The attributes of fibres

Introduction

For thousands of years, humans have exploited the attributes of fibres for the provision of clothing. Sources of natural fibres are wide ranging, but fall into two main categories: cellulosic fibres (chiefly cotton) and protein fibres, which provide the hairy coating of many animals. Wool was used in primitive textiles, and linen-type fabrics were made in North Africa from stem fibres 7000 years ago. Until the advent of synthetic fibres, however, flax, cotton, wool and silk were the only four fibres chosen from all those available.

The chemical and physical properties of natural textile fibres have been thoroughly studied, and the information obtained has been put to good use in many spheres of activity. The studies provided insight into the fibres' long thread-like molecules, in which many relatively simple units are joined together as a chain, and the ways in which the physical properties of a fibre are related to the arrangement of the molecules within it. Using such knowledge, chemists have been able to synthesise materials with properties appropriate for use in almost any conditions, such as heat-resistant materials, glass substitutes, synthetic rubbers, adhesives, and aircraft and rocket components, as well as dozens of different kinds of synthetic fibre.

The total annual world production of fibres today is approximately 30 million tonnes; cotton is the most important in terms of quantity produced. Over 50% of production consists of cellulosic fibres, of which one-fifth is the regenerated cellulose fibre viscose, while cotton accounts for the bulk of the remainder. Wool, although significant in commercial terms, claims a 5% share of world fibre production only, whilst the synthetic fibres make up around 40%, of which polyester fibres account for almost half.

In this chapter we shall look at the properties of fibres in general before examining those of different classes of fibre and outlining the processes of manufacture of synthetic fibres.

Physical properties of fibres

Fibre length

The length of natural fibres varies considerably. The length (*staple*) of cotton fibres is of the order of 12 to 36 mm, depending on the source, whilst wool fibres are from 50 to 400 mm long. There is a minimum useful length of about 10 mm, however, below which the fibres are too short to be spun together into yarn. Furthermore, the characteristics of the yarns depend on the fibre length. A fluffy, spongy yarn with a soft feel is obtained from shorter fibres where many loose ends remain disoriented in the yarn. Longer fibres give smoother, finer yarns with a higher lustre.

A yarn is only as strong as its weakest point, so uniformity of yarn strength is important. To this end a minimum number of around 100 fibres is needed in the cross-section of yarns derived from short-staple fibres, and the finer the fibres the more uniform will be the strength. As the length of the fibres is increased, the degree of twist needed to hold the fibres together and develop a satisfactory strength becomes less and the yarns are correspondingly softer.

Synthetic fibres are produced in the form of continuous filaments, the advantage of which is that they can be either cut into predetermined lengths to suit the type of yarn needed or kept as continuous filaments. Natural and synthetic fibres are often blended together to combine the advantages of both in one yarn. In such cases the length of the synthetic filament may be cut to match that of the natural fibre, thus making it possible to use the same spinning machinery for both fibres.

Fibre fineness

Fibres from different sources show distinctive variations in their cross-sectional shape, but the measured width of a fibre can be taken as the fibre diameter. The theoretical relationship between the diameter and stiffness of a rod can then be invoked to explain the significance of fibre diameter in relation to the practical applications. For example, the stiffness of a fibre is proportional to the fourth power of the diameter, which means that doubling the diameter increases the resistance to bending sixteen-fold! Other factors being equal, this increase will sharply reduce the ability of the fabric to drape over shapes or to hang elegantly.

Fibres with a diameter of more than 40 microns (1 micron (µm) = one thousandth of a millimetre) tend to scratch and stick into the skin because they do not deflect easily. This diameter is

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about that of coarse wool fibres from cross-bred sheep. Usually such fibres are used for the pile in carpets, where more resilient fibres are needed. Other wool fibres range in diameter from 15 to 40 μm, depending on the breed of animal and the position on the fleece on which it grew. Merino sheep produce the finest fibres, with a diameter of 17–25 μm. By comparison, horse hair is of the order of 100–200 μm in diameter, cow hair is coarser still at around 200 μm, whilst hairs from 180 to 250 μm in diameter are stiff enough to be referred to as bristles. (Fibres derived from animals other than the sheep are usually referred to as hairs to distinguish them from sheep's wool; few have proved suitable for specialist textile uses, but more information is available elsewhere [1]. Even though the shorter, softer fibres from different parts of various animals are often also called wool, the description should always be qualified by adding the name of the animal source – for example, cashmere wool.)

Fibres for clothing need to be soft and pliable, that is, their diameter must be small. But if the diameter is halved, the corresponding increase in softness is accompanied by a four-fold reduction in breaking strength. Consequently there are also lower limits needed for the fibre diameter if damage is to be avoided during processing. The minimum practical strength for natural fibres is associated with a diameter of 10 μm, which is found with the finer Sea Island cottons and with Canton and Japanese silks.

Fibre diameter also has a significant influence on the dyeing properties of the fibre, because the surface area of a given mass of fibres is higher for finer fibres. This relative difference between the surface areas of fine and coarse fibres allows the finer fibres to take up dye more rapidly. Fibre diameter can also affect the depth of colour of the dyed goods in relation to the amount of dye applied. For example, fibres with a diameter of 25 μm must absorb about twice as much dye per unit mass as fibres of 44 μm diameter to appear the same depth, because the colour is spread over a larger surface area with the finer fibres.

Fabric lustre

Several factors contribute to fabric lustre, including the fibre diameter and cross-sectional shape (page 66). Such factors influence the way in which light is reflected from the surface of the fabric. The alignment of the fibres in the yarn and the structure of the fabric also have an influence. A harsh shine is associated with large smooth filaments arranged in parallel, whilst finer fibres with a less uniform surface in a yarn with a lower degree of fibre orientation produce multiple reflections and a

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correspondingly subdued lustre. For example, the ribbon-like structure of unmercerised cotton fibres gives a low-lustre fabric. The wavy nature (i.e. the crimp) of wool from some breeds of sheep has the same effect on the sheen of wool fabrics, whilst coarser, straighter wool fibres give a lustre limited by their rough, scaly surface (see page 48). The smoothness of silk filaments is also associated with a characteristic sheen.

Morphological features of fibres

Cotton

Other characteristics of fibres become evident on more detailed study. The intricate structure of cotton fibres only becomes apparent when viewed under the optical or electron microscopes. The cotton fibre is a single-cell structure taken from the cotton plant as a seed hair which develops its characteristic appearance under the microscope as it dries out. As used, it appears as a flat ribbon-like structure with occasional convolutions along its length (Figure 4.1). These prevent parallel

Figure 4.1 *The structure of a cotton fibre, seen (above) diagrammatically and (below) in a photomicrograph*

fibres from slipping past each other, thus contributing to the strength of the yarns when they are twisted together during spinning. The greater magnification possible with an electron microscope has enabled various morphological components of the fibre to be identified.

The outermost layer of the fibre is the thin waxy cuticle, which protects the fibre from its environment. Before cotton can be used as a textile fibre this layer has to be removed by scouring, otherwise the absorption of water-soluble dyes and other reagents is hindered during processing. Beneath this layer is the primary wall of the fibre cell, which is composed of fine threads of cellulose laid down during growth and spiralling round the longitudinal fibre axis at an angle of about 70° (just visible in Figure 4.1). Most of the fibre mass is present as the secondary wall. This also consists of spiralling fibrils, in this case with an inclination to the main fibre axis that varies from 20–30° near the primary wall to around 40° near to the central air-filled channel (the *lumen*). The direction

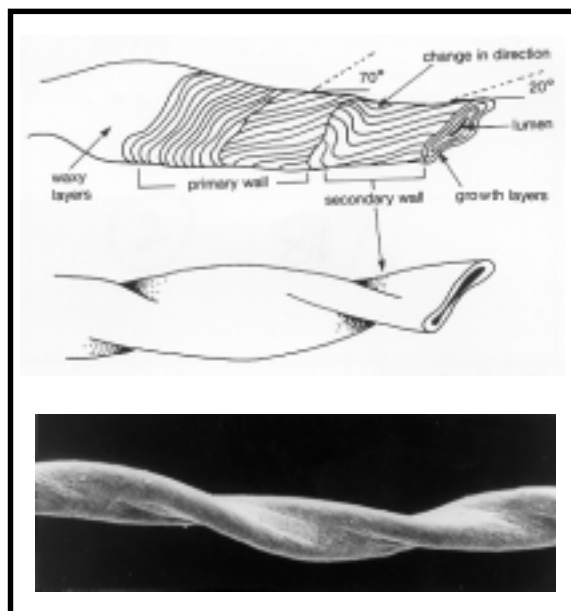of this spiral changes periodically along the fibre length, corresponding to the position of the convolutions mentioned above.

Wool

The appearance of wool fibres is very distinctive, with overlapping scales oriented in the direction of the tip of the fibre (Figure 4.2). The scale structure gives the fibre surface its characteristic roughness, which creates the friction between fibres in a yarn, thus contributing to its strength. Because of the orientation of the scales, however, the friction is greater in the direction of tip to root than from root to tip. This may be readily d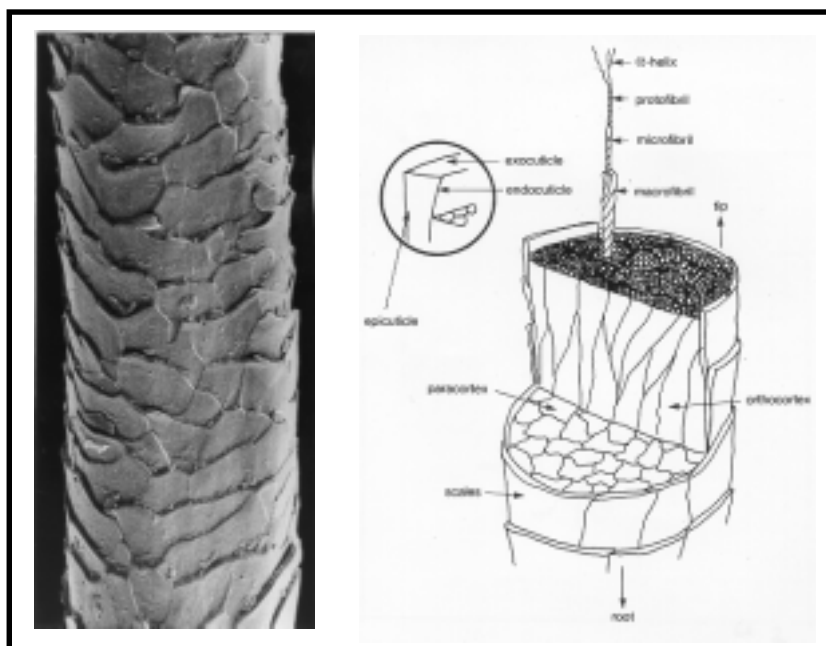etected by lightly gripping a long hair or a wool fibre between the nails of the thumb and forefinger and pulling the fibre through the grip, first one way and then the other: the greater resistance to movement in the tip-to-root direction is evident. This directional friction effect has important technical consequences because, as the fibres are mechanically agitated in the hot wet conditions of processing, they migrate preferentially in the direction of least resistance, i.e. towards the tip of adjacent fibres. If the movement is allowed to go too far, individual fibres begin to form loops and become entangled, and the fabric or yarn structure becomes compacted. The effect can be technically desirable if controlled (as in milling or the manufacture of non-woven felt materials), but serious when it is responsible for the excessive shrinkage of a wool garment during laundering.

Figure 4.2 *The structure of a wool fibre*

The outer scale cells are thin structures that form the main component of the wool fibre

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cuticle. This surrounds the bulk of the fibre material, which is contained in the cellular cortex beneath. The cortex is a complex structure, illustrated diagrammatically in Figure 4.2, which also shows t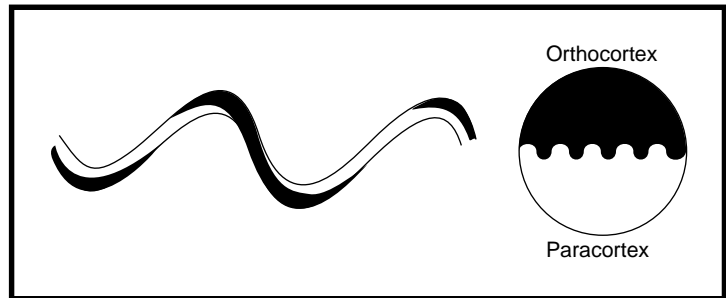he two components of the scale cells (the exocuticle and the endocuticle). The cortex cells are tapering spindle-shaped structures, constructed from component

Figure 4.3 *The distribution of the orthocortex and the paracortex in a wool fibre*

macrofibrils in which the successively smaller microfibrils, protofibrils and finally the helical structure of the protein molecule may be detected. The cortex is heterogeneous and is divided into two regions along the length of the fibre, known as the orthocortex and paracortex. The two halves spiral along the main axis of the fibre, with the more extensible orthocortex always lying on the outer curvature of the fibre (Figure 4.3). They differ slightly in their chemical composition, and the difference is responsible for a difference in their elasticity; this endows the fibres with a characteristic crimp. Other animal fibres are also cellular in structure, but both the scale structure and the crimp frequency vary from one type of animal fibre to another.

The whole fibre is held together by a series of membranes surrounding the cell structure, the outermost of which is the epicuticle.

Silk

Silk, which is also a protein fibre, is produced as a cocoon by the larva of the silk moth *Bombyx mori*. The protein is extruded from two spinnerets, one on each side of the head of the caterpillar, as a pair of continuous filaments between 3000 and 4000 m in length, joined together by a gum called serecin. The gum is removed during processing to release the individual filaments, which have a triangular cross-section and a smooth surface.

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General characteristics of cotton and wool fibres

Comfortable clothing can be made using either cotton or wool fibres; both have the capacity to keep the body comfortable by conducting water from the skin to the atmosphere. Both are hydrophilic

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(water-attracting) fibres, because they possess functional groups that are capable of hydrogen bonding with water molecules. In cellulose they are mostly hydroxyl (OH) groups, but there are several different kinds of hydrophilic group in wool molecules.

In most other respects their chemical and morphological dissimilarities make the attributes of cotton and wool very different. For example, cotton can be safely sterilised in boiling water or by ironing at around 200 °C. Wool, by contrast, becomes harsh and scorched under a hot iron and weak when wet, with detrimental chemical changes taking place at higher washing temperatures. On the other hand, cotton creases very easily, whereas the higher resiliency of wool allows fabric to recover from creasing and retain its shape. Cotton fibres are easier to store because wool protein is palatable to the larvae of certain moths and beetles.

The crimp of wool fibres prevents their close packing in a yarn. Consequently a good deal of the volume of the yarn is air, which makes for a lofty (bulky) warm yarn, the warmth being due to the insulating properties of the static air inside the yarn. Once external pressure is applied (for example, on a windy day), the air begins to flow through the fabric and the warmth of the garments is reduced. In contrast, the flat straight shape of cotton fibres allows them to pack together into a closely structured high-density yarn, which when tightly woven produces a wind-resistant fabric.

The biggest drawback of cellulosic materials, however, is the ease with which they ignite and burn. In this respect wool is superior because it does not readily support combustion, showing only a tendency to become badly singed, due in part to the high nitrogen content of the fibre.

Molecular structure of fibres

In Chapter 3 the formation of molecules was discussed, without considering their size. In general, of course, the more atoms there are in a molecule, the larger it will be. The size of the molecules of most familiar chemical compounds may be deduced precisely from their chemical formulae. But many of the molecules forming the structural material of naturally occurring substances are so immense that simple chemical analysis is no longer an adequate guide to their true structure or shape. Such molecules are referred to as *macromolecules*.

The general concept of structure upon which modern macromolecular chemistry is based was first proposed by Staudinger, who envisaged such molecules as exceptionally long chains of repeating identical units. Each unit is a single simple molecule, but within the chain many such units are chemically linked in a head-to-tail arrangement, like the carriages on a train (Figure 4.4).

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His views have since been adequately confirmed, particularly by the work of Carothers, who was the first person to take simple compounds, synthesise a polymer and adapt its chemical structure to obtain a material with specified physical properties. The resulting nylon fibres soon became appreciated by the public through the hosiery trade during the time of World War 2, when the traditional silk filaments were unobtainable.

The molecule used as the building block in the construction of the long-chain molecule is referred to as the *monomer* and the long molecules themselves are *polymer* molecules, the word polymer being derived from the Greek *poly* (many) and *meros* (parts or segments). The chemical properties of the polymer chains are therefore governed by the monomer, so that a monomer with hydrophilic groups will produce a hydrophilic polymer and a hydrophobic monomer a hydrophobic polymer. Wool and cellulose, for example, are both constructed from hydrophilic monomers, and accordingly the fibres are hydrophilic in character.
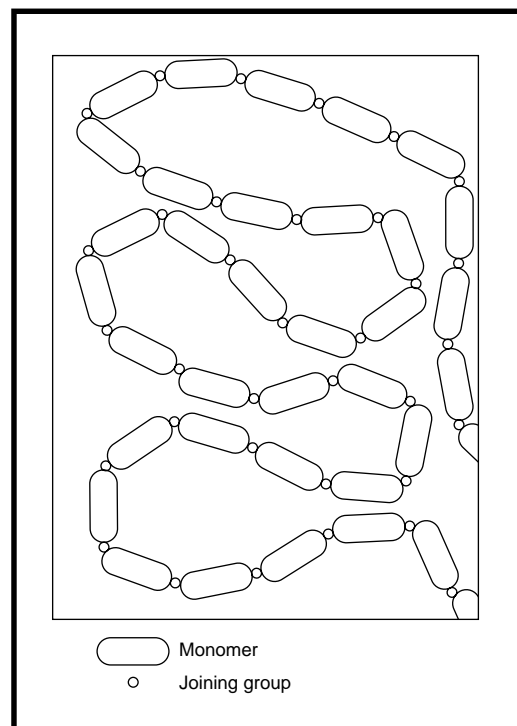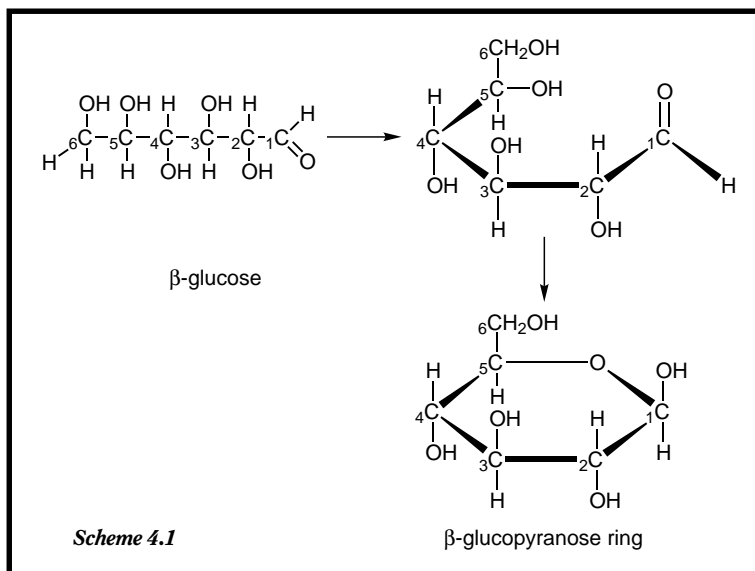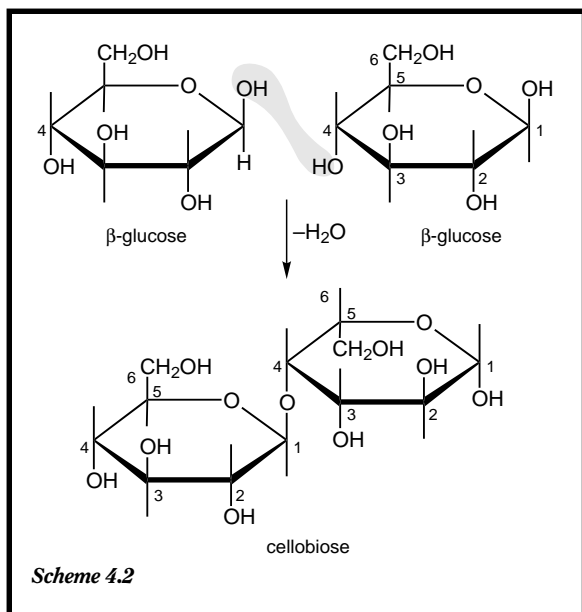

Figure 4.4 *Representation of a step-growth polymer chain*


Scheme 4.1

Structure of the cellulose molecule

The cellulose molecule is closely related to the simple sugar glucose. Glucose forms a ring structure comprising five carbon atoms and one oxygen atom (Scheme 4.1). In this conformational formula

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Scheme 4.2

the thick bonds are taken as being in front of the plane of the paper and the thin bonds behind the plane of the paper, while the tapered bonds indicate the relative dispositions of the adjoining atoms. Glucose is the monomer unit of the cellulose polymer, whilst the repeat unit is cellobiose, a sugar formed by the joining of two glucose units at the terminal hydroxyl groups attached to carbon atoms 1 and 4 with the loss of a molecule of water (Scheme 4.2, in which the hydrogen and carbon atoms incorporated in the ring are omitted for clarity; notice the inversion of the second glucose unit in cellobiose).

Structure *4.1* represents the structure of the cellulose chain; the repeat unit is shown in brackets and marked with a subscript n, to indicate that there are many such units in the chain. For cellulose this number, often called the *degree of polymerisation*, depends on the origin of the sample: for isolated cellulose n is of the order of 3000 (that is, 6000 glucose units) but for cellulose in fibres it may be twice this value, or even more.

4.1   cellobiose
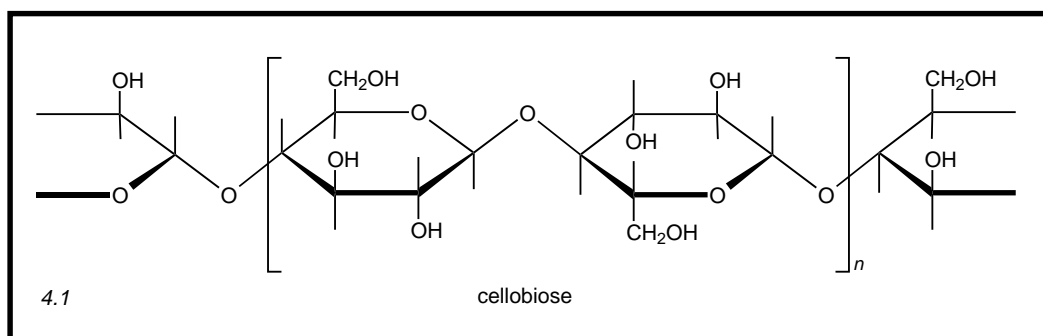
Each glucose ring in the chain contains three hydroxyl groups and it is their presence that allows cotton to absorb moisture and form hydrogen bonds, in particular with certain direct dyes (*4.2*). The formation of hydrogen bonds between adjacent cellulose chains has a particularly important effect, for without them a water molecule would become attached to each hydroxyl group in the cellulose chains and the fibre would dissolve. Cellulose will not dissolve in water, however, and

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in fact is insoluble in all but a few organic solvents. Furthermore, the interaction between the polymer chains is so strong that cellulose does not melt on heating; the chains break down and degrade before the temperature rises to a level at which they could be torn apart to form a liquid.
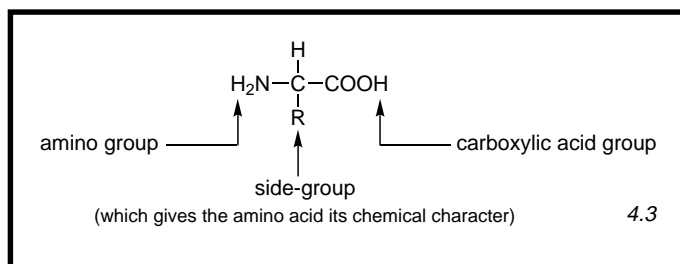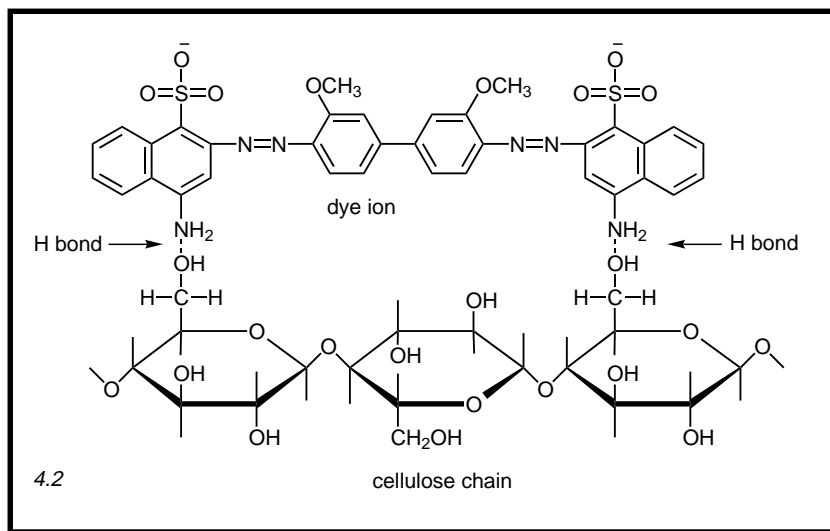

4.2   cellulose chain

Structure of the wool molecule

Wool is a protein, and all protein material is composed of polymer

4.3

chains containing many different *amino acids* as monomer units. The differences between the various proteins lie in the proportions of each acid they contain, and the sequence in which they appear along the length of the polymer chain. All amino acids contain carbon, hydrogen, nitrogen and oxygen, and some contain sulphur too. Some proteins have globular molecules, and these are soluble in water. Others, the fibrous proteins that form the structural material of animal life, are insoluble. Wool is one of the *keratin* group of fibrous proteins, which includes other animal hairs, horn and nails.

Each amino acid contains a carboxylic acid group (—COOH) and a basic amino group (—NH$_2$). This pattern is common to all the amino acids, the simplest of which is *glycine*; structure *4.3* shows the generalised formula. The middle carbon atom in glycine is linked to a carboxylic acid group, an amino group and two hydrogen atoms. One of the hydrogen atoms can be replaced by another group to form a different amino acid and thus a whole series of such acids can be obtained, each containing a different side-group.
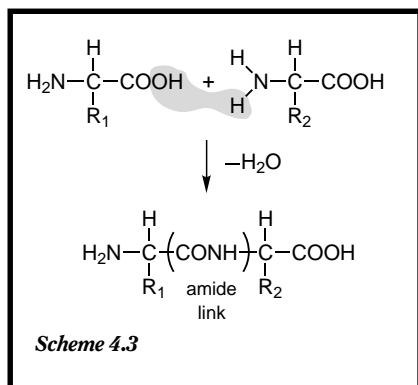
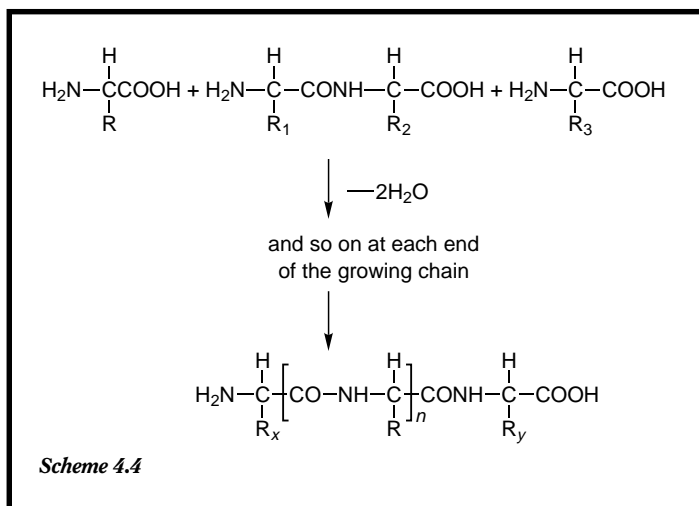Growth of a protein chain requires the amino group of one acid to react with the carboxylic

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Scheme 4.3

Scheme 4.4

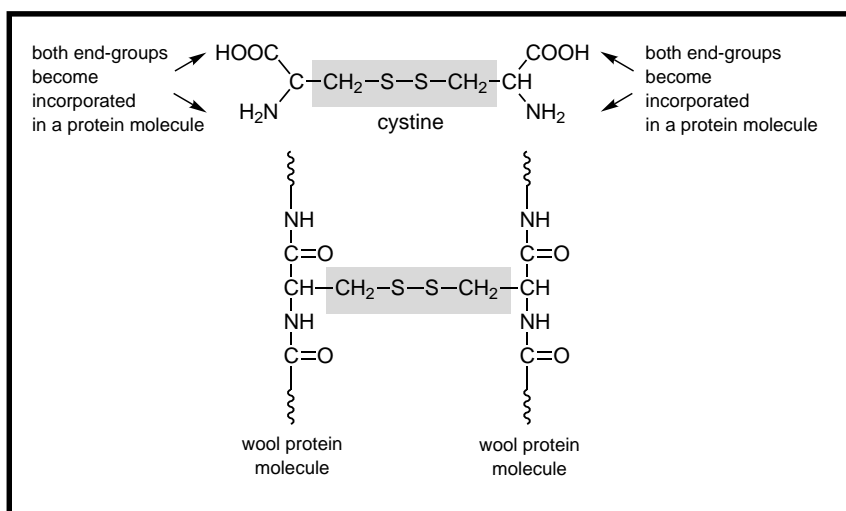**Figure 4.5** *The origin of disulphide crosslinks in wool molecules*

acid group of the next. In the reaction one molecule of water is lost and an amide linkage is formed (Scheme 4.3). This process is repeated at each end of the new molecule, and thus the molecule steadily grows in length (Scheme 4.4). In effect the monomer unit is only one carbon atom long, and because the bonds of a carbon atom are arranged in space as a tetrahedron (Figure 3.4), keratin molecules in the normal state exist with their backbone coiled into a helix. This is alpha (α) keratin, and it will be indicated later how the alpha keratin helix influences the elasticity of wool fibres.

One particular amino acid has a significant influence on wool during wet processing. This is *cystine*, which has two atoms of sulphur in its molecule. The two sulphur atoms bridge the two halves of the molecule, each of which contains one acid group and one amino group. Because of its structure cystine can become incorporated into more than one wool molecule, forming a *disulphide bridge* between them. The formula of cystine and a diagrammatic representation of the

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way in which it bridges (*cross-links*) two wool molecules are shown in Figure 4.5. The disul-phide bridge is susceptible to hot wet conditions and alkaline solu-tions, both of which split the crosslink; other reagents can have the same effect. If the reactions are
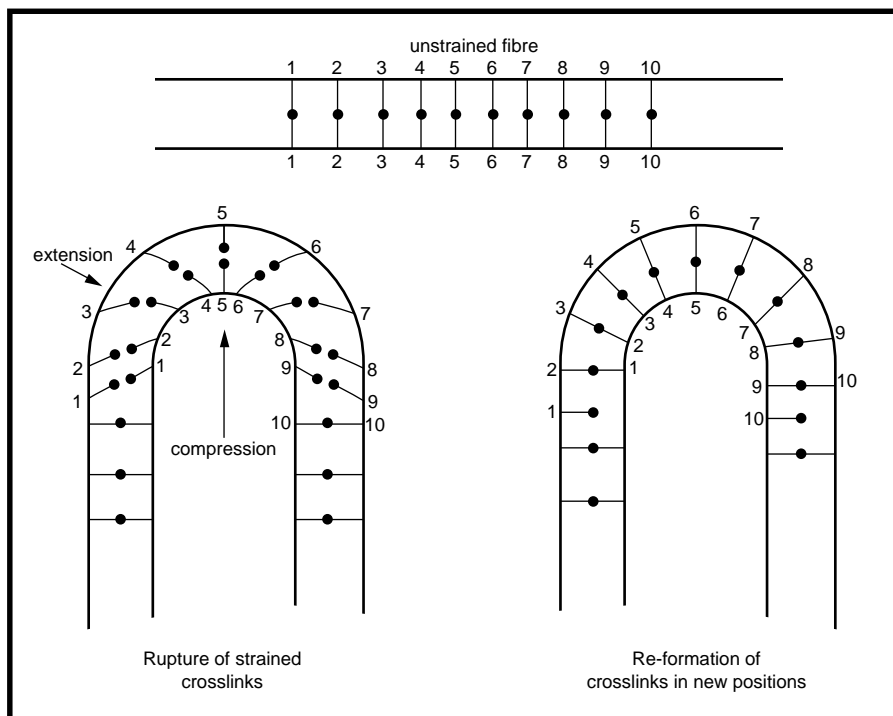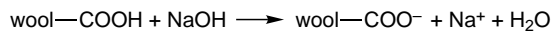

Figure 4.6 *The rupture and re-formation of crosslinks*

not controlled the properties of the fibre are harmed. With care, however, it is possible to manipulate conditions to advantage by allowing the crosslinks to be broken and to match up with different halves, thus forming a new crosslink in a different position (Figure 4.6). In this way creases and pleats may be fixed into the fabric by damp ironing, or fabric may be given a smooth flat appearance. This is also the principle of the permanent waving of human hair, but in this case a chemical reagent is used to split the crosslinks.
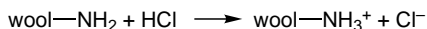
Amphoteric character of wool

All the side-groups of the constituent amino acids are found along the length of the wool protein molecule. Since these include both acidic and basic groups, wool is able to absorb and combine with acids through the basic groups and alkalis through the acid groups. Molecules with this ability are termed *amphoteric*. The acid and basic groups of adjacent chains also react with each other to form salt linkages, and their role in the dyeing of wool with acid dyes is discussed in Chapters 3 and 5.

At high pH values (alkaline solutions) the acidic groups ionise to form negative ions, leaving the wool with a net negative charge (Scheme 4.5). At low pH values (acidic solutions) the situation is

wool—COOH + NaOH $\longrightarrow$ wool—COO$^-$ + Na$^+$ + H$_2$O

Scheme 4.5

wool—NH$_2$ + HCl $\longrightarrow$ wool—NH$_3^+$ + Cl$^-$

Scheme 4.6

reversed, the basic groups reacting with hydrogen ions in the solution to form positive ions and the wool is left with a net positive charge (Scheme 4.6). It follows that there must be a pH at which the numbers of negative and positive charges are equal. This pH is called the *isoelectric point* of the protein.

Fibre structure and elasticity

As well as the chemical differences between wool and cotton, there are also differences in the ways in which the constituent polymer chains are arranged in the fibre. These have a profound effect on their physical properties. Wool garments will easily stretch and recover during use, but their cotton counterparts have very little 'give'. The difference is largely due to the degree of alignment of the polymer chains along the fibre axis. In cotton fibres the cellulose molecules exist as fully extended chains aligned sufficiently close in register to enable crystallisation to occur within the fibre. The crystalline material is difficult to deform and this, together with the already extended configuration of the molecules, makes cotton fibres hard to stretch. All the molecules in the cross-section of the fibre take a share of the imposed stress, and consequently cotton fibres will withstand a high tensile force before breaking. But crystalline material is also brittle and cotton fibres are easily fractured on bending, a property that is associated with a reduced resistance to abrasion.

The protein chains in wool fibres are very different. Reference was made earlier to the coiled configuration of the protein chains and the way in which they are crosslinked through cystine disulphide links. Disulphide linkages also form bridges between coils within the same molecule, and so the fibre becomes an extensive molecular grid structure.

When the fibres are stretched the coils straighten out, but on release of the tensile force the crosslinks cause the chains to spring back to their original helical arrangement. Wool fibres can therefore undergo considerable reversible extension. With this molecular configuration there is very little crystallisation and any strain is distributed unevenly between molecules, which leads to a lower breaking strength. Wool is therefore weak but highly extensible; the balance between the tensile strength and elasticity of wool makes it a very desirable textile fibre.

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Amorphous and crystalline material

Crystalline material is very hard and resistant to the penetration of chemical reagents and dyes, but even with a highly crystalline material such as cotton there still remain some parts of the polymer chains that are less highly organised. This is regarded as amorphous material (a term that somewhat oversimplifies the situation), and it is within these regions that penetration and reaction take place. Any influence that changes the crystalline order also modifies the ease with which dyes and other agents are absorbed. The *mercerisation* process for cellulose is an example. Treatment of cotton with caustic soda causes a marked swelling, which is accompanied by a change to a round cross-sectional shape and a reduction in size, though not in total quantity, of the crystalline material. The fibre lustre is also increased, and there is a marked improvement in both the speed of dyeing and the quantity of dye taken up. On the other hand, the crystallinity and ordered orientation are less and the fibre molecules are more accessible.

Regenerated fibres

Clearly, taken together, cotton and wool possess a wide range of properties desirable for textile fibres. But for many years textile chemists dreamed of discovering how such properties could be obtained by design through synthetic routes.

The first step towards making fibres synthetically was the discovery of how to dissolve waste cellulose and regenerate it into the form of a fibre. The first successful venture of this kind was made by Chardonnet, who converted cellulose into a viscous mass of cellulose nitrate, which was forced through a spinneret to form a filament. This could be spun into a useful textile yarn once the solvent had evaporated, but unfortunately the product was dangerously flammable. The subsequent conversion of cellulose to cellulose acetate (ethanoate) avoided this problem, and cellulose acetate dope was first used by Wherry and Dreyfus for coating the canvas wing covers of aeroplanes in World War 1. Later they turned their attention to the conversion of acetate dope into a useful textile yarn, and such materials are still familiar today. Fabrics made from cellulose triacetate fibres met with particular interest at the time because, as the first hydrophobic fibres, they were the first to be endowed with quick-drying properties.

Fibres have also been regenerated from natural cellulose dissolved in one of two solvents. One was a solution of cuprammonium hydroxide, which gave the now obsolete fibre *cupro* (cuprammonium rayon). The other dates back to the discovery by Cross, Bevan and Beadle in 1892

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that carbon disulphide can dissolve cellulose in the form of wood pulp to give cellulose xanthate. Some time later, in 1905, Courtaulds developed the process for the regeneration of the cellulose from the cellulose xanthate dope to produce the first *viscose* fibres, and their development continues to this day.

When wet the original viscose fibres suffered a drop in tensile strength, but this was later overcome with the development of *polynosic* fibres such as *Vincel 64*, a fibre which in water has properties similar to those of cotton. Polynosic fibres are used extensively in the form of knitted and woven goods for dress and a variety of other fabrics. They are also used in blends with cotton or polyester for sheets, shirtings and rainwear fabrics. A further version is *Sarille*, staples of which have a crimped configuration that imparts a warm handle to the fabric.

Eventually, however, fibres were developed from polymers synthesised directly from simple monomers, imitating the ways in which the natural molecules of cotton and wool are constructed, rather than by modifying natural polymers like cellulose.

Making synthetic fibres

Following the elucidation of the chemical structure of natural fibres, attention was turned to making fibre molecules using simple starting materials. The synthesis of cellulose molecules from carbon dioxide and water by photosynthesis (the chain of reactions that proceeds in all green plants in the light) and the production of fibrous protein from amino acids have so far eluded chemists.
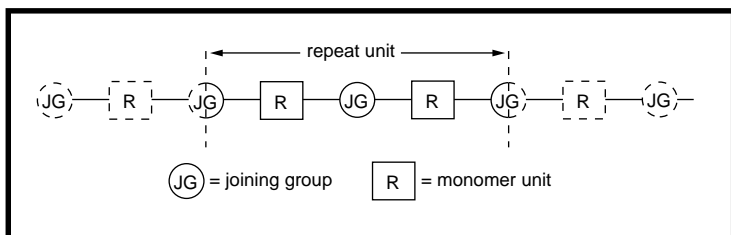

Figure 4.7 The molecular pattern of a step-growth polymer

Nevertheless, many useful textile fibres, such as the familiar and highly successful polyamide and polyester fibres, have been synthesised from simple compounds extracted from crude oil. The general pattern of their cons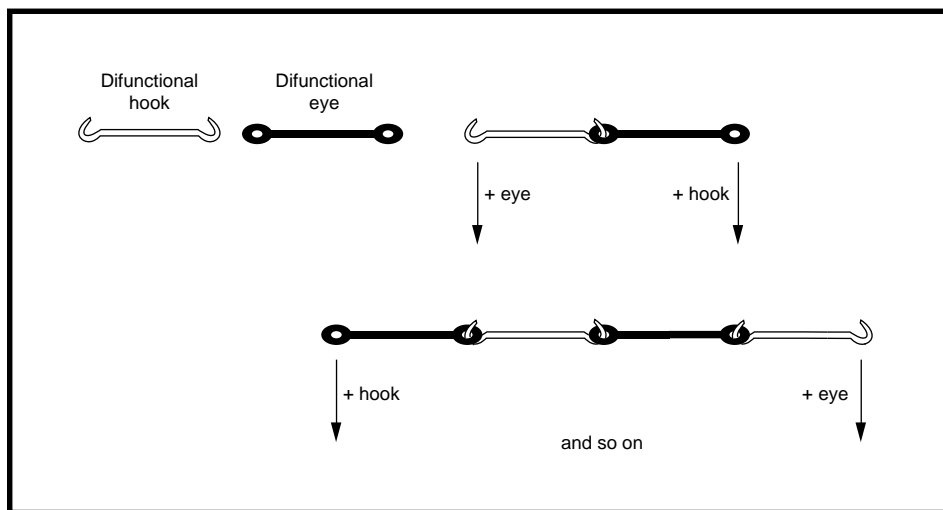truction is shown in Figure 4.7, in which the repeat unit is first made by joining two simple compounds together and then repeating the process at both ends of the new molecule so formed. A simple analogy is a system of hooks and eyes (Figure 4.8).

Figure 4.8 *The stepwise construction of a 'hook and eye' chain*

Step-growth polymers

Nylon fibres

Carothers' discovery nylon, already mentioned, is formed from a monomer made by the reaction of a carboxylic acid with an amine (a compound containing the amino group, —NH$_2$), with the loss of one molecule of water. Carothers deliberately started with difunctional reagents, that is, compounds containing identical functional groups at both ends of the molecule. For example, for the synthesis of nylon 6.6, the first nylon that was marketed, the difunctional acid is hexanedioic acid (adipic acid) and the difunctional base is 1,6-diaminohexane (hexamethylene-diamine). The joining process is repeated 100 times or more and
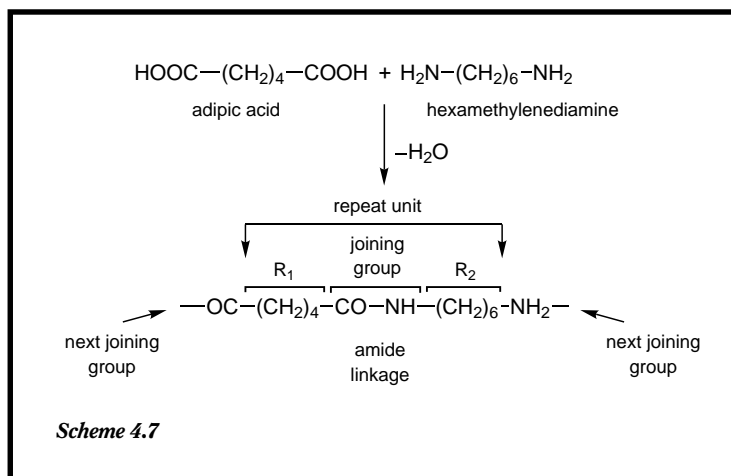
Scheme 4.7

the resulting polymer is designated by reference to the joining group. In the case of nylon it is the amide group (—CONH—). Consequently such polymers are called *polyamides* (Scheme 4.7). Nylon 6.6 is so called to indicate that both the diacid and the diamine contain six carbon atoms. This

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distinguishes this particular polyamide from others made from different starting materials. For example, nylon 6 is made from a single kind of molecule, caprolactam ($H_2N(CH_2)_5COOH$).

Nylon fibres are widely used, particularly in clothing, overalls and menswear. Nylon also improves abrasion resistance when incorporated into a carpet pile.

Although the carbon atoms are represented here by a condensed formula, the actual structure of a row of six carbon atoms is a linear zig-zag arrangement in which the four bonds of each carbon atom point to the corners of a tetrahedron (cf. Figure 3.4). This allows the component carbon atoms to rotate about the carbon–carbon bonds, and it is this freedom of movement that gives the polymer molecules the flexibility usually required in a fibre. This flexibility is to a considerable extent lost in aromatic polyamide or *aramid* fibres, in which the amine component is a benzene ring carrying two amino groups (a benzenediamine). The *para* isomer, benzene-1,4-diamine (*p*-phenylenediamine), is used in the manufacture of *Kevlar* fibres. These have a much higher melting point than that of nylon, and good fire resistance; their textile properties are poor, however, in that their abrasion resistance and flex life are inferior and they cannot be dyed easily. They are nevertheless valuable because of their great mechanical strength and are used as reinforcing fibres for highly stressed articles (vehicle tyres, for instance) and for protective apparel such as bullet-proof vests. *Nomex* fibres are based on the use of benzene-1,3-diamines (*m*-phenylenediamines) as monomers. These fibres have better textile properties and can be used in protective clothing. Recent developments have produced a Nomex fibre which is more readily dyed. The two types of fibre can be combined to make a fabric for protective wear, which has exceptional fire and heat resistance; this provides a good example of a *synergistic* effect, that is, one in which the performance of the components in combination substantially exceeds that which is to be expected from an assessment of their individual properties.

Polyester fibres

Long polymer molecules have also been formed by combining a difunctional alcohol with a difunctional acid. The reaction of an organic acid with an alcohol gives an ester, and it is the ester group (— COO —) that acts as the joining group in the polymer (hence the name 'polyester').

The first commercially successful fibres of this kind were developed by J R Whinfield and J R Dickinson in the 1950s and, like polyamides, they rapidly became established as useful textile fibres. The starting materials in this case were ethanediol (ethylene glycol), a difunctional alcohol, and

benzene-1,4-dicarboxylic acid (terephthalic acid), a difunctional acid (Scheme 4.8), which react together to form poly(ethylene terephthalate). Polyester fibres are noted for their easy-drying properties. They are used extensively in knitted and woven fabrics for apparel and household textiles and in the construction of functional articles such as car seat belts, ropes, nets and sails.

Scheme 4.8

Elastofibres

Elastofibres are based on polyurethane polymers, similar to those used in varnishes and paints.

They are *copolymers*, in which long chains of a polyester or polyether (providing flexibility and stretch) are linked to urethane segments, which bond with each other and hold the structure together. This special molecular construction provides the fibres with a reversible stretch that rivals that of rubber. They are incorporated into activity wear, proving to be strong, hard-wearing and light in weight.

As indicated earlier, polyesters and polyamide polymers are formed in a series of steps, each step in the reaction adding a further unit on an end of the growing chain. For this reason they are called *step-growth polymers*. In theory the polymer chain will grow for as long as the reaction is allowed to continue. In practice, however, there are limits to the length of chain required for fibre formation. If the molecules are too short the fibres will be too weak. On the other hand, if the chain is too long the polymer becomes unmanageable because it can be neither melted at a temperature low enough to avoid decomposition nor dissolved in solvents to be formed into a fibre.

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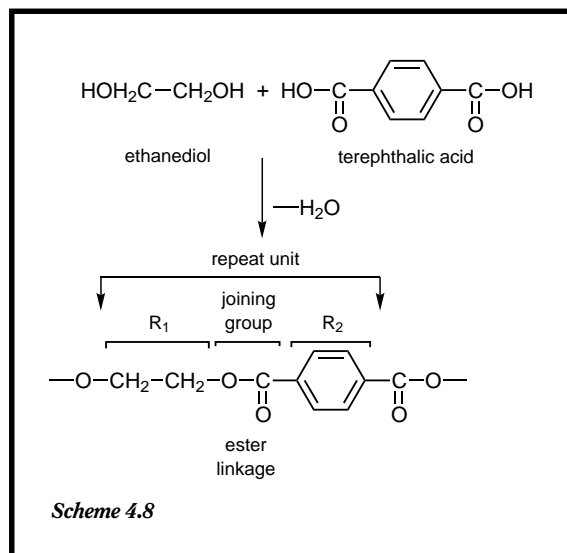
Chain-growth polymers

Other well-known synthetic fibres have been synthesised using a functional group that is very different in behaviour from those involved in step-growth polymerisation. *Acrylic* fibres and those based on *polypropylene* are synthesised through the reactions of *vinyl groups*, in which two aliphatic carbon atoms are joined by a double bond. *Vinyl polymerisation* is possible because of the

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4.4

different character of the two bonds. The two shared electrons forming one of the covalent bonds are firmly bound, as usual in a covalent bond. As explained in Chapter 2, the electrons in the second bond are fairly readily displaced, thus making the bond less stable, i.e. more reactive.
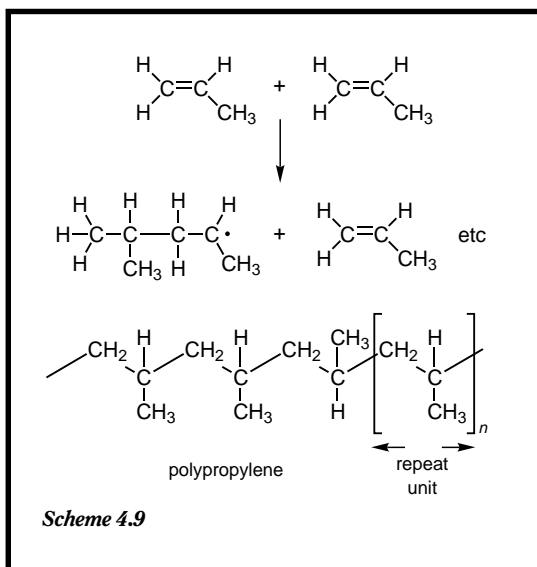
The simplest vinyl monomer is the alkene ethene (ethylene, *4.4)*. Molecules of ethene can be made to react together on the surface of a catalyst, where the two electrons of the less stable bond become unpaired and react rapidly with corresponding unpaired electrons in adjacent ethene molecules. This results in the formation of a stable single bond joining the two molecules together, in the same manner as shown for propene in Scheme 4.9.

One of the hydrogen atoms is added to the terminal carbon atom at one end of the new molecule, leaving the free electron on the carbon

polypropylene

Scheme 4.9

atom at the other end. But electrons cannot remain unpaired, and so a spontaneous reaction occurs with the next vinyl monomer. This continues until the process is halted by other reactions that terminate the growth of the chain. The end result is a long flexible chain some tens of thousands of carbon atoms in length. The polymer is called *polyethylene* or *polythene*, even though its repeat unit is the methylene group ($-CH_2-$).

Olefin fibres

Some of the fibres based on alkene monomers (known collectively, from the traditional name for alkenes, as *olefin fibres*) are useful textile fibres. Polyethylene fibres have been produced, but since their melting point is below the temperature of the coolest iron they are not of much value for textile purposes. *Polypropylene*, prepared from propene (propylene, *4.5*) is a similar but more robust polymer that does have uses for textiles; the head-to-tail reaction of propene molecules forms the polymer (Scheme 4.9).

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In this case the propene monomer is recognisable in the repeat unit. The production of polypropylene relies on the activity of special catalysts that ensure that the reaction takes place specifically in a head-to-tail manner. This catalytic intervention forces all the methyl side-groups to a position on the same side of the backbone of the polymer chain, thereby raising the melting point to 160 °C. These

4.5

fibres are light in weight, and because they contain only carbon and hydrogen atoms they are very hydrophobic. They cannot be dyed and therefore colour is incorporated at the spinning stage. Polypropylene fibres are good for industrial uses such as ropes, filter fabrics and conveyor belts, but their textile applications are largely limited to carpet manufacture.
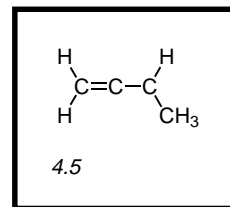
Thin films of both the above polymers can be converted into yarn. The films are converted into thread-like strips, either by slitting or by stretching them until they split (fibrillate), and the strips are then spun into yarn. As such they provide alternatives to string, twine and backings for tufted carpets. The resistance to weathering of olefin fibres also makes them useful for outdoor purposes such as deck chair covers.

4.6   repeat unit
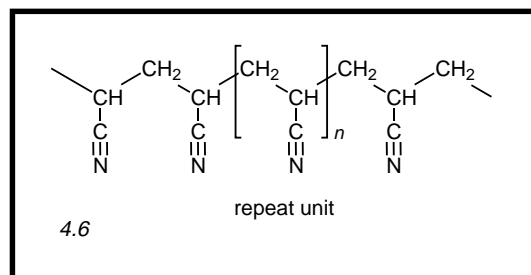
Vinyl polymers derived from *propenonitrile* (acrylonitrile) are used more widely. Pure polyacrylonitrile (*4.6*) proved difficult to convert into fibres. Acrylic fibres cannot be produced from the melt (they decompose before melting) so they must be made from a polymer solution; a suitable solvent is thus essential. But polyacrylonitrile is insoluble in most of the common solvents that were available at the time it was first under investigation. It was many years after the first preparation before suitable solvents became available and acrylic fibres could be formed.

4.7

4.8
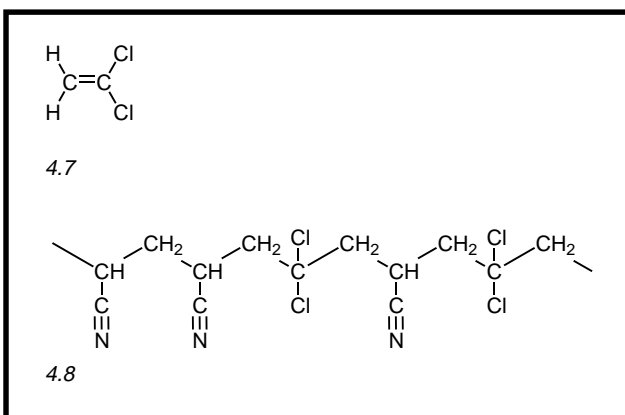
Difficulties associated with the preparation and use of acrylic fibres are also eased by the incorporation of small amounts of a second monomer (a *co-monomer*), such as 1,1-dichloroethene (vinylidene chloride, *4.7*) into the polymerisation mix. In the resultant polymer (*4.8*) the side-

groups on the backbone of the polymer include chlorine atoms as well as nitrile groups. *Teklan* is made in this way; the presence of chlorine atoms in the molecule results in a fibre with improved flame resistance.

Acrilan 16 and Courtelle

Acrilan 16 and Courtelle are two examples of copolymers containing up to 15% of a co-monomer. More recent developments have led to the production of copolymers containing between 35 and 65% of a monomer other than propenonitrile; these can be formed into filaments more easily than polyacrylonitrile itself, and can be dyed more readily. Acrylic fibres modified in this way are grouped together as *modacrylic* fibres, examples of which are given in Appendix 2. Acrylic fibres possess an inherent warmth and soft handle, and come closer to wool than any other fibre. They are used widely in carpet yarns and for knitted goods.

The reaction occurring in the formation of vinyl polymers differs from the step-growth process described for the formation of polyesters and polyamides. For example, when monomers react in step-growth polymerisation molecules of water are lost, whereas in the formation of vinyl polymers all the atoms of the monomer units are to be found in the polymer chain. The biggest difference, however, is in the manner in which the chains grow. In vinyl polymerisation the chain grows at one end only. Moreover, once the process begins it is so rapid that at any one time the reaction mixture consists of fully grown polymer chains and monomer: there are no intermediate stages of the kind found in the step-growth polymerisation of polyamides and polyesters. Consequently the reaction time allowed for vinyl polymerisation affects the amount of polymer formed but not the degree of polymerisation. Such reactions are referred to as *chain-growth polymerisations*.

Whatever the method of polymerisation, the final product is not a mass of macromolecules of identical length. There is always a distribution of molecular sizes, and figures quoted for the degree of polymerisation represent an average around which the values for the majority of molecules will fall.

Conversion of polymers to filaments

The synthetic polymer is presented to the manufacturer in the form of 'chips' or granules with the appropriate degree of polymerisation, and from this state it has to be converted to a filament in a

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manner akin to the spinning of a spider's web or a silkworm's cocoon. In this context spinning refers to the extrusion of a filament through a fine gland, not – as heretofore – to the twisting together of individual fibres or filaments to make a yarn. Thoughts about producing synthetic filaments in this manner were recorded centuries ago, but Ozanam was the first to describe a method in which a solution of real silk could be spun into fibres by extruding through small orifices. His invention,
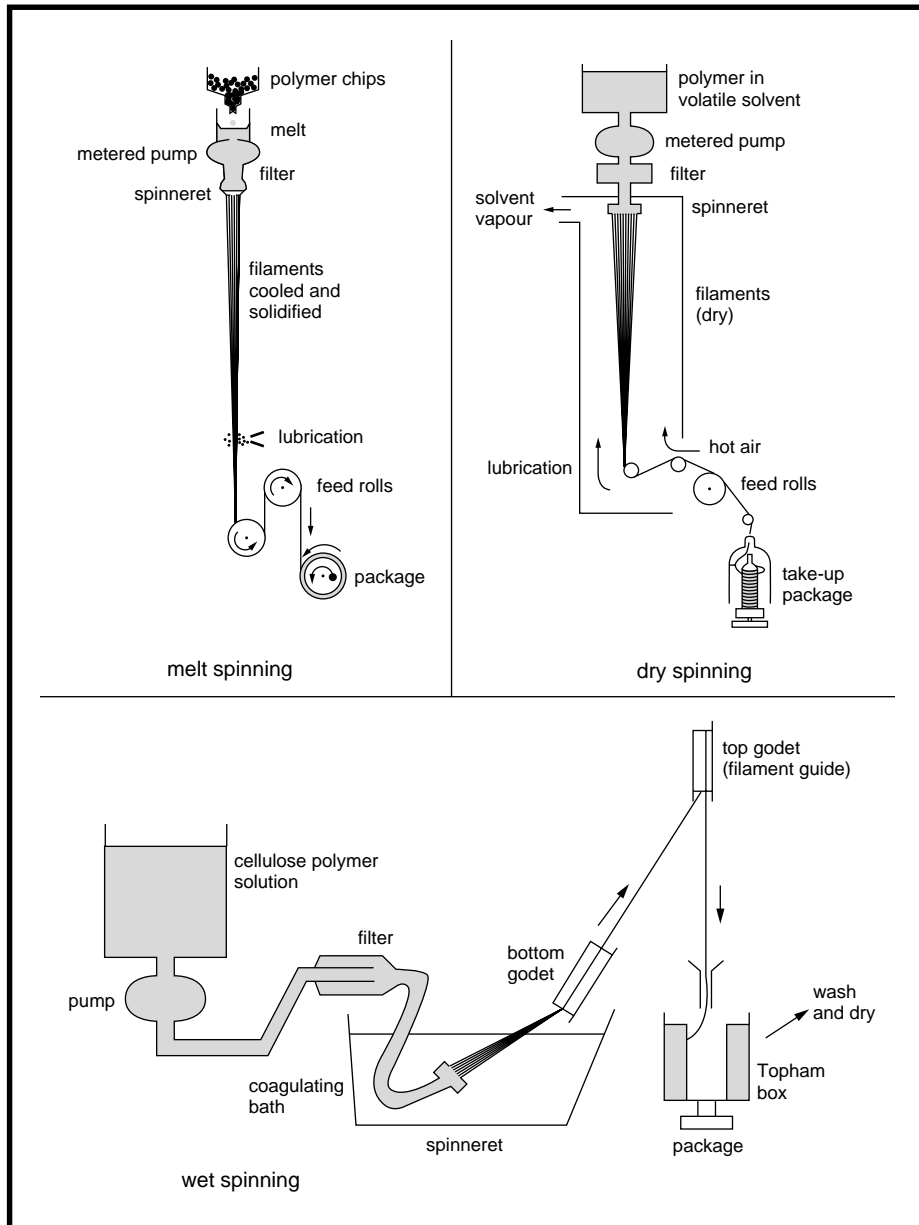

Figure 4.9 *Schematics of the three principal methods of spinning of synthetic filaments*

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which was called the spinning jet or *spinneret*, made possible the present-day developments in spinning.

Three different methods of producing filaments are available at the present time: melt spinning, dry spinning and wet spinning, all of which are represented in Figure 4.9 (page 65).

Melt spinning is appropriate for polymers such as polyester or nylon, which do not decompose at their melting temperature. Molten polymer is pumped through a spinneret, which contains a number of small specially designed orifices. As the filaments enter the atmosphere they cool and solidify as they are wound up on to bobbins.
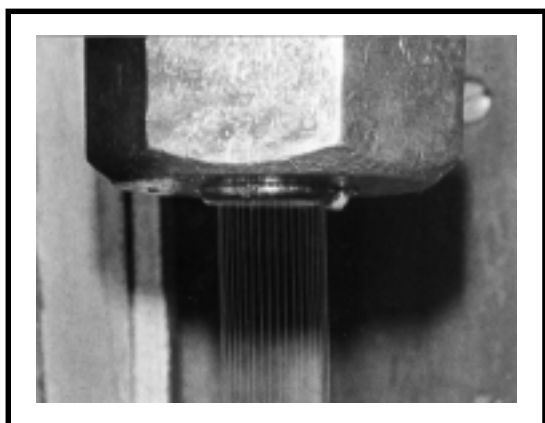
Dry spinning has been designed for polymers such as cellulose acetate, which are more difficult to melt. The polymer is dissolved in a volatile solvent to form a viscous solution, which is then extruded through a spinneret (Figure 4.10). Once the polymer 'dope' reaches the exterior the solvent evaporates in a current of warm air as the filament travels to the take-up bobbin.

Wet spinning is reserved for those polymers that need to be regenerated by some form of chemical action after extrusion. Cellulose dissolved in carbon disulphide, for example, is regenerated in acid solution to form viscose fibre, after which it is dried.

Figure 4.10 *Filaments of cellulose acetate being extruded through a spinneret*

Shape of fibre cross-sections

Extrusion of the filament is the stage at which the choice of cross-sectional shape is made, by choosing an appropriate shape for the orifice of the spinneret (Figure 4.11). The cross-sectional shape of a synthetic fibre is a function of both the method of production and the dimensions of the spinneret orifice; it is sometimes possible to identify which spinning method has been used simply from the cross-sectional shape of the filament. Orifices can be circular, crenellated, trilobal, convex, triangular and hollow, and each shape imparts particular characteristics. For example, ultrafine Trevira polyester filaments can be woven into breathable fabrics; since the cross-sectional area of the filaments is exceptionally low, the spaces between the filaments are so small that surface tension

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prevents water droplets from penetrating, whilst still able to allow water vapour to pass through. Other fabrics, such as reservoir linings, are designed to
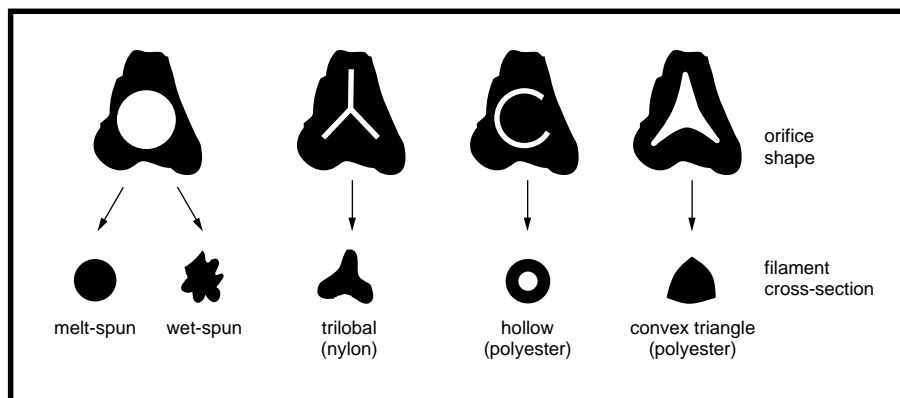

Figure 4.11 Orifice shape and the cross-sections of the resultant filaments

enable water to be retained, while still others prevent the evaporation of water and may, for example, be used for covers over crops in arid regions.

Multilobal nylon fibres are useful in carpet piles because they have a reduced lustre; moreover, some shapes increase their bulk and recovery from compression, in addition to being better able to hide soiling within the pile. The disadvantage is that dirt particles may become stuck in the crevices, thus making cleaning more difficult. The latter problem has been tackled by producing fibres with a smooth surface but four air-filled channels running down the length of the fibre. This reduces the visibility of the soiling through the multiple reflections inside the fibre, and at the same time produces a lighter fibre.

Fibres with a Y-shaped section are more resistant to bending and have better recovery than those with a circular or bean-shaped section, which makes them particularly suited to use as carpet pile. Other circular-sectioned polyester fibres have good insulation properties because of the air trapped within them, making the staple fibres (cut filaments) particularly suited for use as fillings in pillows, duvets and sleeping bags.

Cross-sections and surface appearances of some synthetic fibres are shown in Figures 4.12 (overleaf) and 4.13 (page 69).

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Absorbent fibres

Modification of both the external and internal surface areas of fibres can also powerfully affect the absorption of water. The formation of regenerated cellulosic fibres with a hollow structure provides a method of meeting a demand for high-absorbency fibres for medical uses, such as swabs, and babies'
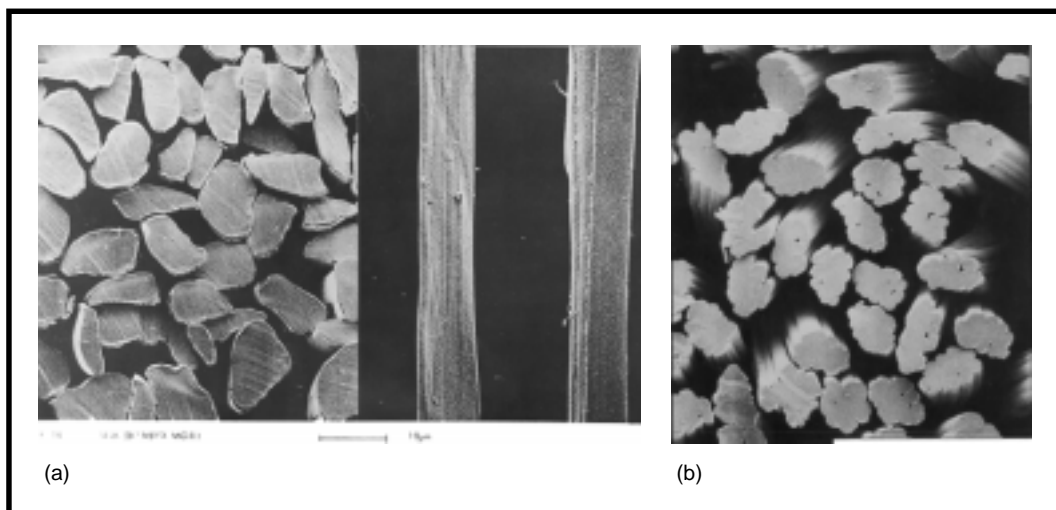
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Figure 4.12 *(a) Silk fibres seen under the scanning electron microscope (left) in cross-section, (right) longitudinal appearance; (b) viscose fibres in cross-section (magnified more than 1000 times)*

nappies. Various chemical expedients can be used to inflate the fibres at the regeneration stage and produce hollow fibres which collapse on drying. *Viloft* and *Courcel* are thin-walled fibres which can absorb an amazing 120 to 380% of their own mass of water [2].

Drawing of synthetic filaments

Fibre formation is incomplete after the spinning stage because the filaments are weak and dimensionally unstable. If they are pulled they stretch irreversibly. In this 'raw' state the polymer chains are disoriented and the structure lacks any coherent molecular arrangement. In the discussion of the structure of natural fibres on page 56 we saw that the degree of molecular alignment of the polymer chains along the length of the fibre axis is associated with the strength of the fibre. If a synthetic fibre is stretched after formation, the disordered polymer chains straighten and become extended along the fibre axis. The molecules slip past each other, but with the increasing order that the stretching imposes they eventually become close enough for intermolecular attractions to develop and to hinder further slippage without fracture. At this stage the filament has developed its maximum strength and the stretching is stopped. The individual polymer chains are now closely aligned and have become bonded to each other.

A process corresponding to this stretching is carried out by the fibre manufacturer, called the *drawing operation*. The filaments are passed around consecutive rollers, each of which rotates faster

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than the one before; the relative speeds of the rollers can be adjusted to impart the required degree of stretch to the filament (Figure 4.14, overleaf). In this way the length of a nylon filament may be increased five-fold, whilst its diameter is reduced and its breaking strength increased.

At this stage it is impossible to change one physical property without affecting others, so the degree of stretch needs to be

Figure 4.13 *Cross-sections of polyester fibres (rod-shaped) and viscose fibres (hollow) in a fibre blend (×750)*

controlled. The close alignment of the polymer chains may allow some crystallinity to develop and this increases the brittleness of the fibre. Although crystallinity increases the strength of the fibre, if the fibre becomes too crystalline it will fracture when bent, and so will have poor abrasion resistance. The fibre will also be more difficult to dye or to be penetrated by chemical reagents or water (permeability to water is an important factor in the comfort of clothing).

Thus by adjusting the *draw ratio* (the ratio of the final length to the original length) these various properties can be controlled. In the final state, therefore, the fibres are composed of polymer chains aligned roughly parallel to the fibre axis with varying degrees of molecular order along the length of the fibre, ranging from crystalline through highly oriented noncrystalline to areas of low orientation (Figure 4.15, overleaf).

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Conversion of filaments to staple

Once the filaments have been obtained they may be twisted together to form a yarn for use in knitting or weaving. Often, however, the properties required for the yarn are better obtained using staple fibre of a predetermined length. For the purposes of blending with natural fibres, the
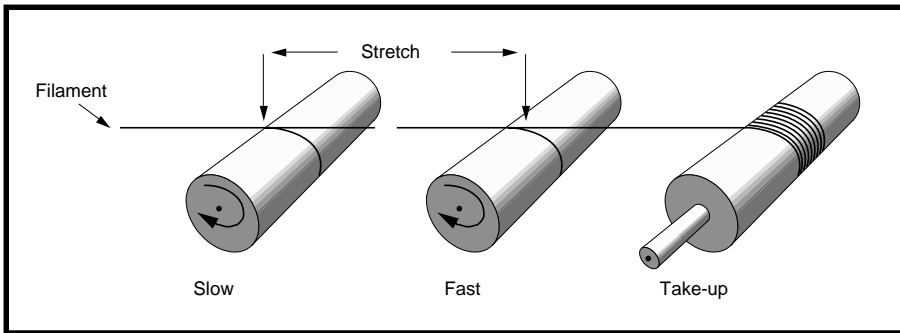
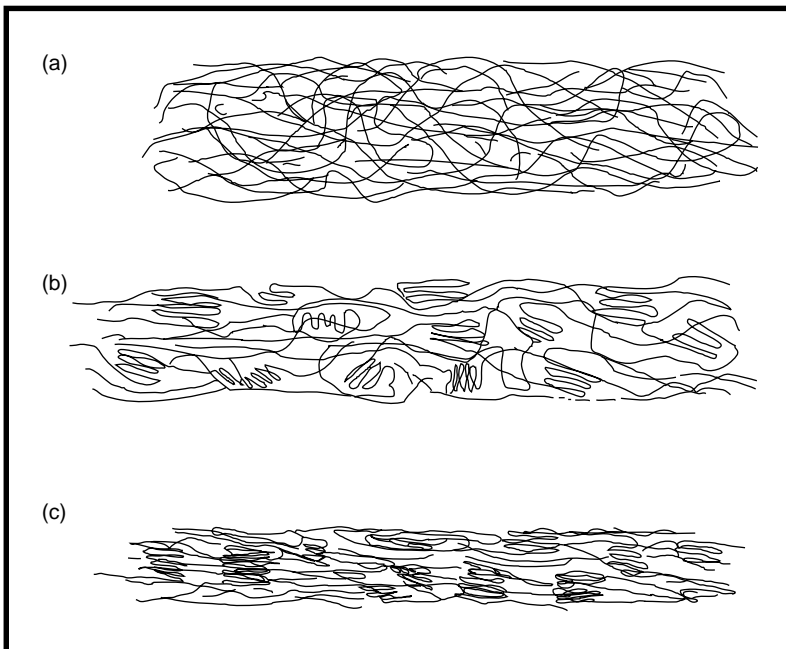**Home**

Figure 4.14 *Drawing filaments*

Figure 4.15 *Changes in molecular orientation in filaments during drawing: (a) as the filament emerges from the spinneret, orientation is mainly random (amorphous); (b) on cooling and stretching some crystalline order appears, with a degree of general orientation along the filament axis; (c) further stretching aligns amorphous and crystalline material along the axis*

synthetic fibres will be cut to correspond closely with the staple length of the natural fibre, but for other purposes such as the preparation of fibres for flocking the chosen length may be as short as a few millimetres. Special guillotine cutters are used for these very short fibres, but fibres intended for general textile uses are usually cut using helical-bladed cutters (similar in shape to those of a lawn mower) mounted on the periphery of a solid rubber roller (Figure 4.16). Hundreds of thousands of parallel filaments are formed into a web, which is passed between the bladed roller and a lower roller made of hardened steel. The length of the staple is governed by the spacing of the cutter blades. The cut is made at an angle to the direction of the movement of the web of filaments so that the cut ends are not coincident with each other. Having passed beneath the cutter, the web is loosened and rolled diagonally to form a continuous sliver for the subsequent conversion into yarn.
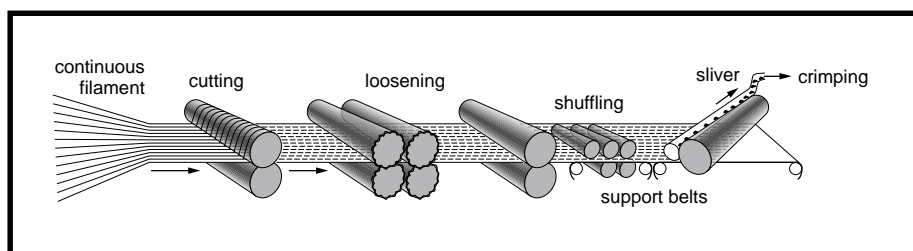
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Figure 4.16 *A cutting sequence in making staple from filaments*

Imparting texture to synthetic fibres

Since the advent of the first synthetic fibres efforts have been continually made to meet consumer demands for synthetic fabrics with greater comfort in wear and pleasanter handle, more akin to those associated with fabrics made from natural fibres.

The effects of variation in the cross-sectional shape on handle have been mentioned already. A major influence on the texture of a fabric is the *crimp* of the fibre, and the 'loftiness' or 'bulkiness' of wool has been imitated with some success by introducing a crimp into the synthetic fibre through a variety of methods. This improves both the appearance and insulation properties of the fabrics subsequently produced, whilst the easy-drying properties are preserved. Furthermore, the greater air space in the fibre allows moisture to be transported more easily from the body to the surrounding air, thus helping to overcome the discomfort often associated with the hydrophobic nature of synthetic fibres worn close to the skin.

Many of the methods for texturising synthetic fibres depend on the fibres' *thermoplastic* nature. When synthetic fibres are heated they do not melt sharply at a certain temperature, as simpler substances do, since the extreme length of the polymer chains prevents them from separating easily. Instead the onset of melting is marked by a change in physical properties; in particular, the fibres become more readily deformed by mechanical stress. This is due to a general increase in the molecular movements of the polymer chains, which at lower temperatures were 'frozen' into position and unable to respond easily to external forces. At a certain temperature, which is a characteristic of the particular polymer, the polymer changes from a rigid substance into a material that is more easily deformed. This temperature is referred to as the *glass–rubber transition temperature* (designated as T_g) and is the temperature at which the polymer molecules become free to take up a new position in response to an external force. Consequently methods have been devised in which fibres held above the T_g are crimped mechanically and then allowed to cool. Such changes

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in a thermoplastic material are reversible but will remain unaffected as long as the temperature of subsequent processing or aftercare treatments remains below the T_g.

Texturising processes

Various methods adopted for texturising are represented in Figure 4.17. In the stuffer box method (Figure 4.17 (a)), yarn is carried into a heating chamber at a rate faster than that at which it is removed, and the compressive action during heating leads to a bulky yarn. Another way of imparting texture is to drag the yarn over a heated knife edge (Figure 4.17 (b)), an action which imparts an unsymmetrical cross-section to the filaments or yarns. When they are subsequently relaxed in hot water curling results, providing the yarn with a stretch. In gear crimping (Figure 4.17 (c)) the heated yarn is passed between heated intermeshing cog wheels before cooling. Still another method
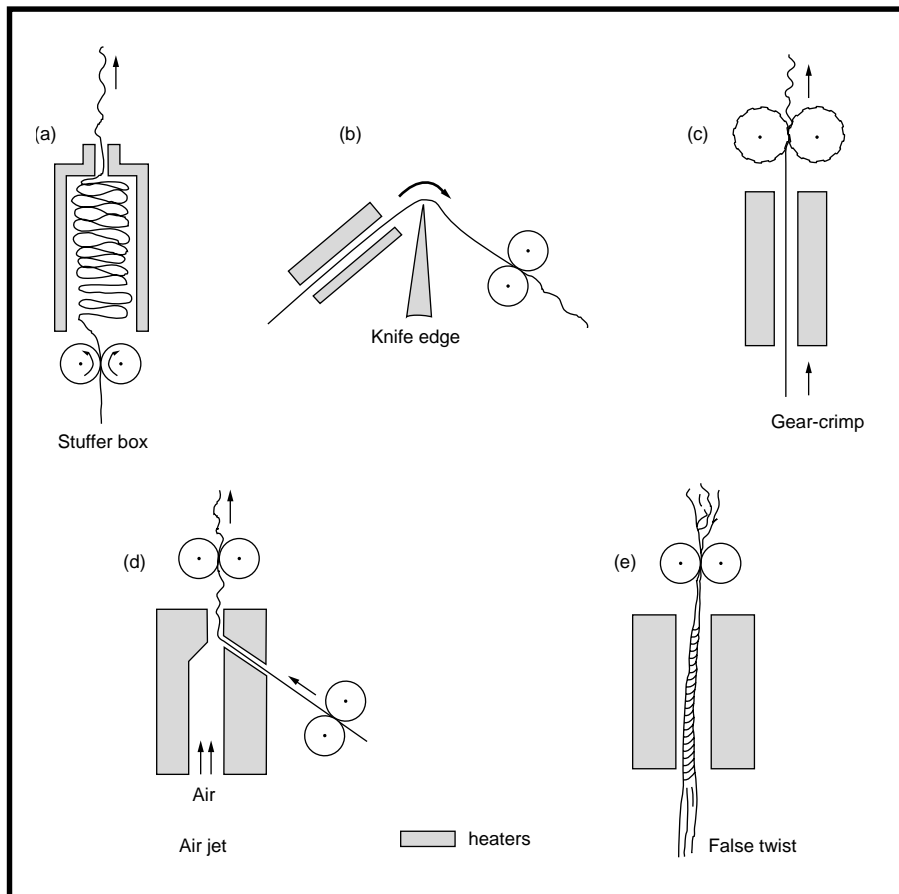

Figure 4.17 *Schematics of fibre crimping*

relies on the disorganisation produced in the yarn structure by a jet of air being forced through the yarn (Figure 4.17 (d)). In a widely used method, a twisted yarn is passed through heaters to set the crimp, and this is followed by an untwisting operation which separates the filaments as distorted coils (Figure 4.17 (e)).

Crimped fibres have also been produced by spinning dual-component fibres, made up of two different polymers lying alongside each other down the length of the fibre. Subsequent heat treatment shrinks both polymers, but to a different extent, and the differential effect leads to the development of a crimp. Such fibres are known as bi-component, conjugate, composite or hetero fibres.

Indicators of the quality of fibre and yarn

Once the yarn has been produced it is necessary to transmit descriptive details to the textile manufacturers, to show that it can meet the design requirements of their products. Yarn is sold by mass, but mass alone is insufficient to inform the weaver of the length of yarn being purchased. Without this information it is impossible to estimate how much yarn will be required for the production run. Consequently various ways of representing the fineness of a yarn (the *count* or *yarn number*) have evolved over the years. These traditional systems were many, varied and confusing; a detailed account has been published [5].

The ISO recommended *tex system*, now universally adopted, expresses the fineness of a yarn terms of the mass (in grams) of 1 kilometre of yarn. So, for example, 1 km of a 30 tex yarn will weigh 30 g.

To avoid the use of small fractions of a unit for very fine yarns a subsidiary unit, the *decitex* (dtex), based on the mass of 10 km of yarn, is used. Thus 10.0 km of yarn with a count of 20 decitex will weigh 20 g.

For single filaments the tex unit is impracticable because the counts involved are very small fractional values. For this purpose the *millitex* (mtex) unit is used, 1 mtex being equal to the mass in grams of 1000 km of filament.

Another important constructional detail for the weaver is the amount of *twist* inserted when spinning the yarn. The degree of twist influences several properties including strength, compactness, compressibility and lustre. The twist is expressed as turns per centimetre, and the

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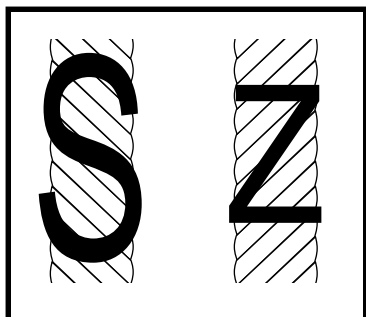
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Figure 4.18 *S-twist and Z-twist*

direction of the twist is indicated by the term 'S-twist' when the fibres slope from left to right across the main axis of the fibre and 'Z-twist' when the slope is from right to left (Figure 4.18).

There are of course many other considerations inherent in the quality and design of yarns and fabrics. These include properties such as tensile strength, tenacity, elongation at break and elasticity, all of which are carefully monitored by the manufacturer. These fall outside the scope of this book, however; more specific works on fabric construction [3] and fibre physics [4] describe these properties and their measurement in more detail.

Presentation of information for the fibre manufacturer

The initial development work on fibres is carried out by chemists and physicists, who need to be aware of the chemical composition of the materials they are using. For this purpose precise chemical names, such as poly(ethylene terephthalate) for a particular type of polyester polymer, are required to confirm the likely chemical responses to any treatment or attempted chemical modification of the properties of the polymer with which they are dealing.

Generic names

Precise chemical names, however, are not essential for the designer or fabric manufacturer. They rely more on the agreed unambiguous generic names defined for international use by the ISO and BSI (ISO R/2076; BS 4815) in describing the chemical origin and type of fibre within any particular group.

Trade names

Very often the generic names of different polymers are also worded in terms of chemical nomenclature, and as such they convey very little information to the general public. A more reliable indicator of quality in this case is a familiar trade name. For instance, some well-known names for polyester fibres are Terylene, Trevira and Dacron, each of which is a polyester fibre from a different manufacturer. Such names are helpful to the consumer because they are often associated with

certification schemes and other ethical merchandising procedures. Consequently through trade names the public can become acquainted with the reliability of a particular product in fulfilling its intended purpose.

Trade names often include the terms 'bright' or 'delustred'. The *bright fibres* are 100% polymer without additives. Fabrics made from these fibres transmit a certain amount of light, which is not always desirable in a garment. The difficulties are eliminated by making opaque or delustred fibres (usually called *dull fibres*) by incorporating a white pigment into the fibre at the spinning stage. Titanium oxide is used for this purpose and the particles of pigment are readily visible in such fibres under the optical microscope.

Some examples of generic, chemical and trade names for fibres are given in Appendix 2, and more extensive information is provided in other sources [1,6,7].

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