3

Polyester fibres

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3.1   Introduction

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

This chapter cannot hope, in the space available, to cover every aspect of such a large and complex topic. Several excellent publications are recommended at the end of the chapter for general reading and for those who would wish to learn more. The author has taken an historical approach, dealing with the history of the discovery of polyesters and their development as fibrous materials and considering each polymer and its physical properties in chronological order. The chemistries of the production processes for individual polyesters are dealt with in turn. The technology of fibre spinning and subsequent treatments such as dyeing is described

in general terms in a separate section. Then follows a discussion of how the chemical properties of the various polyesters affect fibre properties and how these enable each fibre to fit into the appropriate market. Finally, an overview of world fibre demand and the broad economic impact of various polyester fibres and their future is included.

3.2   Brief history of polyesters

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

It was not until the early days of World War II that J. Rex Whinfield and J. T. Dickson, working at the Calico Printers Association Laboratories in England, synthesised high molecular weight PET from terephthalic acid and its purified dimethyl ester by reaction with ethylene glycol.[3] They showed that the new polymer (shorthand name 2GT) was both melt-stable and colourless and could be melt-spun into fibres having very desirable textile properties. During those difficult days of World War II, circumstances were completely against commercialising a new textile fibre. This development had to wait until peace came in 1945. It was agreed that Imperial Chemical Industries (ICI) in Britain would develop the PET fibre under the trade name *Terylene®,* while in the USA the DuPont Corporation introduced the fibre as *Dacron®*. The two brands of fibre became commercial products in the early 1950s on both sides of the Atlantic and were soon successful. One reason may have been a fortuitous trend in ladies' fashions around that time

for accordion-pleated skirts. The excellent pleat-retaining and wash-wear proper-
ties of PET staple fibre in blends with wool and cotton were swiftly recognised and
exploited. Other manufacturers such as Farbewerke Hoechst in West Germany and
Société Rhodiaceta in France took licenses and commercially produced their own
PET fibre versions, under their own brand names (*Trevira*® and *Tergal*®). A
review of the early development of PET fibres has been published by Brown and
Reinhart.[4]

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

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

rate of crystallisation from the melt, an important property in a moulding resin since it allows for short mould-cycle times.

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

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

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

The polymer with ethylene glycol (PEN) is used increasingly in high-performance polyester films and for high softening-point blow-moulded bottles and containers. It was commercialised in 2002 by Honeywell Performance Fibers

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

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

ultimately rather disappointing, as will be seen later. All the polyhydroxyacids are hydrolytically unstable and degrade on exposure to the outdoors or in living systems, but the actual rate of degradation is very much governed by the polymer structure, the ratio of hydrophobic to hydrophilic polymer segments, and the presence of lipases and similar enzymes.

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

3.3.1   Terephthalic acid

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

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

3.3.2   Dimethyl terephthalate

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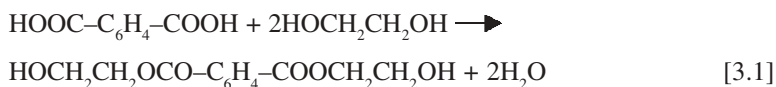
3.3.3   Ethylene glycol

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

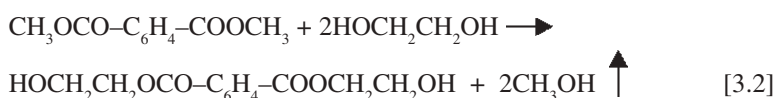### 3.3.4   Bishydroxyethyl terephthalate

Bishydroxyethyl terephthalate (BHET) is not a significant article of commerce, yet it is made and consumed on a very large scale as an intermediate in the production of PET. The first stage of any PET polymerisation process can be considered to be the formation of BHET, usually as a complex mixture with various PET oligomers. The second stage of the polymerisation reaction forms PET-high polymer from

this BHET–oligomer mixture. (The actual amount of free BHET in the reaction mixture depends greatly on the ratio of ethylene glycol to TA or DMT – for economic reasons this tends to be kept as close to 1 : 1 as possible, thus minimising the level of free BHET.) In a direct esterification process, it is simplest to visualise the process as formally a reaction of PTA with excess EG at elevated temperatures to form BHET, by splitting out water, even though the actual levels of free BHET are low.

$$HOOC–C_6H_4–COOH + 2HOCH_2CH_2OH \longrightarrow$$

$$HOCH_2CH_2OCO–C_6H_4–COOCH_2CH_2OH + 2H_2O \qquad [3.1]$$

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

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

$$CH_3OCO–C_6H_4–COOCH_3 + 2HOCH_2CH_2OH \longrightarrow$$

$$HOCH_2CH_2OCO–C_6H_4–COOCH_2CH_2OH + 2CH_3OH \uparrow \qquad [3.2]$$

3.3.5   The melt polymerisation stage

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

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

Quite recently (1998) AKZO-Nobel have developed new titanium catalysts based on TiO_2–SiO_2 compositions made by a technique previously well known in the synthesis of specialised *ceramic* metal oxide compositions. This is the controlled co-hydrolysis in an aqueous alcoholic solution of a mixture of titanium (and zirconium) alkoxides, either alone or with lower alkyl silicate esters, to give a mixed inorganic network molecule.[40] The alcohol is a monohydric lower alcohol

containing one to six carbon atoms. Normally the TiO_2 prepared for use as a white pigment or delustrant (such as that used in PET apparel fibres) is made by the controlled hydrolysis of acidic derivatives such as titanium tetrachloride, $TiCl_4$. Such materials are not active catalysts, but the oxide networks made as described in the AKZO patents can be very active as polymerisation catalysts. Either TiO_2 alone, or as a mixture with SiO_2 or TiO_2/ZrO_2 compositions can all be used. Not every formulation is active: only certain ranges rich in Ti or Zr are good catalysts. The preferred compositions are effective PET polymerisation catalysts at low levels (10–40 ppm based upon the weight of BHET) and do not give the yellow discoloration in the presence of ethylene glycol and hydroxyethyl chain ends that plain titanium alkoxides, such as titanium tetraisopropoxide, do. This invention constitutes something of a breakthrough in polymerisation catalyst chemistry and no doubt more will be heard about it in the near future.[41,42]

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

3.3.6   Solid phase polymerisation

SPP is used when a higher molecular weight is needed than is simply practicable by melt polymerisation. The polymer chips are firstly intensely dried and annealed at a gradually increasing temperature up to the point of maximum crystallisation rate (which is around 160–170 °C for PET) to encourage a high level of polymer chip crystallinity. This process has to be done with some care as the water-quenched polymer chips are almost wholly amorphous and it is most important not to allow them to fuse or sinter together during the annealing step. The reason for this is that once the crystallisation process starts, it is quite exothermic and the chips may locally fuse as a result. The process of SPP is well explained in the
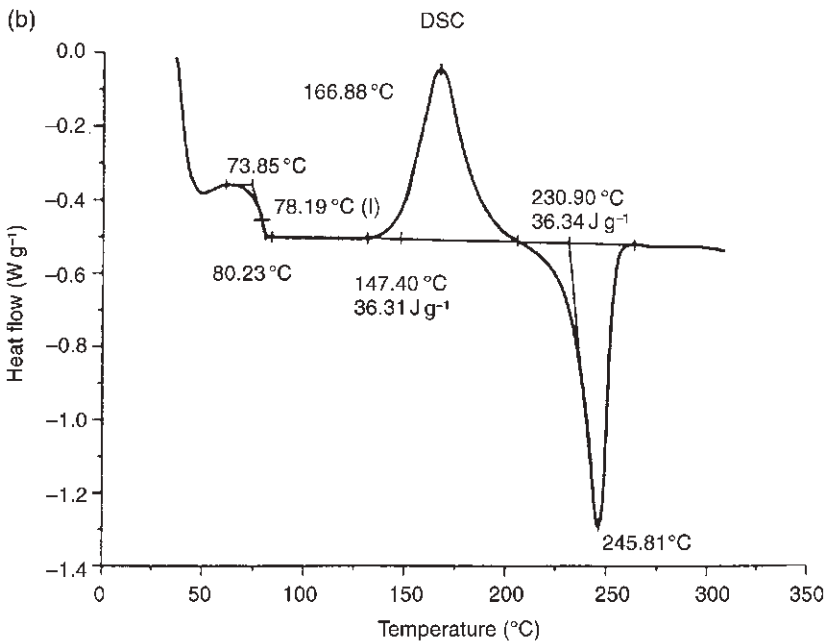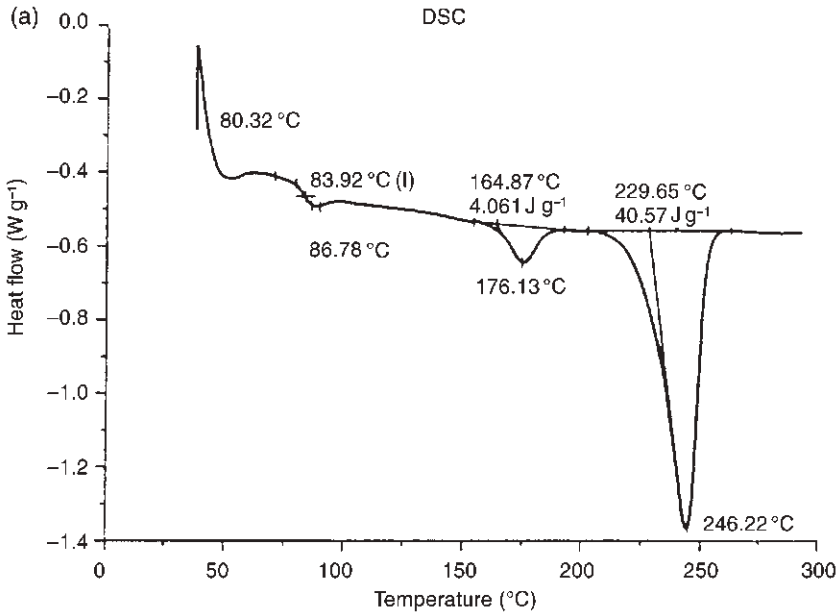
3.1 (a) A typical DSC trace for commercial PET polymer flake;
(b) DSC of the same material after quenching from the melt.
From *Preparative Methods in Polymer Chemistry*, Sorensen *et al.*
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textbook article by Sorensen, Sweeney and Campbell from which the differential scanning calorimetry (DSC) diagrams shown in Fig. 3.1 are taken.[46]

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

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

manufacturers as inferior to nylon for both durability and fibre resilience). When melt-spinning high-tenacity fibres, it may also be necessary to use a SPP polymer with IV > 0.8.

3.3.7   Side reactions and problems with PET melt polymerisation

Nothing in this world is perfect, and melt polymerisation of PET has its share of problems. We have mentioned the fact that chain-breaking reactions occur in addition to chain-forming ones. The degradation of PET is largely a thermal cracking process by which the PET chains break by eliminating a free carboxyl unit, thus leaving a vinyl ester end. The mechanism is generally thought to result from a McLafferty rearrangement, involving a six-membered ring transition state.[50] The vinyl ester end can react with other chain ends to evolve vinyl alcohol in its tautomeric form as acetaldehyde.[36] An acid anhydride link can be formed, at least as a transient species, and acetaldehyde displaced, or the vinyl ester end may react with a hydroxyl chain end to re-form the ester link. Acetaldehyde is always produced during the thermal degradation of PET at over 250 °C. Since melt spinning can take place at up to 300 °C, it will be realised that controlling degradation rates is of great importance in running a robust spinning process. A schematic of the degradation process is shown below:
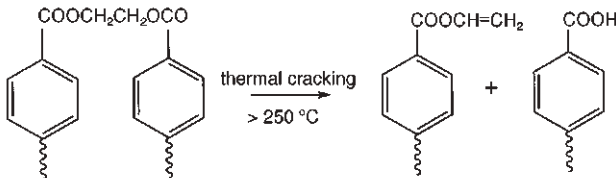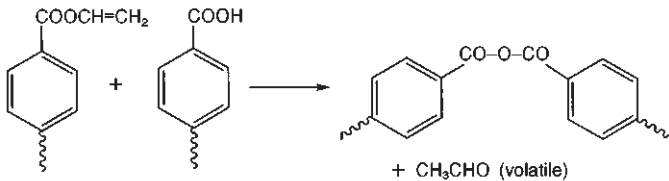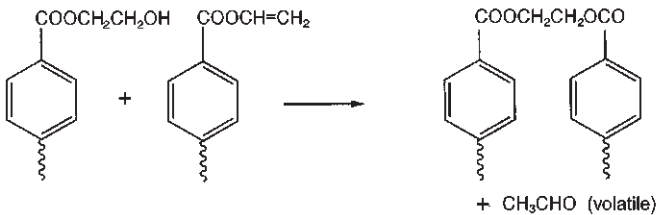
Vinyl ester ends cause many other problems, too. They act as cross-linkers and gelling agents. They polymerise, and the polymers thermally degrade to give yellow or brown polyenes that discolour the final polymer. It is because vinyl ends form intensely yellow-coloured complexes with metals such as titanium and tetravalent tin that they preclude efficient polymerisation catalysts like titanium tetra-alkoxides or dibutyltin oxide being used in PET polymerisation (see Section 3.3.5).

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

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

where m is the molar percentage concentration of DEG.

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

3.3.8   Continuous polymerisation

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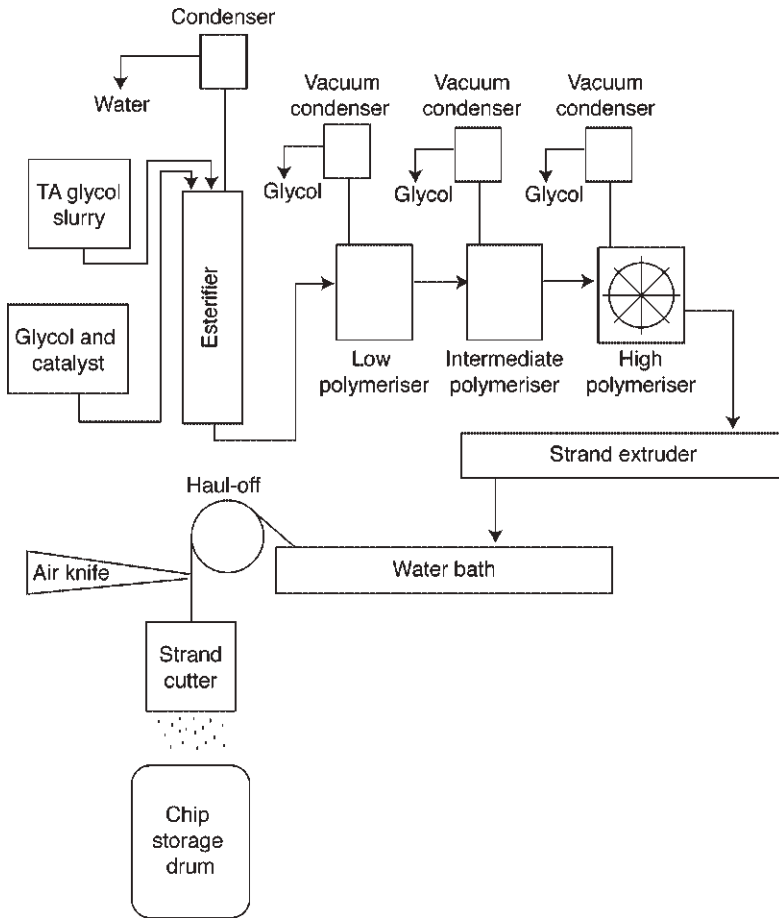
3.2 Schematic of a typical PET continuous polymerisation unit.

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

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

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

3.3.9   Physical properties of PET

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

3.3.9.1   *Intrinsic viscosity and molecular weight*

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

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

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

Table 3.1 Physical parameters of PET

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

Table 3.2   Mark–Houwink constants for PET

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

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

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

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

3.4   Cyclohexanedimethanol polyesters

3.4.1   Introduction

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

3.4.2   Cyclohexanedimethanol and CHDMT polymers

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

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

3.4.3   Physical properties of CHDMT

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

Table 3.3 Crystal parameters for CHDMT

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

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

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

3.4.4   CHDMT: fibre properties and stability

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

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

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

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

3.4.5   CHDMT as a textile fibre

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

property. As mentioned earlier, while CHDMT polymer is largely manufactured nowadays as a moulding resin, there remains a demand for fibrefill and carpet yarn. How this demand will survive competition with newer fibres such as PTT in the same markets remains to be seen.

3.5   Poly(butylene terephthalate) (PBT)

3.5.1   Introduction

A more accurate name for this polymer would be *poly(tetramethylene terephthalate)*, but 'PBT' is a well-established acronym in the engineering moulding resins business. It is another of the fibre-forming polyesters that dates back to Whinfield and Dickson's time in 1941. Its history has been one of ups and downs: originally developed as a textile fibre, it later became much more important as a highly crystallisable injection moulding polymer and an engineering resin. Nevertheless it maintains a fibre presence in the market, chiefly as bulked continuous filament (BCF) carpet fibre, where its resilience is important.[68]
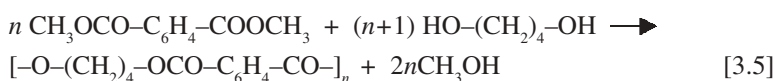
3.5.2   Butane-1,4-diol

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

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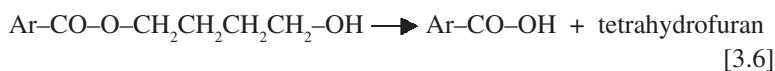
3.5.3   Manufacture of PBT

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

PBT Polymerisation:

$$n\ CH_3OCO–C_6H_4–COOCH_3\ +\ (n+1)\ HO–(CH_2)_4–OH \longrightarrow$$
$$[–O–(CH_2)_4–OCO–C_6H_4–CO–]_n\ +\ 2nCH_3OH \qquad [3.5]$$

Formation of THF from a 4-hydroxybutyl ester end:

$$Ar–CO–O–CH_2CH_2CH_2CH_2–OH \longrightarrow Ar–CO–OH\ +\ tetrahydrofuran$$
$$[3.6]$$

3.5.4   Physical properties of PBT

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

3.5.5   Polymer molecular weight

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

Table 3.4 Crystal parameters for PBT

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

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

Table 3.5 Mark–Houwink constants for PBT

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

3.5.6   Melt-spinning and drawing PBT fibres

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

3.6   Poly(trimethylene terephthalate) (PTT or PPT)

3.6.1   Introduction

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

There seems to be a little confusion on an acronym for this polyester. Shell prefers to use the term PTT (poly(trimethylene terephthalate)) but DuPont and

some earlier trade literature sources call it PPT (poly(propylene terephthalate)). The latter is, strictly speaking, a misnomer, since the term 'propylene glycol' is conventionally applied to 1,2-propanediol. We shall use the Shell nomenclature henceforth and call the polymer PTT, to avoid any possible ambiguity. Furthermore, this acronym emphasises the essential *three-carbon* glycol unit.

3.6.2   Synthesis of PDO and the manufacture of PTT

3.6.2.1   PDO synthesis

Introduction

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

The Degussa process

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

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

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

The Shell hydroformylation process

The more recently introduced Shell process uses the hydroformylation reaction (carbon monoxide plus hydrogen) of ethylene oxide to give 3-hydroxypropanal, using synthesis gas and a transition metal catalyst. The aldehyde is then reduced to propane-1,3-diol. One of the first patented processes was by Beavers (Eastman Kodak) who used a rhodium or ruthenium catalyst.[93] Shell improved upon the

earlier work by using a cobalt catalyst and there has been much patent activity lately concerned with improved hydroformylation catalysts and reaction conditions.[94–97] The hydrogenation of 3-hydroxy-propanal to PDO has also been improved with better catalysts and reaction conditions. Haas and co-workers[98] use a platinum or ruthenium catalyst, while Shell workers disclose nickel–molybdenum.[99] Further improvements result from purifying the crude hydroxy-aldehyde in aqueous solution over active carbon or silica before the hydrogenation step.[100,101]

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

The modified Shell process

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

The DuPont fermentation process

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

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

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

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

3.6.2.2   The PTT polymerisation process

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

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

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

3.6.3   Physical properties of PTT

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

3.6.4   Polymer molecular weight

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

Table 3.6 Crystal parameters for PTT

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

Table 3.7 Mark–Houwink constants for PTT

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

3.6.5   PTT resilience

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

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

3.6.6   Melt-spinning and processing PTT fibres

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

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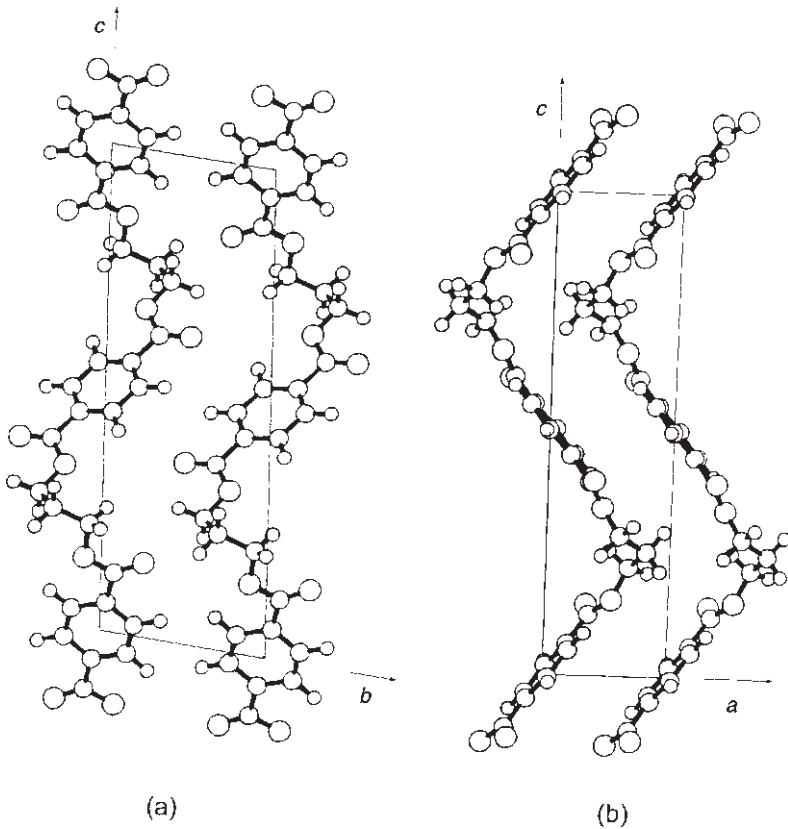
3.3 (a and b) X-ray study of a PTT polymer crystal structure. Reprinted from *Polymer*, **20**, Desborough I. J., Hall I. H. and Neisser J. Z., '3GT', p. 545, 1979, with permission from Elsevier.

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

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

3.7   Biodegradable polyester fibres

3.7.1   Introduction

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

Table 3.8 Biodegradable polyester properties (homopolymers)

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

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

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

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

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

3.7.2   Polyglycolide (PGA)

The polyester from self-condensation of hydroxyacetic acid is usually called polyglycolide after its dimeric lactone, glycolide. Polymerisation is usually done by a ring-opening polymerisation (ROP) of the lactone,[140] often with a Sn(II) salt

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

3.7.3   Polylactide (PLA)

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

3.7.4   Polycaprolactone (PCL)

Caprolactone is the seven-membered ring lactone of ε-hydroxycaproic acid and can be made by a Baeyer–Villiger oxidation of cyclohexanone. In the presence of a stannous octoate catalyst it undergoes ROP to the homopolymer polycaprolactone. This melts at 59–64 °C and has a very low T_g (well below 0 °C). It also has a low modulus but forms strong elastic fibres that are biocompatible. Because it is much more hydrophobic than either lactide or glycolide polymers, it has a long

degradation time, of the order of 2–3 years. It is often combined with other monomers to reduce the degradation time. A block copolymer of caprolactone and glycolide is marketed by Ethicon[145,146] under the brand name *Monacryl®*.

3.7.5   Polydioxanone (PDO)

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

3.7.6   Polytrimethylene carbonate (TMC)

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

3.7.7   Sterilisation and packaging

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

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

3.7.8   Mechanism of degradation

The actual breakdown of the polyesters *in vivo* is quite complex, although it is

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

3.7.9   Disposable fibres

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

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

Biopol is a crystalline thermoplastic with a melting point in the range 170–190 °C. Its structure is analogous to that of isotactic polypropylene, since all the side groups project on the same side of every chain. Like a peptide, the chain has a helical conformation, but unlike peptides, this is due to non-bonded interactions between the carbonyls and the methyl groups. There are no hydrogen bonds, and this helix formation is unique. One practical problem with *Biopol* is that it has a pronounced tendency to embrittle by secondary interlamellar crystallisation. So far, *Biopol* can hardly be called a commercial success, but it has been very thoroughly investigated. A review[163] of PHB polymer and copolymer production by Poirier *et al*. was published in 1995. Again, the author has a personal interest, for while at ICI Fibres in 1977, he was asked to try to melt-spin PHB fibres on a small scale from some of the very earliest samples of ICI's polymer. This was not successful owing to the very high molecular weight of the material. PHB has not been widely investigated as a fibre-forming polymer, although there is talk of biodegradable fishing net monofils. It is less suitable for sutures, for example, since it does not break down readily by simple hydrolysis *in vivo*. It *does* break down both aerobically and anaerobically when

exposed to certain enzymes (lipases), as when composted or exposed to marine environments, so it is likely to be of greater use as a disposable, environmentally friendly, thermoplastic polymer. A recent patent[164] describes the use of copolymers of 3-hydroxy and 4-hydroxalkanoates in medical devices such as sutures, bone screws, etc. These materials have been described[165] by Hori *et al.* and can be produced by a biosynthetic route[166] using recombinant bacteria such as *Escherichia coli.*

3.8   Melt-spinning polyester fibres and associated processing

3.8.1   Introduction

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

3.8.2   Filament yarn melt-spinning

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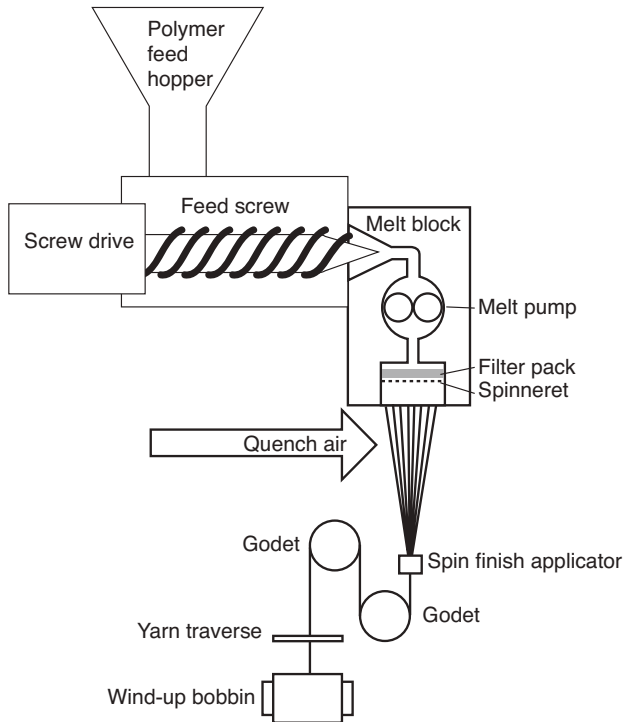
3.4 Schematic diagram of typical F/Y melt spinner.

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

    The molten threadlines emerge from the spinneret and solidify as they fall. The cooling process is accelerated by a controlled flow of non-turbulent quenching air. Passing next around a take-off roll or 'godet', the bundle of filaments are wound up on a yarn package or sent directly to other processing steps. One very important parameter is the thickness of the solid as-spun filament, and this is measured by the *denier count*, which is *the weight in grams of 9 km* of yarn. The official metric

system uses the *decitex count*, which is the weight of *10 km* of yarn (hence decitex is 1.11 × denier); but it seems that the textile industry in much of the world (particularly the USA) resolutely retains the denier count, a measurement dating back to the Lyons silk industry in 18th century France.

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

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

3.8.3   Filament yarn drawing

Although molecular chain orientation has been partly introduced by the draw-down, the main increase in order is usually brought about by a separate *drawing* process.[172] Fibre-forming polymers of adequate molecular weight all show the phenomenon of *cold drawing* on stretching. The undrawn fibre (or a strip of film) will neck down and elongate, and crystallisation will often occur, evident from a change in lustre in the drawn filament due to its optical anisotropy. PET fibres in
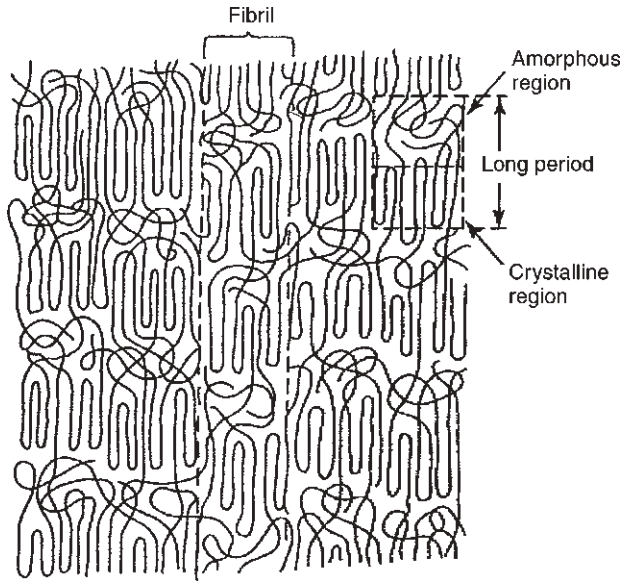
3.5 Morphology of PET fibre showing various features. Reprinted from Mark, 'Polyester fibres' in *Encyclopedia of Polymer Science and Technology* ©2003 John Wiley & Sons, reprinted by permission of John Wiley & Sons Inc.

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

shrinkage, the yarn has to be *heat-set* by passing it over a long hotplate at about 130–140 °C, which is well above the effective T_g (125 °C) of the drawn, oriented and crystallised yarn. The heat setting stage encourages the final development of maximum molecular order and crystallinity; it can be considered as a continuous annealing step. A diagram of the morphology of an oriented, partly crystalline PET fibre is shown in Fig. 3.5.

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

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

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

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

3.8.4   Filament yarn texturising

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

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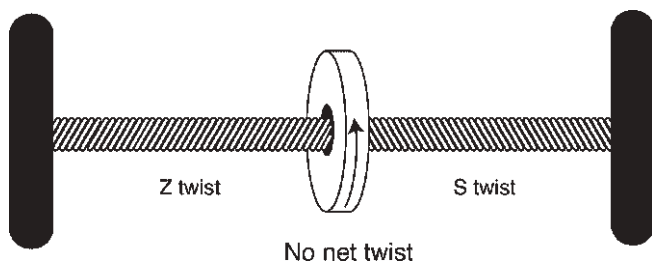
3.6 Principle of false twist bulking.

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

### 3.8.4.1   The principles of false twist bulking

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

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

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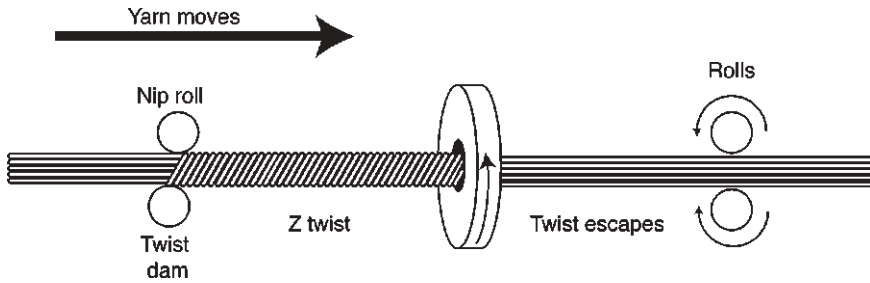
3.7 False twist bulking.
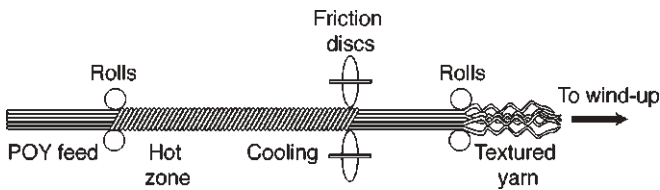
3.8 Friction false twist texturing.

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

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

3.8.4.2   Pin twisters

There are two methods of applying false twist. The older device is the pin twister and the later one the friction twister. The pin twister is a small stainless steel tube with a tiny synthetic sapphire pin (made from fused aluminium oxide) fixed transversely across the bore of the tube. The yarn is looped once around the sapphire pin. The tube is rotated along its axis and as it rotates, it applies a positive twist to the yarn. The level of twist needed is high (approximately 1000 twists m^{-1}) so that if the yarn is running at today's productive speeds, which can be over 1000 m min^{-1}, the rotation speed of the twister tube would have to be extremely

high, more than 1 000 000 r min⁻¹. This would produce truly formidable mechani-
cal problems, and twister pins were made as tiny as possible and driven by friction
wheels or belts or held suspended against magnetic drive wheels, all to eliminate
bearings and their problems. It was generally reckoned that 800 000 r min⁻¹ was
the highest practicable speed for a pin twister drive. Pin texturing gives a high-
quality bulked yarn because the twist drive is 100% positive, and there is no chance
of twist escaping, leaving un-bulked regions ('shiners') in the yarn, but for the
reasons outlined, the overall yarn process speed is much lower than for the friction
twisting bulking process. A typical speed range would be 100–300 m min⁻¹.

3.8.4.3   *Friction twisters*

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

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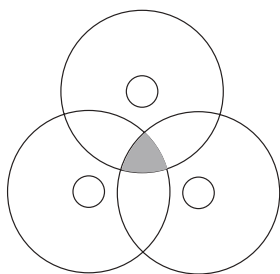
3.9 Arrangement of friction discs.

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

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

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

3.8.4.4   Modern draw texturing machines

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

3.8.4.5   Other F/Y bulking methods

Many other methods have been used to make bulked filament yarns, some very ingenious. There is not the space to cover them in detail, but they include *edge*

crimping, where the yarn is passed over a hot knife-edge which induces an asymmetric shrinkage in the yarn, which in turn develops bulk on relaxing. There are bulking techniques that depend on bicomponent fibres and these will be discussed later in connection with multi-component fibres. Air-jet and steam-jet bulking are similar processes where a feed yarn is heated in a turbulent jet of hot air or steam, which tangles the filaments and blows them into loops, then heat sets the tangles, so that the yarn bulks up after relaxing. Air-jet textured yarns or ATY can be used in a variety of fabric weights from very lightweight apparel up to heavy duty materials for soft luggage fabrics. The feed stock yarn, very often POY, is overfed into a special turbulent flow air-jet: and water is usually sprayed on immediately before the jet to lubricate the yarn. Detailed descriptions of the ATY process can be obtained from the Udo Schweizer website.[176]

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

3.8.5   Industrial filament yarns

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

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

3.8.6   Staple fibres

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

3.9   Modification of polyester fibres

3.9.1   Introduction

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

3.9.2   Spin finishes

All fibres need to be treated with surface finishes that alter the frictional characteristic of the yarn surface. Without these spin finishes, the various processing steps such as drawing, texturising and textile processing would be impossible, because so many of them rely on specific frictional properties on the fibre (for example, friction bush texturising). Spin finishes are often water emulsions of various surface-active agents, either non-ionic or anionic, with various lubricant mineral
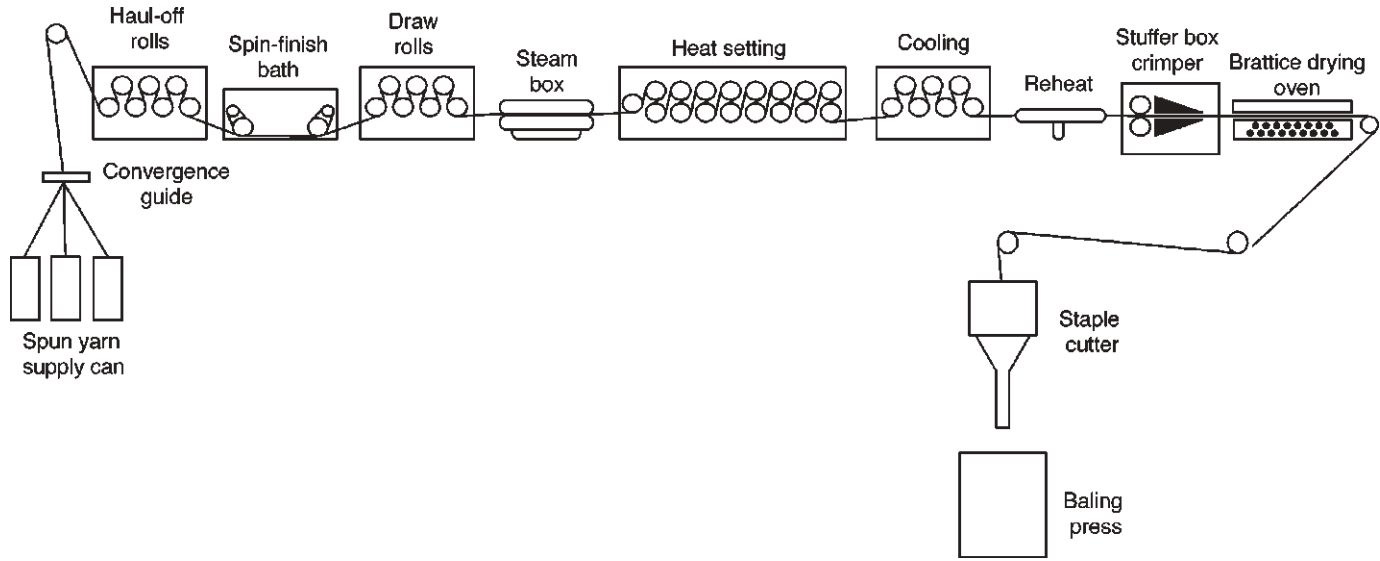
3.10 Diagram of staple draw frame, showing only a single-stage drawing. Two of even three drawing stages are frequently used.

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

3.9.3   Tyre cord treatments

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

To maintain the high strength engineered into the tyre cord, it is essential that the IV drop should be minimised. It was found[188] that the rate of in-rubber degradation

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

3.9.4   Low-pill staple polyester

PET staple blends with wool and cotton were highly successful from the very first introduction of PET in the 1950s. However, before long consumers noted an irritating problem, particularly with wool/PET blends: the formation of small fuzzy balls (called 'pills') on the surface of the woven fabric, which clung remarkably tena-ciously. The phenomenon became known as 'pilling'. It is, in fact, common to all staple fibres (whether they contain PET or not) and is made worse if the level of yarn twist is low, so that the fabric has a rather loose structure. Usually, for pure woollen fabrics and knits, the pills rub off harmlessly, because wool is a relatively weak fibre. PET is a strong fibre (PET staple fibre tenacity is typically ≈ 3.5 g dtex^{-1}) and pills do not rub off: they cling, with deleterious effects to fabric aesthetics. In order to reduce pilling, the IV of the polyester was reduced to make weaker fibres that do not form pills, simply because any pills formed disappear during wear. A polymer IV = 0.42 was selected as the best compromise for a low-pill PET staple fibre, but it caused many practical problems at melt-spinning. The melt viscosity was so low, and the molten threadline so fluid that the process became difficult to run unless controlled very closely. To give a trouble-free and robust melt-spinning process, a way had to be found to raise the effective melt viscosity of the polymer while maintaining the low IV and relatively weak fibres. One method adopted was

to introduce *branching points* into the polymer chain by adding a multifunctional component (either a polybasic acid or a polyhydric alcohol) so as to produce a star-branched polymer. Such polymers are known to have higher melt viscosities for the same (nominal) polymer IV. The branching agent was added at a low level (*ca* 1 mole%) and pentaerythritol (also dipentaerythritol and trimethylolpropane) was the polyfunctional additive of choice.[1] Too much additive leads to gel formation by forming cross-linked polymer networks, but this is not a problem at low levels as used here.

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

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

3.9.5   Non-circular cross-section (NCCS) fibres

Synthetic fibres such as PET and nylon are normally round in cross-section, yet no natural fibre has a perfectly circular cross-section! Wool is scaly and irregular, cotton is 'dog-bone' shaped, and silk is roughly triangular. Consequently, in the early 1970s people began to study the effect of NCCS fibres on yarn and fabric aesthetics, appearance and 'feel'. Fortunately, melt spinning lends itself quite well to production of NCCS fibres by varying the shape of the spinneret orifices, provided the melt viscosity is high enough that surface tension effects do not cause the filament to resume a circular shape. Since the NCCS holes had to be tiny (approximately 0.4 mm overall), machining a multiplicity of them and keeping them all to uniform size and shape is no small engineering problem, particularly in

the very hard metal alloys used for spinneret plates. Spark-erosion machining was one fabrication method used. Nowadays, this problem has been solved by laser-etching. Sometimes it is possible to arrange an array of tiny circular holes in a matrix pattern to make up the final shape – on extrusion, the individual molten filaments fuse into one filament of the desired cross-sectional shape.

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

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

3.9.6   Antistatic and antisoiling fibres

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

Trilobal   Octalobal   Deep-grooved
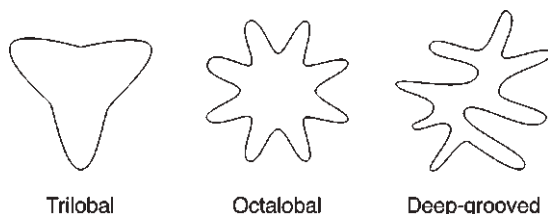
3.11 Non-circular cross-section fibres.

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

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

$$HO–CH_2CH_2O[CH_2CH_2O]_n–OH \hspace{3cm} [3.9]$$

PEG polymer can be made with molecular weights of anything from a few hundred daltons up to several million. Early workers made block copolymers of PET with PEG of molecular weights *ca* 500–2000 Da, and it was possible to permanently incorporate enough PEG without drastically reducing PET properties, thus greatly improving the fibre moisture uptake but at the expense of a severe reduction in the light stability of dyed fibres.[198] Other processes used a PET/PEG melt blend[199] which mitigated the dye light stability problem and also acted as a soil hiding additive, since the PEG near the fibre surface leached out with aqueous treatments (such as dyeing and laundering), leaving a network of fine holes that retained moisture and scattered light, making the fibre more visually opaque. A similar method was the use of PET containing a dispersion of a phosphate ester of PEG.[200] Yet another technique was a PET/PEG block copolymer supplied in an aqueous dispersion as colloidal sized particles. When this was padded and baked onto the fibre as a textile finish, the co-crystallisation of the PET segments in the block copolymer with those in the fibre polymer made the treatment surprisingly washfast.[201] The most satisfactory technique is probably to make a bicomponent fibre

(see Section 3.11.3) with a thin coating of a PET/PEG copolymer on a PET core in a core–sheath configuration. This does not affect fibre properties and minimises the light fastness issue.[202]

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

3.10   Dyeing polyesters

3.10.1   Introduction

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

3.10.2   Disperse dyes

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

–OH and –CH$_2$OH, were developed for both acetate rayon and triacetate. These substitutents gave the dyes a slight degree of water solubility. They were actually dispersed (hence the name) with a surfactant (such as sulphated ricinoleic acid) as fine particles in an aqueous suspension. The dyes were perforce of low molecular weight, and when they were applied to PET this led to problems due to loss of dye by sublimation. PET fabrics usually need to be *stentered* (that is, heat set on a pin frame) after dyeing to remove creases. Since acetate rayon has a poor heat resistance, it was never heated, so dye sublimation was not previously recognised. It was a big headache for PET dyers. It became clear that special dyes would need to be developed especially for PET, based on improved versions of the acetate rayon and triacetate dyes.

As the polyester fibre market flourished, so these novel dyes rapidly advanced, being based upon well-understood dye chemistry. To prevent excessive sublimation, the dyes were made to a higher molecular weight. Typical chromophores were anthraquinones, which gave crimsons, blues and dark greens, while selected azos were used for yellow and orange or red shades. Usually these dyes were most successful if slightly water-soluble, and the ethanolamino group (–NRCH$_2$CH$_2$OH), and its O-benzoate or O-benzene sulphonate ester were often incorporated to give a slight degree of polarity and increased solubility in polyester, but without any ionic or highly hydrophilic character. The higher molecular weight dyes reduced dye sublimation, but at the cost of much slower dyeing and poor dyebath exhaustions. The hydrophobic nature and high level of crystallinity in drawn PET fibres made them much more resistant to penetration than acetate rayon or even triacetate. As a result, pressure dyeing at over 135 °C and the use of dye carriers became widely adopted.

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

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

As already mentioned, to speed up dyeing rates, carriers were introduced, which

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

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

3.10.3   Anionic and cationic dyes for polyester

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

step 1

step 2

step 3
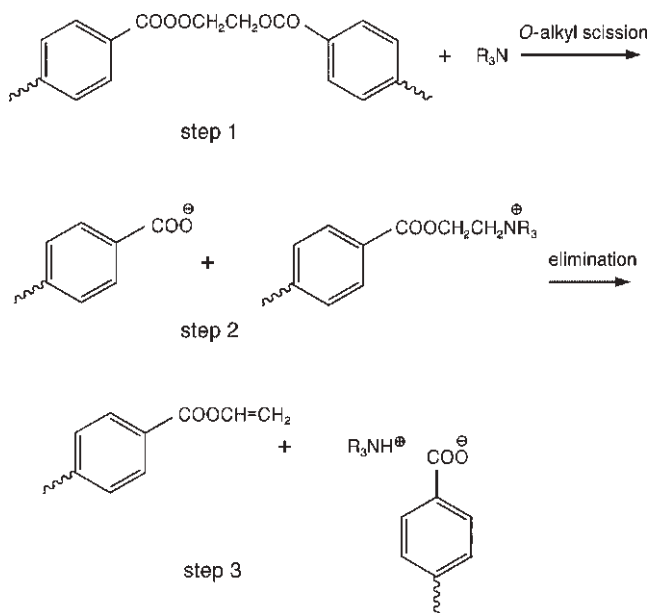
The O-alkyl cracking reaction seems to be general for all terephthalate polyesters. PBT does not degrade as severely as PET; there are no vinyl ester ends formed to generate colour and the spinning temperatures are lower, around 240 °C. IV drop is still a problem but it is more manageable. To make a melt-spinnable PET product, any acid-dyeable basic additive must not be allowed to interact with the polyester at the usual PET melt-spinning temperatures ($\approx$ 285 °C).

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

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

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

3.10.4   Mass dyeing

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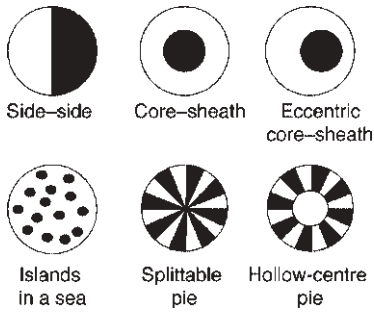
3.12 Cross-sections of various bicomponent fibres.

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

3.11 Bicomponent fibres and microfibres

3.11.1 Introduction

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

3.11.2 Side–side bicomponent fibres

Side–side bicomponent fibres can be used to produce self-bulking yarns. Two PET polymers of different molecular weights, spun as a side/side heterofil, will, on drawing, produce a self-bulking fibre after relaxing because the two spun

birefringences will differ. The relaxed yarn will curl up for the same reasons that a bimetallic strip with different expansion coefficients will curl up and a spiral crimp will result. A self-bulking fibre can also be made by co-spinning PET with a PET copolyester containing a branching agent in a side–side configuration.[214]

3.11.3   Core–sheath bicomponent fibres

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

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

3.11.4   Multiple core bicomponent fibres

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

3.11.5   Hollow fibres

Hollow fibres are yet another type of c/s heterofil: one in which the core is composed of air! They are usually made in the form of crimped staple fibre and spun from a modified staple spinning pack.[219] With advances in melt-spinner design, more complex geometries[220] are available. One patent describes a multiple-core circular polyester staple fibre with six outer hollow cores arranged around a central one.[221] Hollow fibres in the form of filament yarn have specialised uses in markets such as medical devices, but the largest volume market for hollow fibre is staple fibrefill for pillows, duvets, quilts and thermal outerwear. The desired

quality is 'loft' and the lighter and more bulky the fibre, the better. Thermal insulation is a very desirable quality. Hollow polyester fibres are very well suited to this particular end-use: the air entrapped in the hollow cores adds significantly to their insulating properties; more hollow air cores increase this effect. The fibres are frequently crimped by a stuffer-box process or may be made as bicomponent hollow fibres which develop spiral crimp on drawing.[222] Such filler fibres are frequently treated with a permanent polysiloxane finish (called a 'slickening agent') that makes them slippery, so that they slide over each other easily and resist clumping. In this form, they can compete with goose down as a thermally-insulating filling material. For some end-uses, such as fabric interlinings, it may be desirable to stabilise a filled hollow fibre structure by incorporating an additional thermally bondable bicomponent fibre.[223]

3.11.6   Heterofil spinning

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

3.11.7   Microfibres

By microfibres, we mean any individual fibre with a gauge of less than 1.0 dpf. By way of comparison, the normal filament yarn polyester is around 3.0–5.0 dpf. Microfibres are many times finer than a human hair and much finer than the finest silk: allowing for different densities, their diameters are generally less than 10 μm. A typical polyester microfibre has a titre of about 0.5 dpf. Such very fine fibres in the form of yarns have many excellent textile properties. They are very flexible,

giving a soft 'hand', and add excellent drape to fabrics. The extremely high density of fibres per unit area in a typical microfibre fabric makes it inherently windproof and waterproof. There are only very tiny gaps for air to blow through and the fabrics are largely unwettable because surface tension effects prevent water from penetrating the interstices in the fabric. However, as water vapour from perspiration can still easily pass out, these fabrics are comfortable to wear. Their fabric properties make them ideal for women's wear, sportswear, active wear and outdoor wear. They even have (radiant) heat-insulating properties, because the filaments are of the same order of dimensions as the wavelength of infrared radiation. A 0.5 dpf polyester filament (density ≈ 1.4 g cm^{-3}) has a diameter of about 7 μm, right in the middle of the IR wavelength range (2–20 μm). Hence the radiation is efficiently scattered by the microfibres and radiation loss of body heat reduced.

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

3.11.8   Melt-spinning microfibres

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

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

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

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

3.12   World markets, future trends and conclusion

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

Table 3.9 World volume estimates of synthetic fibres

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

Source: *DuPont Annual Report, 2001*

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

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

The market for polyester fibre will certainly continue to grow overall, although as a major commodity item it is likely to be affected very much more than in the past by global economics and trade cycles. Certainly, the price of raw materials such as crude oil and natural gas will have an effect on process costs and markets. Nevertheless, there is still a trend to replace other fibres, both natural and synthetic, with polyester. Nylon is still losing overall markets to polyester. At present, nylon dominates polyester in domestic carpet yarns, but PET has a growing share of the contract carpet trade simply because it is cheaper. The new microfibres and newer easy-to-dye polyesters with excellent resilience (such as PTT) are expected to make big inroads into floor coverings and the apparel markets over the next few

years. It was confidently expected that PTT would have an immediate impact on the carpet business (one place where PET polyester suffers) in 1999–2000 when *Corterra*® was first launched. So far, this has not happened, but fibre price and availability, as always, are major factors. In the long term, there are, as we have seen, new non-oil-based biomass-derived processes in commercial production for making not just intermediates for polyesters but even the polymers themselves. The effect of recycling polyester such as soda bottles into fibrefill and carpet yarns may also have unpredictable effects.

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

3.13   Acknowledgments

3.14   References

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