

# 1

## Fundamental Aspects of Textile Fibres

### 1.1 Textiles

The modern definition of the word *textile*, namely (*n.*) *a type of cloth or woven fabric* [1], reflects the early seventeenth century origins of the word as relating to a woven fabric and the process of weaving. Nowadays, the word has more extensive meanings and associations, such as *textile-filament*, *-fibre*, *-yarn* and *-fabric*, and relates to the preparation of knitted, tufted and non-woven fabrics, as well as woven fabrics. In a similar vein, the modern definition of the word *fibre*, as *a thread or filament from which a vegetable tissue, mineral substance, or textile is formed* [1], also is the result of considerable linguistic evolution since its origins in the early fifteenth century [2] to describe lobes of the liver and entrails [1].

Essentially, textile materials can be considered as principally cohesive, fibrous assemblies in which individual fibres are assembled via friction. A wide range of textiles is commercially available, the different types of such products varying, markedly, in terms of both the geometric arrangement of the fibrous materials (e.g. woven fabric, yarn and non-woven) and the derivation, structure, physical characteristics and chemical properties of the component textile fibres. Since, in its broadest sense, the theory of the dyeing of textiles concerns the nature of the interactions that operate between such fibrous assemblies and dyes, these interactions can be considered in terms of three aspects:

- (1) the gross structural arrangement of the fibrous assembly (e.g. yarn, woven fabric and garment);
- (2) the constituents of the fibrous assembly (i.e. fibre, filament, etc.);
- (3) the composite macromolecules.

Of the large amount of research that has been carried out on dyeing theory, the vast majority has tended to focus less on the physical form of a textile material (i.e. fabric, garment, yarn, etc.) and more on the constituents of the fibrous assembly (fibres, filaments, etc.), with especial attention being placed on interactions that occur at a macromolecular level. Whilst it seems appropriate to consider these three particular aspects of textile physics and chemistry, with emphasis on the constituents of the fibrous assemblies (i.e. textile fibres) from a macromolecular perspective, anything other than an outline of this large and inordinately complex area is neither possible nor required here.

In the context of the gross structural arrangement of fibrous assemblies, textile materials are available in a variety of different physical forms, including, for example<sup>1</sup>:

- yarn
  - staple spun* (comprise staple fibres); e.g. ring spun, air-jet spun, rotor spun;
  - filament* (comprise one or more mono- or multi-filament(s) with/without twist); e.g. untextured (aka flat), textured, interlaced, tape, stretch, bulky;
  - composite* (comprise staple and filament components in at least two strands, one core and a wrap strand); e.g. filament core, staple core;
  - fancy* (comprise deliberate irregularities to achieve effects); e.g. chenille, boucle, fleck, etc.;
  - specialist* (hybrid, triaxial woven, compound);
- cordage;
- flock;
- woven fabric
  - plain-weave*, *twill fabrics*, *satin fabrics*, *complex* (e.g. leno, jacquard, etc.);
- knitted fabric
  - weft-knitted: *single knits* (e.g. jersey, purl, etc.); *double knits* (e.g. interlock);
  - warp-knitted: *tricot*, *raschel*, *net*, *lace*;

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<sup>1</sup> ISO 8159:1987 'Textiles: Morphology of Fibres and Yarns – Vocabulary' discusses the principal terms that are used to describe various textile forms.

**Table 1.1** Stages of textile processing at which dyeing can be undertaken.

fibre	mass coloration <sup>a</sup>	gel dyeing <sup>b</sup>	loose stock <sup>c</sup>	yarn	piece	garment
Cotton	–	–	+	+	+	+
CA/CTA <sup>d</sup>	+	–	–	+	+	+
CV <sup>d</sup>	+	–	+	+	+	+
PA <sup>d</sup>	+	–	+	+	+	+
PAN <sup>d</sup>	+	+	+	+	+	+
PES <sup>d</sup>	+	–	+	+	+	+
Wool	–	–	+	+	+	+

<sup>a</sup> a method of colouring man-made fibres by incorporation of colourants in spinning composition before extrusion into filaments [3].

<sup>b</sup> a continuous tow-dyeing method in which soluble dyes are applied to wet-spun fibres (e.g. acylic or modacrylic fibres) in the gel state (i.e. after fibre extrusion and coagulation, but before drawing and drying) [3].

<sup>c</sup> fibres in the randomised state.

<sup>d</sup> please refer to Figure 1.7 for definitions of the various textile fibre generic names.

- non-woven  
*dry-laid, air-laid, wet-laid, polymer-laid* (and associated bonding processes; e.g. hydroentanglement, needle punching, thermal, chemical, stitching).

Textiles can be dyed at various stages of their manufacture (Table 1.1) depending on the particular manufacturing process used, cost, end use requirements, fastness, etc. Of these various physical forms, yarn and fabric are the two most commonly encountered forms in dyeing.

### 1.1.1 Yarn

Yarn [4–10] is defined as [11] *a product of substantial length and relatively small cross-section, of fibres and/or filaments with or without twist and fabric as a manufactured assembly of fibres and/or yarns that has substantial area in relation to its thickness and sufficient cohesion to give the assembly useful mechanical strength.*<sup>2</sup> Yarn is essentially a transitional product insofar as it is mostly converted into more significant textile products such as woven fabric (by interweaving), knitted fabric (by interlooping) or rope and braid (by intertwisting). Some 90% of fibres are first spun into yarn [5] which is employed in the form of long, fine fibres that consist of either a twisted assembly of staple fibres (fibre of finite, usually short length) or parallel *continuous filaments* (fibres of infinite length). As such, two types of yarn are produced, namely *spun yarn* and *filament yarn*.

It seems appropriate at this point to consider briefly what is meant by the use of the term *spinning* from a textile perspective. Confusingly, *spinning* relates not only to the processes employed in the formation of yarn by the insertion of twist in the case of staple natural or man-made fibres but also relates to the extrusion<sup>3</sup> of filaments from both natural (e.g. silk) and man-made (i.e. polymers) sources.<sup>4</sup>

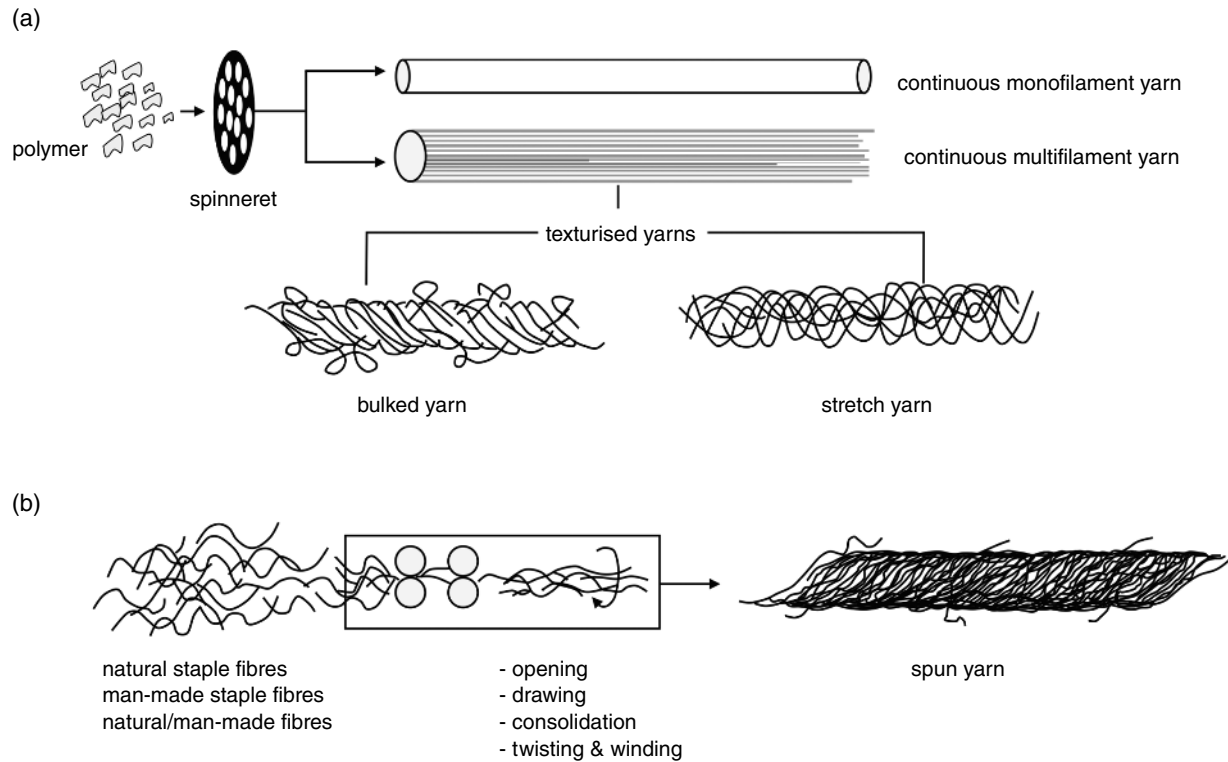
*Filament yarn* is typically represented by man-made fibres although silk is extruded as a natural *continuous filament*. *Monofilament yarn* consists of a single filament as opposed to *multifilament yarn* that comprises several individual filaments. Man-made continuous filaments often are converted into *bulked yarn* via *texturing* prior to being interwoven or interlooped to form woven or knitted fabrics, respectively (Figure 1.1). In contrast, *spun yarns* are manufactured from *staple fibre* of natural, man-made or synthetic origin in which several processes are required to prepare the fibre for spinning (e.g. blending, carding, combing, etc.), this being especially so in the case of natural fibres such as wool and cotton (Figure 1.1).

Yarns can be classified in several ways, according to either their structural complexity (single yarns, plied yarns, etc.), method of fibre preparation (carded, worsted, woollen) or spinning method used (ring spun, rotor spun, etc.). Production methods for yarn were initially developed for spinning natural fibres such as cotton, wool and silk, different processes being devised to accommodate the different physical characteristics of the fibres (e.g. [13–17]). With the advent of man-made fibres, other spinning systems were developed for continuous filament and staple fibres (e.g. [4, 5, 7, 8, 10, 18–20]).

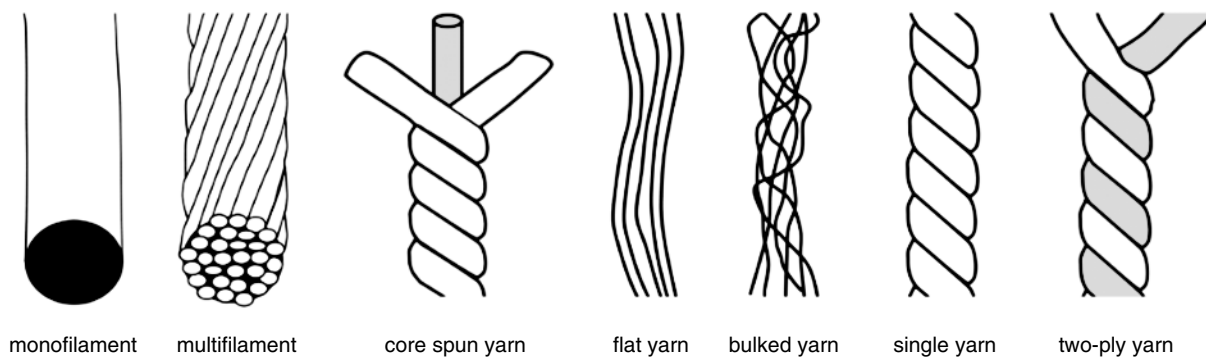
<sup>2</sup> fabrics are most commonly woven or knitted but the term includes assemblies produced by felting, lace-making, net making, nonwoven processes and tufting [11].

<sup>3</sup> solidifying extruded fibres (sometimes also hardened fibres) are drawn so as to impart strength and other properties.

<sup>4</sup> the four common types of spinning process employed for man-made fibres are *melt spinning* (e.g. PA and PES), *dry spinning* (e.g. PAN and CA), *wet spinning* (e.g. CV and CLY) and *gel spinning* (e.g. AR) – for fibre names, see Figure 1.7.



**Figure 1.1** (a) Continuous filament yarns and (b) spun yarns. Reproduced from [12], with permission from Elsevier.

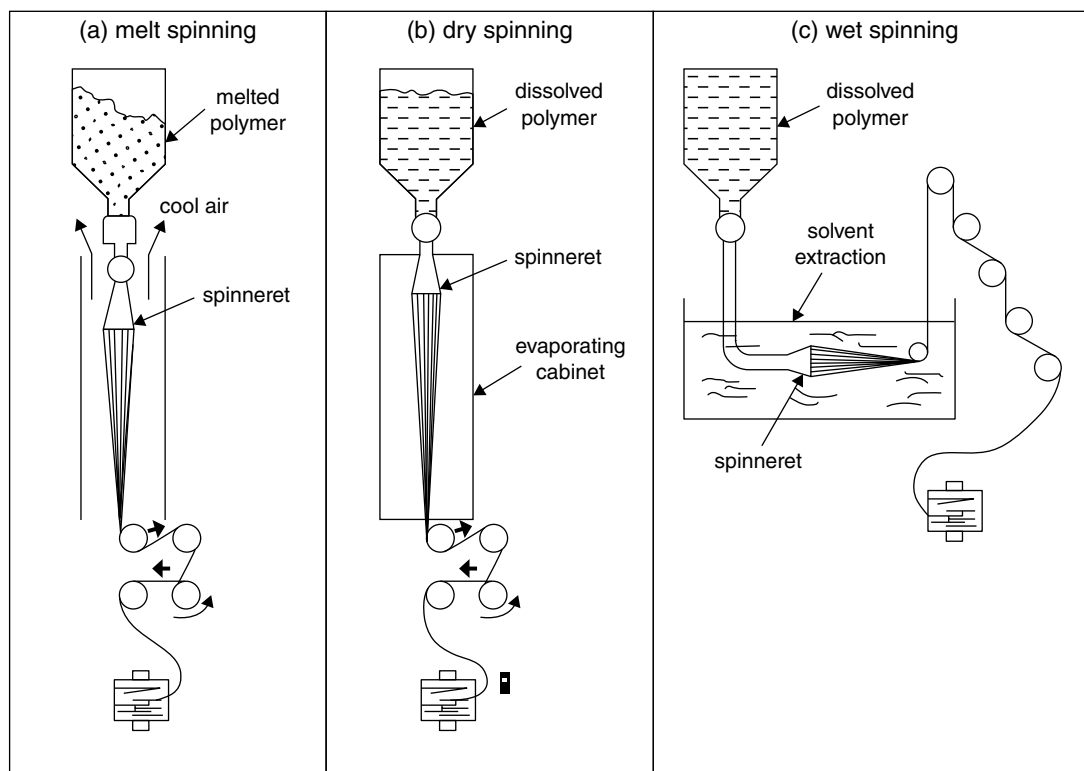


**Figure 1.2** Different types of yarn. (See insert for colour representation of the figure.)

A large number of different types of yarn can be produced depending on fibre type (e.g. natural and man-made) and physical nature (filament, core spun, flat yarn, plied yarn, etc.) (Figure 1.2).

Whilst not all aspects of the highly complex process by which polymers are converted into natural fibres during growth have been entirely resolved, in the case of man-made fibres, the polymers are transformed into fibres commonly via either the molten state (*melt-spinning* (e.g. [18, 21–23])) or solution state (*wet-spinning* or *dry spinning* (e.g. [18, 24])) though other spinning routes (e.g. *electrospinning* and *gel spinning* [18, 25–30]) can be used as appropriate to the particular polymer involved (Figure 1.3). The majority of man-made fibres are produced using melt spinning (e.g. PA, PES fibres) which, generally, offers a lower cost, less complicated route than either of the two solution-based extrusion processes. However, as not all polymers possess a stable melt phase, recourse is therefore made to spinning from solution, of which there are two types of process that can be used:

- (1) *dry spinning* in which the polymer is dissolved in a highly volatile solvent and the fibre is formed by evaporation of the solvent during extrusion (e.g. CA and CTA fibres);
- (2) *wet spinning* in which the polymer can be dissolved only in a solvent of low volatility, the fibre being formed by extrusion into a coagulating medium which removes the solvent (e.g. CV fibres).



**Figure 1.3** (a) Melt, (b) dry and (c) wet spinning. Reproduced from [24], with permission from Elsevier.

Spinning has a marked effect on the structure and properties of the extruded filament. For example, whereas wet spun fibres tend to be round or kidney bean shaped, dry-spun fibres are generally dumbbell-shaped because, during evaporation of the highly volatile solvent from the polymer solution, the outer regions of the extruded fibre solidify before the inner regions, which causes the outer regions to collapse inwards. In this context, many man-made fibres, irrespective of their mode of extrusion, possess a skin/core structure in which the skin and core display differences in physical structure which often are reflected in differences in their dyeability, as exemplified by CV fibres (see Chapter 7).

### 1.1.2 Fabric (e.g. [31–39])

Three types of fabric can be differentiated:

- (1) *woven fabric* in which *warp yarns* (lengthwise) pass under and over *weft yarns* (widthways);
- (2) *knitted fabric* in which yarns are interlooped with adjoining rows either along the length (warp knitting) or across the length (weft knitting);
- (3) *non-woven fabric* (which is usually shortened to *non-woven*) is produced directly without intermediary yarn formation.

Three main methods can be used to mechanically transform yarn into woven and knitted fabrics, namely *interweaving* (more commonly referred to as *weaving*), *intertwining* and *interlooping*, the latter process being most commonly employed in knitting (Figure 1.4) (e.g. [33, 34, 38, 39, 41]).

Non-woven fabric comprises individual fibres or filaments that are bound together in the form of a web by means of friction and/or cohesion and/or adhesion (e.g. [42–52]) (Figure 1.5). As non-wovens typically are not based on intermeshed or interlaced yarns, these fabrics differ fundamentally from conventionally manufactured woven or knitted fabrics; furthermore, yarn spinning and subsequent processing steps such as knitting and weaving are not required in non-woven manufacture. Woven and knitted fabrics are most commonly encountered in aqueous dyeing, the coloration of non-wovens being mostly undertaken using mass coloration or dispersed pigments (e.g. [53, 54]).

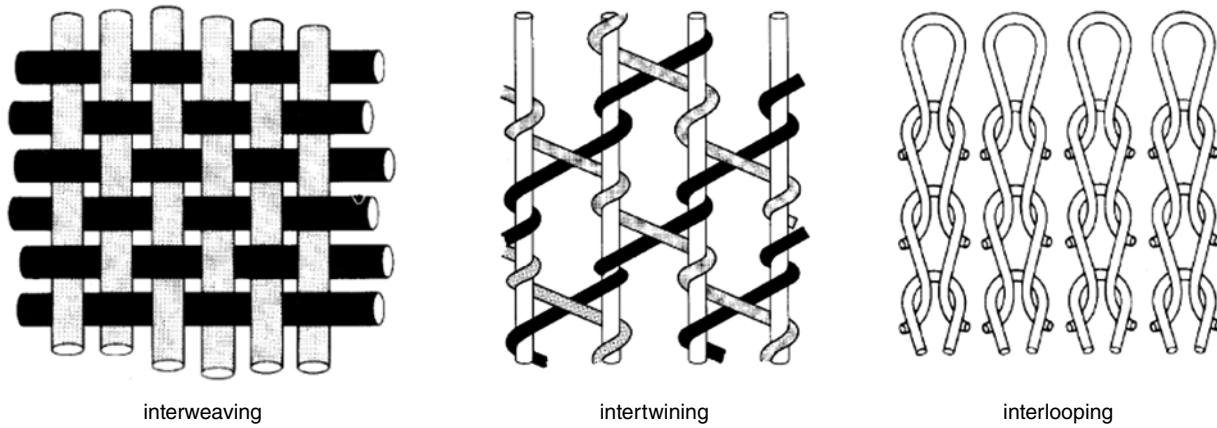


Figure 1.4 Methods used to produce fabrics. Reproduced from [40], with permission from Elsevier.

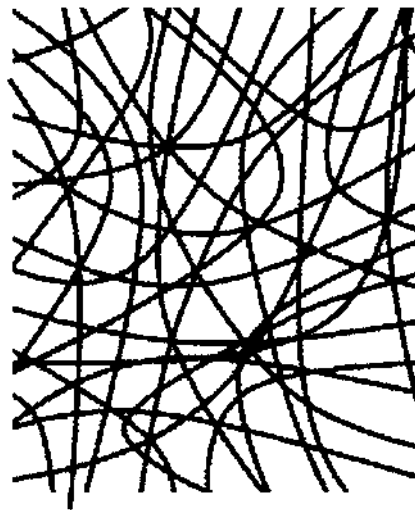


Figure 1.5 Non-woven fabric.

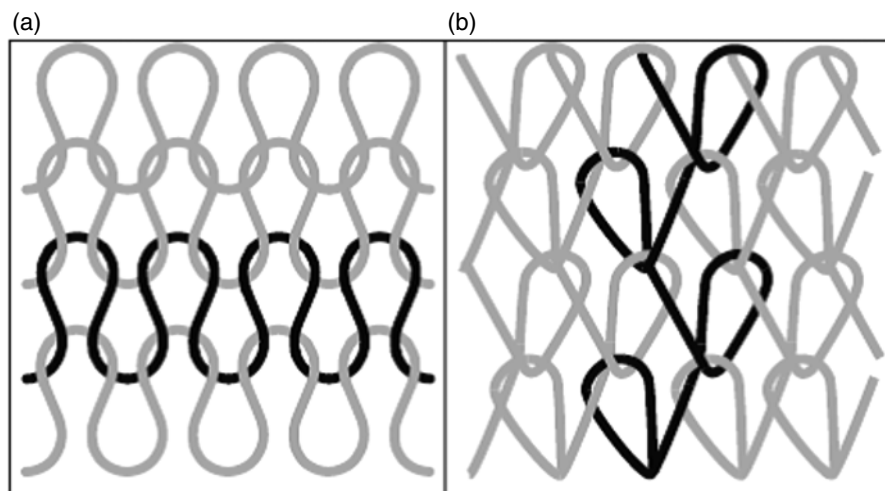


Figure 1.6 (a) Weft- and (b) warp-knitted structures. Reproduced from [32], with permission from Elsevier.

### 1.1.2.1 Knitted Fabrics (e.g. [32–35])

There are two different types of knitted structure, namely *weft-knitted* fabrics and *warp-knitted* fabrics (Figure 1.6) of which there are many variants (e.g. jersey, purl, interlock double, tricot, raschel). In warp knitting, each warp yarn is more or less in line with the direction in which the fabric is produced, whereas in weft-knitting, the weft yarn lies more

or less perpendicular to the direction in which the fabric is produced [11]. Knitted fabrics are available as flat, tubular and shaped structures, whilst a weft knitted fabric can be unravelled, a warp knitted fabric cannot [32].

### 1.1.2.2 Woven Fabrics (e.g. [39, 41, 55, 56])

In a woven fabric, the warp and weft yarns are interlaced (i.e. change direction recurrently from the surface (aka *face*) to the underside (i.e. *back*) of the fabric), perpendicularly to each other. Each warp yarn is referred to as an *end* and each weft yarn is termed a *pick*. The pattern of the interlacing of the warp and weft yarns (i.e. the weave pattern) influences several characteristics of the fabric, including drape, handle, etc. Fabric attributes are also influenced by yarn characteristics, such as colour, fibre constitution, count/linear density, as well as the number of picks and ends per given area. Several basic types of woven structure are produced (plain woven twill, satin) and more complex structures are generated using two or more sets of yarn (e.g. pique, crepe, etc.).

### 1.1.3 Textile Markets

Textiles enjoy manifold applications (e.g. [57–69]) and are traded in four main markets:

- (1) *apparel*: many and varied clothing items, such as shirting, hosiery and lingerie;
- (2) *interior furnishings*: for example carpets, curtains and upholstery in both domestic and contract markets;
- (3) *household textiles*: for example bed linen, towels and blankets in both domestic and contract markets;
- (4) *industrial/technical textiles*: medical-textiles, geo-textiles, agro-textiles, high performance fibres, etc.

For convenience, the four markets are often grouped into two main manufacturing sectors, namely *textiles* (e.g. yarns, household textiles, industrial/technical fabrics) and *clothing* (e.g. apparel, clothing accessories). The global textile and clothing sectors are large and diverse industries that comprise both commodity products that are produced in high volume and at relatively low cost as well as high-value added products for which both research and development are vitally important and fibre technology is a key competitive issue. The textile and clothing industries are very large, complex global manufacturing businesses dominated by small and medium-sized enterprises (SMEs) and encompass several sub-sectors that range from the production of the raw materials, via semi-processed goods (e.g. yarns and woven fabrics) to final products (household textiles, clothing, etc.). In 2011, global clothing and textiles trade reached US\$ 706 billion, the leading importers being the EU-27 and the United States [70]. Textiles and clothing are major global employers: for instance, in 2009, the textiles and clothing sectors within the EU, which account for 29% of world textiles and clothing exports (not including trade between EU member states) and rank second only to China and which generate 40% of global exports [71], employed  $2.3 \times 10^6$  workers across 150 000 SMEs [72]. However, from a worldwide market perspective, despite the considerable scale of the global clothing and textiles sectors, in 2011, clothing (US\$ 412 billion) and textiles (US\$ 294 billion) accounted for only 1.6 and 2.3%, respectively, of world merchandise trade and contrasted markedly with that in chemicals (US\$ 1997 billion; 11.2%) and fuels (US\$ 3171 billion; 17.8%) [70].

## 1.2 Textile Fibres

As mentioned, dyeing theory has tended to focus less on the physical form of a textile material (i.e. fabric, garment, yarn, etc.) and more at the fibre and especially at molecular levels. This section concerns the first of these latter two aspects of textile physics and chemistry, namely textile fibres.

A fibre can be considered [11] as a *textile raw material, generally characterised by flexibility, fineness and high ratio of length to thickness*. However, within this definition, several different types of fibre can be differentiated [11]:

- natural fibre: *a fibre occurring in nature*;
- regenerated fibre: *a fibre formed from a solution of natural polymer or of a chemical derivative of a natural polymer and having the same chemical constitution as the natural polymer from which the solution or derivative was made*;
- chemical fibre: *a literal translation of various non-English terms having the same meaning as manufactured fibre or man-made fibre*;
- manufactured fibre (aka man-made fibre): *a fibre that does not occur in nature, although the material of which it is composed may occur naturally*;

- synthetic fibre: a fibre manufactured from a polymer built up from chemical elements or compounds, in contrast to fibres made from naturally occurring fibre-forming polymers.

These various types of fibre are briefly discussed below.

### 1.2.1 Textile Fibre Classification

Textile fibres can be classified in several ways. That shown in Figure 1.7 follows conventional practice, differentiating six groups spread across two main derivation classes, namely *natural fibres* and *man-made fibres*. Figure 1.7 shows both the generic names (e.g. viscose, polyester) and the appropriate abbreviations (e.g. CV, PES, etc.) that are used for man-made fibres (see Section 1.2.1.1). In this book, the abbreviated fibre names are used preferentially.

**Natural fibres** These are of vegetable (cellulosic), animal (protein) or mineral origin and are staple fibres (i.e. of finite, usually short length), with the exception of silk, which is formed in continuous filaments. In terms of usage, this category is dominated by the cellulosic fibres cotton and flax, as well as the protein fibres wool and silk, with other textile substrates of organic origin, including cellulosic fibres of *seed* (e.g. coir), *bast* (e.g. jute and ramie) and *leaf* (e.g. sisal) derivation, as well as protein fibres derived from hair (e.g. cashmere), providing effectively niche goods. The inorganic fibre asbestos is of course no longer available because of its toxicity. Such is the global popularity of natural fibres that a considerable proportion of global agriculture is concerned with their production.

**Man-made fibres (aka manufactured fibres)** These include *natural polymer* fibres obtained from naturally occurring polymers (mostly cellulose) via chemical transformation (e.g. CV) or derivation (e.g. CA), *synthetic polymer* fibres derived from synthetic materials (e.g. PES) as well as the so-called *inorganic fibres*, such as glass, ceramic and carbon. Whilst man-made fibres are produced as continuous filament, often these are cut to produce staple fibres for use in knitwear or carpets and for blending with natural fibres (e.g. PES/cotton).

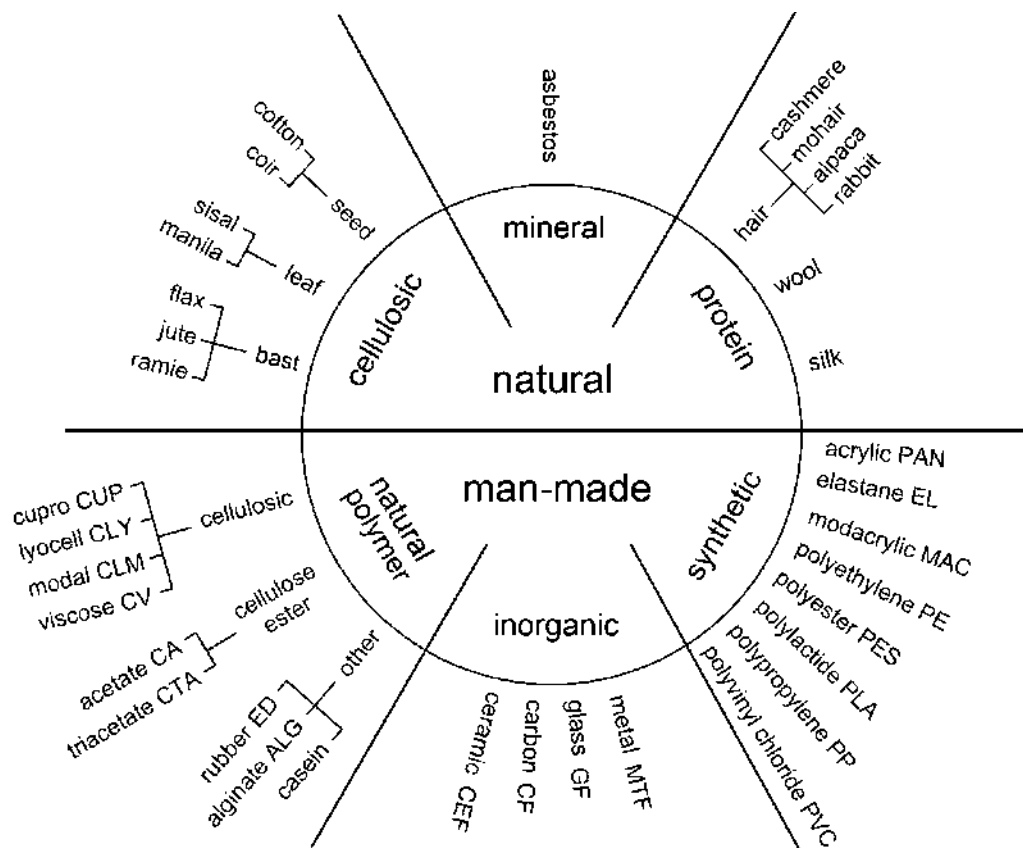


Figure 1.7 Classification of textile fibres.

**Table 1.2** Classification of fibres based on water sorption characteristics.

fibre		dye class
Wool	hydrophilic	Acid, mordant, reactive
Silk		Acid, mordant, basic, vat
CLY		Direct, vat, sulphur, reactive
CV		Direct, vat, sulphur, reactive
Cotton	hydrophobic	Direct, vat, sulphur, reactive
CA		Disperse
CTA		Disperse
PA 6/PA 66		Acid, mordant, direct, disperse, reactive
PAN		Basic, disperse
PES		Disperse

As Figure 1.7 shows, the majority of fibres derived from organic sources (which constitute by far the majority of textile fibres) belong to a relatively small number of chemical classes:

- *natural*: cellulosic and protein;
- *man-made*: polyamide, polyester, polyolefin, polyurethane and polyvinyl.

Furthermore, such fibres, which enjoy traditional, widespread textile usage, for the most part, are composed of partially crystalline, partially oriented, linear polymers. Interestingly, fibres that fall outside these somewhat simplistic parameters, such as glass, ceramic fibres and fluoropolymers, which, for instance, are highly oriented or of pronounced crystallinity, do not enjoy extensive, conventional textile usage.

### 1.2.1.1 Fibre Names

Whilst the names of natural fibres have evolved over several millennia, those of man-made fibres have developed in a far more systematic way in more recent times. Natural fibres are given a *common name* (e.g. cotton, silk and flax) whereas man-made fibres are ascribed a *generic name*; many textile fibres are also given *trade names*.<sup>5</sup> In the context of man-made fibre generic names, in 1971, the *European Commission* (EC) issued a Directive which sought to harmonise the names of textile products as well as their use on labels and in marketing documents [73]. The Directive has been subsequently amended several times and, from 8 May 2012, Regulation (EU) No. 1007/2011 [74], which concerns textile fibre names and related labelling and marking of the fibre composition of textile products (which repealed and replaced former directives 2008/121/EC, 96/73/EC and 73/44/EEC [73, 75]), governs the use of fibre names in the EU [73]. In the United States, textile generic names are allocated by the *Federal Trade Commission* [76]. Unfortunately, for some fibres, different generic names are applied in the United States and the EU, as exemplified by *viscose* (EU)/*rayon* (US) and *elastane* (EU)/*spandex* (US). In this book, the generic names of man-made fibres are those allocated by *la Bureau International pour la Standardisation des Fibres Artificielles* (BISFA) [77], these being shown in Figure 1.7 together with the relevant BISFA abbreviation (e.g. CA and CV).

From the viewpoint of dyeing, textile fibres can be classified as *hydrophilic* or *hydrophobic* in terms of their water sorption properties (Table 1.2), as water sorption is a fibre property of fundamental importance to aqueous dyeing and which varies, markedly, for different fibre types. Whilst the concepts of *hydrophilicity* and *hydrophobicity* are discussed in Chapter 3, in essence, a surface, which when contacted with water, is termed *hydrophilic* when it displays good wettability with water (and generates a *contact angle*<sup>6</sup>  $\theta \leq 90^\circ$ ) and is *hydrophobic* when it displays low wettability with water (and  $\theta > 90^\circ$ ) [78]. For instance, hydrophilic fibres such as natural cellulosic fibres characteristically absorb large amounts of water and undergo sizeable radial swelling, whereas hydrophobic synthetic fibres such as PES absorb almost no water and do not swell. As subsequently discussed, the water sorptive properties of a fibre determine the type of dyes that are employed for its coloration. For example, hydrophilic cotton and wool fibres are readily dyed using water-soluble direct dyes and acid dyes, respectively, whereas the hydrophobic synthetic fibre PES is dyeable only using sparingly water-soluble disperse dyes (Table 1.2). The relative hydrophilicity/hydrophobicity of textile fibres in relation to dyeing are discussed later.

<sup>5</sup> neither the common name nor the generic name is trademark protected.

<sup>6</sup> see Chapter 3 for a discussion of contact angle.



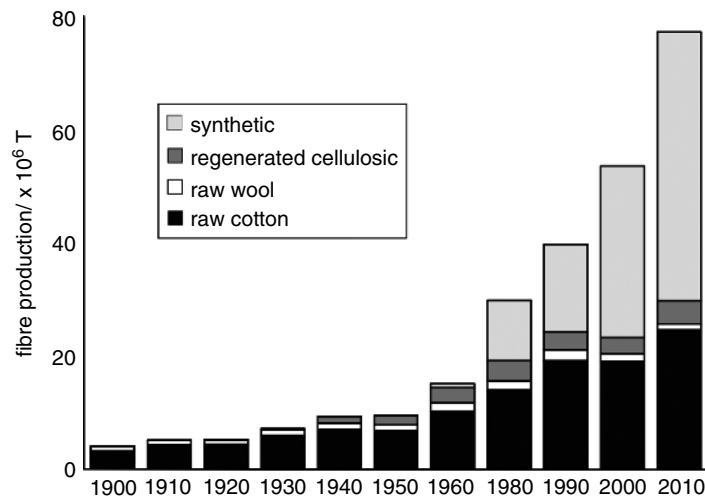


Figure 1.8 World textile fibre production, 1900–2010. Data from [82].

## 1.2.2 Textile Usage

World textile fibre demand in 2012 was  $78.9 \times 10^6$  T [79], resulting in *per capita* consumption of 11.3 kg, assuming a world population of  $\sim 7.0 \times 10^9$  [80, 81]. Of this global textile fibre usage, PES fibres accounted for  $\sim 55\%$  ( $43.3 \times 10^6$  T) and cotton fibres  $\sim 30\%$  ( $23.4 \times 10^6$  T), with wool, silk and other natural fibres making up only a very small proportion ( $\sim 1.5\%$ ;  $1.2 \times 10^6$  T) and other man-made and synthetic fibres comprising  $\sim 13.5\%$  ( $\sim 11 \times 10^6$  T).

As Figure 1.8 shows, between 1900 and 2000, world fibre production grew  $\sim 10$  fold, which contrasts with a 3.8-fold increase in world population and a 2.7-fold increase in *per capita* economic prosperity over the same period [83]. However, between 2000 and 2010, world fibre production grew by  $\sim 45\%$  compared to an increase in world population of only 13% [84]. Such a contemporary high rate of increase in textile demand seems likely to continue for the foreseeable future, not simply because world population is predicted to grow to  $>9$  billion by 2050 and exceed 10 billion by 2100 [85] but also since global economic growth appears set to continue to increase, despite the recent global fiscal austerity, high public debt burden and financial fragility [86]; indeed, it has been estimated that world fibre production will reach  $140 \times 10^6$  T by 2050 [83]. Figure 1.8 also shows the marked increase in global textile production of synthetic fibres that has occurred over the past 30 or so years, a trend that seems unlikely to change.

## 1.2.3 The History and Development of Textile Fibres

As the history and development of textiles and textile fibres has been the subject of many publications, the following serves only as a brief outline of the origins of this significant facet of human progress.

### 1.2.3.1 Natural Fibres

For an overview see Refs. [5, 25, 87–93]. From an historical perspective, precise knowledge of the origins of the use of these substrates and their development as textile materials, which also includes their dyeing, is not possible. As early textiles were of organic origin and, therefore, susceptible to degradation, only very few samples of textiles have survived from prehistory; written records did not appear until around 3100 BCE. Recourse is therefore made to archaeological evidence provided by the few textile remnants, related tools, art, etc.

Whilst the earliest known woven textiles, from the southern Anatolian (present day Turkey) Neolithic settlement, *Çatal Hüyük*, date from 6000 BCE, these are pre-dated by some 100–500 years [90, 94] by nets, mats and other similarly less complex structures. However, it is generally accepted that long before weaving had been developed, prehistoric man was able to join animal hides and skins, use gut, vines and sinew as threads and string and, also, had discovered the importance of twisting fibres to enhance the strength of such threads and strands. Indeed, needles, which could be used for the joining of animal skins, as well as seeds, shells, etc., were first employed in Europe around 26 000–20 000 BCE. Beads that were likely strung with vines, gut, etc. dating from 38 000 BCE as well as three-ply cordage that dates from 18 000 to 15 000 BCE have been found in France [90]. As such, whilst the precise origins of spinning and weaving are unknown, it is likely that spinning, as practiced in the production of cordage, string, etc., preceded weaving. It is commonly accepted that the weaving of textiles on looms began in the Neolithic period, 6000–5000 BCE. The Egyptians are generally considered to be the world's first skilled weavers; linen weaving having become a staple industry in Egypt by  $\sim 5500$  BCE [95].

Although five main types of natural fibre were exploited by primitive man, namely hemp, flax, wool, cotton and silk, other fibre types were also used, such as those derived from, for example, goat, tree bark, rabbit and papyrus. Fibre blends were also utilised in prehistoric times, as exemplified by samples of cotton and raw silk dating from 1500 to 1000 BCE [90]. The two bast fibres, hemp (which provides linen) and flax, were the foremost fibres of prehistory, probably due to their abilities to adapt to a range of habitats and climates and to afford uses other than fibres (e.g. linseed oil and animal feed [90, 96]). Indeed, fragments of woven flax dating from 3000 BCE have been discovered [97] and linen samples dating from 10 000 BCE have been found in Switzerland. Seeds of cultivated flax from 8000 BCE were discovered in Syria [94] and hemp seeds dating from 5500 to 4500 BCE in northern Europe [90].

Although sheep were domesticated by or before 7000 BCE [97], it is unclear as to whether wool was first used independently of the hide for textiles at this time, or the woolly fleece did not develop until the early Bronze Age. Cotton was probably cultivated in Pakistan before 4000 BCE and records of cotton date from around 4300 BCE in Mexico and ~3300 BCE in Peru [98]. The ruins of Mohenjo-daro provide evidence that cotton spinning was practiced in the Indus Valley around 2500–3000 BCE (e.g. [99, 100]) and cotton seeds have been found dating from the second half of the second millennium BCE [100]. It is generally agreed that the Chinese were the first to cultivate the silkworm and manufacture silk, from around 4000 BCE, with the earliest surviving silk samples dating back to 2850–2650 BCE; however, wild silk fibre was woven in India as early as 2500 BCE [101]. Details of the fibre's manufacture remained a closely guarded secret for much of this time, despite the famous trade explorations commonly represented by the *Silk Road* which began around 206–220 CE; indeed, sericulture was introduced to Japan around 195 CE, reaching Constantinople in the seventeenth century and then gradually spreading to the Western world [102].

### 1.2.3.2 *Man-Made Fibres*

See Refs. [25, 103–108] for a summary. The prospects of producing an artificial version of the then most prized of textile fibres, silk, fascinated scientists of the seventeenth and eighteenth centuries. Hooke is generally credited with inspiring this pursuit of 'artificial silk' fibres, by theorising, in 1665, that an 'artificial glutinous composition' similar to that secreted by silkworms might be made which could be 'drawn out' into 'small wires' or filaments [109]. Réaumur (1734) produced coarse fibres using varnish passed through holes in a can, thereby demonstrating the first dry-spinning process and Schwabe (1840) invented the precursor of the spinneret, extruding molten glass filaments. Between around 1850 and 1900, considerable research was undertaken and commercial success achieved in the search to produce 'artificial silk' fibres. All of the ensuing commercially significant fibres were derived from the natural polymer, cellulose, by means of its chemical transformation, entailing cellulose *derivatisation*, *spinning* of filaments and subsequent *regeneration of the cellulose* polymer. As such, the term *regenerated cellulosic* is often applied to such man-made fibres of cellulosic origin, although *regenerated protein* fibres were also produced, as exemplified by *casein*.

The first commercial, man-made fibre, *Chardonnet silk*, obtained from cellulose nitrate, was introduced in 1889. This major landmark in textile fibre development stemmed from Schönbein's discovery (1846) of nitrated cellulose,<sup>7</sup> as well as Audemars' (1855) observation that fibres could be drawn from an alcoholic ether solution of cellulose nitrate, together with the first demonstration of the 'spinning' of 'artificial silk' fibres by Swan (1883). The introduction of *Chardonnet silk* was closely followed by that of *cuprammonium silk* (*Cupro*; CUP; 1899) which arose from both Schweizer's earlier discovery (1857) that cellulose, dissolved in ammoniacal copper oxide, could be regenerated in a coagulation bath as well as from spinning process developments by Despeissis and other researchers (e.g. [110, 111]). The most commercially important of all regenerated cellulosic fibres, *viscose* (CV), resulted from the discovery by Cross, Bevan and Beadle (1891) that cellulose could be dissolved in NaOH and CS<sub>2</sub> and the ensuing *viscous* solution (later called 'viscose') could be coagulated in NH<sub>2</sub>SO<sub>4</sub> to produce fibres. The *viscose process* became industrially viable in 1905, with staple CV fibre being introduced in the 1920s and, in the late 1930s, high-strength CV tyre yarns were launched. In the 1960s, *High Wet Modulus* (HWM) CV fibres were introduced that display properties more similar to their cotton counterparts (e.g. lower shrinkage and more pleasant wet texture) and which are termed *modal* (CMD) fibres (e.g. [89, 112–116]). Although CV has dominated the regenerated fibre market since the fibre's inception, in more recent times, owing to environmental concerns and price competition from synthetic fibres, simpler, less-polluting manufacturing routes to the production of man-made cellulosic fibres were sought. Of various non-aqueous solvents capable of dissolving cellulose directly and which could be readily recovered, *N*-methyl morpholine oxide (NMMO) was commercially utilised to produce *lyocell* (CLY) fibres<sup>8</sup> (1992) (e.g. [116–119]). Whilst Schützenberger first isolated *cellulose triacetate* (CTA) in 1865, commercial applications of the new material were hindered by the high price of the raw materials and the polymer's insolubility in low-cost solvents. Miles (1904) synthesised the acetone-soluble *cellulose acetate* (CA) by the partial hydrolysis of CTA and large-scale textile fibre production

<sup>7</sup> and the explosive material, *Schiesswolle* or gun-cotton.

<sup>8</sup> strictly, CLY fibres are *reconstituted cellulosic fibres*, since their production does not involve cellulose derivatisation prior to regeneration of cellulose.

occurred in 1921. Very strong (high orientation, high crystallinity) CV fibres (*Fortisan*) were introduced in the 1940s and CTA fibres were commercially introduced in 1954<sup>9</sup> (e.g. [112, 120–122]). Although regenerated protein fibres obtained from milk (*casein*) and *gelatin* were investigated as potential ‘artificial silk’ fibres at the end of the nineteenth century, the commercial possibilities of this type of regenerated fibre were revived in the 1930s and, over the ensuing two or so decades, commercial products appeared derived from sources including milk, as well as ground nut protein, corn and soya bean (e.g. [108, 111, 123]). From the mid 1970s, commercial interest also developed in producing fibres from spider silk (e.g. [124–129]). However, with the exception of alginate fibres which are utilised in the form of advanced wound-care non-wovens, regenerated protein fibres have not experienced the widespread commercial use enjoyed by their regenerated cellulosic counterparts.

### 1.2.3.3 Synthetic Fibres

Refs. [25, 111, 130–133] provide an overview of this topic. The development of synthetic fibres has been the subject of a great many articles. The origin of synthetic textile fibres stems from the discovery by Klatte (1913) of a process for wet-spinning *polyvinyl chloride* (PVC) fibres, although commercial realisation was delayed until the 1930s owing to the polymer’s insolubility in commercial-scale solvents; by 1934, PVC was widely used in Germany [134, 135]. However, this discovery and the technical successes achieved by the producers of regenerated cellulosic fibres during the early part of the twentieth century were accomplished despite a marked lack of understanding of textile chemistry and polymer science. This particular situation changed, gradually, owing to the ground-breaking studies made in the 1920s and 1930s, by both Staudinger<sup>10</sup> [137] who showed that compounds such as *natural rubber* were of very high molar mass and were composed of a large number of small molecules that were connected by a covalent linkage via a reaction that he called ‘polymerisation’, and by Carothers<sup>11</sup> on the condensation polymerisation of esters and amides [139].

PVC was first melt-spun in 1932 and the discovery that copolymerisation improved solubility resulted in the introduction of the chlorinated polyvinyl chloride fibre *Pe-Ce* and the vinyl chloride/vinyl acetate fibre *Vinyon* in the mid 1930s [140–142]. What many authors consider to be a landmark in the production of synthetic fibres occurred in 1939 when *PA 66* (aka *nylon 66*) fibre was commercially produced, fibres having been first prepared in 1935 [143]. This was quickly followed by the appearance of many other synthetic fibres such as *PA 6* (aka *nylon 6*) prepared by Schlack in 1938<sup>12</sup> [144] and *polyethylene* (*PE*) in 1939, as well as *acrylic* (aka *polyacrylonitrile*, *PAN*) and *modacrylic* (*MAC*) in the 1940s, and polyester (*PES*), *polypropylene* (*PP*) and *elastane* (*EL*) in the 1950s (e.g. [111, 145–153]). The popularity of synthetic fibres is reflected in the world fibre production data shown in Figure 1.8. Clearly, whilst cotton fibre production has increased, steadily over the past 100 or so years and that of its regenerated counterparts has remained reasonably stable over the past 70 years or so, synthetic fibres have enjoyed sustained, increasing growth since their introduction in the 1950s; wool fibre production has declined in recent decades.

Developments over the past 40 or so years have resulted in what some authors refer to as a ‘second generation’ of man-made fibres which possess significant superiority in one (or more) property compared to conventional textile fibres, such as high strength and stiffness, marked chemical or thermal resistance. Such fibres are referred to as *specialist fibres* or, more commonly nowadays, *high performance fibres*, the latter term mostly relating to fibres that possess *high-modulus* coupled with *high-tenacity* (*HM-HT*).<sup>13</sup> Whilst such fibre types are not widely used in conventional textile markets (i.e. apparel, interior furnishings, household), they nevertheless enjoy widespread industrial, engineering and biomedical applications. In the 1960s, interest in producing specialist fibres resulted in the semi-aromatic polyamide, *PA 6T* and the high-temperature-resistant *m*-aramid fibre poly(*m*-phenylene isophthalamide) (*MPIA* aka *Nomex*). Subsequently, various types of high-performance fibre have been developed including the aromatic, rigid rod, lyotropic liquid crystalline, poly(*p*-phenylene terephthalamide) (*PPTA*; aka *Kevlar*) fibres in the 1970s, thermotropic liquid crystalline polymers (*TLCP*) such as the aromatic polyester fibre *Vectran*, the temperature-resistant and chemical-resistant poly(phenylene sulphide) (*PPS*) fibres (FCT generic name *sulfar*) in the 1980s as well as heterocyclic rigid rod polymers, exemplified by both the high-temperature-resistant *polybenzimidazole* (*PBI*) and *poly(p-phenylene benzobisoxazole)* (*PBO* aka *Zylon*), gel-spun PE fibres (aka *high-performance polyethylene* (*HPPE*) or *high-modulus polyethylene* (*HMPE*)), as exemplified by *Dyneema* fibres as well as high thermal resistant thermosets such as melamine–formaldehyde fibres (e.g. *Basofil*) in the 1980 and 1990s. In addition to organic high-performance fibres such as those mentioned above, several inorganic high-performance fibres are produced, namely carbon fibres, ceramic fibres and glass fibres. The reader is directed elsewhere for fuller accounts of this large area (e.g. [18, 154–161]).

<sup>9</sup> in the manufacture of CA fibres, as CAT is produced prior to the diacetate variant, in many publications, CTA is often referred to as *primary cellulose acetate* and diacetate referred to as *secondary cellulose acetate*.

<sup>10</sup> Staudinger first proposed the term ‘macromolecule’ in 1922 [136].

<sup>11</sup> see, for example [138].

<sup>12</sup> marketed in the late 1940s under the trade name *Perlon* [135].

<sup>13</sup> whilst the maximum strength and modulus of conventional synthetic fibres is about 1 and 15 GPa, respectively, that of high performance fibres is >2 and >55 GPa.

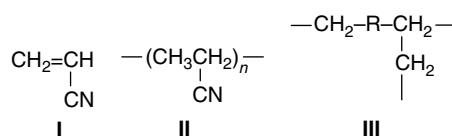
## 1.2.4 Textile Polymers

Both natural and synthetic polymers are an essential part of everyday life, major examples of their use including *plastics* [162, 163], such as low density (aka branched) and high density (aka linear) PE, *elastomers* [164, 165], which include natural rubber and the synthetic variant, styrene-butadiene rubber and, of course, textile fibres. Since, generally, all textile fibres that enjoy widespread usage are organic *polymers*, this section considers some of the fundamental principles and properties of such polymers of relevance to textile fibres.

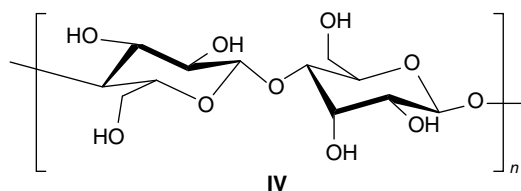
### 1.2.4.1 Polymers

Berzelius first used the term *polymer* in 1832 [166, 167], although this researcher's early definition differs markedly to that in contemporary usage. The origins of *polymer technology* lay in the early nineteenth century as represented by the spreading of masticated natural rubber on cloth in 1820 [168] and the first patents on vulcanised rubber in the 1840s, whilst those of *polymer science* stem from the pioneering work of Staudinger in the 1920s who first introduced the term *makromolekül* (*macromolecule*) to designate long-chain molecules with colloidal nature [166]. This account provides only a brief introduction to the extremely large, diverse and complex areas of polymer chemistry and polymer technology. Comprehensive and informative accounts of the fundamentals of both polymer chemistry and polymer technology are available in several, well-cited textbooks (e.g. [163, 168–174]). Useful definitions in polymer science are available [175] and various polymer terms and definitions are available from IUPAC [176, 177].

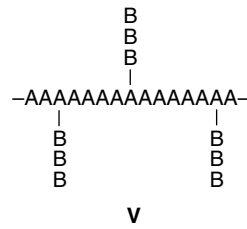
In the latter context, according to IUPAC [175], the term *polymer* refers to a substance composed of macromolecules where the term *macromolecule* (aka *polymeric molecule*) refers to a single molecule; for the purposes of this book, the terms *macromolecule* and *polymer* will be used interchangeably. In simple terms, a *polymer* is a large molecule that is made up of smaller *monomers* that are linked together covalently. A monomer comprises *monomer molecules* which can undergo *polymerisation*, a process by which the monomer is converted into a polymer. Monomers vary in the number of covalent bonds that they can form with other reactants, this being expressed by their *functionality*, *f*. The polymerisation of a *bifunctional monomer* ( $f=2$ ) such as acrylonitrile (**I**) results in a *linear polymer*, in this case poly(acrylonitrile), PAN (**II**) whereas that of *polyfunctional monomers* ( $f>2$ ) yields branched polymers<sup>14</sup>; when branches interconnect, three-dimensionally crosslinked polymers (aka *network polymers*) arise (e.g. phenol-formaldehyde resins, **III**).



A *homopolymer* is formed when only one type of monomer is used, as exemplified by cotton, in which the cellulosic macromolecular chains comprise *D-glucopyranose* monomers joined by  $\beta(1 \rightarrow 4)$  linkages (i.e. the C-1 and C-4 groups of adjacent monomeric molecules link successively through a  $\beta$ -configuration). The repeat unit of cellulosic materials often is depicted as two glucose monomeric units, **IV** (referred to as the disaccharide *cellobiose*) since the  $\beta$  position of the  $\text{---OH}$  groups at C-1 dictates a  $180^\circ$  rotation of the following glucose unit around the 1,4 axis of the pyranose ring. In the case of undegraded cotton fibre, the degree of polymerisation, *DP*, (see Section 1.2.4.4) may be  $>20\,000$  *D*-glucopyranosyl monomer units [25].



<sup>14</sup> which can take several forms such as ladder, comb and star-shaped.



If two or more types of monomer are employed, the ensuing material is a *copolymer*, as exemplified by the polymerisation of *hexamethylene diamine* ( $\text{NH}_2(\text{CH}_2)_6\text{NH}_2$ ) and *adipic acid* ( $\text{HOOC}(\text{CH}_2)_4\text{COOH}$ ) which results in the copolymer, PA 66 ( $\text{---NH}(\text{CH}_2)_6\text{NHCO}(\text{CH}_2)_4\text{CO---}$ ). Copolymers derived from bifunctional monomers are divided into four types based on whether the distribution of the two monomers, A and B, in the polymer is:

- (1) random (*random copolymers*:  $\text{---AABAABBBAAABABB---}$ );
- (2) alternating (*alternating copolymers*:  $\text{---ABABABAB---}$ );
- (3) sequential (*block copolymers*:  $\text{AAABBBAAABBB---}$ ); or
- (4) blocks of monomer are grafted onto another (*graft copolymers* (**V**)).

### 1.2.4.2 Nomenclature

Although polymer science and technology have their origins in the 1920s, there is still no universally adopted system for naming polymers, despite the quite remarkable developments that have occurred within these fields over the past ~100 or so years. As might be expected, this can lead to confusion; indeed, a very wide range of trade names, common names, trivial names, abbreviations and chemical names are employed for polymers. The development of a systematic approach to the naming of polymers was initiated by IUPAC in the 1950s which has continued up to the present time. Although IUPAC has developed a nomenclature system for polymers, it is not universally applied. Briefly, three systems of polymer nomenclature are in general use. The first of these systems, namely *trade names* or *brand names* (and abbreviations), is widely used by manufacturers, processors, fabricators and the like, to describe and differentiate commercial products. The two further types of naming system are based on the *source of the polymer* (i.e. a system that uses the name of the monomer) and a more explicit, *structure-based nomenclature* that can be used when the polymer structure is known. However, traditional polymer names continue to be used.

**1.2.4.2.1 Source-Based Nomenclature System** In this system, the name of the monomer is prefixed by the word *poly*, such as *polyethylene* in the case of polymers derived from single monomers. When the monomer has a very long name or a multi-word name, parentheses are placed around its name, as exemplified by *poly( $\epsilon$ -caprolactam)*<sup>15</sup> or PA 6.

**1.2.4.2.2 Structure-Based Nomenclature Systems** Essentially, two such nomenclature systems are in general use namely a non-IUPAC system and an IUPAC system. In the former case, polymers derived from two different monomers (e.g. PES) are named by prefixing the name of the structural unit, which is enclosed within parentheses, by the word *poly* as in *poly(ethylene terephthalate)*. The IUPAC nomenclature system is based on the use of a preferred *constitutional repeat unit*, CRU, this being the smallest constitutional unit of the polymer and which is named according to the IUPAC procedures employed for the naming of small organic compounds (e.g. [176, 178]). In recognition of the fact that some polymers have well-established, source-based, *trivial* or *traditional* names (e.g. polyethylene and polypropylene), the IUPAC nomenclature system retains such names. The intricacies of the formalised, procedural IUPAC polymer naming system are outside this introductory discussion and the reader is directed elsewhere [178, 179]. Importantly, the CRU differs to the term that is commonly utilised in relation to polymer structure, namely the *repeat unit*, insofar as, for example in the case of PE, whilst the CRU is  $\text{---CH}_2\text{---}$ , the repeat unit is  $\text{---CH}_2\text{CH}_2\text{---}$ . Table 1.3 shows the source-based and structure-based names, as well as repeat units, of some common polymers used in textile fibres.

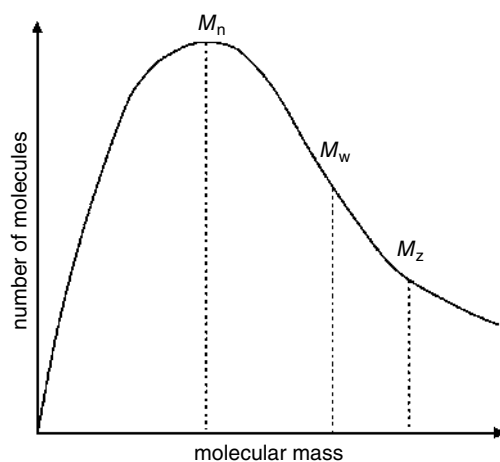
### 1.2.4.3 Molar Mass

The two properties that distinguish polymers from other molecules are their very large molecular size and long chain structure. The size of a polymer molecule can be defined in terms of either its *molar mass* or its *degree of polymerisation*,

<sup>15</sup> which often is also named as the equivalent *poly(6-aminocaproic acid)*.

**Table 1.3** Structure- and source-based names of some polymers.

common name	structure-based name	source-based name	repeat unit
Polyethylene	Poly(methylene)	Polyethylene	$-(\text{CH}_2\text{CH}_2)_n-$
Polypropylene	Poly(1-methylethane-1,2-diyl)	Polypropylene	$-(\text{CHCH}_2)_n-$   $\text{CH}_3$
Acrylic	Poly(1-cyanoethane)	Polyacrylonitrile	$-(\text{CHCH}_2)_n-$   $\text{CN}$
Polyester	Poly(oxyethane-1,2-diylxyterephthaloyl)	Poly(ethylene terephthalate)	$-(\text{O}(\text{CH}_2)_2\text{OOC}-\text{C}_6\text{H}_4-\text{CO})_n-$
Nylon 66	Poly(imino (1,6-dioxo-1,6-hexanediyl) imino-1,6-hexanediyl)	Poly(hexamethylene adipamide)	$-(\text{NH}(\text{CH}_2)_6\text{NHCO}(\text{CH}_2)_4\text{CO})_n-$
Nylon 6	Poly(imino(1-oxohexane)-1,6-diyl)	Poly( $\epsilon$ -caprolactam) or poly(6-aminocaproic acid)	$-(\text{NH}(\text{CH}_2)_5\text{CO})_n-$

**Figure 1.9** Idealised molecular mass distribution.

the latter parameter being a measure of the number of monomeric units in the polymer chain molecule. Rather than molar mass, the term *molecular weight* is often (inaccurately) used to describe the size of a polymer molecule, this being the dimensionless *relative molar mass*,  $M_r$  (aka *relative molecular mass*; *molecular weight* [177] or *RMM*), of a uniform polymer molecule (aka *monodisperse polymer*<sup>16</sup> or polymer composed of molecules of the same mass), which is the mass of the molecule relative to that of  $^{12}\text{C}$ . To convert the dimensionless quantity,  $M_r$ , to molar mass,  $M$ , which is the mass of 1 mole of the polymer (unit:  $\text{g mol}^{-1}$ ),  $M_r$  is multiplied by the unified *atomic mass unit*,<sup>17</sup>  $u$ , or *dalton*<sup>18</sup> (symbol  $\text{Da}$ ), the latter parameter often being used as a unit for the molar mass of a polymer. However, since polymers usually comprise molecules that are non-uniform with respect to their molar mass (i.e. they are *non-uniform polymers* or *polydisperse polymers*) and contain molecular chains of varying lengths, their molar mass is related to their degree of polymerisation. Thus, linear and branched polymers (with the exception of some naturally occurring polymers) consist of molecules with a *molar mass distribution*, as illustrated by the idealised, simple molecular mass distribution in Figure 1.9.

Such a distribution can be described in terms of several averages, the two most commonly employed being the *number average*,  $\bar{M}_n$ , and the *mass average* (aka *weight average*),  $\bar{M}_w$ , Eqs. 1.1 and 1.2, where  $N_i$  is the number of molecules of molar mass  $M_i$  and  $\sum$  denotes summation over  $i$  molecules.<sup>19</sup> As  $\bar{M}_w$  is influenced by the relatively smaller number of large molecules,  $\bar{M}_w > \bar{M}_n$ .

<sup>16</sup> IUPAC no longer recommends the use of the terms *monodisperse polymer* or *polydisperse polymer* [180].

<sup>17</sup> atomic mass unit, AMU, is equal to 1/12 the mass of one atom of  $^{12}\text{C}$  ( $=1.6606 \times 10^{-27}$  kg).

<sup>18</sup> 1 Da =  $1 \text{ g mol}^{-1}$ , although strictly it is a unit of molecular mass (i.e. 1 Da =  $1.660538782(83) \times 10^{-27}$  kg).

<sup>19</sup>  $\bar{M}_v$ , and the *z-average*,  $\bar{M}_z$ , are less widely used.

$$\bar{M}_n = \frac{\sum N_i M_i}{\sum N_i} \quad (1.1)$$

$$\bar{M}_w = \frac{\sum N_i (M_i)^2}{\sum N_i M_i} \quad (1.2)$$

The ratio of the two average molar masses, which depends on the breadth of the molar mass distribution, is referred to as the dimensionless parameter, *molar mass dispersity*,<sup>20</sup>  $\mathcal{D}_M$  ( $\mathcal{D}_M = \bar{M}_w / \bar{M}_n$ ). The term *dispersity* describes the dispersions of distributions of molar masses as well as of relative molecular masses or of molecular weights [180]. For a uniform polymer,  $\mathcal{D} = 1$ , whereas, in practice,  $\mathcal{D} > 1$  for most polymers. Values of  $\mathcal{D}$  vary according to the type of polymerisation reaction used, as exemplified by *condensation*  $\sim 2$ , *free-radical addition* 1.5–10 and *network polymers* 2– $\infty$  [181]. Usually, polymers are characterised using  $\bar{M}_n$  together with reference to dispersity. For example, polymers used in the manufacture of PES and PA fibres typically display a narrow molar mass distribution ( $\mathcal{D} = 2$ ) and their  $\bar{M}_w$  is usually  $< 50\,000$  whilst that of polymers used in PAN fibres range between 90 000 and 140 000, with  $\mathcal{D}$  ranging from 1.5 to 3 [182]. Various methods can be employed to determine the average molar mass distribution of polymers, such as light scattering, colligative properties, chemical analysis, sedimentation and viscometry (e.g. [170, 181, 183, 184]).

#### 1.2.4.4 Polymerisation

*Polymerisation* (aka *polymerization*) describes the process by which a monomer mixture is converted into a polymer [177] (e.g. [163, 170, 171, 185, 186]). Depending on the *polymerisation mechanism* involved there are two types of reaction by which monomers can be converted into polymers, namely *step-growth* and *chain-growth*. Confusingly, the terms *step* and *chain* are often used interchangeably with the terms *condensation* and *addition*, respectively, since polymers often are classified as being either *condensation polymers* or *addition polymers* based on the *type of polymerisation* reaction involved. However, not all condensation polymers are produced using step polymerisation and not all addition polymers are produced using chain polymerisation processes. In *step-growth polymerisation* (aka *step polymerisation*), bifunctional (or multifunctional) monomers react initially to form a *dimer* molecule (monomer + monomer), then *trimer* (monomer + dimer), *tetramer* (dimer + dimer; monomer + trimer) or larger *oligomer*<sup>21</sup> molecule and, ultimately, a polymer molecule. In step polymerisation, the reactions involved can occur between any of the variously sized species (monomer, dimer, trimer, etc.) that are present in the reaction system. In contrast, *chain-growth polymerisation* (aka *chain polymerisation*) occurs by a monomer molecule adding to a reactive centre (free radical, anion or cation) present within a growing polymer. Monomer molecules, one at a time, add only onto the reactive centre via a *chain reaction*, the addition of each monomer propagating the reactive centre; monomers, dimers, trimers, etc. do not react with each other.

The *degree of polymerisation*, *DP* (which is synonymous with *chain length*), is a measure of the number of monomer units in a polymer (or oligomer) molecule, which, in the case of a homopolymer comprising only one type of monomer, is given by either the *number average degree of polymerisation*,  $X_n$ , Eq. 1.3, where  $M_n$  is the *number average molar mass* of the polymer or the *weight average degree of polymerisation*,  $X_w$ , Eq. 1.4, where  $M_w$  is the *weight average molar mass* of the polymer and, in both cases,  $M_0$  is the molar mass of the monomer.

$$X_n = \frac{\bar{M}_n}{M_0} \quad (1.3)$$

$$X_w = \frac{\bar{M}_w}{M_0} \quad (1.4)$$

For example, the DP of cellulose varies depending on its source. In the case of undegraded cotton, the DP may be  $> 20\,000$  *D*-glucopyranose monomers corresponding to an  $M_r$  of 3 240 000 Da [187]. The DP of native cellulose may be as high as 14 000 but this may be reduced to 1000–2000 by alkali-based purification processes [188]. The previously mentioned term *dispersity* also describes the dispersions of distributions of degrees of polymerisation,  $\mathcal{D}_X$  ( $\mathcal{D}_X = \bar{X}_w / \bar{X}_n$ ) [180].

<sup>20</sup> the term *dispersity* replaces the much used term *polydispersity index*.

<sup>21</sup> an oligomer is a molecule of low molar mass that comprises a low number of monomer molecules (at least two); e.g. dimer = 2 monomer molecules; trimer = 3 monomer molecules, etc.

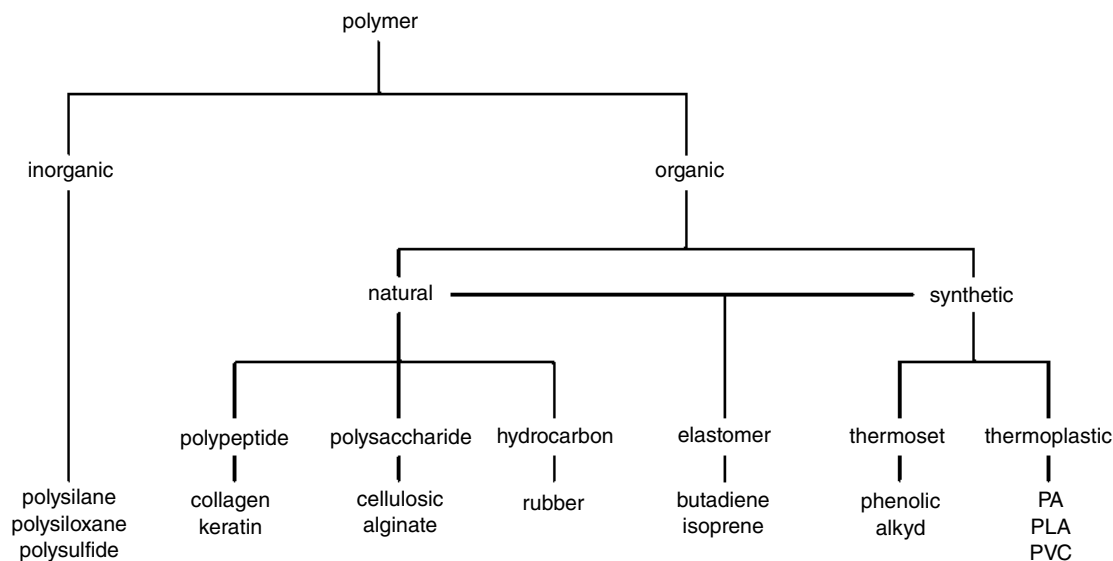


Figure 1.10 Classification of polymers.

### 1.2.4.5 Classification

Polymers can be classified in many ways, for instance, according to origin (e.g. natural, synthetic), structure (e.g. linear, branched, network), thermal behaviour (e.g. thermoplastic, thermoset, elastomer), polymerisation mechanism (step-growth and chain-growth), type of polymerisation reaction (condensation or addition), type of linkage (e.g. polyamide, polyester, etc.) and, of relevance to the nature of the polymers used in textile fibres, according to their long-range order (crystalline, amorphous or semi-crystalline nature). Whilst there is no agreed method for classifying polymers, the scheme depicted in Figure 1.10 seems apposite.

## 1.2.5 Textile Fibre Morphology and Fine Structure

In the context of textile fibres, the term *morphology* refers to various characteristic properties, such as cross-sectional shape, fineness, lustre, colour and length which are apparent visually, including those observable using either optical or electron microscopy (SEM or TEM<sup>22</sup>). The term *fine structure* is widely used to describe the three-dimensional arrangement of the composite molecular chains within a polymer and also the interactions between individual polymer chains and aggregates that comprise several polymer chains. As such, *fibre fine structure* concerns the nature and relative extent of *order* within the macromolecule and the effects which this has on both the physical and chemical properties of the fibre. Thus, fine structure considerations involve the concepts of *crystallinity* and *orientation*, as well as several other related characteristics that derive from the three-dimensional arrangement of the polymer chains in textile fibres.

The structural features of textile fibres and those of the polymers from which they are derived (i.e. natural, man-made and synthetic polymers) have been the subject of substantial research interest over many decades. However, despite such attention, which continues to the present time, the precise nature of the structure of both fibres and polymers has not been fully resolved, a situation that seems unlikely to change in the foreseeable future. Since this book concerns textile fibres and, therefore, the polymers that are used for such materials, structural aspects of textile fibres will now be considered.

As mentioned, a wide range of different textile fibres is available, from high volume commodity materials, such as cotton and PES to low volume variants, exemplified by the high-performance aramids and HM-HT fibres. The majority of fibres, in particular those that enjoy widespread usage, can, in essence, be considered to be assemblages of *semi-crystalline, partially oriented, linear polymers*,<sup>23</sup> although some fibres fall outside these somewhat rudimentary structures, as exemplified by glass which is completely amorphous. In essence, all organic textile fibres consist of two physical regions namely one that displays a high degree of *order* which often is referred to as *crystalline* material and

<sup>22</sup> SEM, scanning electron microscopy; TEM, transmission electron microscopy.

<sup>23</sup> linear polymers fall into two main classes: *homochain polymers* (containing only C atoms in the main chain) normally prepared using addition or chain-reaction polymerisation (e.g. PE) and *heterochain polymers* (containing atoms other than C in the main chain) typically prepared using polycondensation or step-reaction polymerisation (e.g. PA).



one that exhibits a low degree of order which is commonly referred to as *non-crystalline* or *amorphous* material.<sup>24</sup> The relative extents of these two materials (which often are referred to as *regions* or *domains*) vary for different fibres and, for a given fibre type, the extent of the crystalline and amorphous domains often varies as a function of the particular production conditions used (filament extrusion, drawing, etc.). Although several models have been proposed to describe the structural arrangement of semi-crystalline (i.e. partially ordered) fibres (and polymers), the precise nature of the fine structure of textile fibres is not fully understood. This section presents an overview of fibre fine structure; IUPAC recently published definitions relating to crystalline polymers [189].

### 1.2.5.1 Orientation, Order and Crystallinity

Orientation, order and crystallinity are three different but interrelated facets of fibre structure.

**1.2.5.1.1 Orientation** All textile fibres are *anisotropic*<sup>25</sup> which is reflected in anisotropy in such as their mechanical and optical properties, such characteristic directional dependency being a consequence of *orientation*. However, the term *orientation* refers to two aspects of textile structure: *fibre orientation* (the parallelism of the component fibres to the longitudinal (fibre) axis) and *molecular orientation* (the parallelism of the constituent polymer chains to the fibre axis). In the case of man-made and synthetic fibres, orientation is introduced during processing operations (e.g. spinning and drawing). Some fibres, such as PPTA (aka *Kevlar*) and HPPE or HMPE fibres are very highly oriented materials that enjoy specialised applications.

*Fibre Orientation* In the context of the orientation of the fibrous assembly (i.e. the parallelism of the component fibres with respect to the fibre axis), the spinning processes employed in both the formation of yarns from staple natural and man-made fibres (via sequential thinning and twisting steps) as well as the spinning (i.e. melt-spinning, wet-spinning, dry-spinning, dispersion-spinning or gel-spinning) of man-made and synthetic fibres (via both extrusion and drawing) result in the fibres being oriented parallel to the fibre axis. The orientation of fibres within a fibrous assembly has a major effect upon the geometrical and mechanical properties of the fibre as well as its liquid-permeability and liquid-absorption characteristics. For example, fluid permeability is greater and a fibre is both stronger and stiffer in the direction of fibre orientation. In the case of regenerated fibres, the degree of orientation depends on the extent of stretching imparted during spinning, often this being reflected by the *orientation factor*, as determined from birefringence measurements.

*Molecular Orientation* The component polymer chains in general purpose fibres are oriented more or less parallel to the fibre axis. Although such molecular orientation is an inherent, fixed characteristic for natural fibres that is determined during growth, as exemplified by the helical structure of cotton, in the case of man-made and synthetic fibres, the extent of molecular orientation is determined by the production conditions used (extrusion, drawing, etc.). In the latter context, within an extruded, undrawn man-made fibre, both the crystalline and non-crystalline regions have little orientation. Subsequent drawing (i.e. stretching) orientates the polymer chains, and, therefore the crystalline and amorphous material also, along the fibre axis, with the result that in drawn, man-made and synthetic fibres, the polymer chains usually lie mostly parallel to the fibre axis. For both extruded amorphous and semi-crystalline, as spun-fibres, as represented by, for example, PAN and PA fibres respectively, crystallinity is likely to be developed post-extrusion (e.g. during wind-up or drawing), the level of orientation being determined by the particular conditions employed (temperature, rate of drawing, etc.). In the case of synthetic fibres in particular, *crystal orientation* (i.e. the orientation of the polymer crystals within the fibre) can occur during spinning (e.g. melt spinning of PA fibres) or subsequent drawing [190]. Molecular orientation is of major significance to all textile fibres. In the case of man-made fibres in particular, if molecular orientation is not fully developed during fibre production, the ensuing materials will be weak, and undergo excessive stretch in response to small applied loads and display poor recovery from deformation. The extent of molecular orientation can be described mathematically, using a formalism that employs order parameters [191].

Both *molecular orientation* (the polymer chains are oriented along the fibre axis) and *fibre orientation* (i.e. the fibres are oriented along the longitudinal (fibre) axis) contribute to the high anisotropy of fibres and that of many of their properties. The mechanical properties of fibres are influenced by the degree of orientation insofar as, in general, increasing orientation lowers extensibility but increases strength. Many industrial textiles are highly oriented and several theoretical models have been developed to relate fibre mechanical properties to orientation (e.g. [192]). The degree of orientation can be determined using several techniques such as X-ray diffraction, dichroism, IR spectrometry and birefringence.

<sup>24</sup> it is unclear as to whether the ordered regions in PAN fibres constitute a crystalline phase.

<sup>25</sup> they display different behaviour in different directions.

**1.2.5.1.2 Order** Order, from the viewpoint of textile fibre structure, relates to the lateral, longitudinal and directional correlation of adjacent polymer chains (i.e. the arrangement of the composite molecular chains in three-dimensional space). *Short-range order* concerns nearby chains whereas *long-range order* extends over long molecular distances.

The degree of molecular orientation in fibres is far from perfect and varies for different types of fibre. In the case of general textile fibres, the long, linear polymer molecules pass through regions of high *order* as well as regions of low order. The degree of order ranges from regions in which the chains are closely aligned and tightly packed, corresponding to *crystalline* regions, to those in which the chains are less tightly packed and aligned, which are referred to as *amorphous* regions. In practice, the degree of order in a fibre lies somewhere between the perfect order of a crystal lattice and the perfect disorder of an amorphous polymer such as glass.

**1.2.5.1.3 Crystallinity** *Crystallinity* is defined as *the presence of three-dimensional order on the level of atomic dimensions* [193]. In essence, a crystal comprises a three-dimensional, regular, repeating array in which the repeat unit is defined in terms of the crystal *unit cell* and the repeat pattern is described in terms of the *crystal lattice*. The crystal unit cell describes the spatial arrangement of atoms within a given type of crystal and is defined in terms of the cell's *lattice parameters* (*cell edge length*, denoted  $a$ ,  $b$ ,  $c$  and the *angles between these* which are denoted  $\alpha$ ,  $\beta$  and  $\gamma$ ).<sup>26</sup> When packed together, unit cells describe the bulk arrangement of atoms within a crystal. Unit cells vary in their symmetry and seven different 3D *crystal systems* or types of unit cell are distinguished, namely *cubic*, *tetragonal*, *monoclinic*, *orthorhombic*, *trigonal*, *hexagonal* and *triclinic*, which can stack together to provide 14 different *Bravais*<sup>27</sup> *lattice systems* (*cubic*: simple, body-centred, face-centred; *tetragonal*: simple, body-centred; *monoclinic*: simple, end-centred; *orthorhombic*: simple, body-centred, face-centred, end-centred; *rhombohedral*; *hexagonal* and *triclinic*).<sup>28</sup> A *paracrystalline* lattice arises from variations in unit cell dimensions whilst disturbances in the crystal lattice result in *crystal defects*.

In a crystalline polymer, the lateral, longitudinal and directional correlation of adjacent polymer chains (i.e. order) extends over long distances, resulting in a regular structure. However, whilst small molecules such as NaCl can be obtained in complete three-dimensional order in the form of crystals wherein the component atoms or molecules are arranged in a precise, ordered manner that extends in all three spatial dimensions, larger molecules, such as the polymers of organic origin that constitute fibres, are obtained as semi-crystalline materials that comprise mixtures of crystalline material that displays a high degree of order as well as amorphous material that shows a low degree of order. In a completely amorphous material there is no lateral, longitudinal or directional correlation of adjacent polymer chains and the constituent atoms and molecules are randomly arranged.<sup>29</sup> The main feature that determines whether or not a polymer will crystallise is chain regularity. Even the most crystalline polymer will often possess lattice defects that contain non-crystalline material and, therefore, crystalline polymers usually possess some level of irregularity and, therefore some amount of amorphous material. Partial crystallinity, which is manifest in many polymers, arises from a particular stereoregular arrangement of the composite macromolecules. If the chain repeat unit is simple and regular then crystallinity will be highly developed (e.g. PE) whereas in the case of, for example, PP in which the repeat units are complex and contain (bulky) side groups, crystallisation will occur only when the side groups are positioned in a *tactic* arrangement.<sup>30</sup>

The crystalline domains in fibrous polymers, which often are referred to as *crystallites*, differ characteristically to those displayed by small molar mass crystalline solids (e.g. NaCl) which tend to be hard and brittle insofar semi-crystalline fibres (e.g. PA) tend to be soft and easily deformed, often even at low temperatures. Indeed, the crystallinity in polymers such as those that form the basis of textile fibres differs to that displayed by many other crystalline materials insofar as both crystalline and amorphous regions are present in the same polymer, the size of the crystalline domains being very small (~10 nm) in at least one dimension whilst the level of imperfection within the crystalline regions can be quite large [196].

In the case of natural fibres such as wool and silk, the relative extents of crystalline and amorphous regions are an intrinsic feature of the growth conditions employed, whereas for both man-made and synthetic fibres, the nature of both the crystalline and amorphous domains vary, widely, for different types of polymer and, for a given type of fibre (e.g. PES, PA), vary as a function of the particular production conditions employed, especially both the thermal and mechanical profiles involved.

The mechanism of crystallisation in semi-crystalline polymers has received considerable attention and lies outside the scope of this account. For example, [163 and 196–203] provide general accounts including a recent review of the use of indentation hardness as a means of studying the kinetics of crystallisation from the glassy state [204]). The nature of

<sup>26</sup> for example, the unit cell of PET is triclinic, with  $a = 0.456$  nm,  $b = 0.594$  nm,  $c = 1.075$  nm,  $\alpha = 98.5$ ,  $\beta = 118$  and  $\gamma = 112$  [194].

<sup>27</sup> named after the French crystallographer, Auguste Bravais, who derived the 14 lattice modes, e.g. [195].

<sup>28</sup> the term *trigonal* refers to a *crystal system* and not to a *lattice system*: rhombohedral crystals belong to the trigonal crystal system but some crystals can belong to either the rhombohedral or hexagonal lattice systems.

<sup>29</sup> such a completely amorphous material can be described as being *isotropic*.

<sup>30</sup> the substituent groups are attached to the same side of the polymer chain.

the crystallisation process in semi-crystalline polymers such as those used in PES and PA fibres is complex and, despite studies over several decades, is not yet completely understood. In essence, when a polymer such as PA 6 is allowed to cool from the melt in an unoriented state, crystallites develop in the form of thin, flat lamellae in which polymer chains fold back and forth (Section 1.2.5.1.3). The crystallites are dispersed within an essentially randomly oriented (isotropic) amorphous phase, though a small fraction of the amorphous phase will possess some level of orientation in the direction of extrusion. Depending on the crystallisation conditions, especially in the case of polymers crystallised from the melt, spherulites (Section 1.2.5.2) may form that comprise stacks of densely packed parallel lamellae, the stacks being randomly oriented. At the surface of the crystallites, polymer chain folding and chain reentering occurs, creating loops within the amorphous phase that lie between the lamellar crystallites. Chains also may pass through the amorphous region linking one lamellae to another; short chains (aka *cilia*) as well as long chains that are not incorporated within the crystalline domains may also be present in the amorphous phase. The structural components of the ensuing semi-crystalline structure range in size from ones to tens of nanometre (individual lamellar crystal), sub-micron (lamellar stacks) and micrometre to centimetre (spherulites) [205]. When the oriented material is drawn, as in fibre production, the chains in the oriented amorphous fraction are preferentially oriented, and, subsequently, both less oriented and randomly oriented chains of the amorphous phase unfold and merge with the oriented amorphous region [206]. Lamellae and crystallites also are oriented in the direction of drawing which may result in crystallinity being further developed. As discussed later, drawn fibres such as PA 6 are thought to comprise a fibrillar structure in which aggregates of crystallites are linked by means of *tie molecules* within the amorphous regions.

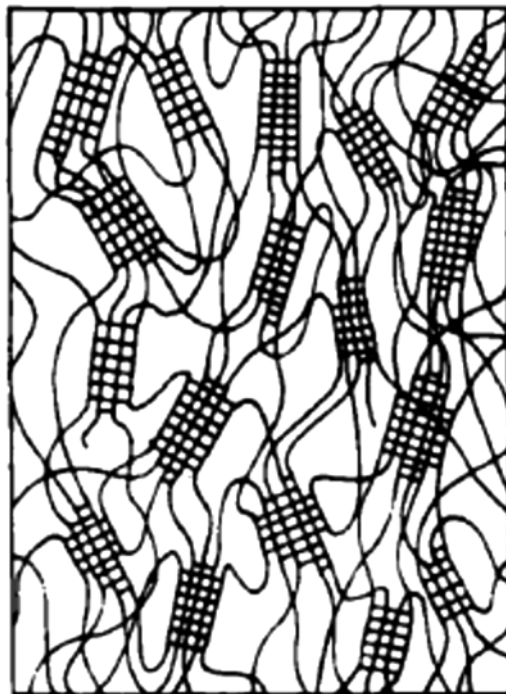
The extent of crystallinity in fibres, expressed as percent by mass or volume, can be determined using both physical and chemical methods, such as density, X-ray diffraction, thermal analysis, IR spectroscopy,  $^{13}\text{C}$  NMR or water sorption. By way of example, reported values for the crystallinity of fibres, which will vary according to the method of determination employed and the precise nature of the fibres examined, range from upto 85–95% in the case of aramids [207], ~70% for flax [208], ~60% [26]<sup>31</sup> to 70% [210] for cotton, 60% for CLY [211], 40% for CV [26], 38% for HWM CV [210] ~65% for silk (B. mori) [212], ~50% for PA [209, 213], 50–65% for PP [145], 25% for CTA and 16% for CA [214] whilst values of 60–80% are given for isotactic PE [215]; some HM-HT fibres can have degrees of crystallinity approaching 100% [216]. The degree of crystallinity varies markedly with temperature, as exemplified by that of PA 66, which decreases from ~75% at 20°C to ~40% at 100°C and 0% at 120°C [26]. In the case of fibres derived from cellulose, the *crystallinity index*, *CI*, is sometimes used to describe the relative amount of crystalline material present (e.g. [217]). The dimensions of crystals in polymers are not uniform but instead adopt a distribution that depends on the conditions employed for crystallisation. Rates of crystallisation vary for different polymers: for example, the rate of crystallisation of PA 66 > PA 6 and that of poly(1,4-butylene terephthalate) (PBT) > PES [216]. Indeed, the low propensity of PES to crystallise at room temperature results in *as-spun yarns* produced at low spin speeds being amorphous. Although such fibres possess molecular orientation, crystallinity is imparted only by subsequent drawing (at draw ratios of 1.5–6 [218]). High spin speeds impart stress-induced crystallisation, resulting in crystalline as-spun yarn which can display 50% crystallinity [219].

### 1.2.5.2 Models of Fibre Structure

Although several models have been proposed to describe what often is referred to as the *fine structure* of textile fibres, and both drawn and undrawn polymers in general, no single interpretation of fibre structure is applicable to the broad range of available fibre types. Current views of fibre fine structure are, in effect, collations of information secured from experimental evidence obtained using various analytical techniques over many decades (e.g. microscopy: optical, electron, atomic force; spectrometry: IR, NMR; diffraction: optical, X-ray, electron; thermal analysis; physical: density, moisture sorption), as no single technique can provide an unequivocal description of fibre structure ([220] reviews the structural models and analytical methods used in relation to drawn polymers). Furthermore, the models that are employed to describe the fine structure of fibrous polymers (i.e. textiles), some of which are discussed below, are also used to describe the morphology of non-fibrous polymers. However, confusingly, different names and terms are sometimes used by textile and polymer researchers for the same structural model and its components.

The use of X-ray diffraction to study the crystallinity of polymers stems from the 1920s when natural polymers such as cellulose and its derivatives as well as other natural polymers were first examined. The use of X-ray diffraction for determining polymer crystallinity has persisted to the present day; a succinct account of the historical aspects of crystallinity determination in polymers is available [196]. Each of the various polymer/fibre structure models, which first appeared in the 1930s, are, in effect, attempts to portray the structural regularity of partially ordered polymers and fibres, often using graphical representations (see [221]). As described below, the first widely used model focussed on the existence of two distinct physical regions within the fibre, namely crystalline and amorphous

<sup>31</sup> a crystalline : amorphous region ratio of 2 : 1 is suggested from X-ray diffraction analysis [209].



**Figure 1.11** Fringed micelle model of semi-crystalline polymers. Reproduced from [237], with permission from John Wiley & Sons, Inc.

phases.<sup>32</sup> Subsequent advances in polymer structure, notably the discoveries of spherulites and polymer chain folding, resulted in this model being modified and the development of other two-phase models as well as three-phase structural models. In contrast, several investigators view fibre structure as a continuous phase rather than comprising separate ordered and disordered phases.

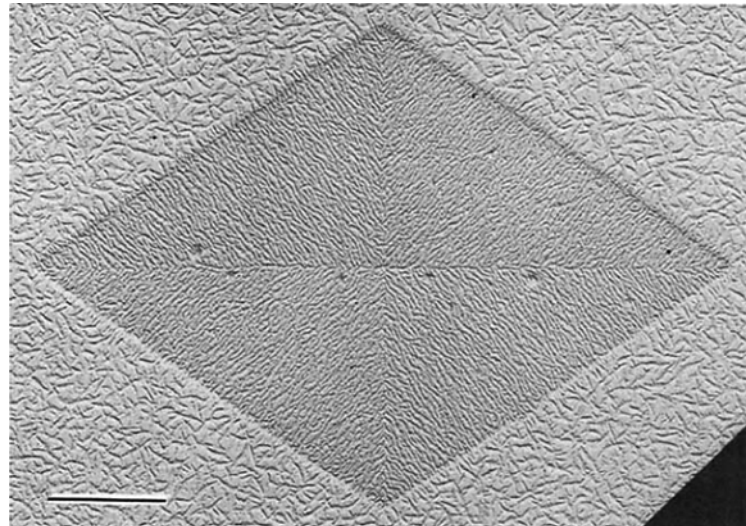
The following is intended as a guide to this somewhat convoluted but nonetheless interesting subject. In the contexts of fibre and polymer structure, the reader is directed to detailed accounts (e.g. [25, 162, 163, 183, 197, 198, 209, 220, 222–229]). Current ideas of fine structure are articulated within each of the six chapters that discuss the dyeing of the main types of fibre (i.e. Chapters 7, 8, 9, 10, 11 and 12).

**1.2.5.2.1 Two-Phase Models** During the early part of the twentieth century, experimental results obtained from investigations of the natural and man-made polymers and textile fibres available, using the then recently introduced technique of X-ray diffraction as well as mechanical properties and sorption phenomena, were interpreted in terms of a two-phase model in which crystalline *micelles* were embedded within an amorphous matrix, the *micellar concept* of Nageli [230] having its origins in the nineteenth century.<sup>33</sup> X-ray diffraction analysis of fibrous materials [231, 232], such as those for cellulose that were first reported [233, 234], revealed sharp diffraction patterns, indicative of three-dimensional order exhibited by simple, low molar mass crystalline solids; however, these discrete reflections were also accompanied by diffuse scattering that was indicative of disordered (amorphous) material. This duality of fibre X-ray diffractograms was interpreted as indicating that fibres were semi-crystalline in nature, as they contained two physical domains namely one that displayed a high degree of *order* (crystalline regions) and one that showed low degrees of order (amorphous regions).

The first widely used model that sought to explain the wide-angle X-ray scattering (WAXS) patterns that provided evidence of both crystalline and amorphous regions in semi-crystalline polymers was the *fringed micelle model*, originally suggested for gelatin in 1930 [223, 235, 236] (Figure 1.11), of which several variants were proposed up to the 1950s [225]. In essence, according to this model, which has been used to describe the fine structure of many different types of polymer (see [238] and the references therein), the crystalline regions are envisaged as being embedded within the disordered, amorphous medium, which, together comprise the semi-crystalline polymeric structure. Polymers/fibres are considered to comprise randomly arranged, entangled polymer chains amongst which regions exist in which

<sup>32</sup> in this context, the terms 'crystalline' and 'amorphous' stem from von Laue's discovery of the diffraction of X-rays by crystals (for which he was awarded the Nobel Prize for Physics in 1914) and the pioneering X-ray crystallography of WH Bragg and his son, WL Bragg, for which they were jointly awarded the Noble Prize for Physics in 1915 (WL Bragg was the youngest ever Nobel Laureate).

<sup>33</sup> the Swiss botanist Nägeli used the term 'micelle' to describe material extracted from starch, cellulose and proteins that comprised sub-microscopic crystalline particles embedded in a matrix of inter-micellar material.



**Figure 1.12** Decorated (Decoration is the name of a technique used in SEM to enhance the resolution of solid surfaces) single crystal of a PE fraction ( $M_w = 20000$ ;  $M_w/M_n = 1.1$ ) grown from a dilute solution ( $\sim 0.1\%$ ) of a mixture of tetrachloroethylene and *p*-xylene (scale bar =  $1\ \mu\text{m}$ ). Reproduced from [244], with permission from John Wiley & Sons, Inc.

neighbouring polymer chains aggregate and form crystalline *micelles*, some  $0.005\ \mu\text{m}$  wide and  $\sim 0.05\ \mu\text{m}$  thick. The micelles are arranged more or less randomly throughout the structure and a polymer molecule *fringes* (meanders) in and out of these micelles (Figure 1.11). The *fringes* are the regions of the polymer chains that travel from the crystalline region to the surrounding amorphous region, each polymer chain passing alternately through the crystalline micelles and amorphous regions. The crystalline micelles in effect act as physical crosslinks within the fibre.

Although the fringed micellar model interpreted the earlier experimental results obtained and explained many of the characteristic properties of fibres, during the 1950s, advances in both textile and polymer physics, namely the discovery of *spherulites* (spherical aggregates), *polymer chain folding* and the observation of fine *fibrils*,  $\leq 0.01\ \mu\text{m}$  wide and of apparent infinite length in both natural and man-made fibres, provided evidence that was inconsistent with the fringed micelle concept [239, 240]; thus, alternative views of fibre structure were developed.

**Chain Folding** In 1957, single crystals of synthetic polymers were isolated for the first time grown from solution, [241–243]<sup>34</sup> as exemplified by crystals of PE obtained from dilute ( $\sim 0.01\%$ ) *p*-xylene solution. The observations<sup>35</sup> that, in these thin, lamellar (flat, plate-like) single crystals ( $0.01\text{--}0.02\ \mu\text{m}$  ( $10\text{--}20\ \text{nm}$ ) thick and  $\sim 10\text{--}20\ \mu\text{m}$  wide and long;  $\sim 40\text{--}80$  PE repeat units) (Figure 1.12), the PE chain axis was approximately perpendicular to the crystal basal plane (i.e. the chain axis lays across the thickness of the lamellae), whereas the molecules of PE are typically  $1\ \mu\text{m}$  ( $1000\ \text{nm}$ ) long, meant that then the PE molecules must *fold* within the crystal (Figure 1.13) [163, 222, 223, 226, 241–243, 246, 247].

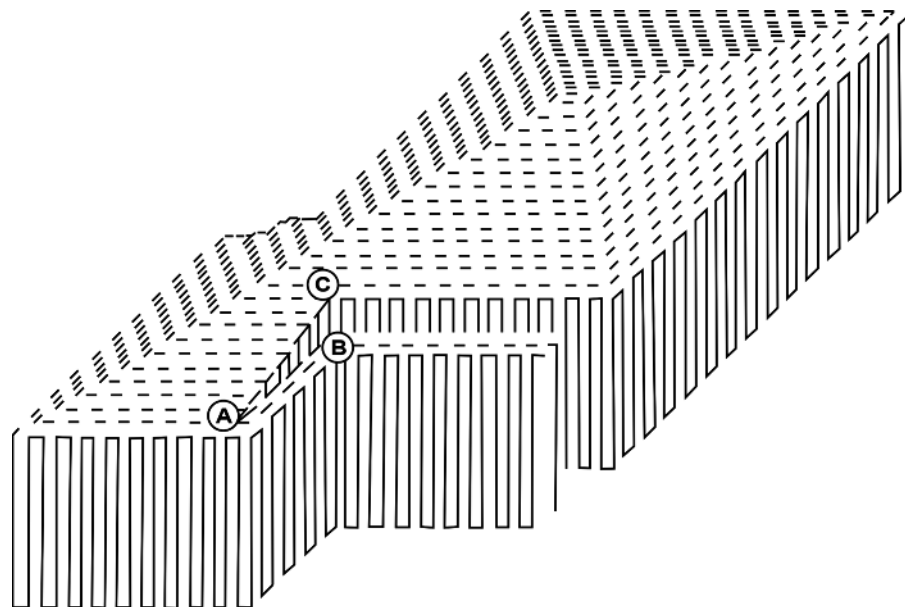
Thus, in such chain folding, a single polymer chain will pass through the same crystal many times by folding regularly on the crystal base (Figure 1.13) such crystals being referred to as *chain-folded lamellar crystals*. In Figure 1.13, the straight lines represent straight segments of molecules connected top and bottom by crystal folds; the diagram is drawn to a scale such that the straight segments of the molecules (the thickness of the lamellae) is  $\sim 100\ \text{\AA}$  [245]. The pyramidal shape of the single PE crystals (Figures 1.12 and 1.13) arises from small vertical displacements imparted by *chain folding* (the chain axis is tilted at  $\sim 30^\circ$  w.r.t. the normal of the lamella); similar displacements are found in many types of crystal (corrugations are often observed produced by the collapse of the single crystal).

During the late 1950s and early 1960s, the structure of single crystals grown from solution was reported for a wide range of polymers [196, 222, 248, 249]. Lamellar structures and chain folding have been observed for many polymers and various crystal shapes reported for the single crystals of different materials obtained from both dilute solution and the melt [248–253], such as flat ribbon (PEST), lozenge (PA 6) and irregular hexagonal platelet tending to flat ribbon (PA 66). The concept of polymer chain folding, which is commonly attributed to the isolation of single crystals in 1957 [222, 241], although the first report of chain folding was made by Storks [254] in a 1938 electron diffraction study of thin films of gutta-percha<sup>36</sup> formed by evaporation from chloroform, is now a well-known aspect of polymer and fibre

<sup>34</sup> interestingly, this was reported independently by the three individual researchers.

<sup>35</sup> made notably using the, then newly introduced, technique of Transmission Electron Microscopy (TEM).

<sup>36</sup> a natural rubber trans-polyisoprene.



**Figure 1.13** Schematic of a re-entrant face of a pyramidal PE crystal. The molecule grows at A, with new growth occurring on AB to provide a new fold surface; the exposed old growth face ABC may generate spiral growth. Reproduced from [245], with permission from John Wiley & Sons, Inc.

crystallisation and structure.<sup>37</sup> Indeed, a lamellar crystal is nowadays accepted as being the fundamental structural form by which most partially ordered polymers generally crystallise both from solution and melt. Crystallisation from the melt (e.g. [196]) is more complicated than that from solution and several conformation models have been proposed to describe chain folding in polymer crystals, as exemplified by the *Erstarrungsmodell* (*solidification model*) [255], *random re-entry* or *switchboard* model [246, 256], *adjacent re-entry* model [257] and *variable-cluster* model [258].

In the case of cellulosic fibres, the question as to whether polymer chain-folding occurs is unresolved. As discussed in Chapter 7, whilst the parallel arrangement of the cellulose chains in cellulose I (e.g. cotton) is inconsistent with chain-folding, the fact that the anti-parallel arrangement in cellulose II (e.g. regenerated cellulosic fibres) is compatible with chain folding continues to be the subject of research interest.

**Spherulites** In 1945, it was shown that crystallites are not randomly arranged but, rather, form regular structures which have circular symmetry. A common structural component in materials crystallised from the melt is the *spherulite* or *spherical aggregate of crystals*<sup>38</sup> that comprise radiating arrays of periodic lamellar stacks (Figure 1.14).

Spherulites were first observed by Bunn and Alcock [259] and have a variety of shapes (as described in the excellent review paper by Magill [260]) depending on both chemical (e.g. structure and molar mass) and physical properties (e.g. crystallisation conditions and crystal lattice). Spherulites comprise both crystalline and amorphous domains, their size ranging from a few to hundreds of microns. Spherulites grow outwards, radially, in three-dimensions from a nucleus, their shape and size depending on the particular nucleation process involved, which often is heterogeneous (via the presence of foreign particles), before impinging on neighbouring spherulites and forming polyhedra. The spherical, optical symmetry of spherulites [261] results in two unique refractive indices (tangential,  $\eta_t$ , and radial,  $\eta_r$ ) which permit their optical characterisation using polarised light (i.e. spherulites give a characteristic Maltese cross pattern when viewed under polarised light; Figure 1.15).

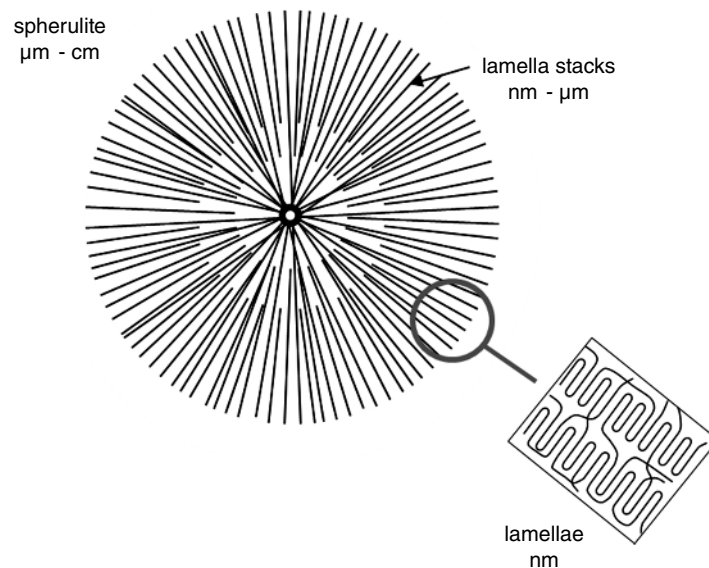
Negatively birefringent spherulites are most commonly observed in polymers, positive birefringent spherulites being less common and non-birefringent examples being rare [260]. Although optical microscopy was originally used to observe spherulitic morphology, more recently *Atomic Force Microscopy*<sup>39</sup> (*AFM*) has been used to study lamellar and spherulitic morphology [264, 265]. The growth of spherulites occurs by the formation of *fibrils* that spread outwards, in bundles, from the nucleus into the amorphous material, branching to form a spherical pattern.

To take into account such developments in polymer analysis, a *modified fringed micelle* structure was proposed [237, 266] (Figure 1.16a), which incorporated chain folding and fringing into *tie-molecules* at the edge of each micelle. In the latter context, several researchers consider that a single polymer chain located within one crystalline lamella can

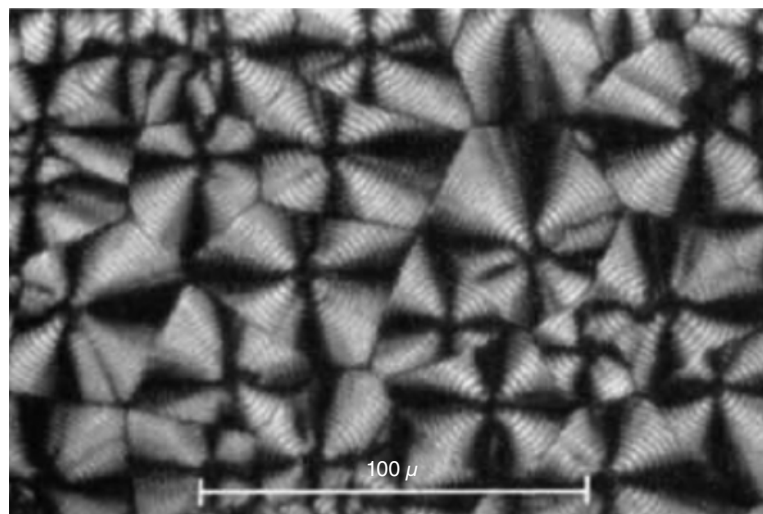
<sup>37</sup> see Wunderlich for a thorough account [222].

<sup>38</sup> spherulites occur in various materials (e.g. volcanic rocks, metals) and their study dates back to the C19th.

<sup>39</sup> a powerful technique for submicron investigation of polymer surface properties [263].



**Figure 1.14** Idealised distribution of lamellae and lamellae stacks in spherulite.



**Figure 1.15** Linear PE cast on glass. Reproduced from [262], with permission from John Wiley & Sons, Inc.

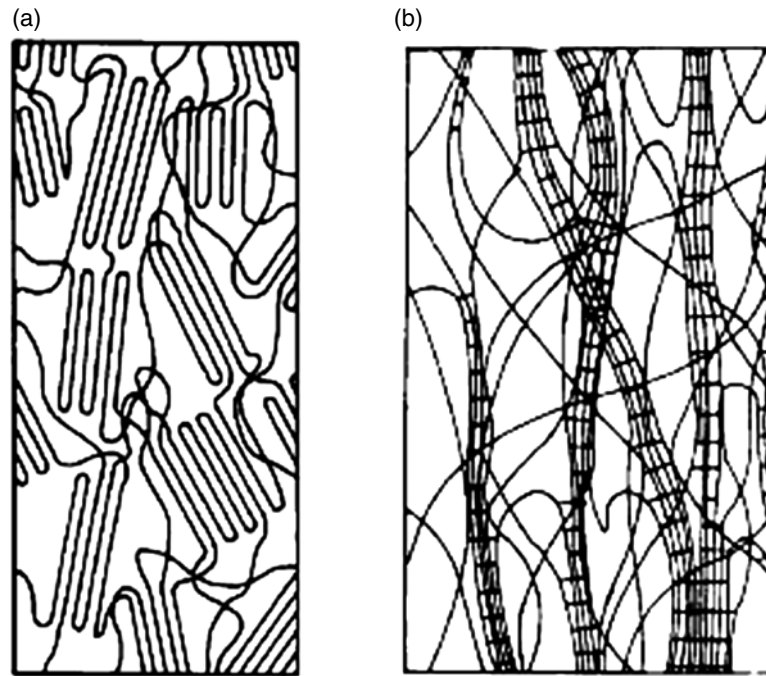
extend across the amorphous region to join another lamella; as such, *tie molecules* can connect different lamellae [267–269]. Models of this type are considered to offer the best working model for fibres such as PA and PES [228, 270]. The *fringed fibril* model (Figure 1.16b) [221, 271, 272] took into account experimental evidence [273] of the presence of long fibrils<sup>40</sup> in some fibres. According to this model, fibrils are long crystals composed of relatively short segments of polymer chain bundles. A given polymer is considered to pass alternately through several such crystalline fibrils and also through the surrounding non-crystalline regions (i.e. fibrils are the crystalline sections of a continuous system of polymer chains). This fringed fibrillar model is considered as the most appropriate for most regenerated cellulosic fibres [274]; it describes the observed properties of regular CV fibres, with crystalline micelles being linked via tie-molecules in amorphous regions [275], though the fringed micelle model can also apply [116].

Models that depict a two-phase, pseudo-fibrillar assembly of crystallites that comprise folded polymer molecules at their ends and which are linked by means of tie molecules within the amorphous regions are considered to explain the behaviour of many fibre types, as exemplified by PA (e.g. Figure 1.17).

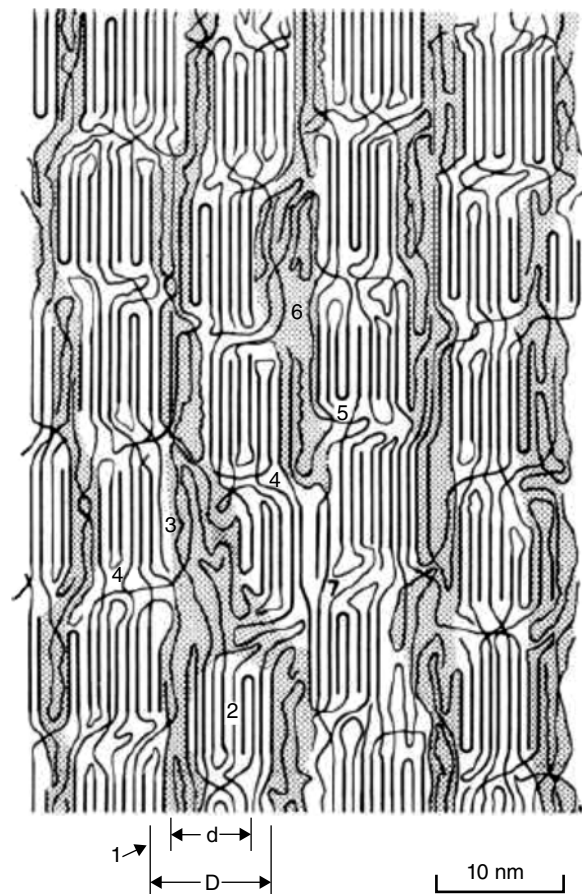
In the case of drawn PP fibres, it is believed that *microfibrils*<sup>41</sup> comprise alternating units of folded-chain crystals and amorphous regions that are mainly chain folds. Tie molecules located on the microfibril surfaces extend through

<sup>40</sup> although the word *fibril* has several meanings from a textile viewpoint, in the context of the current discussion, the following definition applies: *structural sub-units of fibres, formed from bundles of linear polymer molecules in crystalline or semi-crystalline organisation* [11].

<sup>41</sup> the term 'microfibril' is also (unhelpfully) often abbreviated to 'fibril' in the context of fibre fine structure.



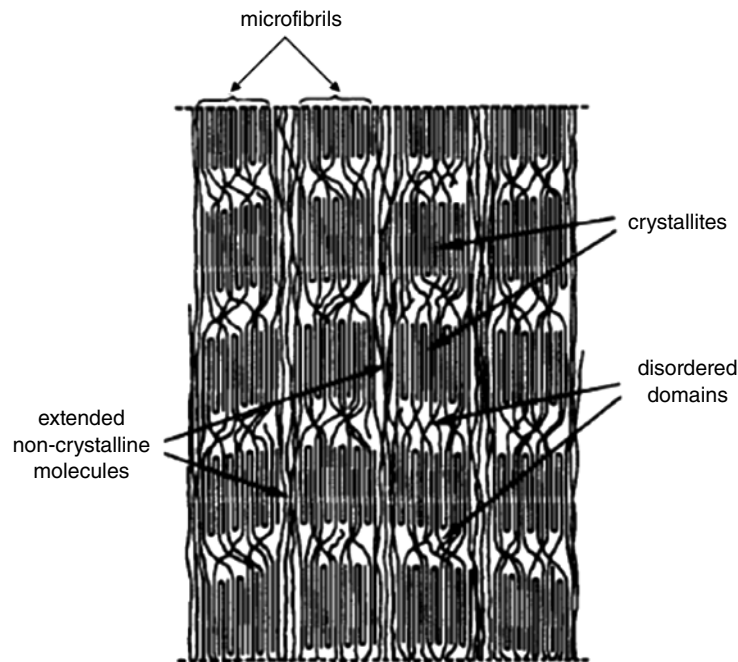
**Figure 1.16** Fringed fibril model. Reproduced from [237], with permission from John Wiley & Sons, Inc.



**Figure 1.17** Structure of PA 6 fibre to interpret WAXS and WAXD data. Reproduced from [269], with permission from John Wiley & Sons, Inc.

the amorphous regions along several crystal units [145]. Peterlin [276] and Prevorsek *et al.* [277] both conclude that the strongest element of fibre structure is the microfibril. In the case of PA 6 and PES fibres, the interfibrillar domains consist of extended, as opposed to folded, chain molecules [277]. A two-phase model proposed for PAN fibres





**Figure 1.18** Structural model of PA 6. Reproduced from [277], with kind permission from Springer Science and Business Media. (Figure 3 on page 2313 of reference [277].)

considers that fibrillar sub-units contain amorphous and laterally bonded crystalline phases, the latter having a lamellar texture oriented at right angles to the long fibre axis [151]. Whilst both single- and two-phase models have been proposed for PAN fibres, the latter is considered the most likely, although the two phases are likely to display much lower differences in order compared to conventional melt-spun fibres [151]. The fine structure of wool [278] consists of cortical cells that are composed of crystalline *macrofibrils* of 0.1–0.3  $\mu\text{m}$  width, which comprise 500–800 microfibrils ( $\sim 0.007 \mu\text{m}$  diameter [209]; also known as *Keratin Intermediate Filaments* or *KIFs*) that make up  $\sim 40\%$  of the fibre [209], embedded within a matrix of *Keratin-Associated Proteins* (*KAPs*). Regenerated fibres are considered [279] to possess a two-phase structure that is independent of the transformational production and fibre-forming processes, in which elementary fibrils comprise a succession of crystallites and intermediate less-ordered amorphous regions, with tie molecules connecting laterally adjacent amorphous regions.

**1.2.5.2.2 Three-Phase Model** Several authors consider that a *three-phase microfibrillar model* (aka *Swiss cheese fibre model*) best describes the fine structure of PA fibres (e.g. [280–282]). In this model, which was proposed for PA 6 fibres but is considered applicable to both PA 66 and PES fibres [277, 281] (Figure 1.18), the fibre consists of three types of domain namely *crystallites*, *amorphous domains* and *interfibrillar matter* (aka *fibre matrix*) that differ in terms of density and order. The fibre is seen to comprise microfibrils that contain both crystalline and amorphous regions dispersed within a dense matrix. The density and degree of order of the intermicrofibrillar domains (i.e. the fibre matrix) is greater than that of the amorphous regions of the microfibril but is lower than that of the crystalline regions [281]. Intrafibrillar tie molecules are distributed more or less uniformly over the cross section of the microfibrils and the fibre matrix comprises interfibrillar amorphous tie molecules [282]. The three-phase model has been used to explain the multiple thermal transitions observed for some polymers [238]. The two types of amorphous domain within both PES and PA 6 fibres are those which connect two adjacent crystallites as well as extended chain<sup>42</sup> amorphous domains that represent the extended tie molecules proposed by Peterlin [283].

However, Prevorsek and Bukosek [282] consider that whilst the three-phase model is applicable to high-tenacity PA 6 fibres, it does not apply to aliphatic PA 6 fibres produced using standard melt spun processing. Clearly, the issue of the fine structure of melt spun polymers such as PA 6 is not resolved.

**1.2.5.2.3 Continuous Models** Although the above two-phase and three-phase models of fibre structure interpret the crystalline and amorphous regions as being clearly differentiated, several workers have sought to interrogate this concept of well-defined crystalline and non-crystalline regions. In 1932, Staudinger [284] considered that a high molar

<sup>42</sup> the term *extended* means the opposite of *folded*.

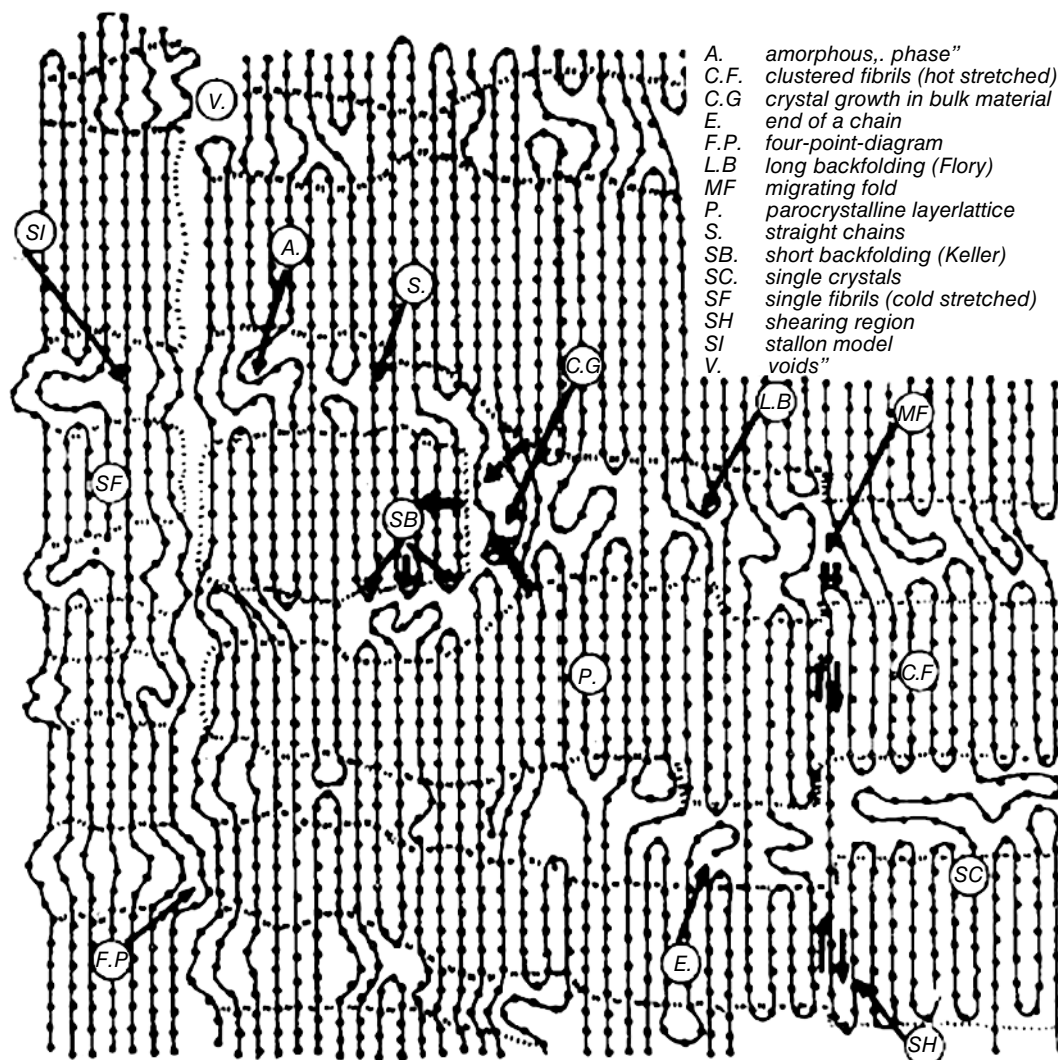


Figure 1.19 Paracrystalline model of stretched PE. Reproduced from [289], with permission from Elsevier.

mass polymer would form a large, continuous, imperfect crystal in which end-groups would provide local imperfections; other researchers at the time favoured such a continuous structure model [285, 286].

Kargin proposed that in the case of some fibre types, crystallinity need not necessarily exist insofar as order could arise from the mutual alignment of polymer molecules within an essentially amorphous system [287]. Reneker [288] proposed in the case of PE that disorder may result from crystal defects occurring at various points within the crystal. In the 1960s, Hosemann proposed the concept of *paracrystalline structure*<sup>43</sup> in polymers [289, 290] (Figure 1.19), according to which, small, random disturbances of the crystal lattice result in local distortions, caused by irregularities in chain conformation and imperfect polymer geometry, which impart a loss of long-range order but do not effect short-range order. In effect, structure can range from perfect crystals, through paracrystalline to amorphous. As such, paracrystallinity enables order and disorder to coexist but without recourse to distinct phases. In the latter context, the paracrystalline nature of several natural and synthetic fibres as well as polymers have been examined [291].

Although the fine structure of cotton has been the subject of considerable investigation and speculation, and aspects still remain unresolved, the fibre is considered to comprise thin, crystalline *macrofibrils* that consist of bundles of *microfibrils* which, in turn, are made up of *elementary fibrils* of smaller width. Although cotton is considered as being essentially 100% crystalline, experimental studies (e.g. water sorption, fibre density and X-ray diffraction) reveal the presence of approximately one-third disordered material [275] which can be attributed to imperfect packing of microfibrils and crystal defects [209, 292, 293]. The precise nature of the microfibrils remains a matter of debate insofar as the presence of light and dark regions along the length of microfibrils as revealed by X-ray diffraction has been interpreted as implying that the microfibril comprises a continuous crystalline structure whereas an alternative view is that it suggests the presence of crystalline and amorphous regions, respectively [294].

<sup>43</sup> a paracrystalline material has short/medium range order but lacks long-range order.

**1.2.5.2.4 Unified Parametric Approach** As mentioned, none of the above models of fibre structure is applicable to the broad range of available textile fibres. It has been suggested that fibre structure can be described in terms of six quantitative parameters that characterise differences between the structure of the various fibres [209, 237, 295] namely *degree of order, degree of localisation of order, length/width ratio of localised units, degree of orientation, size of localised units and molecular extent*.

**1.2.5.2.5 Summary** It is apparent that the precise fine structure of textile fibres has not been fully resolved and it seems unlikely that this situation will change in the near future. It is generally considered that fibre structure is more complicated than suggested by the various models and, since different fibres have different structures, different models are likely to provide the most realistic representation of structure [209]. Fibres may display characteristics from several models [225, 295]; for example, the structure of PA and PES fibres likely takes the form of a modified fringed micelle which comprises crystalline regions that display folding and fringing from their ends, arranged in a pseudofibrillar array and which are linked by tie molecules [209, 275]. A fringed micelle model may be appropriate in the case of the cellulose II crystal variant in regenerated fibres such as regular CV [228] and CLY fibres [296, 297].

As mentioned, within each of the six chapters that discuss the dyeing of the main types of fibre (i.e. Chapters 7, 8, 9, 10, 11 and 12), current views of fibre fine structure are discussed.

## 1.3 General Physical and Mechanical Characteristics of Textile Fibres

The following account provides a brief introduction to some of the general physical and mechanical characteristics of textile fibres of relevance to aqueous dyeing and which, it is hoped, might help explain some of the terms and definitions that often are encountered in the published literature concerning dyeing theory.

Fibres that are used for textiles have several common characteristics, noteworthy examples being *fineness, flexibility, high surface area : mass ratio and high strength*. Fibres are also *flexible*, reasonably *uniform* in shape and size and also display *adequate mechanical, chemical and thermal stabilities*; however, they are seldom homogenous and are not isotropic. The following account is far from inclusive and more detailed and extensive discussions are available (e.g. [89, 111, 209, 298–306]).

### 1.3.1 Length

Natural fibres are of finite, usually short in length (staple fibre), such as cotton (~1.2–3.8 cm) or merino wool (~6–7.5 cm), the exception being silk, which is obtained as continuous filament some  $15 \times 10^4$  cm long [307]. Man-made fibres are produced as continuous (infinite length) filaments, either as monofilament yarns or more commonly, as multifilament yarns, although often continuous filament fibres are cut to a particular staple length; durable crimps, loops, coils, etc. can be imparted to continuous filament yarns by *texturing*. Indeed, yarns produced from staple fibres are softer, bulkier and warmer than are yarns comprising untextured or *flat* continuous filaments. Whilst the shortest textile fibres are ~1 cm in length, the majority of staple fibres are ~2–50 cm long. Yarn strength is related to fibre length insofar as longer fibres enable a greater number of contact points between individual fibres thereby resulting in greater frictional forces between the component fibres; fibres <12 mm in length are generally unsuitable for spinning [308].

### 1.3.2 Fineness

*Fibre fineness*<sup>44</sup> is one of the most important fibre attributes not only because it is a commonly used indicator of fibre quality but also because it influences several other fibre characteristics, such as specific surface area, stiffness, handle, torsional rigidity, fibre cohesion, yarn uniformity, capillary wetting and wicking. Fineness stems from fibres being long and thin, which is characterised by a high *aspect ratio* (length : diameter ratio of at least 100 : 1 and commonly  $\geq 1000$  : 1 and up to 10 000 : 1; e.g. wool: 3000; cotton: 1500 [309]) that is intrinsically related to high specific surface area.

Although fibre diameter might appear to be a convenient way to express fibre fineness, this is not the case, as textile fibres are rarely homogenous, often are of non-circular and irregular cross-section and, in many cases, their width is not

<sup>44</sup>in the United States, *fibre size*.

uniform along their length. Fineness is therefore determined either by measuring the mass of a known length of fibre or by measuring the length of a known mass of fibre. Two systems are used:

- (1) A *direct system* in which fineness is expressed in terms of *mass per standard length of fibre* via the *average linear density* (generic name *titre*). A standard length is used, measured in either metre or yards.<sup>45</sup> The SI unit for linear density is the *tex* (g/1000 m; symbol  $T_t$ ) [310], although the related *dtex* (g/10 000 m) is more commonly used as this is close to the value of the older *denier* unit (g/9000 m; symbol  $T_d$ ) (1 dtex = denier  $\times$  1.1111); 1 dtex = 0.1 tex.
- (2) An *indirect system* that expresses fineness in terms of the *count* of a yarn (aka *yarn count*; *yarn number*) which is a measure of the *length of fibre per standard mass* (i.e. is the reciprocal of mass per unit length). The particular standard length used depends on the manufacturing route employed to produce the yarn; for example, the English *cotton count* (symbol: either *c.c.* or  $Ne_c$ ) is the number of 840 yd lengths of yarn in 1 lb and the *woollen (American cut) count* (symbol: either *w/c* or  $Na_c$ ) is the number of 300 yd lengths of yarn in 1 lb.

Conversion factors are available to convert various count systems relative to tex [11, 311].

Yarns are often characterised in terms of their fineness, as exemplified by *super fine* 2–7.5 tex; *fine* 7.5–16 tex; *medium/coarse* 16–40 tex; *coarse* >45 tex [5]. Fineness has long been used as a way of grading natural fibres, as exemplified by both the wool [312, 313] and cotton [314] count systems wherein the higher the count, the finer is the fibre (e.g. *wool count system* – merino wool: 80s–100s<sup>46</sup>; coarse wool: <44 s; *cotton count system* – medium/average cotton yarn: 50s–150s; coarse cotton yarn: <50s). For natural animal fibres (e.g. wool and mohair), fineness is also expressed as *mean fibre diameter* (e.g. merino: 17–25  $\mu\text{m}$ ; Romney: 33–37  $\mu\text{m}$ ). Fibre diameter is also used as a grading system for wool fibres in which the parameter is related to wool yarn count [312, 313] (e.g. 80s  $\approx$  17.7–19.14  $\mu\text{m}$ ; coarser than 36 s  $\approx$  >40.2  $\mu\text{m}$ ); tex is related to cotton count in another grading system (e.g. 30 count  $\approx$  25 to 15+ tex) [314].

$$D = 20 \left( \frac{\text{dtex}}{\pi\rho} \right)^{0.5} \quad (1.5)$$

The relationship between fibre diameter and linear density is given by Eq. 1.5, assuming a circular fibre cross-section, where  $D$  is diameter ( $\mu\text{m}$ ) and  $\rho$  density ( $\text{g cm}^{-3}$ ). Figure 1.20 shows the diameters of different types of fibre of various linear densities (assuming a circular fibre cross-section). In the case of regular textile fibres, fibre fineness ranges from ~1 to 30 dtex, corresponding to diameters of up to ~60  $\mu\text{m}$ .

The fineness of multifilament man-made fibre yarns is often denoted in terms of *dtex per filament*, *dtexpf*, which is the decitex of the yarn divided by the number of filaments within that yarn. For example, 78f68, in which the number 78 refers to the yarn dtex and the number 68 refers to the number of filaments within that yarn; hence each component filament within this particular yarn is of 1.15 dtex. Coarse yarns often are produced by twisting together one or more yarns,<sup>47</sup> the fineness of the ensuing *plied* or *folded* yarns being the sum of the component yarns (e.g. one 30 dtex and one 20 dtex yarn will produce a 50 dtex folded yarn). A *doubled yarn* is obtained when yarns of the same count are combined (e.g. a 50 dtex yarn comprising two 25 dtex yarns), the resulting yarn being denoted 50/2 dtex (in the case of an indirect system, such as the cotton count, two single, say 50s yarns plied together are designated 50s/2).

### 1.3.2.1 Microfibres

A microfibre is a man-made fibre (typically CV, CLY, CMD, PES, PA or PAN<sup>48</sup>) of very low linear density [315]. This somewhat vague description reflects the fact that, as yet, there is no internationally agreed definition of the term microfibre, insofar as, the fineness range of microfibres is not precisely defined. Generally, such fibres are of 0.3–1 dtex (<10  $\mu\text{m}$  diameter) [315], although finer fibres in the range 0.1–0.3 dtex are available which are referred to as *super microfibre* or *ultrafine microfibre* [314] as well as yet finer, *nanofibres*, which vary in diameter from 1 nm (0.001  $\mu\text{m}$ ) to ~100 nm (0.1  $\mu\text{m}$ ), as exemplified by a PA 46 nanofibre of 0.0016  $\mu\text{m}$  ( $\approx 2.4 \times 10^{-8}$  dtex) [316].

An appreciation of the fineness of both micro- and nanofibres compared to that of some common types of fibre is presented in Figure 1.23<sup>49</sup>; Figure 1.21 provides examples of dtexpf ranges for PES yarns. Detailed reviews of microfibres are available [315, 318].

<sup>45</sup> a standard length in yards is referred to as a *hank* or *skein*.

<sup>46</sup> the notation to express count is the number of hanks followed by an 's', e.g. 10s, 80s, etc.

<sup>47</sup> by a process referred to as plying, folding or twisting, the twist imparted during plying being opposite to that of the component yarns.

<sup>48</sup> PES is by far the most dominant of fibre types used for microfibre.

<sup>49</sup> the diameter of human hair varies from ~45 to 110  $\mu\text{m}$  [317].

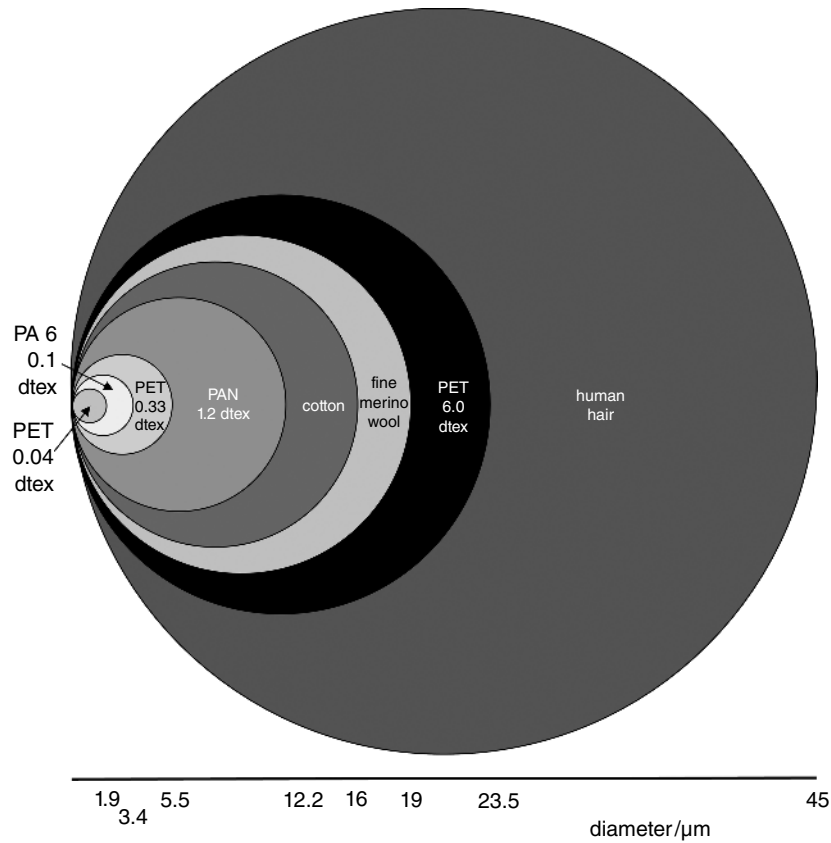


Figure 1.20 Representation of fineness of different fibres assuming round cross section.

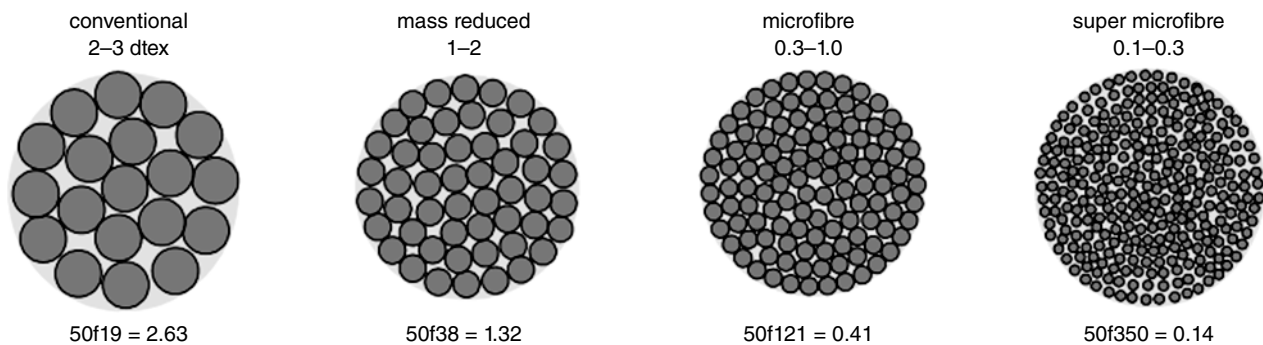


Figure 1.21 Examples of dtexpf range for PES yarns.

Although fibres of very low linear density were spun in the 1950s and 1960s, these were not commercialised for use as microfibre. In the mid 1960s, *bicomponent spinning* technology was developed for the production of microfibre which, in 1970 [319, 320], resulted in the introduction of *artificial suede*, a non-woven, composite fabric comprising PES microfibres within a PU base.<sup>50</sup> Microfibres are produced as either continuous filament using *direct spinning* and also *conjugate spinning*, or as staple microfibre produced using several types of spinning process. Microfibres are produced as both fully drawn and partially oriented yarn; the yarn can also be texturised. Of the three main types of polymer used in microfibre production (PES, PA and PAN), PES predominates.

**1.3.2.1.1 Direct Spinning** Direct spinning is akin to the ‘conventional’ spinning of the appropriate man-made and synthetic fibres (e.g. melt: PA, PES; wet: PAN). It produces a single-component microfibre (e.g. 0.1 dtex PET [319]) and is also the simpler of the two production methods and does not necessitate subsequent splitting/dissolution processes to separate the two components.

<sup>50</sup>as exemplified by the commercial product *Alcantara* ([www.alcantara.com](http://www.alcantara.com)) which comprises 60% PES (typically 0.1 dtex; 0.4 μm) and 40% PU [321].

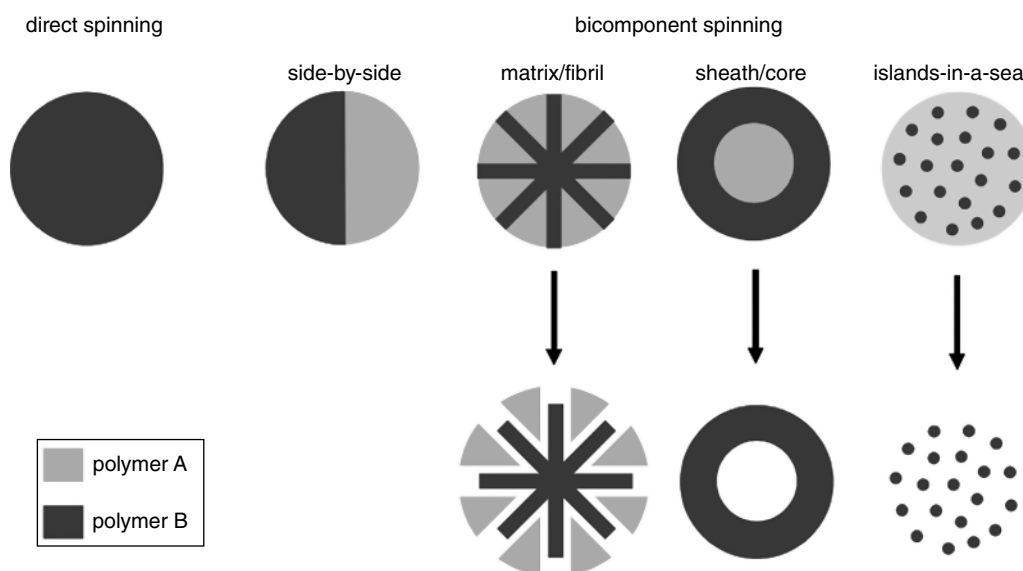
**1.3.2.1.2 Bicomponent Spinning** Essentially, in bicomponent spinning, two or more strongly adherable but separable polymers of different chemical constitution/physical properties are spun, either joined together or parallel to each other. A post-extrusion process (dissolution or splitting) is then used to separate the components. For example, in the case of PA and PES, the two molten polymers are brought together either before they enter the spinneret or within the spinneret, at which time they fuse together so that the ensuing single yarn filaments comprise at least two joined components; subsequent dissolution or splitting separates the two component polymers. There are four variants of the bicomponent spinning method [11] namely *side-by-side* (aka *conjugate*), which imparts a helical crimp to the fibre as a result of differential heat shrinkage of the component polymers, *islands-in-a-sea*, in which one component is dissolved subsequent to extrusion, *sheath-core* which can produce symmetrical or non-symmetrical filaments and/or crimp as well as *matrix-fibril* which comprise fibrils of one component polymer that are embedded within a matrix of another component polymer but which do not extend along the full length of the fibre (Figure 1.22).

**Dissolution Processes** These typically comprise an extruded bicomponent fibre from in which the *sea* or sheath (e.g. polystyrene, 2-ethylhexyl acrylate copolymer) is dissolved leaving the *islands* or core (e.g. PA, PET). In these dissolution methods, a single-component microfibre (e.g. 0.1 dtex PA) is produced.

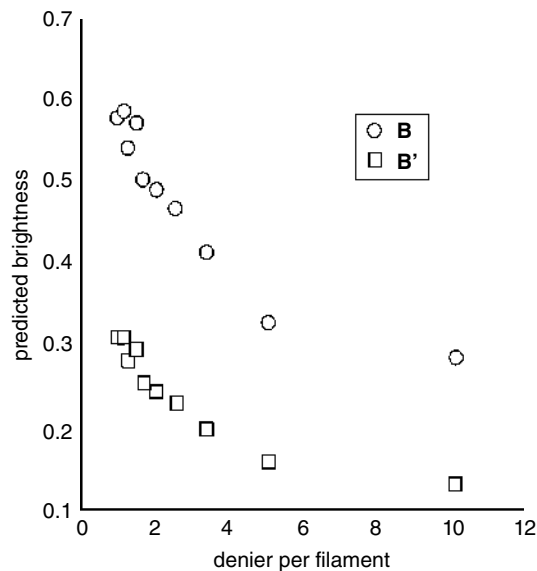
**Separation (Splitting) Processes** Splitting of the extruded bicomponent filament can be achieved mechanically, by the use of water or using solvents which shrink one of the components; for example, in a PA/PES bicomponent fibre, the PA is shrunk using benzyl alcohol. Splitting generates a multi-component fibre that contains two different types of polymer (e.g. PA and PES) which clearly has implications for subsequent processing (including dyeing). Hollow filaments can be produced by employing a core component that can be subsequently removed (e.g. by dissolution).

**1.3.2.1.3 Staple Microfibre Production** Several processes can be used to obtain staple microfibre [319] including *melt blowing* (aka *jet spinning*), *spun bonding*, *flash spinning*, *centrifugal spinning* and *polymer-blend spinning*, details of which are available (e.g. [26, 319, 322]).

**1.3.2.1.4 Characteristics of Microfibres** Fibre diameter effects several fibre characteristics. In essence, the smaller the diameter of a given fibre, assuming a circular cross-section, the greater, for example, will be its *aspect ratio* (length : diameter ratio), *flexibility* (*flexural rigidity* = stiffness  $\propto$  diameter<sup>4</sup>), *lustre*, *fineness* ( $\propto$  diameter<sup>2</sup>), *drapeability*, *surface area* ( $\propto$  diameter), *rate of water sorption*, *yarn packing density* and *yarn uniformity*. As a result, it is perhaps not surprising that microfibrils, employed either alone or in blends with coarser fibres (e.g. cotton and CV), enjoy extensive use in many apparel markets (e.g. functional sportswear and technical textiles) because of their greater comfort as well as superior aesthetic and tactile properties [315, 323]; in addition, microfibrils are widely employed in areas such as



**Figure 1.22** Comparison of direct and bicomponent spinning processes used in microfibre production.



**Figure 1.23** Predicted values of brightness (B, no dye present in filaments; B', dye present in filament). Reproduced from [324], with permission from SAGE.

filtration, domestic and industrial cleaning,<sup>51</sup> synthetic leather and medical applications. Microfibres are available with different cross-sectional area (solid or hollow), cross-sectional shape (e.g. *circular* or *profiled* – trilobal, angular, serrated, ribbon-like); bicomponent fibres (e.g. sheath-core) are also produced.

A corollary of the increase in specific surface area that attends a decrease in linear density is that the greater reflection of light from the finer fibre surface (Figure 1.23) results in more dye having to be applied in order to secure the same visual depth of shade as that of a dyed coarser fibre.

As a consequence of having to use greater amounts of dye on finer fibres, for dyeings of the same visual depth of shade, the wet fastness of dyed finer fibres will be lower than that of their dyed, coarser counterparts. The influence of linear density on colour strength and fastness was observed several decades prior to the introduction of microfibres (e.g. [325–327]). Indeed, as the path length of light within a dyed fibre decreases with decreasing diameter, Fothergill [328] proposed in 1944 that Eq. 1.6 could be used to predict the amount of dye,  $C$ , required to achieve the same visual depth of shade on two fabrics comprising similar fibres, 1 and 2, of differing dtex,  $t$ . However, the equation is provisional only, since the amount of dye required to achieve a given visual depth of shade will depend on other factors such as fibre cross-sectional shape and amount of delustrant.

$$C_2 = C_1 \left( \frac{t_1}{t_2} \right)^{0.5} \quad (1.6)$$

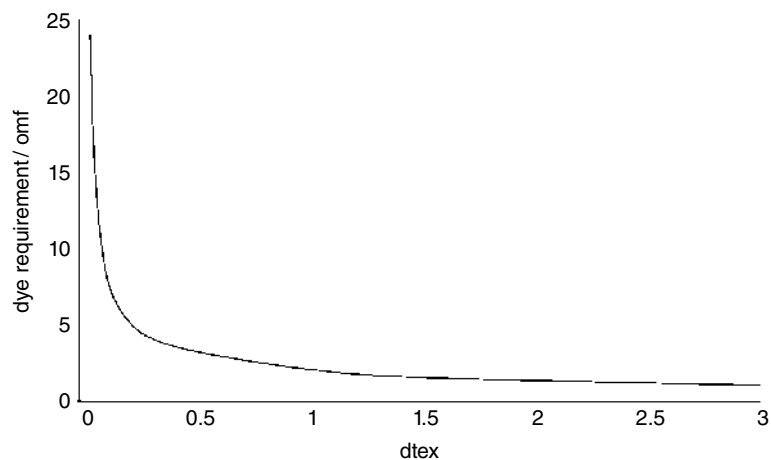
Nevertheless, by way of example, Eq. 1.6 shows that in order to obtain the same visual depth of shade on 0.3 dtex PES microfibre as that secured using 2% omf dye on 1.5 dtex conventional PES fibre, 4.47% omf dye would be required; to achieve the same depth of shade on 0.05 supermicrofibre suede would necessitate the use of 10.96% omf dye. The relationship between fibre fineness and dye requirement predicted by Eq. 1.6 is depicted graphically in Figure 1.24. Alternative approaches to that described by Eq. 1.6 have been proposed by other workers (e.g. [324, 329–331]; see [315, 332] and the references therein).

The greater surface area of microfibres also affects dyeability, this being reflected by microfibres exhibiting a faster rate and greater extent of dye uptake; these aspects are discussed in the chapters that describe the dyeing of PES, PAN and PA fibres.

### 1.3.2.2 Mass Reduced PES Fibres

Microfibre spinning technology was not the first commercial method for producing synthetic fibres of low linear density. In 1950, shortly after the commercial introduction of PES fibres, Waters [333] reported that the diameter of 2 denier (2.2 dtex) PES filaments was reduced by treatment with aq. KOH solution at 98°C, the first patent on the use of alkali to

<sup>51</sup> the cleaning ability of microfibre is essentially a combination of high surface area, high packing density and capillary action that results from the very small size of the segmented, often wedge-shaped filaments.



**Figure 1.24** Dye required as a function of dtex based on a 2% omf dyeing of a 1.5% dtex fibre.

reduce the mass (and linear density) appearing 2 years later [334]. Such *mass reduction* (aka *weight reduction*, *alkali dewighting*, *alkali treatment*) of PES relies on the ability of hot, aq. alkalis (commonly NaOH) to hydrolyse the polymer. In addition to reducing linear density, this topochemical treatment (i.e. it is confined to the surface of the fibres), which can be controlled by means of the temperature, duration, alkali concentration, catalyst and liquor ratio used [315, 335], also effects other fibre characteristics namely improved wettability, handle and softness. Whilst alkali treatment imparts mass losses of ~10–25% [315] and enables fibres of reduced linear density to be secured (e.g. conventional PES filament: 2–3 dtexpf; mass reduced PES filament: 1.2–1.6 dtexpf), the level of fineness achieved are not those provided by microfibre spinning technology. In response to a trend towards fabrics with silk-like handle [336], the alkali treatment of PES gained in popularity in Japan during the 1970s and remains an area of research interest (e.g. [337, 338]). Details of the treatment including mechanistic aspects and effects on fibre structure and properties are available (e.g. [315, 321, 335]).

### 1.3.2.3 *Shingosen*

In Japan during the 1960s, research efforts began to focus on mimicking silk fibres using PES fibres; during the 1970s efforts were also directed towards increasing the apparel use of PES continuous filament yarn. Whilst there is no precise definition of the word *shingosen*, which means literally *new synthetic fibres*, the term refers to a range of textile materials derived mainly from continuous filament PES that display novel fabric characteristics [336]; typically shingosen include the fineness range <0.3–2.0 dtex [339]. Although the term first appeared in 1987, the concept has its origins in the 1960s when the primary aim was to reproduce the lustre, drape and stiffness of silk. Shingosen<sup>52</sup> has continued to evolve and develop till the present day, utilising various innovative technologies, such as alkali mass reduction, air-jet entanglement, polymer modification, surface modification and microfibre spinning, in order to generate the current range of materials that display four types of characteristics, namely *super-soft* (peach skin), *super-bulky*, *worsted-like* and *super-drape* (dry touch) (e.g. [315, 336, 340]).

### 1.3.2.4 *Nanofibres*

Nanofibres [157, 341] of diameter ~0.001 to 0.1  $\mu\text{m}$  (1–100 nm) are commonly produced using *electrospinning*, in which polymers are either wet-spun or melt-spun in a strong electric field (e.g. [342–345]). Owing to their very small diameter, nanofibres display features related to their very high specific surface area such as high moisture absorption, as exemplified by a PA nanofibre of 44 dtex (composed of  $1.4 \times 10^6$  filaments) which has a surface area 1000 times greater than that of conventional PA fibres and displays moisture absorption 2–3 times greater than conventional PA fibres [157].

## 1.3.3 Twist

Spun yarn is obtained by combining individual fibres or filaments together often by means of twist, as a result of which, the fibres follow a helical path around the yarn axis. Twist is characterised in terms of *direction*, *level*, *angle* and *twist multiple*.

<sup>52</sup> The term shingosen is sometimes incorrectly assumed to mean ‘microfibre’ which is incorrect since not all shingosen comprise microfibre and not all microfibre is shingosen.



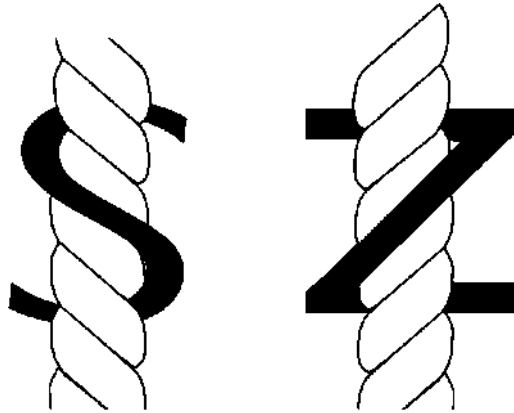


Figure 1.25 S-twist and Z-twist.

The *direction of yarn twist*, which depends on the transverse orientation of the fibres and is denoted by the letters *S* (counterclockwise spiral direction of twist: helices inclined left to right: \\\) and *Z* (clockwise spiral direction of twist: helices inclined right to left: //), affects the surface appearance of both knitted and woven fabrics (Figure 1.25). The angle of twist<sup>53</sup> describes that between the path of the yarn element and the yarn axis whilst the *level of twist* is measured in terms of twist per unit length (e.g. turns per meter or turns per inch) and affects both the density and strength of a yarn. *Twist multiple* relates twist level and fibre fineness/count being referred to as *twist factor*, *TF*, or *alpha metric*,  $\alpha_m$ , in the cases of imperial and metric units, respectively.

Both yarns and fabrics are highly porous structures that comprise solid fibre and air voids. Only 80% of a yarn is occupied by fibre [308] irrespective of the particular technical arrangement involved. The porosity of fabrics ranges from 50 to 95%, depending on fibre fineness, yarn twist, fabric construction, etc. [346]. Since for fibres of a given linear density, an increase in yarn twist increases yarn compactness, it follows that yarns of high twist level are more difficult to dye as the closely packed component fibres hinder both the removal of air from between the fibres and the penetration of aqueous dye solution to the yarn interior [308].

### 1.3.4 Fibre Specific Surface Area, $S_m$ or $S_v$

Whilst surface area is the total area of a solid (e.g. fibre), the specific surface area of a solid is either the *surface area per unit mass*,  $S_m$  (unit:  $\text{m}^2 \text{kg}^{-1}$ ), or the *surface area per volume*,  $S_v$  (unit:  $\text{m}^{-1}$  i.e.  $\text{m}^2 \text{m}^{-2}$ ).<sup>54</sup> According to Eq. 1.7 [309], where  $q$  is the *shape factor* (see Section 1.3.5), the finer the fibre (i.e. the lower the dtex) the greater is specific surface; also, for a given fineness (dtex), specific surface increases with increasing density of the fibre.

$$S_m = 2\sqrt{\pi} \left( \frac{1+q}{\sqrt{\rho \cdot \text{dtex}}} \right) \quad (1.7)$$

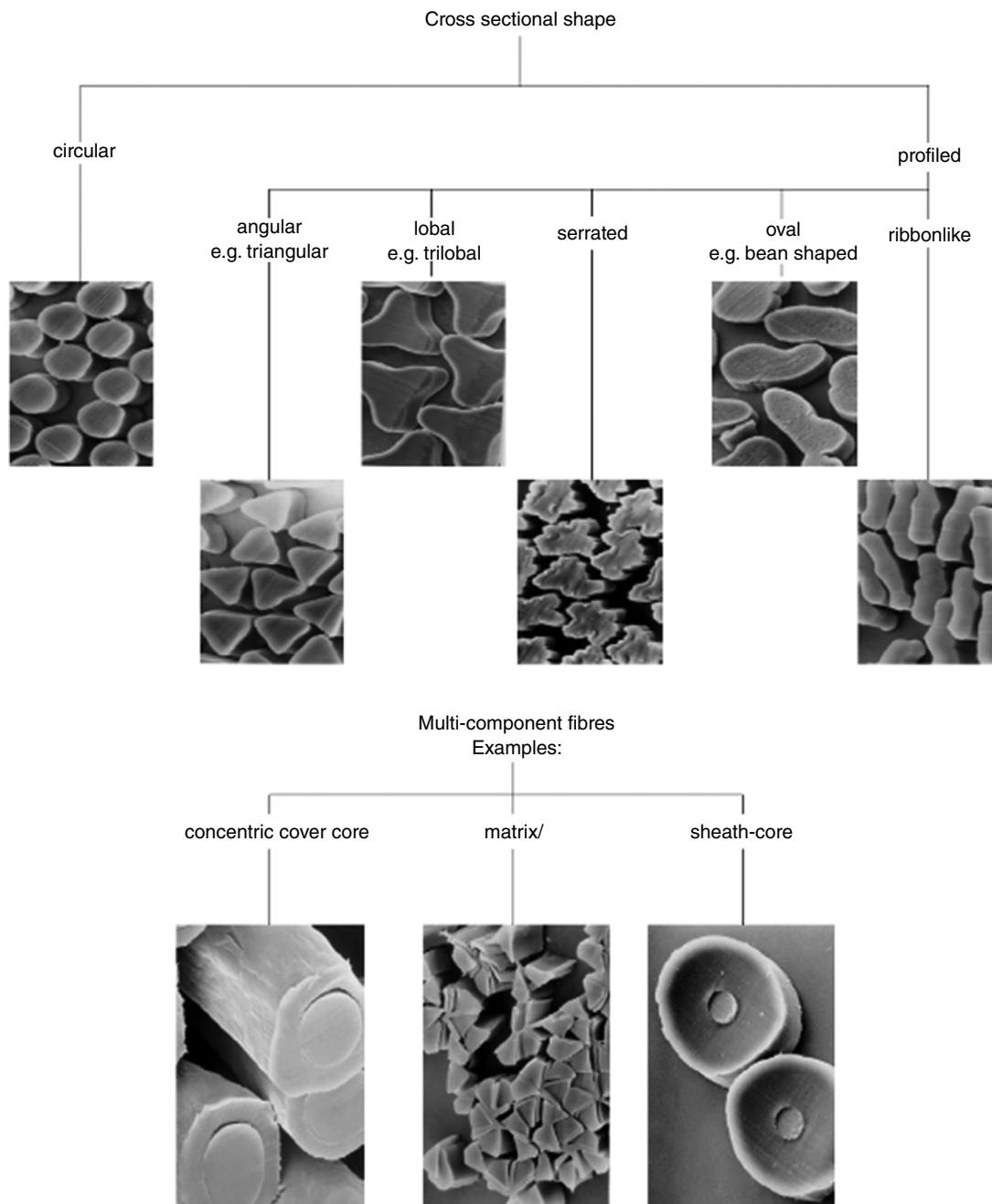
The densities of conventional textile fibres range from  $\sim 0.9$  (PP) to  $1.6$  (cotton)  $\text{g cm}^{-3}$  whilst those of some high modulus fibres vary from  $1.7$  to  $2.5$  (e.g. carbon fibre:  $1.8\text{--}2.0 \text{g cm}^{-3}$ ; E-glass fibre:  $2.55 \text{g cm}^{-3}$  [347]). The majority of fibres have densities greater than that of water ( $1 \text{g cm}^{-3}$ ). When fibres absorb water, their density often changes.

### 1.3.5 Cross-Sectional Shape

In the case of natural fibres, fibre cross-sectional shape is determined during growth, and a variety of cross-sectional shapes are represented, as exemplified by dogbone or flat ribbon (cotton), circular or elliptical (wool), triangular (silk) and polygonal (flax). Man-made and synthetic fibres that are spun from either the molten or solution states are produced with different cross-sectional area (solid or hollow), cross-sectional shape including *circular* or *profiled* (trilobal, angular, serrated, oval, ribbon-like) and cross-sectional form (smooth, structured); multi-component fibres (e.g. sheath-core and concentric cover-core) are also produced [77] (Figure 1.26). Non-cylindrical fibre shapes can be used to create

<sup>53</sup> Often denoted  $\alpha$ .

<sup>54</sup> For example, consider a round fibre of radius  $r$  and density  $\rho$ : per unit length, as surface area is  $2\pi r$  and fibre volume  $\pi r^2 h$  then specific surface area per unit mass  $S_m = 2/r\rho$  and specific surface area per volume  $S_v = 2/r$ .



**Figure 1.26** Typical cross-sectional shapes of man-made and synthetic fibres. Reproduced with permission from [77]. © BISFA.

different optical effects in fibres via reflection and scattering of light. As discussed in Section 1.3.2.1.2, in bicomponent spinning, two strongly adhered but separable polymers (e.g. PA and PES) are co-spun.

Cross-sectional shape affects several fibre attributes (e.g. [348, 349]) including specific surface area and also provides functionality, such as lustre or moisture transport. Non-circular shapes have greater surface areas than circular cross sections. According to Eq. 1.7, the shape of the fibre cross section can be taken into account via the cross-sectional *shape factor*,  $q$ , which ranges from 0 for a circular fibre cross section to 0.09–0.12 for triangular cross sections and  $>0.60$  for irregular saw cross sections [309]. By way of example, the specific surface area of a 1.5 dtex PES filament ( $\rho = 1.36 \text{ g cm}^{-3}$ ) produced in triangular cross section ( $q = 0.10$ ) is  $272.6 \text{ m}^2 \text{ kg}^{-1}$  compared to a value of  $247.8 \text{ m}^2 \text{ kg}^{-1}$  for a similar dimensioned PES filament of circular cross section ( $q = 0$ ). Fibre cross-sectional shape also influences both *flexural rigidity* (bending) and *torsional rigidity* (twisting) [209] as well as the packing of filaments in yarns. Multifilament yarns comprise several monofilaments collected together to form a coherent body usually by the introduction of twist. The way in which the component monofilaments pack together is influenced by their cross-sectional shape and surface structure. In essence, circular fibres with smooth surfaces promote close packing and the production of dense, compact and uniform yarns. Non-circular filaments discourage close packing and favour the production of bulky yarns.

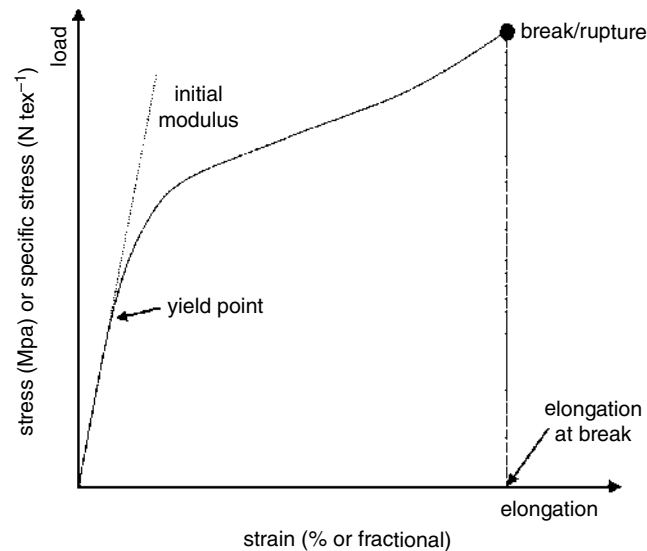


Figure 1.27 Idealised load-elongation curve for a textile fibre.

## 1.4 Properties of Textile Fibres

As mentioned, the very wide range of textile materials that are commercially available enjoy a diverse range of applications, for which differing properties, mostly governed by end-use requirements, are required, for example, from softness and moisture absorbency for apparel to high tenacity and elongation in the case of tough industrial materials. Some of these properties of relevance to dyeing are discussed below.

### 1.4.1 Mechanical Properties

The responses of fibres to applied forces that induce bending, tension, torsion and compression are important from both processing and performance viewpoints. Since textile fibres are sensitive to both temperature and moisture (i.e. *Relative Humidity, RH*; see Chapter 3), the determination of fibre properties must be carried out under known, constant, environmental conditions. Thus, textiles are *conditioned* prior to and during testing according to which, the substrate is allowed to equilibrate within a *standard atmosphere*<sup>55</sup> and testing is undertaken within the same controlled atmosphere. A commonly used standard atmosphere is 20°C ( $\pm 2^\circ\text{C}$ ) and 65% relative humidity (*RH*)  $\pm 4\%$  RH [350].

#### 1.4.1.1 Load-Elongation (Stress-Strain) Curves

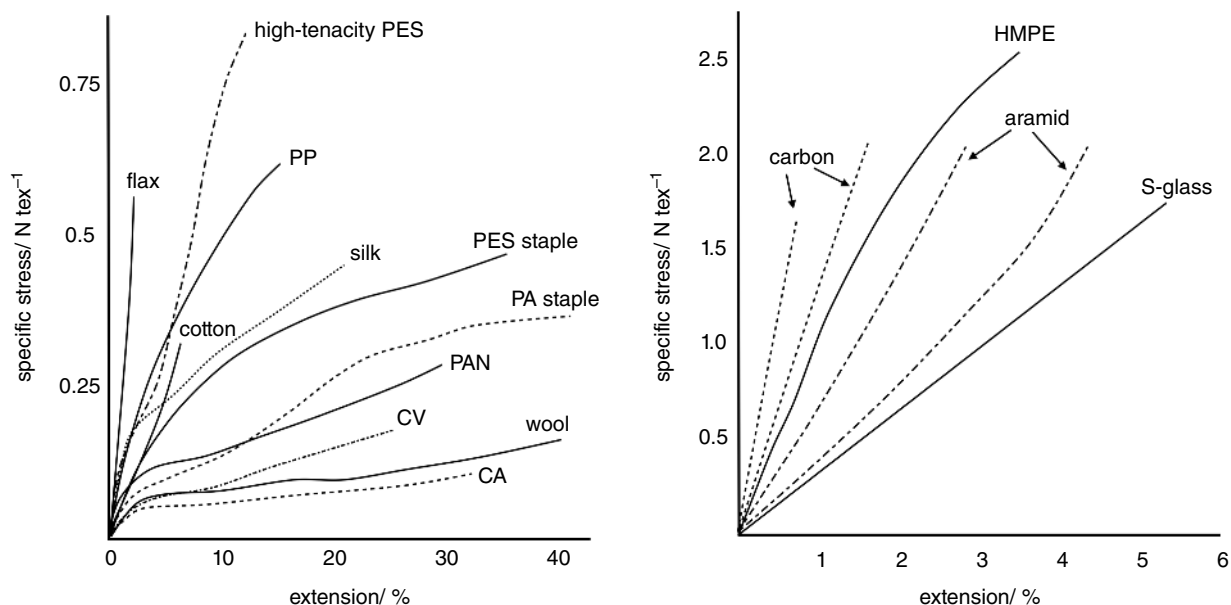
Several mechanical properties of fibres are determined from *load-elongation* (aka *stress-strain*) curves in which a progressively increasing load is applied to a fibre and the resulting deformation is determined. Typically, fibres are subjected to tensile testing in which a uniaxial force is applied that imposes a controlled, constant rate of elongation up to the point of breakage. Although stress-strain curves are often ascribed a 'typical' shape, such as that shown in Figure 1.27, load-elongation curves for textile fibres vary, sometimes quite markedly (e.g. see Figure 1.28), between different fibre types, as exemplified by curves for cotton and some other natural cellulosic fibres often being quite different to those secured for many other types of fibre. The following account related to Figure 1.27 is intended to be instructive only and readers should consult more detailed texts such as Ref. [209].

Confusingly, various terms are used for such plots and different units of measurement employed. If *load* is measured in *N*, *elongation* will be expressed in centimetre. However, load is often replaced by *stress* (load/cross-sectional area) of unit  $\text{Nm}^{-2}$  ( $1 \text{ Nm}^{-2} = 1 \text{ Pa} = 1 \times 10^{-6} \text{ MPa}$ ) or, since for many textile fibres, as cross-sectional area is neither well-defined nor uniform, linear density is used and the resulting *specific stress* (load/linear density) has units of  $\text{N tex}^{-1}$  (or for similarity with the older unit linear density,  $\text{g denier}^{-1}$ ,  $\text{cN dtex}^{-1}$ ). *Elongation* can be replaced by either fractional or percentage *strain* (Figure 1.27).

With reference to Figure 1.27, when a fibre<sup>56</sup> is subjected to a small amount of stress, the fibre undergoes strain (deformation); if the fibre recovers completely from the deformation when the stress is removed, the fibre has

<sup>55</sup> 'standard' simply means that the temperature and RH are *controlled*.

<sup>56</sup> in the case of crimped fibres, the crimp is removed prior to measurement.



**Figure 1.28** Stress-strain properties of textile fibres (65% RH; 20°C). Reproduced from [275], with permission from Elsevier.

undergone *elastic strain*.<sup>57</sup> In this initial region of a stress–strain curve, stress and strain are linearly proportional, the proportionality constant being the slope of the (straight line) plot and is known as the *initial modulus* or *Young's Modulus*,  $E$ , the ratio of stress to strain when the material behaves elastically.<sup>58</sup> When stress and strain are not directly proportional,  $E$  is given either by the *tangent modulus*, the slope of the tangent at any given position on the stress–strain curve, or the *secant modulus*, the slope of a line from the origin to any point on the stress–strain curve. After the application of an initial amount of stress, the *yield point* is reached which corresponds to the stress at which the fibre, if subjected to greater stress, will no longer return to its original shape. Two methods are available for determining yield point, both involving the construction of tangents to the stress–strain curve [209, 307]. A related parameter is the *elastic limit*, which is the greatest amount of stress that can be applied to the fibre without causing permanent deformation; whilst brittle materials break at or about their elastic limit, ductile materials continue to deform at applied stress above the elastic limit. Non-linear stress/strain deformation beyond the elastic limit indicates that the fibre is undergoing *non-elastic deformation* (aka *plastic deformation*) during which, irreversible (permanent) deformation occurs; typically, textile fibres (and ductile materials in general) have a large non-elastic deformation region. Eventually, the application of further stress results in *rupture* (also referred to as *fracture* or *breakage*) of the fibre.<sup>59</sup> Breakage can be quantified using three parameters, namely *elongation at break* (also known as *break extension* or *breaking extension*), *work of rupture* (determined as the area under the load–elongation curve upto the point of break) and *strength*, which for an individual fibre is given by the *breaking strength* (aka *tensile strength*), this being the maximum tensile force used in extending a fibre to breaking point, whereas for comparing different fibres, the *specific stress at break* is measured, which is referred to as *specific strength* or *tenacity*.

The mechanical properties of a textile fibre are commonly described in terms of attributes, for which, confusingly, different terms are used, that include strength (tenacity), extensibility (elongation at break), elasticity (elastic recovery), stiffness (modulus) and toughness (work to rupture). The *strength* (*tenacity*) of a fibre is commonly expressed in relation to fibre fineness, often as the maximum stress applied to the fibre at its breaking point. Natural fibres and the early regenerated fibres have tenacities of  $\sim 0.1\text{--}0.6\text{ N tex}^{-1}$ , those of synthetic fibres and industrial fibres are in the range  $0.4\text{--}0.6\text{ N tex}^{-1}$  and  $0.6\text{--}1.0\text{ N tex}^{-1}$ , respectively, whilst HM-MT fibres are in the range  $1.0\text{--}3.0\text{ N tex}^{-1}$ . The *elongation at break* (aka *extension at break*) describes the extent of deformation of a fibre imparted by a given stress and is commonly expressed as the fractional increase in length of the fibre when it breaks. Whilst cotton has relatively low elongation ( $\sim 6\text{--}10\%$ ), that of wool ( $\sim 25\text{--}50\%$ ) is of a similar value to many synthetic fibres; elastane fibres typically have values of elongation of  $>400\%$ . *Elastic recovery* refers to the amount by which a stretched fibre recovers to its original dimensions when the deforming stress is released; often, stretch-recovery cycles involve hysteresis, so that 100% recovery is not achieved. PA fibres typically display much higher recovery from low amounts of stress than PES fibres; consequently, PA fibres rather than PES fibres therefore enjoy extensive use in ropes and cordage as well

<sup>57</sup> the majority of fibres are inelastic except at very low levels of extension.

<sup>58</sup>  $E$  is a measure of *stiffness*, having the same units as stress ( $\text{Nm}^{-1}$  or Pa or MPa).

<sup>59</sup> fibre fracture comprises a large subject matter in its own right, e.g. [351].

as in hosiery. Elastane fibres characteristically can be stretched to several times their length and rapidly revert to essentially their unstretched length when the tension is removed.

Collectively, the tensile strength (tenacity), elongation (extensibility) and elastic recovery (elasticity) describe the strength, robustness and ability of a fibre to assume a given shape and to recover its original dimensional attributes.

*Fibre stiffness* describes the resistance of a fibre to deformation. The *initial modulus* (aka *Young's modulus*), which often is used as a measure of the ability of a fibre to resist extension, is the ratio between the stress applied to a fibre and the strain that results from the application of that stress. Initial modulus values range from ~2 to 20 N tex<sup>-1</sup> for conventional textile fibres, ~30 and 100 N tex<sup>-1</sup> in the case of industrial fibres and up to >300 N tex<sup>-1</sup> for HM-HT fibres. *Toughness* is expressed as the amount of energy needed to break the fibre. The unit of work of rupture is mN tex<sup>-1</sup>, as toughness is proportional to fibre fineness. Tough fibres, such as PA and PES, also tend to display reasonably high tenacity and elongation.

Absorbed moisture reduces modulus, but both elongation to break and elongation at break increase. The strength of cotton and other cellulosic fibres increases, whereas the strength of other fibres is reduced by the presence of moisture. Whilst temperature imposes similar effects to those of moisture, they are more fibre-specific [209].

## 1.4.2 Thermal Properties

As textile materials are multiphase systems that comprise individual fibres as well as *interstices* (*pores*) filled with a medium (e.g. air, water and dye liquor), the transfer of heat through the fibrous assembly necessitates transmission through the various phases (i.e. fibre, dye liquor, etc.); furthermore, textile fibres are anisotropic. As such, thermal conduction in fibrous assemblies<sup>60</sup> is a complex process that has attracted considerable attention and which requires the use of complex mathematics. This large and multifaceted area is outside the scope of this book and the reader is directed elsewhere (e.g. [352–354]).

### 1.4.2.1 Heat Capacity

*Heat capacity*,  $C$ , is the amount of heat required to change the temperature of a material by a given amount, the SI unit of heat capacity being J K<sup>-1</sup>. Heat capacity can be measured either at constant pressure or at constant volume, denoted by  $C_v$  and  $C_p$ , respectively. As the heat capacity of a material depends on its mass, the *specific heat capacity*,  $c$ , (aka *specific heat*) (SI unit: J kg<sup>-1</sup> K<sup>-1</sup>) describes the amount of heat required to increase the temperature of a unit mass of material by a given amount. Although heat capacity is a macroscopic variable, it is linked to molecular structure and vibrational molecular motions [355]. Values of the specific heat capacity of various polymers [355] and fibres are available (e.g. PVC: 0.8–0.9; PES: 0.5–1.0; cotton: 1.3; PA 66: 1.5–1.8 kJ kg<sup>-1</sup> K<sup>-1</sup> [93]). Interestingly, the absorption of water ( $c_p \sim 4.2$  J kg<sup>-1</sup> K<sup>-1</sup>) does not increase the specific heat capacity of fibres to an amount predicted by a simple mixing law, possibly because the absorbed water may be behaving more like ice ( $c_p \sim 2$  kJ kg<sup>-1</sup> K<sup>-1</sup>) than liquid water or it may change the specific heat capacity of the polymer [209].

### 1.4.2.2 Thermal Conductivity

Thermal transfer occurs by three main physical processes, namely conduction, convection and radiation. Whilst all three processes are feasible in the case of textile materials, conduction is the dominant process [356]. In essence, *thermal conductivity*,  $k$  (sometimes denoted by  $\kappa$  or  $\lambda$ ; SI unit: W m<sup>-1</sup> K<sup>-1</sup>), which is a measure of the ability of a material to transfer heat, is the proportionality constant in *Fourier's Law of Conduction*, Eq. 1.8, shown in its general (vector) form for multidimensional conduction, where  $q$  is the flux (amount of thermal energy flow),  $T$  the temperature and  $\nabla$  the Del (Nabla) operator.<sup>61</sup>

$$q = -k\nabla T \quad (1.8)$$

The well-known (related) partial differential *heat equation* describes the temperature distribution within a given region as a function of time, a form of the equation of relevance to fibrous systems [356] being given by Eq. 1.9, where  $t$  is the time,  $\rho$  the density,  $\Phi$  the heat generating rate within a given volume,  $\nabla^2$  the Laplace operator and  $a$  the *thermal diffusivity* (thermal conductivity divided by *volumetric heat capacity*, i.e.  $\rho c_p$ ), the latter parameter being a measure of how quickly a body can change its temperature and which has the same dimensions as mass diffusivity,  $D$  (i.e. m<sup>2</sup> s<sup>-1</sup>).<sup>62</sup>

<sup>60</sup> a topic that also includes areas such as clothing and textile composites.

<sup>61</sup> the negative sign indicates that heat transfer occurs in the direction of decreasing temperature.

<sup>62</sup> when  $\Phi = 0$  (i.e. there is no heat generation), Eq. 1.9 is of the same form as the time-dependent mass diffusion equation.

$$\frac{\partial T}{\partial t} = \alpha \nabla^2 T + \frac{\Phi}{\rho c_p} \quad (1.9)$$

Of course, to solve the above differential equation (Eq. 1.9), boundary conditions of the problem and initial conditions are required (e.g. constant heat flux, constant surface temperature and initial temperature distribution).

The thermal conductivity of polymers is influenced by several properties including density, chain orientation and crystal structure [357]. Values of the thermal conductivity of various polymers [357] and fibres [93] are available, though, as fibres are anisotropic, so too are values of thermal conductivity, with longitudinal values being several orders of magnitude greater than those measured in the transverse direction. Typically, transverse values tend to be used, ranging from 0.1–0.3 (PP) to 0.3–0.6 (cotton)  $\text{W m}^{-1} \text{K}^{-1}$ , although it is suggested that such values act as guidelines only since thermal conductivity can be effected by molecular orientation [307].

### 1.4.2.3 *The Glass Transition Temperature, $T_g$*

As mentioned, organic natural, man-made and synthetic fibres comprise (mostly linear) semi-crystalline polymers that contain regions which display a high degree of order (crystalline material) as well as regions that display a low degree of order (amorphous material). In a crystalline material, the lateral, longitudinal and directional correlation of adjacent polymer chains (i.e. order) extends over long distances, resulting in a regular structure whereas in a completely amorphous material, there is no lateral, longitudinal or directional correlation of adjacent polymer chains and the constituent atoms and molecules are randomly arranged. In the case of semi-crystalline polymers, and therefore textile fibres, the crystalline and amorphous domains display different, but interrelated, thermal behaviour. From the viewpoint of dyeing, two important thermal transitions<sup>63</sup> can arise in polymers and textile fibres namely *melting* (aka *crystalline melting temperature*),  $T_m$ , which is a characteristic feature of the crystalline regions of the polymer and the *glass transition*,  $T_g$ ,<sup>64</sup> which relates to the amorphous regions. Both melting and glass transition are important parameters of major relevance to the processing of polymers insofar as they define the upper and lower temperature limits for many applications, including dyeing.

The glass transition in an amorphous material or the amorphous regions within a semi-crystalline polymer has been described as *a temperature-, time- (or frequency-) and composition-dependent, material-specific change in physical state, from a glassy mechanical solid to a rubbery viscous liquid (capable of flow in real time)* [359]. The nature of the glass transition in polymers has been the subject of great interest over many decades, this interest continuing till now. In this context, the reader is directed to general, well-cited texts and reference works for detailed accounts of the topic (e.g. [162, 170, 224, 360–364]). According to IUPAC [189], phenomena occurring at the  $T_g$  of polymers remain areas of ongoing scientific investigation and debate.

As discussed below, although glass transition presents features of a second-order transition (i.e. at  $T_g$ , the molar Gibbs energy, enthalpy and specific volume of the melt and glass are equal), the heat capacity and coefficient of thermal expansion are discontinuous.  $T_g$  is generally not viewed as a thermodynamic transition owing to the difficulty in attaining equilibrium in both a polymer melt and glass at temperatures near to  $T_g$  [189].

**1.4.2.3.1 *Crystalline and Non-crystalline Regions*** As previously discussed, partial crystallinity, which is displayed by many polymers, especially those utilised in textile fibres, arises from the particular arrangement of the composite macromolecules. If the monomeric unit is simple and regular, crystallinity is highly developed (e.g. PE), whereas if the monomer units are complex and contain bulky side groups, crystallisation will be less developed (e.g. PP). Even the most crystalline polymer usually possesses some level of irregularity, such as lattice defects, and, therefore, some non-crystalline material. The characteristics of the crystalline regions in fibrous polymers differ from those displayed by small molar mass crystalline solids, such as NaCl. Whilst crystals of salt are hard and brittle, semi-crystalline fibres, such as PA, are soft and readily deformed, especially when heated. In terms of the response of polymers towards applied thermal energy, two types of polymer can be distinguished namely:

- (1) *thermoplastic polymers* which soften when heated above  $T_g$  but harden again when cooled below this particular temperature, this cycle being repeatable;
- (2) *thermoset polymers* [365, 366] which undergo irreversible curing when heated above a particular temperature, resulting in a hard, cross-linked material that cannot be softened by reheating.

<sup>63</sup> transitions can be considered as *narrow intervals of temperature or frequency over which polymer properties change by large amounts* [358].

<sup>64</sup> although the SI unit for  $T_g$  is the Kelvin, in this book, values of  $T_g$  are given in Celsius, as this is the most commonly used unit in textile-related publications.

$T_g$  concerns the effects of heat on the thermoplastic properties of polymers; this account focuses on semi-crystalline, mostly linear polymers.<sup>65</sup>

**1.4.2.3.2 The Glass Transition** Many compounds exist in three physical states, namely solid, liquid and gas. The transitions between these states or *phases* (e.g. melting, vapourisation) are characteristically sharp and are *first-order transitions* insofar as the transition involved is accompanied by a sudden change in a *primary thermodynamic function* (enthalpy, entropy, volume). However, the situation for polymers is much different and more complicated. Many polymers decompose before vapourisation occurs, whilst polymers in which strong intermolecular interactions arise, such as H-bonded cellulosic polymers such as cotton, decompose before melting occurs. Furthermore, for many polymers, the transition from solid to liquid (i.e. melting) is not sharp but often occurs gradually over a small temperature range.

As mentioned, in the case of semi-crystalline polymers (i.e. textile fibres), two important thermal transitions can arise. The first of these is melting, which is denoted by the crystalline melting temperature,  $T_m$ , this being a transitional feature of the crystalline regions of the polymer in which the crystal structure is destroyed and a disordered, amorphous liquid is formed. The second important thermal transition is the *glass transition*,  $T_g$ , which is a characteristic property of only the amorphous region within a semi-crystalline polymer. Owing to the stronger intermolecular forces that operate between crystallites within the crystalline domains compared to those that operate between the essentially randomly arranged molecular chains within the non-crystalline regions, more thermal energy is required to overcome bonding in the crystalline regions. Thus,  $T_g < T_m$  and, therefore, the crystalline regions remain crystalline during the glass transition. Clearly, the degree of crystallinity within a semi-crystalline polymer influences both  $T_m$  and  $T_g$ , the glass transition becoming less significant as the degree of crystallinity increases; indeed, for many polymers, an increase in crystallinity is accompanied by an increase in  $T_g$ . Dramatic conformational changes in polymer structure occur at both  $T_m$  and  $T_g$  which impart marked changes in several physical properties, including, for example, specific volume, heat capacity and modulus [181, 364]. However, the thermal transitions that occur at both  $T_m$  and  $T_g$  are not sharply defined in polymers but, instead, take place over a range of temperatures, even though single values of  $T_m$  and  $T_g$  often are quoted for polymers and fibres.

Figure 1.29 illustrates the changes in specific volume for both an idealised 100% crystalline polymer as well as an idealised 100% amorphous polymer, as a function of temperature; also shown are changes in specific volume that can occur in the case of an idealised partially crystalline polymer. If a 100% crystalline polymer is heated, its specific

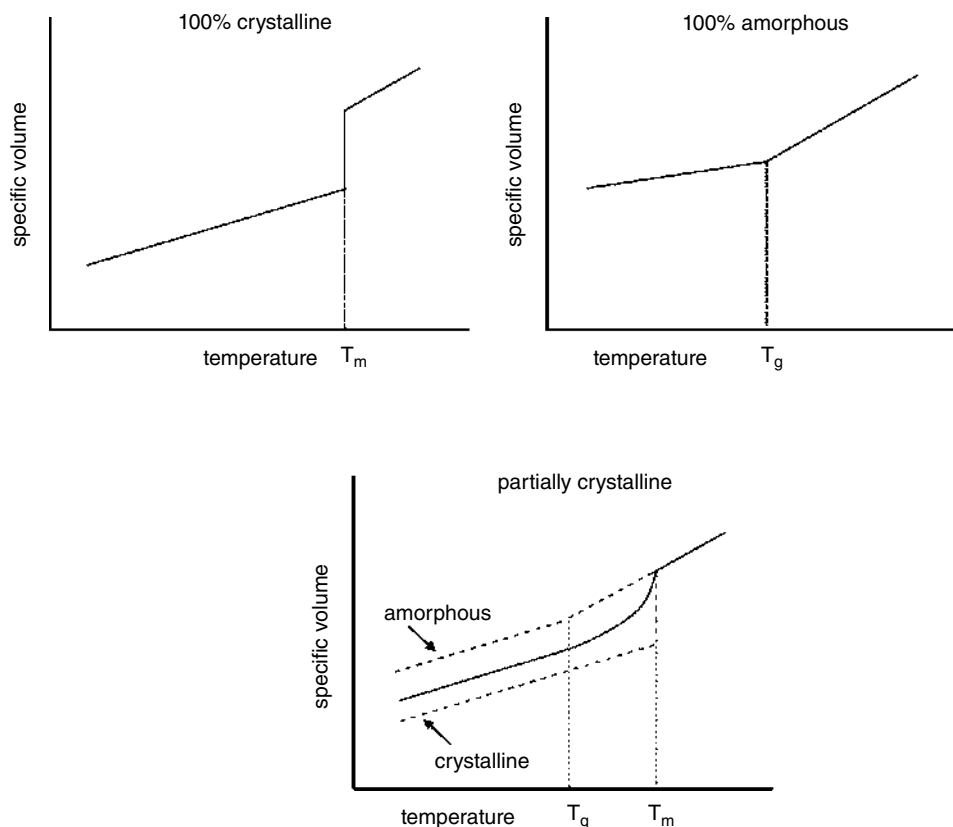


Figure 1.29 Idealised representation of  $T_m$  and  $T_g$ .

<sup>65</sup> which comprise mostly linear (or lightly branched) macromolecular chains.

volume increases steadily until, at the crystalline melting temperature,  $T_m$ , the crystalline material melts, which is accompanied by a large increase in volume (Figure 1.29). Whereas small perfectly crystalline materials characteristically have a well-defined melting temperature (e.g. NaCl = 801°C [367]), polymers are never completely crystalline since they possess both amorphous material and crystallites of varying dimensions. Thus, the  $T_m$  of a crystalline polymer occurs over a range of temperatures: the melting of crystalline material of shorter chain segments begins at a temperature below  $T_m$  whilst longer chain length crystallites melt at higher temperatures. In the case of a 100% solid, amorphous polymer (Figure 1.29), at temperatures  $<T_g$ , its properties resemble those of a *glass* (i.e. hard, rigid and brittle), the macromolecules being able to undergo only weak vibrations. Upon heating, these vibrations increase in amplitude until, at the  $T_g$ , the polymer begins to soften. At temperatures just above  $T_g$ , increased vibrational and rotational changes occur and the polymer becomes rubbery and its specific volume increases (Figure 1.29); at higher temperatures, the polymer's properties now resemble those of a highly viscous liquid. If the molten amorphous polymer is cooled, it continues to behave as a rubber-like material until the glass transition is reached, below which, the polymer behaves as a glass. In the case of a semi-crystalline polymer (Figure 1.29), which comprises both crystalline and amorphous regions, at temperatures below  $T_g$ , the solid is glassy. Whilst the material softens at  $T_g$ , due to changes in the amorphous regions, relatively small changes in specific volume occur since the crystalline regions remain solid. As  $T_m$  is approached, the crystallites begin to melt and, at temperatures above  $T_m$ , the polymer will be rubbery, viscoelastic or liquid depending on its molar mass. If the semi-crystalline polymer is cooled from above  $T_m$ , the crystalline regions become ordered when  $T_m$  is reached, below which, the polymer is a flexible crystalline solid and, below  $T_g$ , the polymer is glassy (Figure 1.29). Some partially crystalline polymers display two glass transitions, a lower one that stems from wholly amorphous material and a higher one that arises from amorphous material that is incumbered by neighbouring crystallites. Usually, the changes that accompany  $T_g$  do not occur at a particular, well-defined temperature but, rather, occur over a range of temperature.

As mentioned, strong intermolecular interactions occur in some polymers, such as cellulose in which extensive, H-bonding results in high crystallinity and an inability to soften or melt; often, such polymers possess a value of  $T_m$  that is greater than the temperature at which decomposition occurs. Both natural and man-made fibres of both cellulosic (e.g. cotton, CV, etc.) and keratinous (e.g. wool) derivation, as well as synthetic polyamides (e.g. PA 6, PA 66) generally display high values of glass transition temperature because of the predominance of H-bonding.

Values of the  $T_g$  of many polymers are available in tabulated form (e.g. [363, 364]). A wide range of factors influence the  $T_g$  of polymers, including, for example, molar mass, chain flexibility, crystallinity, tacticity, pressure, thermal history, molar mass and, of relevance to dyeing, plasticisers and moisture (e.g. [170, 173, 183, 185, 315, 363, 364]). The  $T_g$  and  $T_m$  values for various polymers are given in Table 1.4. The two thermal transitions depend similarly on several polymer characteristics and enjoy a general correlation insofar as polymers with high  $T_g$  values have high  $T_m$  values, while low  $T_g$  and low  $T_m$  values tend to coincide; also, the ratio  $T_g/T_m \approx 2/3$  (temperature expressed in K) applies to many polymers [192].

**1.4.2.3 Measurement of  $T_g$**  As mentioned, the dramatic alteration in the motion of polymer chains at  $T_g$  results in significant changes in a variety of physical (mechanical, electrical and thermodynamic) properties, which,

**Table 1.4** Glass transition temperature and crystalline melting temperature for some polymers.

fibre	$T_g/^\circ\text{C}^a$	$T_m/^\circ\text{C}^a$
PE	-30 to -128 <sup>a</sup>	137.5 <sup>a</sup>
PP <sup>b</sup>	-3.2 <sup>a</sup>	174 <sup>a</sup>
PA 6	40 <sup>c</sup>	223 <sup>c</sup>
PA 66	50 <sup>c</sup>	265 <sup>c</sup>
PES	61 <sup>c</sup>	270 <sup>c</sup>
PAN	85-95 <sup>a</sup>	320 <sup>d</sup> ; decomp. ~250 to -320 <sup>a</sup>
CTA	157 <sup>e</sup>	306 <sup>a</sup>
Silk	175 <sup>f</sup>	Decomp. ~250 <sup>f</sup>
Cellulose	230 <sup>g</sup>	Decomp. 150 <sup>a</sup>

<sup>a</sup> [210].

<sup>b</sup> isotactic.

<sup>c</sup> [185].

<sup>d</sup> [368].

<sup>e</sup> [369].

<sup>f</sup> [173].

<sup>g</sup> cotton.



theoretically, could be used to determine  $T_g$ . As  $T_g$  is not thermodynamically stable, its determination is highly dependent on the conditions employed, being a function of the heating rate and measurement frequency. For example, a method that employs a rapid temperature change will generally provide higher values for  $T_g$  than if a slower change in thermal conditions were adopted.

Several methods are used to measure the glass transition temperature of polymers in practice, which, in essence, can be divided into two categories depending on the rate at which determination is undertaken namely *static* (slow rate) or *dynamic*. In the former, a particular sample parameter (e.g. heat capacity) is monitored as temperature is changed slowly to allow the sample to equilibrate whereas in dynamic methods, glass transition is denoted by a rapid change in modulus that occurs in response to an applied stress (deformation), the observed transition observed being frequency-dependent. Generally, the  $T_g$  values obtained using dynamic methods are higher than those obtained using static methods. *Thermal analysis* (e.g. [370–372]) is the name given to a group of techniques in which a physical property of a substance is measured as a function of temperature whilst the substance is subjected to a controlled temperature programme [373], which includes several techniques that seek to determine a polymer's response to being heated or cooled (or held isothermally). A wide range of such techniques can be used, including established variants such as *Differential Scanning Calorimetry* (DSC) [374], *Dynamic Mechanical Analysis* (DMA) [375], *Thermomechanical Analysis* (TMA) [376], *Thermogravimetric analysis* (TGA) [377], IR [378] and *Dielectric analysis* (DEA), as well as relatively more recent derivatives such as *Quasi-isothermal temperature modulated DSC* (TMDSC [379]) and others (e.g. *Positron Annihilation Lifetime Spectroscopy*; PALS) [250, 371, 372, 376, 380–382]. However, care must be exercised in interpreting glass transition values since they vary markedly depending on the following:

- the particular method used for determination (e.g. DMA vs. DSC vs. TMA), as exemplified by values for the  $T_g$  of poly(methylmethacrylate) which ranges from 105°C determined using thermal expansion, 120°C (penetrometry) to 160°C obtained using a rebound elasticity technique [163];
- the experimental procedure employed (such as whether the sample was heated, cooled and held isothermally) as evidenced by static methods, such as dilatometry, providing values of  $T_g$  in the range 40–55°C for both PA 6 and PA 66 compared to 90–100°C in the case of dynamic methods [149];
- the thermal history of the polymer;
- the particular chemical nature of the polymer;
- the presence of impurities such as plasticisers, oligomers and unreacted monomers;
- molar mass and its distribution.

Hence, in considering the value of  $T_g$  for a given polymer, as exemplified by tabulated values for different polymers (and polymer blends) (e.g. [210, 383–385]), consideration must be given as to the nature of its determination, especially since  $T_g$  is markedly affected by the presence of moisture and polymers and fibres that contain hydrophilic groups, such as cellulose and PA, usually contain some amount of moisture, as is discussed later.

**1.4.2.3.4 The Nature of  $T_g$**  The glass transition is a highly complex phenomenon and despite considerable research interest over many decades, its precise character remains unclear. Two main opposing approaches have been adopted to interpret the glass transition, namely that it is a *thermodynamic transition* or a *kinetic occurrence*, these having their origins in the 1930s and 1940s [386], respectively. A detailed discussion of these models is outside the scope of this section (e.g. [170, 386–391]).

*Thermodynamic Approach to  $T_g$*  Briefly,  $T_g$  is considered to represent a thermodynamic *second-order phase transition*.<sup>66</sup> Ehrenfest (1933) [392, 393] first proposed a classification of phase transitions based on the continuity of the *free energy*,  $G$ , and its derivatives. A first-order transition arises when a first derivative of free energy (e.g. entropy) exhibits discontinuity with respect to a thermodynamic variable (e.g.  $T$ ); thus, melting is a *first-order phase transition*. A *second-order phase transition* occurs when a first-order derivative is continuous but a second derivative of free energy (e.g. heat capacity) is discontinuous (e.g. [394]). In the case of the glass transition, since the first derivatives of Gibbs free energy (i.e. volume and entropy) are continuous but the second derivatives (e.g. heat capacity) display (apparent) discontinuity,  $T_g$  is considered to resemble a second-order transition. However, this particular approach is doubtful since the observed discontinuities are not sharp but spread over a range temperature and, also, the polymer's glassy state is thermodynamically unstable and therefore not defined by normal state variables; in addition, the value determined for  $T_g$  is highly method-dependent and also varies according to the sample's age and history [364, 389, 391]. Indeed, the glass

<sup>66</sup> a *phase transition* occurs when a thermodynamic system changes from one phase (or state) to another as a result of temperature and/or pressure change, as exemplified such as by solid/liquid and liquid/gas phase changes.

transition has been considered to be a *psuedo* or *quasi* second-order transition [389], the observed discontinuities not being sharp but rather spread over a range of temperature.

*Kinetic Approach to  $T_g$*  An alternative view that  $T_g$  is a kinetically controlled phenomenon stems from the fact that polymer viscosity increases, markedly, as a polymer melt is cooled ( $\sim 10^{11}$ – $10^{12}$  Pa s [390, 395]) and that the accompanying changes, for example, coefficient of thermal expansion, elastic modulus and diffusivity that are employed to define  $T_g$ , are the consequence of the time-related frequency of molecular motions within the polymer, rather than the existence of a thermodynamic second-order transition [364, 389, 390].

Several other theories have been devised to describe the phenomenon of glass transition, including the *cooperativity approach* and the *mode-coupling theory* [391, 396].

**1.4.2.3.5 Free Volume** This is a widely used model of molecular mobility in relation to  $T_g$ , which has been employed to develop theories of the diffusion of low molar mass materials in polymers, as well as thermal conductivity and the behaviour of solutions [386], though other theories have been proposed [388] (for detailed accounts see for example [186, 388]). Essentially, the amorphous regions in semi-crystalline polymers contain holes or cavities of atomic or molecular dimensions that arise from the inefficient/irregular packing of the macromolecular chains. These holes/cavities are described as *free volume* which can be considered as the space in a solid or liquid polymer that is not occupied by the component macromolecules and expressed as Eq. 1.10 where the free volume,  $V_f$ , is the difference between the volume,  $V$ , occupied by the polymer at a particular temperature and the van der Waals volume,  $V_o$ , of the polymer at 0 K. Free volume is a measure of the amount of the space available in which polymer chains can readily change their conformation.

$$V_f = V - V_o \quad (1.10)$$

Briefly, the use of free volume,  $V_f$ , in the context of temperature-dependent molecular mobility within polymers, is the result of advances made by several authors. Doolittle proposed the concept of *free volume* (or rather *free space*) in the context of the temperature-dependence of viscosity of low molar mass liquids (*n*-paraffin hydrocarbons) [397], whilst Fox and Flory described the relevance of free volume to the glass transition in polymers [395], and its contribution to molecular transport was proposed by Cohen and Turnbull [398].

Free volume describes the amount of space within a polymer in which the molecules can undergo rotational and translational motion. In the case of an amorphous polymer (or the amorphous regions within a semi-crystalline polymer or fibre), at temperatures  $< T_g$ , the constituent polymer chains are prevented from changing position by neighbouring chains. Thus, in the glassy state, constituent atoms can only undergo vibrations. As the temperature increases, the amplitude of these vibrations increase and sufficient energy will be introduced into the polymer to enable bond rotation to occur within the macromolecular chains. The small amounts of free volume that are present begin to coalesce and form larger regions of free volume, which allows polymer segments that lay between two simultaneously rotating bonds in the same chain to change position. Such change of position is referred to as a *segmental jump*, which provides a vacated space into which another polymer segment can move, this process being repeated throughout the polymer. This segmental movement continues until it is sterically hindered by adjacent polymer molecules. The energy barrier to this cooperative segmental mobility is overcome over the narrow temperature range of the glass transition temperature and is accompanied not only by a marked increase in free volume but also by an equally dramatic change in the physical character of the polymer from glassy to rubbery. Above  $T_g$ , an increase in temperature results in a marked increase in free volume and a corresponding increase in the frequency of segmental jumps.

Figure 1.30 shows a representation of the occupied and free volumes within a polymer. With increasing temperature, the occupied volume increases gradually, owing to thermal expansion of the polymer, until, at the glass transition, polymer volume dramatically increases owing to a sudden increase in expansion of free volume. Above  $T_g$ , the amount of free volume within the polymer is high and molecular motion can occur relatively easily, as the constituent molecules can move and change their conformations readily within the available space. In this region, the amount of free volume increases markedly with increasing temperature, owing to increased molecular motion. As the temperature is lowered, the amount of free volume reduces until, at  $T_g$ , there is insufficient space to permit large-scale segmental motion of the chains to occur. Below  $T_g$ , the amount of free volume available remains essentially constant, regardless of further decrease in temperature, as the macromolecular chains are immobilised.  $T_g$  is considered to signify the beginning of cooperative movements involving chain segments of  $\sim 20$ – $100$  chain C-atoms [163] and of 2–10 nm in length [399].

The application of free volume theory to the interpretation of the  $T_g$  of polymers has been widely practiced; its use to describe the effect of temperature on the diffusion of dyes in semi-crystalline polymers is also well documented [315]. At temperatures  $< T_g$ , amorphous polymers behave as rigid solids in which the segmental mobility of the constituent macromolecular chains is, in effect, zero. As temperature increases, the segmental mobility of the polymer chains

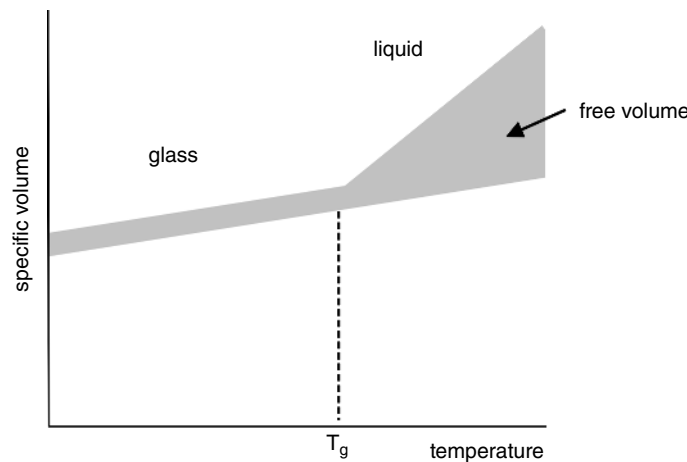


Figure 1.30 Representation of free volume within a polymer.

increases. At the same time, the limited amount of free volume available within the amorphous regions begins to coalesce, forming larger voids which, in turn, allow increased segmental mobility. Such changes in segmental mobility occur over a very narrow temperature range and are accompanied by a marked increase in free volume.  $T_g$  is the temperature at which these changes begin, and in passing through  $T_g$ , the polymer changes from a rigid solid glass to a highly viscous, rubbery liquid. According to this interpretation,  $T_g$  is the particular temperature below which the free volume is not large enough for molecular movement; however, at or  $>T_g$  sufficient energy is available for molecular movement and the free volume increases sharply with increasing temperature (Figure 1.30). This dependency of volume on temperature causes an increase in the coefficient of thermal expansion and, consequently, it is common to express the temperature coefficient of free volume as the difference between the thermal expansion coefficients of the material above and below  $T_g$ , as follows.

**1.4.2.3.6 WLF Equation** The *Williams, Landel and Ferry (WLF)* equation describes the temperature-dependence of several mechanical and electrical properties of polymers, as well as those of super-cooled fluids, including viscous flow, dielectric dispersion, dynamic light scattering and viscoelastic response [400, 401], of which the latter aspect is of relevance in the context of the dyeing of textile fibres derived from synthetic polymers. The WLF equation is a consequence of the *time-temperature superposition principle*, which enables temperature-dependent mechanical properties of viscoelastic<sup>67</sup> polymers to be determined from known properties at a (chosen) reference temperature.

As described below, time-temperature superposition (aka *time-temperature equivalence*) is based on the principle that the mechanical properties of a polymer are governed by a simple relationship between time and temperature, as a result of which, viscoelastic data (e.g. modulus or creep compliance) obtained at a particular temperature can be superimposed on data secured at another temperature by *shifting* one of the curves along the time axis to an extent that is described by the *shift factor*,  $a_T$ . The WLF equation enables this temperature shift factor to be estimated for temperatures other than those originally employed. Although the equation is derived empirically, as discussed later, it can be rationalised theoretically in terms of free volume theory by assuming that a polymer behaves as a viscoelastic material.

**1.4.2.3.7 Time-Temperature Superposition Principle** In essence, the underlying premise is that the rate at which the molecular relaxation processes occur within a polymer increases with increasing temperature and, also, that the timescale over which these processes occur is reduced at higher temperatures. According to time-temperature superposition, viscoelastic behaviour (e.g. modulus) observed at one particular temperature can be related to that at another temperature by transposing (i.e. shifting) the timescale (for fuller accounts, see [192, 361, 388, 402–404]).

At (or about)  $T_g$ , the change from glassy to rubbery states, which is accompanied by marked changes in polymer properties such as density and modulus, is both time- and temperature-dependent. Owing to the nature of the viscoelastic relaxations in polymers, the effect of an increase in temperature on such physical properties is equivalent to an increase in time. For example, a polymer that displays rubbery behaviour under one set of particular time/temperature conditions can exhibit glassy behaviour either by reducing temperature or by increasing time at initial temperature. According to the time-temperature superposition principle, which was introduced in the early 1940s

<sup>67</sup> a viscoelastic material displays both elastic and viscous characteristics when subjected to deformation; they exhibit time-related strain in response to applied stress.

[405, 406], viscoelastic data obtained at one temperature can be transformed to another temperature by a simple manipulation of the time scale. A wide range of viscoelastic properties of polymers display such time-temperature equivalence, as exemplified by the pioneering work of Tobolsky *et al* on the *stress relaxation*,  $E_r$ , of polyisobutylene [407, 408]. Superposition is often employed experimentally to determine mechanical response since instruments are unable to cover the time scale (or frequency scale) of the viscoelastic behaviour of polymers from  $T_g$  to flow [409].

By way of explanation, if a particular polymer property, of arbitrary symbol  $M$ , is determined as a function of time,  $t$  (e.g. 0–100 h), over a wide range of temperatures,  $T$  (e.g.  $-50$  to  $+50^\circ\text{C}$ ), when values of  $M$  are plotted as a function of  $\log t$ , the set of curves shown in the left-hand panel in Figure 1.31 is obtained for each temperature.

It was found empirically that each of these *data curves* could be superimposed by keeping one curve fixed and shifting the others by different amounts horizontally. For example, if  $0^\circ\text{C}$  was chosen as the reference temperature ( $T_{\text{ref}}$ ), then data obtained  $>0^\circ\text{C}$  are shifted to the right and those secured  $<0^\circ\text{C}$  are left shifted. The extent of this shift, which is termed the (temperature) *shift factor*,  $a_T$ , corresponds to a displacement along the  $\log t$  axis of  $(\log T_{\text{ref}} \pm \log T)$ . According to the time-temperature superposition principle in its simplest form, a plot of  $M$  versus  $\log t/a_T$  enables the various data curves obtained at different temperatures to be superimposed into a single, *master curve*, shown in the right panel of Figure 1.31. The ensuing master curve shows the particular viscoelastic property,  $M$ , for the polymer at a given reference temperature,  $T_{\text{ref}}$  (in this case  $0^\circ\text{C}$ ), as a function of time. In this master curve, each of the separate curves of  $M$  as a function of  $t$  obtained at different temperatures are transposed by the shift factor,  $a_T$ , which is a function only of temperature. The relationship between time and temperature (i.e. the values of  $\log a_T$  required to superpose the various data curves onto the single master curve) is shown in the inset within Figure 1.31.

In the context of time-temperature superposition, Williams, Landel and Ferry proposed that the temperature shift factor,  $a_T$ , could be expressed by Eq. 1.11. The master curve approach obtained by superposition describes well the mechanical properties of polymers and the WLF equation can be used to predict mechanical character outside the range of experimental values used (i.e. temperature and frequency or time).

**1.4.2.3.8 Free Volume and the WLF Equation** The origins of free volume theory stem from Doolittle's proposal [397] that the non-linear behaviour of the viscosity of a liquid is related to the *relative free space* (i.e. *relative free volume*),  $\Phi = V_f/V_o$ , where  $V_f$  is the free space (free volume) at a given temperature and  $V_o$  the volume at 0 K (Eq. 1.11).

$$\eta = A \exp^{B/\phi} \quad (1.11)$$

In the context of the temperature-dependence of both mechanical and electrical relaxation processes in polymers, Williams *et al.* [410] employed the *fractional free volume*,  $f = V_f/V$ , rather than  $\Phi$ , where  $V$  is the total volume of a polymer

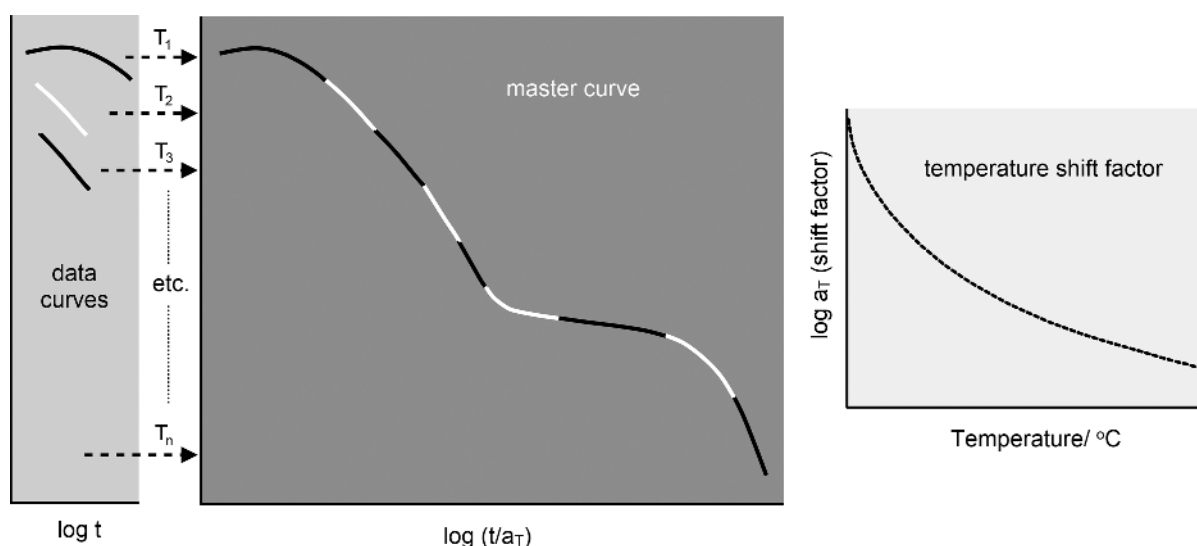


Figure 1.31 Idealised representation of the time-temperature superposition principle.

which contains a volume that is occupied by the free volume,  $V_f$ . At the glass transition,  $f$  is given by  $f_g$ , with the assumption that  $f$  varies linearly with temperature (Eq. 1.12), where  $\alpha_f$  is the *thermal expansion coefficient* of the free volume.  $\alpha_f$  is the difference in thermal expansion coefficient of the polymer,  $\Delta\alpha = (\alpha_r - \alpha_g)$ , above ( $\alpha_r$ ) and below ( $\alpha_g$ )  $T_g$ ; values of  $\alpha_f$  are commonly equal to those for the constant  $C_2$  in the WLF equation (Eq. 1.16) since  $C_2 = f_g/\alpha_f$  [411].

$$f = f_g + \alpha_f(T - T_g) \quad (1.12)$$

Values of  $f_g$  are  $\sim 0.025$  as  $T_g$  is approached and, for many polymers, remain constant at this value as the temperature is lowered  $< T_g$ . The latter observation has been interpreted in the context of  $T_g$ , in which  $f_g$  is an *effective free volume* (sometimes referred to as the *WLF free volume*) that is relevant to specific relaxation experiments whereas the actual free volume is  $\sim 10$ – $15\%$  less [411].

Rewriting Eq. 1.11 as Eq. 1.13, the viscosity at a given temperature,  $T$ , above  $T_g$  is given by Eq. 1.14, where  $a_T$  is the *shift factor*.

$$\ln \eta = \ln A + B \left( \frac{1}{f} \right) \quad (1.13)$$

$$\ln \left( \frac{\eta_T}{\eta_{T_g}} \right) = \ln a_T = B \left( \frac{1}{f_T} - \frac{1}{f_g} \right) \quad (1.14)$$

Inserting Eq. 1.12 into Eq. 1.14 gives Eq. 1.15 which is identical in form to the empirically derived *WLF* equation (Eq. 1.16) in which  $C_1$  and  $C_2$  are constants and  $T_{\text{ref}}$  is a (chosen) reference temperature.

$$\log \left( \frac{\eta_T}{\eta_{T_g}} \right) = \log a_T = - \frac{(B/2.303f_g)(T - T_g)}{f_g/\alpha_f + (T - T_g)} \quad (1.15)$$

$$\log a_T = - \frac{C_1(T - T_{\text{ref}})}{C_2 + (T - T_{\text{ref}})} \quad (1.16)$$

In the context of time-temperature superposition, Williams, Landel and Ferry proposed that the shift factor,  $a_T$ , could be expressed by Eq. 1.16. If  $T_{\text{ref}}$  is taken as the  $T_g$  (i.e.  $T_{\text{ref}} = T_g$  in Eq. 1.16) then the ensuing equation, Eq. 1.17, holds well for many polymers between  $T_g$  and  $T_g + 100^\circ\text{C}$  [168]. Although the values of the two constants  $C_1$  and  $C_2$  vary for different polymers (for values see [409]), if a dilatometric (i.e. static method) is used to measure  $T_g$  then the two constants in Eq. 1.17 are often considered to be *universal*, with values of 17.44 and 51.6 K, respectively, insofar as they provide shift factors that are reasonably close to measured values.

$$\log a_T = - \frac{C_1(T - T_g)}{C_2 + (T - T_g)} = - \frac{17.4(T - T_g)}{51.6 + (T - T_g)} \quad (1.17)$$

Thus, the WLF equation, although derived empirically, is justified theoretically in terms of free volume theory by assuming that the polymer behaves as a viscoelastic material that has a relaxation time ( $\tau$ ) and, for which, viscosity ( $\eta$ ) varies only with temperature [162, 224, 361], as depicted by Eq. 1.15 which is of an identical form to the WLF equation (Eq. 1.16) and infers that  $f_g$  and  $\alpha_f$  should be the same for different polymers. Indeed, the values of 17.44 and 51.6 K in Eq. 1.17 mean that for most amorphous polymers,  $f_g = 0.025$  (and thus the fractional free volume is  $\sim 2.5\%$ ) and  $\alpha_f = 4.8 \times 10^{-4} \text{ K}^{-1}$ .

The WLF equation describes the exponential, temperature-dependent nature of a diffusion-controlled relaxation process at a given temperature,  $T$ , as a function of the rate of relaxation at a lower reference temperature, in this case,  $T_g$ . An indication of the significance of the WLF equation in relation to a temperature-related change in a diffusion-controlled process, such as water or dye diffusion within a polymer, is provided by considering that according to the exponential relationship described by Eq. 1.16, for values of  $(T - T_g)$  of 0, 1, 2, 5, 10 and 15, the corresponding relaxation rates would be 0,  $\sim 2$ ,  $\sim 34$ ,  $\sim 1668$  and  $\sim 8300$ , respectively.

**1.4.2.3.9 Significance of  $T_g$  in Relation to Fibre Properties** In terms of man-made and especially synthetic fibres,  $T_g$  plays a major role during drawing, setting and texturing, insofar as these processes rely upon the inherent plasticity of the fibre that arises at or about the glass transition.  $T_g$  profoundly influences the dyeability of many man-made and

synthetic fibres insofar as both the rate and extent of dye uptake  $<T_g$  are very low and unacceptably so in commercial terms. In essence, this is due to the very low diffusional ability of dye molecules within the polymer at temperatures below the glass transition because of the limited amount of free volume that arises from insufficient segmental mobility of the macromolecular chains at temperatures  $<T_g$ . Whilst this important aspect is discussed in Chapter 8 (i.e. dyeing of PES) briefly, acceptable dyeing rates of, for example, PES, PA and PAN fibres can be secured at temperatures  $>T_g$ , for which the plasticising action of water is of major significance; the latter aspect is discussed in Chapter 3.

As discussed, in extruded filaments of man-made and synthetic fibres, the component fibres are oriented parallel to the longitudinal (fibre) axis whereas the constituent polymer chains are only loosely orientated. Subsequent drawing orientates both the crystalline and non-crystalline regions along the fibre axis which promotes crystallinity and increases strength. In the case of, for example PES and PAN, drawing is usually carried out at temperatures between  $T_g$  and  $T_m$  so as to minimise fracture. Although drawn, orientated thermoplastic fibres, such as PES and PA, possess high tenacity and elasticity, they display poor dimensional stability. Thus, *setting* is carried out so as to stabilise the fibre, yarn, fabric or garment, such treatment being carried out at temperatures  $>T_g$ , under which conditions, thermally induced relaxation processes release the metastable structure imparted by extrusion and drawing and, upon cooling to  $<T_g$ , a more stable molecular structure is secured. *Texturing* of synthetic fibres is carried out to impart increased bulk, enhanced softness and fullness, etc. through the creation of a curvilinear axial profile. In the case of the most significant commercial texturing process, *false-twist texturing*, thermoplastic fibre filaments are stretched and then heated, twisted and finally cooled to  $<T_g$  before being untwisted.

**1.4.2.3.10 Setting (e.g. [130, 209, 412, 413])** As mentioned above, setting is carried out, in the cases of natural, man-made and synthetic fibres, in order to stabilise a fibre, yarn, fabric or garment either in an existing condition or after deformation (e.g. insertion of pleats). Two main levels of set can be achieved: *temporary*, where the effect is lost during use, and *permanent* insofar as the effect cannot be reversed except by employing more severe setting conditions. Setting can be achieved using either chemical or thermal treatments in the presence or absence of tension. Heat setting can be used to impart fabric dimensional stability as well as other properties such as increased volume, wrinkle resistance or temperature-resistance. Several mechanisms have been proposed to explain the nature of the various thermal, mechanical and chemical processes employed in setting [209, 412].

In the case of thermoplastic synthetic fibres, such as PA and PES, after drawing, the fibres display thermal shrinkage when heated  $>T_g$  but  $<T_m$ , owing to molecular relaxation processes. The extent of such shrinkage depends on various fibre properties (e.g. degree of crystallinity and level of orientation) and environmental conditions (e.g. temperature and humidity). Hence, whilst drawn, orientated fibres possess high tenacity and elasticity, and they display poor dimensional stability. Thus, fabrics, and to a lesser extent yarns, comprising man-made and synthetic fibres are often heat-set, using hot air, hot water or steam, to stabilise them in either their current physical condition or after deformation. Essentially, in this process, heating the fibres eliminates internal tensions introduced during extrusion and drawing and rapid cooling sets the fibre in its new state. Heat setting is carried out at temperatures  $>T_g$  under which conditions, the metastable structure imparted by extrusion and drawing is released through thermally induced relaxation processes and, upon cooling to  $<T_g$ , a more stable molecular structure is attained. In the case of both PA and PES fibres, steam setting (or hydro-setting) enables lower temperatures to be used than in dry-heat setting, as the water acts as a plasticizer, lowering  $T_g$ .

Although both dry-heat setting and steam setting increase the crystallinity of PA fibres, especially when carried out under tension, the modulus of the fibre is increased by dry-heat setting but is decreased by steam setting [315]. The latter effects are of significance to dyeing in that steam setting increases whereas dry-heat setting decreases the dyeability of PA fibres with anionic dyes [315]. Optimum setting conditions (temperature, duration and heating medium) vary for different fibres (e.g. PES steam: 140°C, 10–30 min; CTA dry-heat: 180–190°C, 0.5–2 min [413]; PAN dry-heat: 170–190°C, 15–60 s [414]) and, for a given fibre type, vary according to the type of heat setting medium employed (e.g. PA 6 water: 100°C, 120–180 min; steam: 108–121°C, 10–30 min; dry-heat: 175–190°C, 0.25–0.5 min) [413].

From the viewpoint of natural fibres, as cellulose ethers are very stable, etherification reactions of cotton are widely used to impart crease resistance, as well as other durable and non-durable effects; esterification reactions have been explored as a means of securing formaldehyde-free crease-resistant finishes. When wet swollen CLY fibres are subjected to mechanical stress, small fibrillar hairs are abraded from the fibre surface, giving rise to the phenomenon of *fibrillation* [415] (Chapter 7). Although fibrillation has been utilised to create distinctive fabric aesthetics for CLY fibres (e.g. *peach skin effects*), chemical treatments [415] including crosslinking using colourless compounds carrying various electrophilic groups typically employed in reactive dyes [416, 417] have been utilised to reduce fibrillation tendency and impart improved wet resistance; chemical cross linking has been utilised in commercial CLY fibre variants [418]. In *crabbing*, by means of which wool fabric is stabilised towards subsequent processing, the fabric is treated under tension in hot or boiling water, the tension being maintained as the water is allowed to cool.

**1.4.2.3.11 Texturing (e.g. [4, 19, 321, 419–422])** The majority of natural fibres have an *inherent* crimp, which takes the form of a bend, wave, twist or curl along their length and which imparts bulk and softness to yarns. For example, wool has a marked, regular crimp whereas cotton has a slighter, more irregular crimp. Whilst synthetic fibre monofilament or multi-filament yarn are used without crimp (i.e. as flat yarn), a large proportion of synthetic fibre output is in the form of textured yarn. The prime reason for texturing is to impart a curvilinear axial profile, thereby creating increased bulk that also benefits from enhanced softness and fullness, improved moisture transport, greater insulation capacity and improved matte appearance. In essence, texturing is a multi-stage process in which the filament is deformed longitudinally by twisting and the applied deformation is retained so that adjoining filaments assume a bulked structure. Two types of texturing method are used: one employs *heat setting* to retain the deformation, which is applicable to thermoplastic fibres such as PES and PA, and the other uses *friction* to retain the applied deformation in the case of non-thermoplastic materials. A variety of different types of texturised yarns are available which are classified into several types according to their appearance, properties and/or the way they are manufactured [31, 321].

Several texturing processes have been developed since the first twist process was devised for bulked CA filaments in the 1930s. Each of the various methods produces yarn of different crimped character, the two most significant processes being *false-twist texturing* and *air-jet texturing*. In the case of the most commercially employed texturing method, *false twist texturing*, the yarn is heated, highly twisted and then cooled before being untwisted. The process causes the yarns to contract, as a result of which they display high stretch (~fivefold in length) and good recovery from stretch. Textured yarn is often referred to as *Draw Textured Yarn (DTY)*; nowadays, the most commonly used feed yarn for texturing is *Partially Oriented Yarn (POY)* continuous filament. By way of explanation, earlier processes for the production of textured yarns comprised three discontinuous stages namely *spinning/winding*, *drawing/twisting* and *texturing*. Although process developments have not as yet enabled a continuous spin-draw-texture process to be developed, modern texturing is carried out in two stages. The high-speed winding of extruded filaments obtained using high-speed spinning partially orients the composite molecular chains within the filaments, resulting in *partially oriented yarn (POY)* (aka *partially drawn yarn*); subsequent drawing/texturing is carried out simultaneously in one operation. Two types of false twist process are used namely *single-* and *double-heater*. The use of a single heater, which raises the temperature of the yarn to  $>T_g$  prior to twisting, enables high-stretch yarns to be obtained. The use of a second heater positioned after the twisted, high-stretch filaments have been cooled and slightly relaxed reduces the high-stretch character of the bulked yarns. False twisting refers to a process that imparts no net twist to a yarn. Briefly, if a filament yarn is twisted at its middle by turning, it will twist equally on both sides of the middle point. Each side will be twisted in opposite directions, one side having an 'S' twist and the other side a 'Z' twist (i.e. 'S' =  $\backslash\backslash\backslash\backslash$  and 'Z' =  $/\!/!\!/!$ ). When the twist is released, both the S and Z twists disappear because a 'false twist' has been imparted. In *air-jet texturing*, the process of texturing is not reliant upon the thermoplastic behaviour of the fibres, insofar as filaments are heated and then passed through a turbulent hot air jet which opens up the component filaments in the yarn, which is then cooled. Whilst POY is the most common feed yarn for air-jet texturing, *Air Textured Yarns (ATY)* differ to DTY's as loops are formed at the surface of the ATY filaments which impart a distinct handle and appearance. *Bulked Continuous Filament (BCF)* yarns are heavier dtex PP or PA yarns employed in carpet (e.g. 50–400 dtex in the case of PA filaments) which are textured using either hot air or fluid jet. BCF yarns have a random crimp composition that provides bulk but little stretch.

**1.4.2.3.12 Other Transitions (Relaxations)** Many authors consider that  $T_g$  is a *primary thermal transition* or *relaxation*, as it involves motion of large sections of the main macromolecular chains. However, polymers often are subject to a number of other *secondary transitions* that arise at temperatures below  $T_g$ , because side chains and small segments of the macromolecule, such as chain end groups, require less energy for mobility than the larger, main chain segments associated with  $T_g$  (e.g. [423–427]). Several techniques can be used to detect such transitions in polymers, including dynamic mechanical analysis, dielectric loss factor measurements and NMR [425].

Relaxation transitions in polymers are commonly labelled alphabetically in descending order of the temperature at which they occur (i.e.  $\alpha$ ,  $\beta$ ,  $\gamma$ ,  $\delta$ , etc.), the highest temperature transition being the  $\alpha$  relaxation or glass transition,  $T_g$ , in the case of amorphous polymers (or the amorphous region in a semi-crystalline polymer). However, the label ascribed to secondary relaxations, which sometimes are termed *sub- $T_g$  transitions*, do not imply similarity of origin of the transition insofar as the  $\beta$ -transition in one polymer may well arise from a different molecular motion to the  $\beta$ -relaxation in another polymer. Whilst  $T_g$  usually spans several degrees of temperatures, sub- $T_g$  relaxations tend to extend over a much broader temperature range. The various transitions are interpreted in terms of both the relative motions of the composite macromolecular chains, side groups and branches, as well as cooperative motions of the crystalline and non-crystalline regions. In essence, the  $\beta$ -relaxation is commonly associated with local chain or sub-group motion and may well extend over 100°C. The  $\gamma$ -relaxation, which often can be resolved into several components corresponds to side group or end group motion in amorphous polymers and, in the case of crystalline material, to the  $\beta$ -relaxation processes within the amorphous region; the  $\delta$ -transition is of similar derivation to the  $\gamma$ -relaxation [428]. The various relaxations, which have been classified according to the possible modes of molecular motion involved [409], are

sometimes referred to in terms of the temperature at which they occur, namely  $T_\alpha$ ,  $T_\beta$  and  $T_\gamma$ , ( $T_\alpha > T_\beta > T_\gamma$ ) and are effected by crystallinity and orientation, moisture, pressure, stereoregularity, etc.

Some polymers show three, clearly resolved relaxation processes, as exemplified by linear and branched PE which displays an  $\alpha$ -relaxation at 60–80°C,  $\beta$  at –20 to –30°C and  $\gamma$  at –120 to –130°C [210]. The  $\alpha$ -transition occurs close to the  $T_m$  and is attributable to motion of the chains associated with the crystalline phase, whilst the  $\beta$ -transition involves amorphous regions which are influenced by the crystalline regions and the  $\gamma$ -relaxation stems from mobility of either branches or chain end groups in the amorphous regions [429]. Other polymers show only two transitions, as represented by PAN containing vinyl acetate or methyl acrylate comonomers, that display two transitions, at ~80–110°C and ~140°C [368], the former being considered to correspond to molecular motions within the paracrystalline region whilst the latter relates to dipole–dipole interactions between the cyano groups (–CN) in the amorphous regions [430], although the precise nature of the two transitions remain unresolved.

Interpretation of the various secondary transitions is especially difficult in the case of semi-crystalline polymers owing to the presence of both crystalline and non-crystalline phases. For example, PES displays relaxation behaviour that is sensitive to crystallinity (e.g. [404, 431, 432]) namely an  $\alpha$ -transition at ~80°C, associated with segmental motions within the amorphous regions, which becomes broader and is shifted to higher temperatures with increasing crystallinity, and a  $\beta$ -relaxation at approximately –40°C that is insensitive to the degree of crystallinity. However, oriented, semi-crystalline PES has been shown to display three relaxation peaks at around 100°C ( $\alpha$ ), –70°C ( $\beta$ ) and –230°C ( $\gamma$ ) [433]. The three major relaxations in PA 6 (see [434]) occur at approximately +80°C ( $\alpha$ ), –40°C ( $\beta$ ) and –120°C ( $\gamma$ ) [435]: the  $\alpha$  relaxation, which corresponds to the  $T_g$  of dry PA 6, reflects motion in long chain segments in amorphous regions; the  $\beta$  relaxation arises from motion of non-H-bonded amide groups and in the presence of water, polymer–water units [436], whilst the  $\gamma$  relaxation reflects motion of short polymethylene segments with some involvement of adjacent amide groups.

As discussed briefly above and in detail in Chapter 3, moisture markedly effects the temperature of the  $\alpha$  relaxation (i.e.  $T_g$ ) of many amorphous and semi-crystalline polymers, which is perhaps most dramatically illustrated in the case of PA materials such as PA 46, for which the  $T_g$  of the dry material is reduced from +80 to –40°C when the substrate contains 12.4% water [437]. Water also affects both the magnitude and temperature-range of some secondary relaxation processes in polymers. For example, in the case of dry PA 4, whilst an  $\alpha$ -transition located at 81°C and a  $\gamma$ -relaxation at –111°C were observed, no  $\beta$  transition was detected. However, the addition of water resulted in the appearance of a  $\beta$ -relaxation at –60°C and the temperature of all three transitions decreased with increasing water content [438].

### 1.4.3 Optical Properties

Textile fibres are dyed for various reasons, most notably to enhance their appearance. This section concerns some of the characteristics of both undyed and dyed fibres. The large and multifaceted area of colour physics is not discussed and readers are directed elsewhere (e.g. [439–443]).

As textile fibres are anisotropic, their optical properties (as with others of their physical properties) vary with fibre direction. Accordingly, textile fibres are *birefringent* (*optically anisotropic*) in that their *refractive index* depends on *polarisation* by light and varies with the direction of propagation of the light.

#### 1.4.3.1 Polarisation (e.g. [209, 306])

Confusingly, the term *polarisation* (aka *polarization*) refers to several scientific phenomena,<sup>68</sup> of which perhaps the most commonly known involves the selective orientation of the electric oscillations of electromagnetic waves (visible light), as exemplified by *polaroid* sunglasses which employ *dichroism* to reduce glare. Electromagnetic waves comprise both electric and magnetic fields (vectors) that oscillate (vibrate), in phase, at right angles to each other, the two oscillations also being perpendicular to the direction of propagation of the wave. Polarisation refers to the orientation of the wave's electric field (which may be oriented in a single direction or may rotate as the wave travels), all directions of vibration being equally probable. In essence, non-polarised light can be converted into *polarised light* using an optical filter (*polariser* or *polarizer*) that allows the passage of light of a specific polarisation but which prevents passage of waves of other polarisations. For example, the filter restricts the electric vibrations to a single *plane* thereby producing *plane polarised* (aka *linearly polarised*) light in which the electric vectors are *plane parallel* (or *plane-polarised*) with respect to the direction of propagation.<sup>69</sup>

<sup>68</sup> for example, *dielectric polarization* (charge separation), *wave polarization* (electric flux), *spin polarization* (elementary particles).

<sup>69</sup> Polaroid sunglasses function by allowing the passage of only vertically polarised light, thereby preventing passage of horizontally polarised light that is reflected from surfaces and which gives rise to 'glare'.



In the context of the optical properties of fibres, the term *polarisation* refers to the tendency of an electron cloud within an atom or molecule to be (temporarily) distorted by an externally applied electric field such as that produced by a nearby ion or dipole or, of relevance here, light (i.e. electromagnetic radiation). As implied by the foregoing, there are several mechanisms of polarisation, such as *ionic polarisation* (displacements between positive and negative ions in ionic crystals, e.g. NaCl), *molecular polarisation* (polar molecules in an electric field can experience torque which causes them to align with the applied field) and, of relevance to the optical properties of textile fibres, *electronic polarisation* (aka *electric polarisation*). Electronic mechanisms only occur during the interaction between light and fibres because only electrons are sufficiently light enough to respond to the very high frequency of the light waves involved.

As light passes through a (transparent or translucent) fibre, the applied electric field polarises the electron cloud of the fibre's constituent atoms/bonds/molecules. As discussed in Chapter 5, the ease with which the electron cloud arrangement in a non-polar species can be distorted by the presence of the electric fields of neighbouring molecules is a measure of the *polarisability* of the atom or molecule. The distortion of the electron cloud induces a dipole moment in the originally non-polar atom or molecule, the induced dipole moment being related to the polarisability of the molecule or atom and the strength of the electric field. Polarisability is commonly expressed as *polarisability volume*, values for which often are of similar magnitude to molecular volumes. Accordingly, the larger the volume occupied by electrons, the greater the polarisability of those electrons; polarisability also increases with increasing number of electrons per unit volume. Polarisability decreases with increasing electronegativity because the electron cloud (or electron density) is more tightly held. This particular characteristic is a feature of the concept of *soft* and *hard* compounds, the former having diffuse electron clouds and are polarisable whereas the latter are poorly polarisable owing to their tightly held electron clouds.<sup>70</sup>

The polarisability of a given bond is influenced by neighbouring atoms and, therefore, polarisability is differentiated into three aspects namely one *longitudinal* aspect (i.e. along a molecular or bond axis) and two *transverse* aspects (perpendicular to the molecular or bond axis). In the case of textile fibres, although the constituent molecular chains assume a parallel or near parallel arrangement along the fibre axis, owing to the axial symmetry of the fibre, the two transverse aspects are identical.

### 1.4.3.2 Refractive Index

Refractive index (aka *index of refraction*),  $n$ , is a dimensionless quantity that describes the nature of the propagation of light through a medium. A consequence of the polarisation of a transparent or translucent material by light is that the velocity of light within a medium varies for different media, for which Eq. 1.18 applies where  $\nu$  is the velocity of light. As light travels more rapidly in a vacuum than in a medium  $n \geq 1$  (e.g.  $n_{\text{water}} = 1.33$ ).

$$n = \frac{\nu_{\text{vacuum}}}{\nu_{\text{medium}}} \quad (1.18)$$

An alternative derivation of refractive index describes the fact that when light passes from one medium to another it is *refracted* (bent), Eq. 1.19, where  $i$  is the angle of incidence and  $r$  that of refraction.

$$n = \frac{\sin i}{\sin r} \quad (1.19)$$

Refractive index varies with density, since electron density also increases with density and, therefore, so does electronic polarisability; values of  $n$  for polymers are available [444].

As a consequence of the anisotropy of fibres, refractive index varies as a function of direction of passage of light through the substrate, and, therefore, fibres have two principal refractive indexes (parallel and perpendicular), as discussed below.

### 1.4.3.3 Birefringence

Whilst the refractive index of an isotropic material is identical for all directions of measurement, the refractive index of an anisotropic material, such as a crystal or textile fibre, varies with direction of measurement. A fibre is generally characterised by two refractive indices, one measured along the fibre axis,  $n_{\parallel}$ , and one perpendicular to the fibre axis,  $n_{\perp}$ . The difference between the two refractive indices ( $\Delta n = n_{\parallel} - n_{\perp}$ ) is the *birefringence*, which reflects the different polarisability of the fibre to light oscillating along and normal to the fibre axis. Birefringence is observed in materials as

<sup>70</sup> the concept of Hard and Soft compounds is related to that of Lewis acids and bases, the former being synonymous with a nucleophile and the latter an electrophile.

**Table 1.5** Birefringence of some fibres [440].

fibre	$n_{\parallel}$	$n_{\perp}$	$\Delta n$
PA 6	1.580	1.530	0.050
PA 66	1.582	1.519	0.063
CA	1.539	1.519	0.02
CV	1.539	1.519	0.02
Cotton	1.578	1.532	0.046
Aramid	2.267	1.605	0.662

the result of mechanical orientation in either the solid or liquid states (i.e. *stretch* and *flow* birefringence, respectively); thus, polymers melt under forced flow or under tension display birefringence, as also do solid polymers after orientation [440].

The birefringence of the majority of fibres is positive, ranging from 0.010 (wool) to 0.662 (Kevlar 49) [307] (Table 1.5), since  $n_{\parallel} > n_{\perp}$ , indicating that the atoms/bonds along the chain are less polarisable than are those disposed laterally. However, PAN, CTA and PVC fibres are negatively birefringent, although only weakly so [307, 445]. Birefringence can be used to determine the degree of molecular orientation in fibres, irrespective of the size and nature of the crystalline and amorphous regions [307].

**1.4.3.3.1 Dichroism** As a corollary of the anisotropy of textile fibres, dyed fibres often are *dichroic* insofar as the depth of shade or colour of the dyeing may vary according to the angle of viewing (i.e. direction of the incident light) owing to orientation of the dye molecules together with that of the polymer molecules in the fibre. For this effect to occur, several aspects must be satisfied [209, 446, 447] namely:

- the dye molecule must itself be *dichroic*, as observed for asymmetrical dyes in which light absorption occurs along one axis, as exemplified by the essentially linear oscillator axis in the case of planar azo direct dyes or vat dyes;
- the dye molecule must be adsorbed in the fibre in such a manner that the axis corresponding to light absorption is aligned either essentially parallel to or perpendicular to the polymer chain molecules in the fibres;
- the polymer chain molecules in the fibre must be preferentially oriented.

Several workers have used the first two aspects to quantify the orientation of the polymer chains in a fibre by equating the extent of dichroism of the adsorbed dye molecules to the orientation of the fibre molecules [446–449]. The dichroism of dyed cotton has been used as a means of describing the mechanism of dyeing [450] in which context Sumner *et al.* [451] employed dichroism to determine the effects of soaping treatments on vat dyed cellulosic materials.

$$\frac{A_{\parallel}}{A_{\perp}} = \frac{k_{\parallel}c}{k_{\perp}c} = p \quad (1.20)$$

In the case of a dichroic dyed fibre, the respective amounts of polarised light parallel and perpendicular to the fibre axis absorbed by the fibre,  $A_{\parallel}$  and  $A_{\perp}$ , respectively, can be used to determine the *dichroic ratio*,  $p$ , via Eq. 1.20 where  $k_{\parallel}$  and  $k_{\perp}$  are the absorption constants and  $c$  the dye concentration [446].

#### 1.4.3.4 Lustre

Most textiles are examples of a *gonioapparent materials*<sup>71</sup> and lustre is one of several key attributes of the appearance of textile materials, others include, for instance, colour and texture. Lustre is a particular *goniometric property* which can be defined as *the display of different intensities of light, reflected both specularly and diffusely, from different parts of a (fibre, yarn and fabric) surface exposed to the same incident light* [11]. Lustre is a complex sensation that depends on both the characteristics of the textile material being viewed (e.g. fibre and yarn type, woven/knitted/non-woven construction) and the viewing conditions employed. Despite much research attention over many decades, which continues till recent times (e.g. [209, 452–457]), no objective quantitative parameter has yet been developed to describe fibre lustre and, consequently, subjective (visual) assessment of this important fibre property is routinely employed [453, 458] with adjectives such as *shiny*, *lustrous*, *matt* and *dull* being common. Nonetheless, several equations have

<sup>71</sup> one whose appearance changes with change in illumination or viewing angle.

been developed to describe fibre lustre employing data obtained using *goniophotometers*; recently, fuzzy logic and image processing have been applied to lustre determination in textiles [456, 457].

In simple terms, a surface is perceived as being lustrous if its brightness differs under different angles of observation or illumination. Lustre can be considered as textile fibre *gloss* which is a function of several fibre characteristics, such as the refractive index, cross-sectional shape and smoothness of a fibre, fibre surface regularity (e.g. hairiness), fibre fineness, the structure and arrangement of yarn in a fabric, filament/yarn crimp and twist, and, in the case of synthetic fibres, the presence of delustrant (see Section 1.4.3.4.1). As such, fibres that are uniform will display high lustre, as observed in the cases of silk filaments which have a characteristic smooth surface, as well as man-made and synthetic fibres. In contrast, natural fibres (with the exception of silk) tend to be irregular in terms of uniformity. Indeed, Adderley [459] proffered that the characteristic dullness of cotton was attributable to the fibre's irregular shape and that the marked improvement in lustre imparted by *mercerisation* (Chapter 3) could be attributed to the fibres assuming a more regular, round cross-sectional shape.

**1.4.3.4.1 Delustrants** Extruded man-made and synthetic fibres are typically transparent and highly lustrous. The addition of a delustrant reduces lustre and also increases opacity (and covering power), the most common delustrant being powdered  $\text{TiO}_2$  (particle size range: 0.3–0.4  $\mu\text{m}$  in the case of PES fibres [219]), although other compounds such as  $\text{ZnS}$ ,  $\text{Al}_2\text{O}_3$  and synthetic resins [321] can be used. Only a small amount of  $\text{TiO}_2$  (e.g. 0.2% in the case of PA fibres [213]) is required to reduce transparency whilst additional levels are employed to secure fibres of differing lustre, these being referred to as *clear* (aka *bright*) in the case of fibres that do not contain delustrant, *semi-matt* (aka *semi-dull*) and *matt* (aka *dull*), the latter two variants being produced using additions of 0.5% and up to 2%  $\text{TiO}_2$ , respectively, in the case of PA fibres [213]. The presence of delustrant within the fibre will reduce lustre because the small particles of typically  $\text{TiO}_2$  scatter the transmitted light thereby increasing the extent of diffuse reflection.

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