example, that extended exposure to oxygen plasma causes pitting of PE fibre surfaces.³ This pitting is helpful in promoting adhesion between PE fibres and resin in composites, because the pitted structure can be penetrated by the resin to confer better mechanical keying.

To obtain a clearer understanding of the effects of plasma treatments on polyolefin fibre surfaces will require a combination of sophisticated experimental techniques. While changes in wettability can be readily assessed by the determination of contact angles of drops of water on a fabric, it has also been shown that environmental scanning electron microscopy can be utilised to determine the

contact angle of water (and oils) on individual fibres in the fabric.¹¹⁸ Furthermore, advanced microscopy techniques are needed to study the changes in surface topography, and indeed the value of atomic force microscopy in this respect has recently been reported.¹¹⁹ For studying the chemical changes induced at the fibre surface, X-ray photoelectron spectroscopy is a valuable tool.

5.14 Conclusion

In commercial terms, by far the majority of melt-spun polyolefin fibres are PP fibres,^{6,7} and these look to have a bright commercial future. Their technological advantages render them well placed to meet the variety of innovative demands they are likely to face over the coming years. At the same time, many of their inherent disadvantages are being steadily overcome by the use of suitable additives, as discussed in Section 5.6. Nonetheless, in order to meet future technological demands, improvements in polyolefin fibre performance will continue to be required.

The achievement of these improvements can embody a number of approaches. Thus, systematic experimental design techniques, of the kind outlined in Section 5.13.3, will provide useful ways of gauging which fibre processing conditions, and which combinations of them, have significant influences on a set of required technological applications. Processing conditions to meet these specifications can then be optimised. Following optimisation, neural networks and other suitable techniques can be applied as forecasting tools to link polyolefin fibre processing and performance.¹⁰¹

However, useful though all these techniques are, the future of polyolefin fibre processing on an industrial scale will need to be underpinned by even more detailed understanding of the structural changes occurring during fibre processing. While it is evident that considerable progress has been made over the last decade or so, notably with polyethylene,⁹⁰⁻⁹² the application of advanced microscopic techniques, such as scanning probe microscopy and environmental scanning electron microscopy (ESEM) should help to progress our understanding still further. Particularly exciting are the possibilities that ESEM offers for real-time *in situ* studies of polyolefin fibre drawing.

The next few years may also see further innovations in the effectiveness of additives, particularly flame-retardant, antimicrobial and antistatic additives, and even antioxidants. The dyeing of polyolefin fibres still remains one of the most elusive challenges.

Finally, the coming years are bound to witness more stringent demands and legislation for the recycling and regeneration of synthetic fibres; the recycling of polyolefin fibres has been already discussed in Section 5.12. Moreover, the technologies used for the production of polyolefin fibres will require to be 'clean'. However, in comparison to many other synthetic fibres, polyolefin fibres are arguably well set to meet these important environmental challenges.¹²⁰

5.15 Acknowledgment

The assistance of Dr R. D. Yang and Dr O. K. Risnes in the preparation of this chapter is gratefully acknowledged.

5.16 References

1. McIntyre J.E. and Daniels P.N., editors, *Textile Terms and Definitions*, 10th ed, The Textile Institute, Manchester, 1995.
2. Buchanan D.R., 'Olefin fibres' in *Kirk-Othmer Encyclopedia of Chemical Technology*, Vol.16, 3rd ed, John Wiley and Sons, New York, 1981, pp. 357–385.
3. Ward I.M. and Cansfield D.L.M., 'High-performance fibres' in *Advances in Fibre Science*, editor Mukhopadhyay S.K., The Textile Institute, Manchester, 1992, pp.1–24.
4. Anon., 'Hochfeste polyethylenfaser Tenfor', *Chemiefasern/Textilindustrie*, July/August 1989, **39/91**, T177.
5. Anon., 'Celanese enters race to market high-strength polyethylene fibre', *European Chemical News*, August 20/27, 1984, 22.
6. Anon., 'Global PP fiber capacity 7.6 million tons', *Chem Fibers Int*, 2001, **51**, 318.
7. Anon., 'Worldwide olefin fibers production and producing capacity by product type: 1997 to 2002', *Fibre Organon*, June 2001, 110–111.
8. Van Parys M., 'PP fiber and textile engineering', *Chem Fibers Int*, 2001, **51**, 317.
9. Oertel C.G., 'Applications' in *Polypropylene Handbook*, editor Moore E.P., Hanser, Munich, Vienna and New York, 1996, pp. 349–379.
10. Peckstadt J.-P., 'Market perspectives in the West European polyolefin textile industry', *Chem Fibers Int*, 1998, **48**, 362.
11. Van Dingenen J.L.J., 'Gel-spun high-performance fibres' in *High-performance Fibres*, editor Hearle J.W.S., Woodhead Publishing Ltd, Cambridge, 2001, pp. 62–92.
12. Weedon G., 'Solid-state extrusion high-molecular weight polyethylene fibres' in *High-performance Fibres*, editor Hearle J.W.S., Woodhead Publishing Ltd, Cambridge, 2001, pp. 132–155.
13. Cook J.G., *Handbook of Polyolefin Fibres*, Mero Publishing Company Ltd, Watford, 1967.
14. Koslowski H.-J., '40 years of PP fibers', *Chem Fibers Int*, 2000, **50**, 150–153.
15. Albizzati E., Giannini U., Collina G., Noristi L. and Resconi L., 'Catalysts and polymerizations' in *Polypropylene Handbook*, editor Moore E.P., Hanser, Munich, Vienna and New York, 1996, pp. 11–111.
16. Cowie J.M.G., *Polymers: Chemistry and Physics of Modern Materials*, 2nd ed, Blackie, Glasgow and London, 1991.
17. Cossee P., 'Ziegler–Natta catalysis I. Mechanism of polymerization of α -olefins with Ziegler–Natta catalysts', *J Catalysis*, 1964, **3**, 80–88.
18. Schmenk B., Miez-Meyer R., Steffens M., Wulfhorst B. and Gleixner G., 'Polypropylene fiber table', *Chem Fibers Int*, 2000, **50**, 233–253.
19. Ahmed M., *Polypropylene Fibers – Science and Technology*, Elsevier, Amsterdam, Oxford and New York, 1982.
20. Wishman M. and Hagler G.E., 'Polypropylene in fibres' in *Handbook of Fiber Science and Technology*, Vol. IV, editors Lewin M. and Pearce E.M., Dekker, New York, 1985, pp. 371–502.
21. Sinn H. and Kaminsky W., 'Ziegler–Natta catalysis', *Advances in Organometallic Chemistry*, Vol. 18, Academic Press, New York, 1980, pp. 99–149.

22. Kaminsky W., Külper K., Brintzinger H.H. and White F.R.W.P., 'Polymerization of propene and butene with a chiral zirconocene and methylalumoxane as cocatalyst', *Angew Chem Int Ed*, 1985, **24**, 507–508.
23. Brintzinger H.H., Fischer D., Mühlaupt R., Rieger B. and Waymouth R.M., 'Stereospecific olefin polymerization with chiral metallocene catalysts', *Angew Chem Int Ed*, 1995, **34**, 1143–1170.
24. Gleixner G. and Vollmar A., 'Fibers of metallocene polyolefines', *Chem Fibers Int*, 1998, **48**, 393–394.
25. Van Parys M., 'PP fiber engineering: latest developments', *Chem Fibers Int*, 1998, **48**, 317–322.
26. Scott N.D., 'Metallocenes and polypropylene – new solutions to old problems in textile end-uses?', *Chem Fibers Int*, 1997, **47**, 125–126.
27. Gibson V. and Wass D., 'Iron age polymers', *Chemistry in Britain*, 1999, **35**, 20–23.
28. Ward J.H., Shahar A. and Peppas N.A., 'Kinetics of 'living' radical polymerizations of multifunctional monomers', *Polymer*, 2002, **43**, 1745–1752.
29. Hagimoto H., Shiono T. and Ikeda T., 'Living polymerization of propene with a chelating diamide complex of titanium using dried methylaluminoxane', *Macromol Rapid Commun*, 2002, **23**, 73–76.
30. Morton W.E. and Hearle J.W.S., *Physical Properties of Textile Fibres*, 3rd ed, The Textile Institute, Manchester, 1993.
31. Nielsen A.S., Batchelder D.N. and Pyrz R., 'Estimation of crystallinity of isotactic polypropylene using Raman spectroscopy', *Polymer*, 2002, **43**, 2671–2676.
32. Tomka J.G., Johnson D.J. and Karacan I., 'Molecular and microstructural modelling of fibres' in *Advances in Fibre Science*, editor Mukhopadhyay S.K., The Textile Institute, Manchester, 1992, pp. 181–206.
33. Hearle J.W.S. and Greer R., 'On the form of lamellar crystals in nylon fibres', *J Text Inst*, 1970, **61**, 240–244.
34. Wunderlich B. and Grebowicz J., 'Thermotropic mesophases and mesophase transitions of linear, flexible macromolecules', *Adv Polym Sci*, 1984, **60/61**, 1–59.
35. Lotz B., Wittman J.C. and Lovinger A.J., 'Structure and morphology of poly(propylenes): a molecular analysis', *Polymer*, 1996, **37**, 4979–4992.
36. Miller R.L., 'Existence of near-range order in isotactic polypropylenes', *Polymer*, 1960, **1**, 135–143.
37. Cohen Y. and Saraf R.F., 'A direct correlation function for mesomorphic polymers and its application to the "smectic" phase of isotactic polypropylene', *Polymer*, 2001, **42**, 5865–5870.
38. Bunn C.W., 'The crystal structure of long-chain normal paraffin hydrocarbons. The 'shape' of the $>CH_2$ group', *Trans Faraday Soc*, 1939, **35**, 482–491.
39. Peterlin A., 'Molecular model of drawing polyethylene and polypropylene', *J Mater Sci*, 1971, **6**, 490–508.
40. Samuels R.J., *Structural Polymer Properties, the Identification, Interpretation and Application of Crystalline Polymer Structure*, John Wiley and Sons, New York, 1974.
41. Hautajarvi J. and Leijala A., 'A morphological study of melt-spun polypropylene filaments by atomic force microscopy', *J Appl Polym Sci*, 1999, **74**, 1242–1249.
42. Risnes O.K., Mather R.R. and Neville A., 'Probing the morphology of polypropylene fibres by scanning probe microscopy', *Polymer*, 2003, **44**, 89–100.
43. Moore E.P., 'Fabrication processes' in *Polypropylene Handbook*, editor Moore E.P., Hanser, Munich, Vienna and New York, 1996, pp. 303–348.

44. Wulffhorst B. and Meier K., 'Polypropylen fasern', *Chemiefasern/Textilindustrie*, 1989, **39/91**, 1083–1090.
45. Goswami B.G., 'Spunbonding and melt-blowing processes' in *Manufactured Fibre Technology*, editors Gupta V.B. and Kothari V.K., Chapman and Hall, London, 1997, pp. 560–594.
46. Bajaj P., 'Spin finishes for manufactured fibres' in *Manufactured Fibre Technology*, editors Gupta V.B. and Kothari V.K., Chapman and Hall, London, 1997, pp. 139–169.
47. Becker R.F., Burton L.P.J. and Amos S.E., 'Additives' in *Polypropylene Handbook*, editor Moore E.P., Hanser, Munich, Vienna and New York, 1996, pp. 177–210.
48. Sen K., 'Polypropylene fibres' in *Manufactured Fibre Technology*, editors Gupta V.B. and Kothari V.K., Chapman and Hall, London, 1997, pp. 457–479.
49. Allen N.S., 'Photodegradation and photooxidation of polyolefins: importance of oxygen-polymer charge transfer complexes', *Polym Degrad Stab*, 1980, **2**, 155–161.
50. Gijisman P., 'New synergists for hindered amine light stabilizers', *Polymer*, 2002, **43**, 1573–1579.
51. Gugumus F., 'Possibilities and limits of synergism with light stabilizers in polyolefins I. HALS in polyolefins', *Polym Degradation Stability*, 2002, **75**, 295–308.
52. Dwyer S.M., Boutni O.M. and Shu C., 'Compounded polypropylene products' in *Polypropylene Handbook*, editor Moore E.P., Hanser, Munich, Vienna and New York, 1996, pp. 211–235.
53. Ciba Specialty Chemicals, European Patent 0829520.
54. Holme L., McIntyre J.E. and Shen Z.J., 'Electrostatic charging of textiles', *Text Prog*, 1998, **29**, 1–90.
55. White W.C., Monticello R.A., Krueger J.W. and Vandendaele P., 'Antimicrobials for polypropylene: their promise and environmental impact', in *Polypropylene in Textiles*, editors Gandhi K.L. and Pearson J.S., World Congress, Huddersfield, July 2000, pp. 237–242.
56. Wright T., 'AlphaSan: a thermally stable silver-based inorganic antimicrobial technology', *Chem Fibers Int*, 2002, **52**, 125.
57. Burkinshaw S.M., Froehling P.E. and Mignanelli M., 'The effect of hyperbranched polymers on the dyeing of polypropylene fibres', *Dyes Pigments*, 2002, **53**, 229–235.
58. Kaul B., Ripke C. and Sandri M., 'Technical aspects of mass-dyeing of polyolefin fibres with organic pigments', *Chem Fibers Int*, 1996, **46**, 126–129.
59. Horrocks A.R., Mwila J., Miraftab M., Liu M. and Chohan S.S., 'The influence of carbon black on properties of oriented polypropylene. 2. Thermal and photodegradation', *Polym Degrad Stab*, 1999, **65**, 25–36.
60. McKay R.B., 'Control of application performance of classical organic pigments', *J Oil Col Chem Assoc*, 1989, **72**, 89–93.
61. Mather R.R., 'Surface character and performance of organic pigments', *Chem Ind*, 1981, 600–605.
62. Richter E. and Bott R., 'Waxes for colored polypropylene fibers', *Chem Fibers Int*, 2000, **50**, 188–190.
63. Sprague B.S., 'Relationship between structure and properties of 'hard' elastic fibers and films', *J Macromol. Sci Phys B8(1–2)*, 1973, **8**, 157–187.
64. Cannon S.L., McKenna G.B. and Statton W.O., 'Hard-elastic fibers (a review of a novel state for crystalline polymers)', *J Polym Sci Macromol Rev*, 1976, **11**, 209–275.
65. Tomka J.G., 'Polypropylene – the world's strongest fibre?', *Textile Month*, October 1996, 40–43.

66. Northolt M.G. and van der Hout R., 'Elastic extension of an oriented crystalline fibre', *Polymer*, 1985, **26**, 310–316.
67. Wang I.-C., Dobb M.G. and Tomka J.G., 'Polypropylene fibres: an industrially feasible pathway to high tenacity', *J Text Inst*, 1995, **86**, 383–392.
68. Wang I.-C., Dobb M.G. and Tomka J.G., 'Polypropylene fibres: exploration of conditions resulting in high tenacity', *J Text Inst Part 1*, 1996, **87**, 1–12.
69. Ziabicki A., *Fundamentals of Fibre Formation: The Science of Fibre Spinning and Drawing*, John Wiley and Sons, New York, 1976.
70. Gupta V.B. and Bhuvanesh Y.C., 'Basic principles of fluid flow during fibre spinning' in *Manufactured Fibre Technology*, editors Gupta V.B. and Kothari V.K., Chapman and Hall, London, 1997, pp. 31–66.
71. Brandao J., Spieth E. and Lekakou C., 'Extrusion of polypropylene. Part 1: Melt rheology', *Polym Eng Sci*, 1996, **36**, 49–55.
72. Han C.D., Lamonte R.R. and Shah Y.T., 'Studies on melt spinning. III. Flow instabilities in melt spinning: melt fracture and draw resonance', *J Appl Polym Sci*, 1972, **16**, 3307–3323.
73. Sheehan W.C. and Cole T.B., 'Production of super-tenacity polypropylene filaments', *J Appl Polym Sci*, 1964, **8**, 2359–2388.
74. Piccardo S., Saiu M., Brucato V. and Titomanlio G., 'Crystallisation of polymer melts under fast cooling. II. High-purity iPP', *J Appl Polym Sci*, 1992, **46**, 625–634.
75. Choi C.-H. and White J.L., 'Comparative study of structure development in melt spinning polyolefin fibers', *Int Polym Processing*, 1998, **13**, 78–87.
76. Yang R.D., Mather R.R. and Fotheringham A.F., 'Relationship between structure and spinning processing of as-spun PP fibres', *Int Polym Processing*, 1999, **14**, 60–68.
77. Spruiell J.E. and White J.L., 'Structure development during polymer processing. Melt spinning of polyethylene and polypropylene', *Polym Eng Sci*, 1975, **15**, 660–667.
78. Nadella H.P., Henson H.M., Spruiell J.E. and White J.L., 'Melt spinning of isotactic polypropylene: structure development and relationship to mechanical properties', *J Appl Polym Sci*, 1977, **21**, 3003–3022.
79. Fan Q., Xu D., Zhao D. and Qian R., 'Effects of molecular weight distribution on the melt spinning of polypropylene fibers', *J Polym Eng*, 1985, **5**, 95–123.
80. Broda J. and Wlochowicz A., 'Influence of pigments on supermolecular structure of polypropylene fibres', *European Polym J*, 2000, **36**, 1283–1297.
81. Kitao T., Ohya S., Firukawa J. and Yamashita S., 'Orientation of polymer molecules during melt spinning. II. Orientation of crystals in as-spun polyolefin fibers', *J Polym Sci, Polym Phys*, 1973, **11**, 1091–1109.
82. Fung P.Y.F., Orlando E. and Carr S.H., 'Development of stress crystallised morphology during melt spinning of polypropylene fibers', *Polym Eng Sci*, 1973, **13**, 295–299.
83. Sheehan W.C. and Wellman R.E., 'Relationship between molecular orientation and draw ratio of polypropylene monofilaments', *J Appl Polym Sci*, 1965, **9**, 3597–3603.
84. de Vries H., 'The relationship between birefringence and draw ratio of man-made fibers', *J Polym Sci*, 1959, **34**, 761–778.
85. Nadella H.P., Spruiell J.E. and White J.L., 'Drawing and annealing of polypropylene fibers: structural changes and mechanical properties', *J Appl Polym Sci*, 1978, **22**, 3121–3133.
86. El Maaty M.A.I., Bassett D.C., Olley R.H., Dobb M.G., Tomka J.G. and Wang I.-C., 'On the formation of defects in drawn polypropylene fibres', *Polymer*, 1996, **37**, 213–218.

87. Samuels R.J., 'Quantitative characterization of deformation in polypropylene fibers', *J Polym Sci, A-2*, 1968, **6**, 2021–2041.
88. Qin Y., Miller M.M., Brydon D.L., Cowie J.M.G., Mather R.R. and Wardman R.H., 'Fiber drawing from blends of polypropylene and liquid-crystalline polymers', in *ACS Liquid-crystalline Polymer Systems – Technological Advances*, editors Isayev A.I., Kyu T. and Cheng S.Z.D., ACS Symposium Series 632, American Chemical Society, Washington D C, 1996, pp. 98–109.
89. Yang R.D., Mather R.R. and Fotheringham A.F., 'The application of factorial experimental design to the processing of polypropylene fibres', *J Mater Sci*, 2001, **36**, 3097–3101.
90. Amornsakchai T., Olley R.H., Bassett D.C., Al-Hussein M.O.M., Unwin A.P. and Ward I.M., 'On the influence of initial morphology on the internal structure of highly drawn polyethylene', *Polymer*, 2000, **41**, 8291–8298.
91. Amornsakchai T., Bassett D.C., Olley R.H., Unwin A.P. and Ward I.M., 'Remnant morphologies in highly-drawn polyethylene after annealing', *Polymer*, 2001, **42**, 4117–4126.
92. El-Maaty M.I., Olley R.H. and Bassett D.C., 'On the internal morphologies of high modulus polyethylene and polypropylene fibres', *J Mater Sci*, 1999, **34**, 1975–1989.
93. Horrocks A.R. and D'Souza J.A., 'Degradation of polymers in geomembranes and geotextiles' in *Handbook of Polymer Degradation*, editors Hamid H.S., Amin M.B. and Maadheh A.G., Marcel Dekker, New York, 1992, pp. 433–506.
94. Horrocks A.R., Mwila J., Miraftab M., Liu M. and Chohan S.S., 'The influence of carbon black on properties of orientated polypropylene. 2. Thermal and photodegradation', *Polym Degrad Stab*, 1999, **65**, 25–36.
95. Mukhopadhyay S.K. and Partridge J.F., 'Automotive Textiles', *Text. Prog.*, 1999, **29**(1/2), 1–128.
96. Fung W. and Hardcastle M., *Textiles in Automotive Engineering*, Woodhead Publishing Limited, Cambridge, 2001.
97. Rigby A.J., Anand S.C. and Horrocks A.R., 'Textile materials for medical and healthcare applications', *J Text Inst Part 3*, 1997, **88**, 83–93.
98. Horrocks A.R., Richards A.F. and Ghosh S., 'Inclusion of waste polymer on the performance of oriented polypropylene geotextile tapes'. Part I: Effect on textile properties', *Text Res J*, 1995, **65**, 601–606.
99. Horrocks A.R. and Ghosh S., 'Inclusion of waste polymer on the performance of oriented polypropylene geotextile tapes'. Part II: Effect of tape structure and morphology', *Text Res J*, 1998, **68**, 473–478.
100. Christiani C., Klason C. and Shishoo R., 'The effect of reprocessing of polypropylene on fiber spinning', *J Appl Polym Sci*, 1999, **73**, 1859–1867.
101. Allan G., Yang R., Fotheringham A. and Mather R., 'Neural modelling of polypropylene fibre processing: predicting the structure and properties and identifying the control parameters for specified fibres', *J Mater Sci*, 2001, **36**, 3113–3118.
102. Logothetis N. and Wynn H.P., *Quality Through Design*, Clarendon Press, Oxford, 1989.
103. Ross P.J., *Taguchi Techniques for Quality Engineering*, McGraw Hill, New York, 1988.
104. Fisher R.A., *Design of Experiments*, Oliver and Boyd, Edinburgh, 1966.
105. Shin Y.-W., Uozumi T., Terano M. and Nitta K., 'Synthesis and characterization of ethylene-propylene random copolymers with isotactic propylene sequence', *Polymer*, 2001, **42**, 9611–9615.

106. Kumar S., Doshi H., Srinivasarao M., Park J.O. and Schiraldi D.A., 'Fibers from polypropylene/nano carbon fiber composites', *Polymer*, 2002, **43**, 1701–1703.
107. Qin Y., Brydon D.L. and Mather R.R., 'Production of thermally stable polypropylene fibers', *J Appl Polym Sci*, 1996, **61**, 1287–1292.
108. Lakes R.S., 'Foam structures with a negative Poisson's ratio', *Science*, 1987, **235**, 1038–1040.
109. Pickles A.P., Alderson K.L. and Evans K.E., 'The effects of powder morphology on the processing of auxetic polypropylene', *Polym Eng Sci*, 1996, **36**, 636–642.
110. Alderson K.L. and Evans K.E., 'The fabrication of microporous polyethylene having a negative Poisson's ratio', *Polymer*, 1992, **33**, 4435–4438.
111. Alderson K.L., Alderson A., Smart G., Simkins V.R. and Davies P.J., 'Auxetic polypropylene fibres. Part 1. Manufacture and characterisation', *Plastics, Rubbers Composites*, 2002, **31**, 344–349.
112. Evans K.E., 'Tailoring the negative Poisson ratio', *Chem Ind*, 1990, 654–657.
113. Tsai P.P., Wadsworth L.C. and Roth J.R., 'Surface modification of fabrics using a one-atmosphere glow discharge plasma to improve fabric wettability', *Text Res J*, 1997, **67**, 359–369.
114. Radu C.-D., Kiekens P. and Verschuren J., 'Surface modification of textiles by plasma treatments' in *Surface Characteristics of Fibers and Textiles*, editors Pastore C.M. and Kiekens P., Surfactant Science Series, Vol. 94, Marcel Dekker, New York, pp. 203–218.
115. Occhiello E., Morra M., Morini G., Garbassi F. and Humphrey P., 'Oxygen-plasma-treated polypropylene interfaces with air, water, and epoxy resins', *J Appl Polym Sci*, 1991, **42**, 551–559.
116. Gross Th., Lippitz A., Unger W.E.S., Friedrich J.F. and Woll Ch., 'Valence band region XPS, AFM and NEXAFS surface analysis of low pressure d.c. oxygen plasma treated polypropylene', *Polymer*, 1994, **35**, 5590–5594.
117. Sigurdsson S. and Shishoo R., 'Surface properties of polymers treated with tetrafluoromethane plasma', *J Appl Polym Sci*, 1997, **66**, 1591–1601.
118. Wei Q.F., Mather R.R., Fotheringham A.F. and Yang R.D., 'Observation of wetting behavior of polypropylene microfibers by environmental scanning electron microscope', *J Aerosol Sci*, 2002, **33**, 1589–1593.
119. McCord M.G., Hwang Y.J., Hauser P.J., Qiu Y., Cuomo J.J., Hankins O.E. and Bourham M.A., 'Modifying nylon and polypropylene fabrics with atmospheric pressure plasmas', *Text Res J*, 2002, **72**, 491–498.
120. Van de Velde K., 'Recycling of polypropylene', *Chem Fibers Int*, 2002, **52**, 59–61.