CHAPTER 1

FIBRE SPINNING (with Special Emphasis on MELT SPINNING)

1.1 Introduction

1.1.1 Fibres [1]

A **fibre** may be defined as a flexible, macroscopically homogeneous body having a high ratio of length to width and a small cross-section. A large segment of the world's agricultural activity is concerned with the growth and harvesting of natural fibres. The production of synthetic fibres is an important activity of the worldwide chemical industry. The textile and paper industries are the primary converters of fibres into products with properties directly related to the unique characteristics of fibres. Textile fibres may be classified according to origin as being either naturally occurring or synthetic. Natural fibres are those derived directly from the animal, vegetable, and mineral kingdoms. These fibres are known as **staple** fibres; an estimate of their length is their staple length. Synthetic fibres, on the other hand, are manufactured from organic polymers, such as polyesters and polyamides (Nylons). The basic physical element of both types of fibre is what is termed a **filament**, i.e., an individual strand of continuous length. Depending on the manufacturing method used, the final fibre product may consist of just one or more than one filament.

1.1.2 Manufacturing Methods [2,7]

In the traditional methods of synthetic fibre manufacture, filaments are obtained in continuous form. When several such filaments are combined and slightly twisted to maintain unity, the product is called a **multifilament yarn**, and typically may contain up to

100 single filaments. Individual filaments, considerably larger in cross-section, and called **monofilaments**, may also be used in certain applications.

Frequently, it is desirable to obtain fibres in finite lengths for subsequent manufacture into **spun yarns** by conventional spinning operations. In this case, thousands of continuous filaments are collected together into a continuous rope of parallelized filaments called a **tow or roving**. The tow is converted into staple-length fibre by simply cutting it into specified lengths. The staple length produced depends on the system of yarn manufacture that is to be used. Twisting together two or more yarns forms **cord**. Various yarn structures are shown in Fig. 1.1.

1.1.2.1 Spinning of Fibres [1,2,4,6]

Synthetic fibre manufacture is based on three common methods of fibre formation or spinning. The term **spinning** should be reserved for the textile manufacturing operation where staple fibres are formed into continuous textile yarns by several consecutive attenuating and twisting steps. A yarn so formed from natural or synthetic staple fibres is a staple or spun yarn. In the context of synthetic fibre manufacture, spinning refers to the overall process of polymer extrusion and fibre formation. The three principal methods are **melt spinning**, **dry spinning** and **wet spinning**, although there are many variations and combinations of these basic processes (Table 1.1).

Spinning refers to the process of converting a suitable synthetic polymer to the fibre form, usually from its melt or from its solution in a selected solvent. Of the different spinning techniques, melt spinning is the simplest, requiring no handling of solvents or non-solvents and hence requiring no post-spinning solvent evaporation, precipitation or coagulation and drying. Melt spinning is the most economical, but can only be applied to polymers that are stable at temperatures sufficiently above their melting point or softening point to be extended in the molten state without substantial degradation.

Solution spinning is practised when melt spinning cannot be carried out. Solution spinning may be of two kinds: dry spinning and wet spinning.

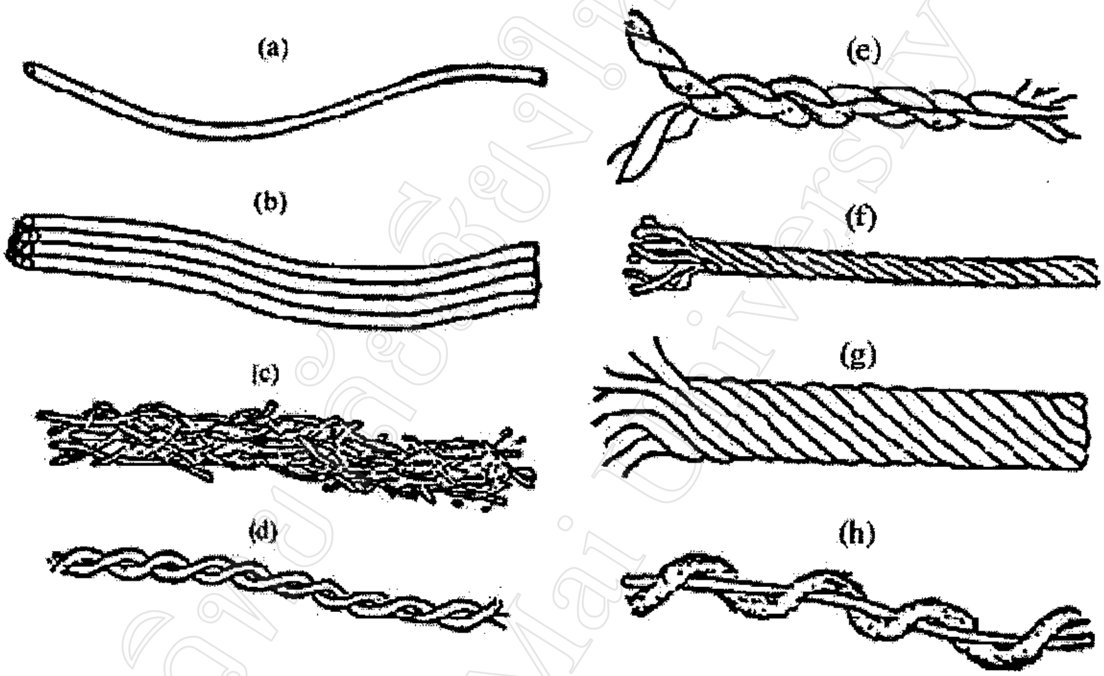


Fig. 1.1 Idealized diagrams of various yarn structures [3].

(a) Monofilament : solid, single strand of unlimited length
(b) Multifilament : many continuous filaments with some twist
(c) Staple : many short fibres twisted tightly
(d) Two-ply yarn : two single yarns twisted together
(e) Multiple yarn : plied yarns twisted together
(f) Thread : hard, fine-ply yarn
(g) Cord or cable : many plied yarns twisted into a coarse structure
(h) Combination : two dissimilar yarns plied together

Table 1.1 Comparison of the three principal methods of fibre spinning [15].

Wet Spinning	Dry (or Solvent) Spinning	Melt Spinning
1. Chemicals dissolve raw material 2. Fibre is spun into a bath 3. Fibre solidifies when coagulated	1. Resin solids are dissolved by solvent 2. Fibre is spun out into warm air 3. Fibre solidifies by evaporation of solvent	1. Resin solids are melted 2. Fibre is spun out into air 3. Fibre solidifies on cooling
Oldest process Most complex Weak fibres until dry Washing, drying, bleaching, etc., required before use	Direct process Solvent required Solvent recovery required No washing, etc., required	Least expensive Direct process High spinning speeds No solvent, washing, etc., required Fibres shaped according to spinnerette hole

In melt spinning, the polymer is heated above its melting point and the molten polymer is forced through a **spinnerette**, a die with one or more small orifices which may be varied in their diameter and shape. The jet of molten polymer emerging from each orifice in the spinnerette is guided to a cooling zone where the polymer solidifies to complete the fibre formation process. In dry spinning, the polymer is dissolved in a suitably volatile solvent and the solution is extruded under pressure through a spinnerette. The jet of polymer solution is guided to a heating zone where the solvent evaporates and the filament solidifies. In wet spinning, the polymer is also dissolved and the solution forced through a spinnerette which is submerged in a coagulation bath. The polymer is either precipitated or chemically regenerated from a soluble derivative such as a salt. In most instances, the filaments formed by melt, dry, or wet spinning are not suitable textile fibres until they have been subjected to one or more successive drawing operations.

Drawing is the hot or cold stretch and attenuation of synthetic filaments in order to achieve an irreversible extension, induce molecular orientation with respect to the fibre axis, and develop a fine structure within the fibre. This fine structure is generally characterized by a high degree of crystallinity and by an orientation of both the crystallites and the polymer chain segments in the non-crystalline domains. The fine structure and physical properties of synthetic fibres are often further modified by thermomechanical annealing treatments. In melt spinning, the two processing steps of spinning (extrusion) and drawing (structure development) are increasingly being combined into a single high-speed spinning process.

In summary, all of these spinning processes proceed roughly according to a scheme of four stages. In the first stage, the liquid to be spun is extruded through the orifice(s) of a spinnerette. The length of filament that can be obtained is governed by the spinnability. In the second stage, the actual filament begins to form. In this transition region, internal stresses equilibrate. In the first two stages, the filament retains its external shape. In the third stage, the still semi-liquid filament is drawn or stretched under its own weight causing a slight orientation of the polymer chains to occur. In the fourth stage, the filament is drawn.

Typical cross-sections of fibres produced by these three types of processes are shown in Fig. 1.2 while the processes themselves are compared in Fig. 1.3.

The dimensions of filament or yarn are expressed in the unit called **tex**. This measure of **fineness** or **linear density** is defined as 1 g / 1000 m (10^{-6} kg/m). This unit has replaced **denier**, which is expressed as 1 g / 9000 m (1.111×10^{-7} kg/m);

1 denier = 0.1111 tex. This linear density of a filament is related to its diameter, provided that the filament has a circular cross-section, by the relationship :

$$\text{Diameter } (\mu\text{m}) = 2 \times 10^{3} \sqrt{\frac{1}{\pi} \times \frac{\text{Linear density (tex)}}{\text{bulk density (kg/m}^{3}\text{)}}}$$

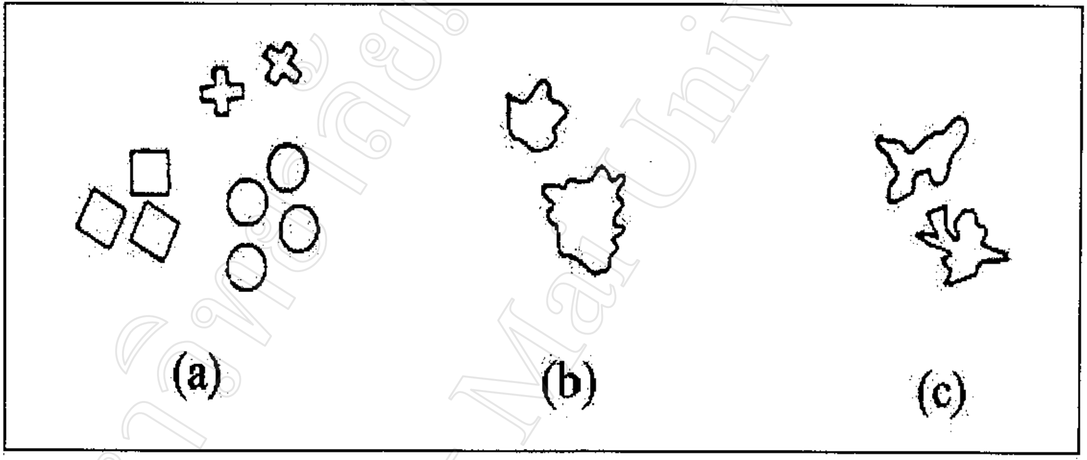


Fig. 1.2 Typical cross-sections of fibres produced by the three different spinning processes [2].

(a) melt-spun nylon from various shaped orifices

(b) dry-spun cellulose acetate from round orifices

(c) wet-spun viscose rayon from round orifices

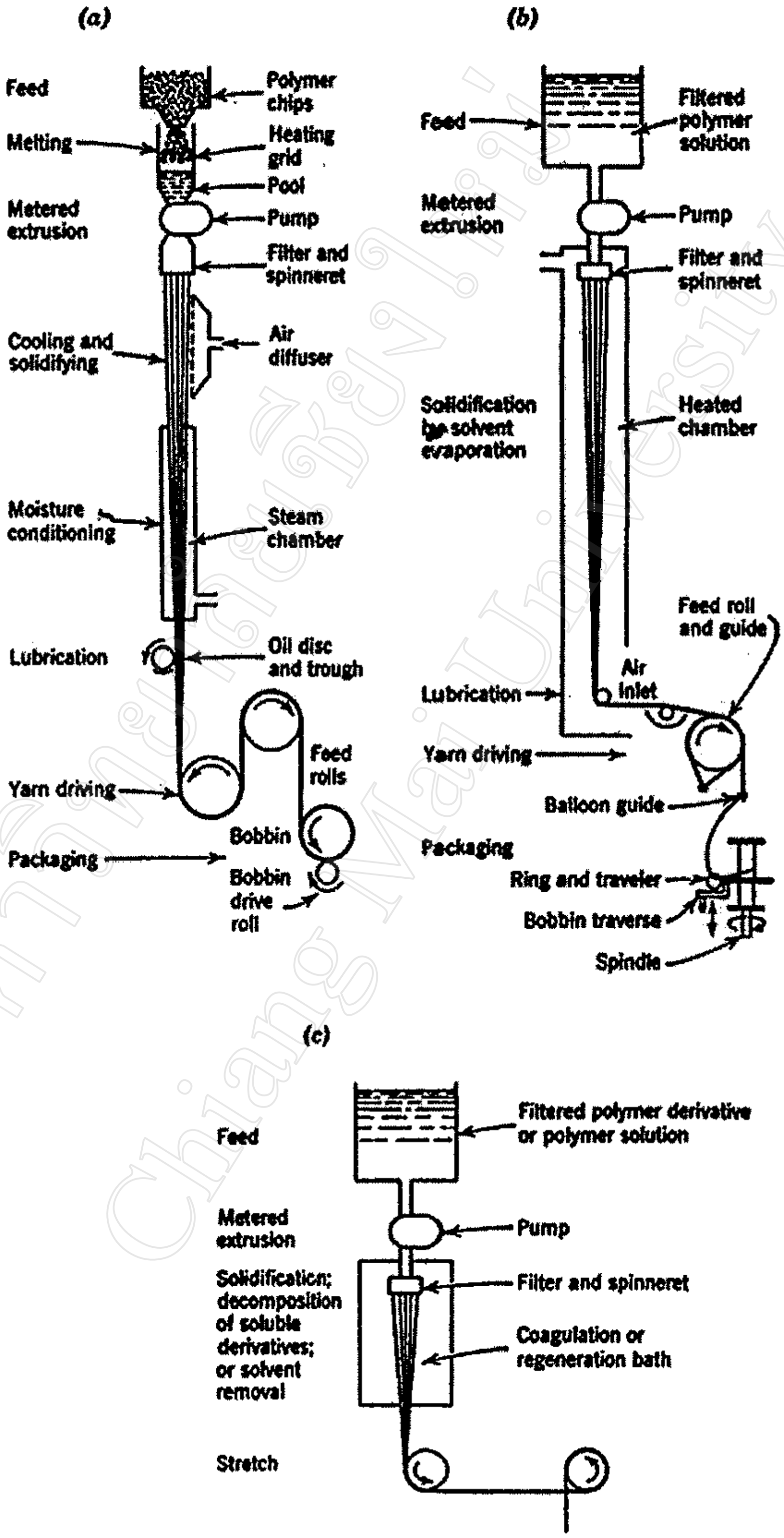


Fig. 1.3 Schematic diagrams of the three principal types of fibre spinning: (a) melt spinning ; (b) dry spinning ; (c) wet spinning [8].

1.2 Melt Spinning

1.2.1 Development of Melt Spinning [5]

The viscous rayon method was developed towards the end of the last century and the melt spinning method for synthetic fibres was established in the early part of the 1930s. In the beginning of the history of spinning, progress in spinning techniques was mainly made by accumulating empirical facts; that is to say, by repeating a set of procedures such as setting a spinning condition and measuring the resultant properties and structures of the spun fibres. There were few studies on physico-chemical changes and on structural formation in the spinning fibres between the spinnerette and the take-up device. With the rapid advances of the synthetic fibre industry in the 1940s, a strong need arose to understand the basics of the spinning process in order to improve the productivity and quality control of fibres. Consequently, toward the end of the 1950s, the melt spinning process started to be analyzed mathematically as an engineering problem and then later, in about the middle of the 1960s, a method for the quantitative description of the melt spinning process based on hydrodynamics, rheology and the theory of thermal conduction was established. Since then, studies on structure formation and crystallization during the spinning process have been extensively carried out such that interrelationships between the various factors, as shown in Fig.1.4, are now more clearly understood.

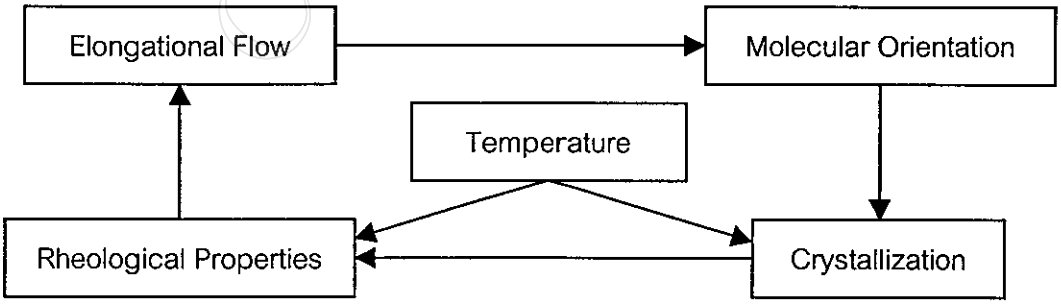


Fig. 1.4 Correlation between the main factors governing the melt spinning process [6].

1.2.2 Melting of the Polymer [1,9]

In the simplest controlled form of melt spinning, the polymer is introduced into a cylindrical well, the lower part of which is heated from the wall. The polymer is displaced downward through the melting zone towards a spinnerette by applying pressure to a ram that acts as a piston applied to the top of the unmelted polymer in the well. The extruded filaments are collected continuously on a wind-up bobbin. This simple batch–type discontinuous method is suitable for small-scale experimental work but not for large-scale commercial production.

The lower limit of the melt spinning temperature is the temperature at which the polymer is completely molten, usually around 20-40°C higher than nominal melting point. When very high polymer molecular weights are used, it may be necessary to increase the melt temperature further in order to lower the melt viscosity. However, it must be remembered that the total amount of heat imparted to the polymer will have to be removed later in the cooling zone, so every attempt at elevating the spinning temperature beyond the absolutely necessary minimum should be given very serious consideration.

The upper limit of the melting temperature is usually governed by the polymer's thermal stability and does not require very extensive comment. In the case where the operable temperature range is wide, it is preferable to gravitate towards the lower end of the scale. The upper limit is set by the temperature at which appreciable thermal degradation begins.

Nowadays, most commercial melt-spinning plants melt the polymer with the aid of screw extruders. The extruder is fed directly with polymer in powdered or chip form and can forward molten polymer of high melt viscosity. A single extruder may supply several spinning positions through a series of branching pipes or tubes. The manifold leading from the extruder must be designed in such a way as to minimize path lengths and therefore any differences in thermal history and residence time between the supplies of molten polymer to different spinning positions. The feed rate to individual spinning units is controlled by an accurately machined metering gear pump which delivers molten polymer at a constant rate into a filter assembly. Metering pumps are capable of feeding against high back pressures of at least up to 50 MPa (7250 psi) without change of feed rate.

Before reaching the spinnerette, the molten polymer is usually filtered through a so-called **screen pack** or **filter** comprising one or more sintered or fibrous metal gauzes or a bed of graded fine refractory material, such as sand or alumina, held in place by metal screens. Filtration removes large solid or gel particles that might otherwise block spinnerette holes or, if passed through, occupy sufficient cross-sectional area in the filament to affect its processing or tensile properties. Smaller particles, such as delusterants, are not retained by the filter. Filtration also provides a shearing action and can thus also influence rheological behaviour.

1.2.3 The Spinnerette [1,9-11]

The spinnerette is the element of spinning hardware which serves to change the polymer shape into infinitely long cylinders. For melt spinning, the spinnerette is made of stainless steel or a nickel alloy and is a flat plate, flush with or recessed in its mounting. Spinnerettes for molten polymers, where the extrusion pressure may be as high as 20 MPa (2900 psi), are relatively thick (3-10 mm). Individual hole diameters are usually in the range of 0.1 - 1 mm at the exit, the larger diameters being for the more viscoelastic melts. The spinnerette's capillary section (see Fig. 1.5(b)) is shorter than the plate thickness with a length : diameter ratio of usually between 1 and 10. The entrance to each hole is comparatively wide but the cross-section is often shaped to give a gradual rather than abrupt reduction in diameter in order to avoid flow discontinuities.

It is important to note here that the spinnerette hole does not directly control the linear density of the filament. Linear density is controlled by the throughput of polymer per hole, W (g/min), and the wind-up speed, V (m/min). The linear density (tex = g/km) of a melt spun fibre is then $10^3 W / V$. The relationship between the linear density and the ratio of the extrusion and the wind-up speeds, V_0 / V, where V_0 is the mean extrusion velocity, is give by the equation :

$$\text{Linear density} = \frac{A\rho W_p V_0}{V}$$

where A = cross-sectional area (mm^2) of the orifice

ρ = density (kg/m^3) of the extrudate at the extrusion temperature

W_p = weight fraction of polymer in the extrudate as it leaves the spinnerette. (For melt spinning, $W_p = 1$)

While spinnerettes are serving the purpose for which they were intended and are serving it quite well, there are a number of side phenomena taking place during the extrusion of a polymer through a capillary. These side phenomena, which result mainly from the shearing action on the extruding polymer, have a strong influence on both some engineering tasks and on the behaviour of the polymer in the further processing stage up to the alteration of the final properties. In this respect, the spinnerette has, to a certain extent, a similar action to the screen (or filtering) pack previously mentioned. Some typical spinnerettes used in melt spinning are shown in Fig.1.5.

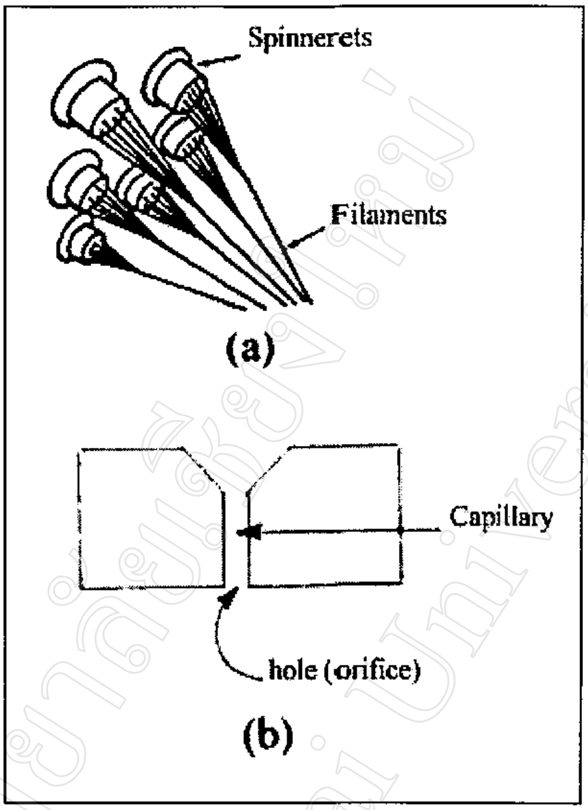


Fig. 1.5 Typical spinnerettes used in melt spinning [12].

(a) a series of multiple-hole spinnerettes

(b) internal design structure of a single-hole spinnerette

1.2.4 Spinnability [13]

The maximum achieveable filament length for a spinning process is known as the **spinnability** and depends on the viscosity, η, of the polymer melt and the rate, ν, of spinning. The filament length, L, passes through a maximum as the value of the product $\eta\nu$ increases.

The occurrence of a maximum in the $L = F(\eta\nu)$ function means that the spinnability is governed by at least two processes: the cohesive fracture (or swell effect) and the capillary fracture (melt break or capillary break). A certain amount of elastic energy is, of course, stored in every viscoelastic fluid. This amount of energy also depends on the cohesive energy of the material. If a certain amount of stored energy is exceeded, then the fibre undergoes what is known as cohesive fracture. On the other hand, the capillary fracture depends on the surface tension of the liquid as well as on its viscosity and the speed of the spinning process.

The first of these two mechanisms to occur causes a break in the filament. If the rate of spinning and/or the viscosity is too low, capillary fracture occurs and the liquid degenerates into single droplets because of the dominating effect of surface tension. Relaxation times which are too large because of viscosities being too high causes cohesive fracture, which is a brittle fracture. Viscosities can be too high because of, for example, high molecular weight, fast gel formation, or too low spinning temperature.

1.2.5 Cooling and Drawing [1,15]

As molten polymer passes through a spinnerette hole, it is drawn away and attenuated by a draw-down force applied by a forwarding or wind-up roll; simultaneously, its temperature rapidly decreases. The diameter immediately below the hole and before attenuation begins is larger than the hole diameter. This so-called die swell is due to relaxation of the viscoelastic stress induced in the hole. When spinning oxidation-sensitive polymers, it is useful to blanket a narrow zone immediately below the spinnerette with inert gas in order to prevent deposition of degradation products around the orifices. A short cylindrical cowl, known as a shroud, extending downward for a short distance around the space immediately below the spinnerette, maintains a blanket of hot gas around the nascent thread line and is used particularly where a spun yarn of low orientation but high orientability is required, as in the production of high tenacity yarns.

Immediately below this region, cool filtered air is blown across the thread line at a controlled rate to encourage uniform cooling [14]. Thereafter, the thread line is protected from stray drafts by enclosing it in a protective chimney until close to the point where the filaments converge to form a yarn or small tow. Unconditioned yarn may slough off the bobbin during storage due to moisture absorption and further crystallization.

The filaments as spun are almost completely unoriented. Most of the stretching that occurs between the spinnerette and wind-up does so while the filament is still molten and so there is sufficient time for molecular orientation to relax before the polymer cools and crystallizes. Consequently, a separate drawing step is usually necessary to produce the orientation of the crystallites which gives rise to the required physical and mechanical properties. In the drawing step, somewhat lower speeds are required than in spinning. A typical drawing (only) process is represented in Fig. 1.6 below. However, it should also be mentioned here that developments in fibre spinning technology have now enabled these two steps to be combined into one continuous process [15].

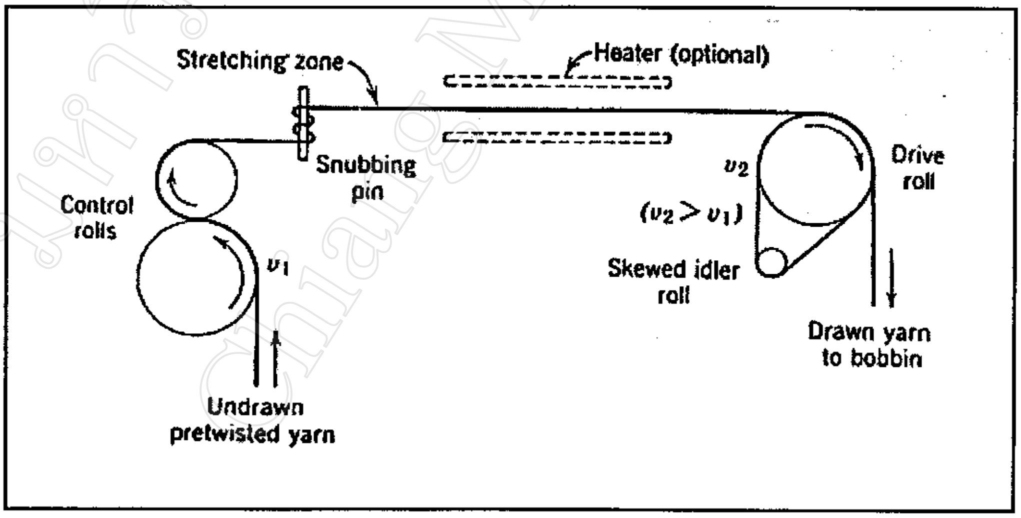


Fig. 1.6 Schematic diagram of a typical fibre drawing process [15].

The drawing step utilizes two sets of rolls, as shown in Fig. 1.6, one to feed the undrawn yarn from a supply package at velocity v_1 and the other, moving about four times as fast, to collect the drawn yarn at velocity v_2 . The filaments may pass over a metal pin between the two sets of rolls; drawing is localized in the neighborhood of the pin. The yarn is then collected on a strong metal bobbin. Freshly draw yarn has a tendency to contract somewhat in length.

The combined spin-draw process was developed conventionally in the 1960s by coupling the spinning and drawing processes in series, as shown in Fig. 1.7.

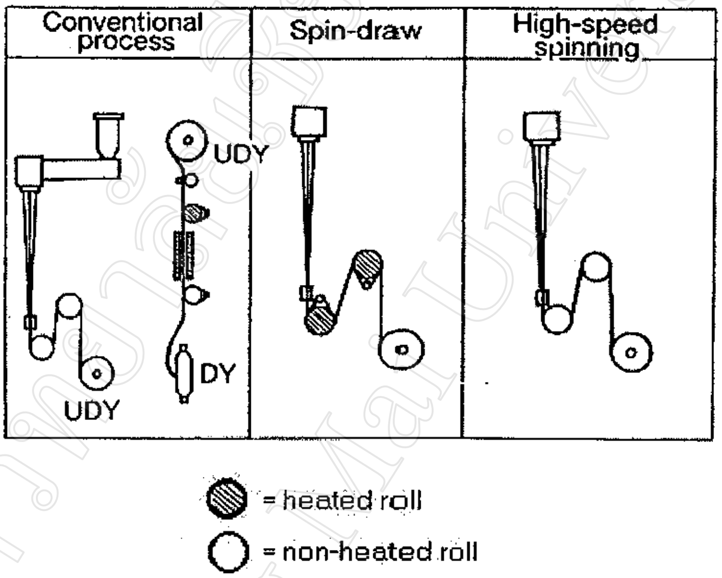


Fig. 1.7 Schematic diagrams of the production processes used for making poly(ethylene terephthalate) (PET) yarn [5].

UDY = undrawn yarn
DY = drawn yarn

For continuous-filament yarn production, the orientation of the spun yarn depends upon the speed at which it is forwarded or spun. For the principal commercial products, speeds below about 1500 m/min are employed to make spun yarn of low orientation, and above about 2500 m/min to make partially orientated yarns. The orientation increases progressively up to about 6000 m/min [16]. At higher speeds, other stress-induced processes prevent further orientation [17].

Products of low orientation must be drawn to a relatively high **draw ratio** to produce so-called **fully oriented yarn**. Drawing may be carried out as a separate step in which the spun yarn is first wound up onto a bobbin or it may be integrated with spinning as a spin-draw process in such a way that the yarn is removed from the spinning zone relatively slowly, forwarded to a drawing zone (or two or more successive drawing zones) in which it is oriented, and finally wound up at a high speed, e.g., 6000 m/min.

Monofilament fibres are produced at relatively low spinning speeds because of the problem of heat removal. Monofilaments are usually quenched by passing into cold water or onto a cold quench roll immediately after extrusion. The ribbon of cooled filaments is dried, if necessary, by an air blast and drawn between sets of feed rollers and draw rollers at draw ratios ranging from 4 to about 20, depending upon polymers and products. Drawing can be carried out either separately (off-line) or in series with spinning (on-line).

The main structure changes that take place in the fibre during the drawing (stretching) process are as follows [18]:

1. The molecules slide over each other; it would be quite impossible to draw any fibres in which the molecules were crosslinked (like the rungs in a ladder) by more than about 100 percent.
2. The molecules turn into the direction of draw so that, after being drawn, they are oriented parallel to the fibre axis.
3. The crystallinity of the fibre is increased.
4. The properties of the fibre are modified by the increases in the degree of orientation and crystallinity.

1.3 Orientation and Crystallinity [5]

In the spinning process, the molecular chains are oriented by three processes: flow orientation outside or inside the spinnerette orifices and orientation by deformation. For the orientation of the molecular chains that occurs in the spinnerette to be effective in orienting the filament, the rate of stabilization of the filament must be greater than the reciprocal relaxation time. This requirement applies only to the surface and not to the interior of the filament. The orientation of the molecules within the spinnerette thus has little influence on the orientation of the molecules in the finished filament.

Outside the spinnerette, the molecules also become oriented by elongational flow. As the distance from the spinnerette mouth increases, the optical birefringence (the specific index of birefringence is the difference between the index of the axial refraction and the index of transverse refraction) increases slowly at first and then rapidly up to a limiting value, as determined by the rigidity of the filaments and then the resulting limited mobility of the molecules. This process produces the greatest observed proportion of orientation. Generally, fibres are expected to have positive birefringence because of the better alignment and orientation of the molecules along the fibre axis in both the crystalline and non-crystalline domains [19]. Finally, a smaller contribution comes from yet a third process, namely, orientation through deformation of the physical network which is formed.

1.3.1 The Arrangement of the Molecules in a Fibre [18]

Evidence has shown that in drawn fibres the long molecules are arranged more or less parallel to the longitudinal axis. There is a close and real analogy between the arrangement of the fibres in the yarn and the arrangement of the fibrous molecules in the fibres. The main sources of evidence for this state of affairs are: (1) anisotropic swelling (2) birefringence, and (3) X-ray analytical data. It should be noted that the parallelisation of the molecules in natural fibres is not perfect and that it varies considerably from one kind of fibre to another. This variation plays a notable part in determining the properties of natural fibres.

In the case of synthetic fibres, it is often possible to control the degree of orientation. The means by which the orientation is increased is invariably that of stretching. Consider a filament which has been extruded without any stretching being applied to it; the molecules will approximate to a random arrangement, as shown in Fig. 1.8, although there will probably be a slight degree of orientation of the molecules parallel to the fibre axis caused by the directional flow through the spinnerette.

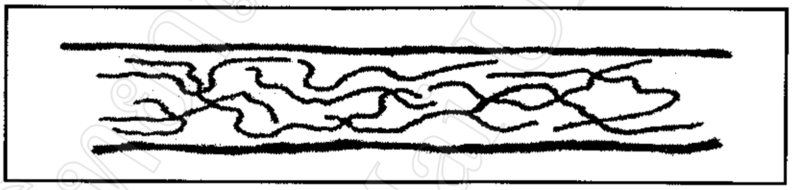


Fig. 1.8 Random arrangement of molecules in a fibre.

If, however, a material which consists of randomly arranged molecules is stretched in one direction, the molecules tend to orient themselves in that direction, as shown in Fig. 1.9.

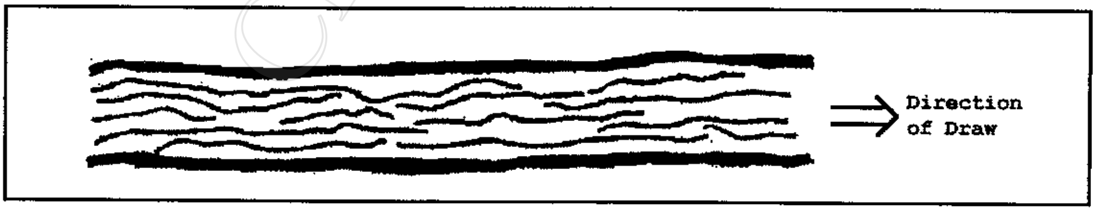


Fig. 1.9 Orientation of molecules in a fibre after drawing.

1.3.2 Crystalline Regions

Evidence of birefringence, dichroism (an optical effect which it has been possible to link with fibre orientation) and X-ray analysis has been adduced to support the view that fibres are crystalline, but it is supposed that they are not entirely crystalline. A fibre, as described previously, is made up of a large number of very long fibrous molecules. We can imagine that if care were taken to impose no stretching or flow during spinning, the molecules would be in random order, as shown in Fig. 1.8, but that as soon as the fibre is stretched, the molecules turn into line with the fibre axis.

Whereas at first they lack any order, the time will come, as they are turned into line, when they will arrange themselves one with another in an orderly way. Arrangement in an orderly and regular way encourages crystallization to take place, crystals simply being ordered arrangements of molecules. If the molecules are long and flexible and have no cumbersome side chains, they will tend to fall readily into place with one another, as shown in Fig. 1.9, and the crystals will soon form and grow. Diagrams showing both ordered (crystalline) and random (amorphous) regions in fibres of different degrees of crystallinity are compared in Fig. 1.10.

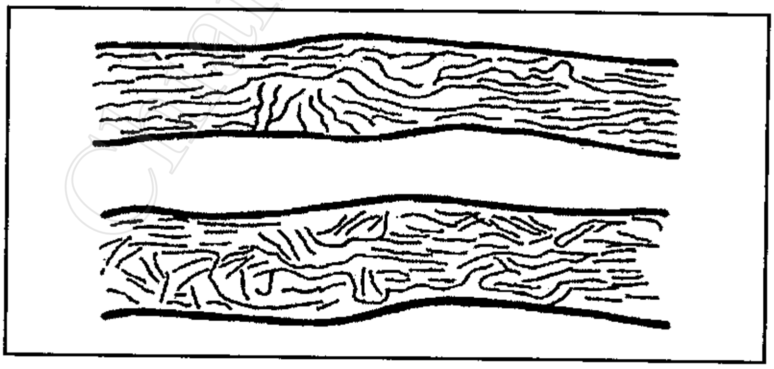


Fig. 1.10 Diagrams representing both ordered (crystalline) and random (amorphous) regions in the same fibre. (Lower diagram represents a lower degree of crystallinity than the upper. Note that in either case the longest molecules can pass from one crystalline region right through an amorphous region to another crystalline region.)

1.3.3 Structure Formation During Spinning [18]

Crystallization arising from the state of molecular orientation in the polymer in a polymer solution, melt or amorphous solid is term 'oriented crystallization'. Crystallization during spinning is a typical example of oriented crystallization. Structure formation in oriented crystallization is of great interest because it is a phenomenon reflecting the nature of the macromolecule. The following are general features of oriented crystallization:

1. The morphology of the crystallized materials changes according to the degree of molecular orientation.
2. With increasing degree of molecular orientation, the temperature which gives the maximum rate of crystallization goes up and, in some cases, the maximum rate itself also increases by several orders of magnitude.
3. The mechanism of orientated crystallization may be very different from that of non-oriented crystallization.

1.3.3.1 Oriented Crystallization from the Melt [5]

The knowledge that we have so far acquired of structure formation from oriented melts of flexible polymers can be summarized as follows:

1. In advance of crystallization, a spatial non-uniformity of density occurs [20]. A domain with higher density has a rod-like shape elongated along the direction of molecular orientation. The diameter of the domain depends strongly on the degree of molecular orientation and decreases with increasing degree of orientation. The domain, generally speaking, is of a size which can be seen with a light microscope.
2. Within such a domain, density fluctuations on a scale of several tens of nm occur within a stacked lamella-structure in which constituent 'lamallae' are developed perpendicularly to the direction of molecular orientation. The fluctuation can be detected by meridional small-angle X-ray scattering [21].

At this stage of structure formation, wide-angle X-ray diffraction from the crystalline state is still not observed (small-angle scatterings appear first before wide-angle scatterings). In conclusion, there exists a mesomorphic state during transformation from the amorphous state to the crystalline state.

3. When polyethylene is crystallized from solution (concentration 0.5-5%) by stirring the solution, what is called the shish-kebab structure [22] is formed. In the shish-kebab structure and the row structure (a structure showing an appearance like a Japanese mat, 'Tatami'), crystalline lamellae are stacked in the direction of molecular orientation. Such morphology was interpreted by Keller and co-workers [23] as a structure consisting of folded-chain lamellar crystals grown epitaxially on a long and slender nucleus composed of extended chains. Row structure, however, can readily emerge even from very weakly oriented melts, and in a thin film of the polymer we can observe many nuclei which are aligned in a line in the rod-like domain [24]. In thin films crystallized under molecular orientation with a rather high degree of orientation, a crystalline domain of about 200 nm in length and about 15 nm in width was identified by high-resolution electron microscopy as a domain in which lattice fringes are observable [25]. Accordingly, of course, we cannot deny the existence of extended-chain crystals. Hence, in order to gain a better understanding of the structure formation during crystallization under flow (oriented crystallization), the overall conformation of specific molecular chains in the material should be determined, for example by neutron scattering.

1.3.3.2 Development of High-Speed Spinning [5]

In order to improve the productivity of fibres and to open up new avenues for their use, the process of high-speed melt spinning [26] has been developed as an attempt to produce highly oriented filaments by a single-stage process without the need for separate off-line drawing after spinning. Since a commercial winder with a take-up speed of about 6000 m/min became available in the latter half of the 1970s, studies on high-speed spinning have been greatly advanced. For example, in the case of the commercial production of poly(ethylene terephthlate) (PET) fibres, the main features of high-speed spinning are as follows:

1. PET does not crystallize appreciably in normal melt spinning, but does at a spinning speed of about 4000 m/min or more.
2. An abrupt necking-like change of diameter of the filaments during high-speed spinning is recognized and closely related with crystallization.
3. The resultant spun filaments have a skin-core structure: the skin region is highly oriented and crystallized, but the core region has weak orientation and low crystallinity.
4. The spun filaments have rather high extensibility, and accordingly are utilized only for special purposes.
5. A spinning speed of 7000 m/min or more lowers the quality of spun filaments.

Experimental observations have shown that chain orientation and crystallinity are improved considerably by **necking**, i.e., the rapid thinning phenomenon of filaments at one point in the spinline during the high-speed spinning of PET. When the chain orientation improves, PET forms a pre-crystalline structure which promotes easy filament drawing and eventually the velocity gradient increases. Accordingly, the chain orientation further improves, the crystallization is accelerated, and the oriented meso-phase is formed. The elongational viscosity then increases due to crystallization and, finally, the system is fixed. This situation is shown schematically in Fig. 1.11.

During necking, it can be predicted that crystallization will take place very suddenly and the filament temperature will rise quickly by 10°C or more. Practically, however, it is probable that the crystallization rate is not so great in the latter half of the crystallization process where secondary crystallization plays an important role. This, together with the temperature dependence of the crystallization rate and its dependence on the degree of orientation, is attracting considerable research attention at the present time. For a full understanding of the necking phenomenon, precise on-line measurements and further structural investigations are needed.

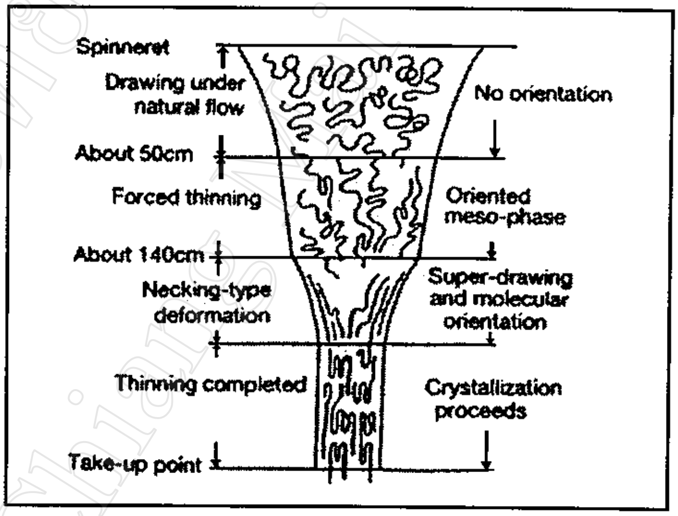


Fig. 1.11 Change of fibre structure in high-speed spinning [27 ,28].

1.4 Theoretical Variables in Fibre Formation [9]

The number of process variables in fibre formation is usually seriously underestimated. Theoretical variables in fibre formation consider the most important properties of a polymer and the necessary changes the polymer must undergo to be transformed into a fibre. These theoretical variables in the melt spinning process may be enumerated as follows:

1.4.1 Number-Average Molecular Weight

In 1932, Mark [29] published his observation that, in the melt spinning process, with the essential variables equivalent, the maximum obtainable fibre tenacity increased with increasing molecular weight of the polymer up to a certain molecular weight level (which was characteristic for the polymer) after which it became constant. Sookne and Harris [30] found that the polymer molecular weight had a similar influence on the modulus of elasticity of the fibre.

1.4.2 Shear History of the Polymer

In the plastics industry, it was frequently noticed that a product made from the same polymeric raw material but on different machinery had different mechanical properties. Later, this phenomenon was recognized as a result of differences in thermal or shear histories, or both. Careful analyses of melt-flow properties showed that some of the flow properties may be changed for the same polymer depending on whether or not the specimen had been previously extruded.

1.4.3 Shear in Spinnerette Capillary

The shear in the spinnerette capillary is as important as the shear the polymer experiences prior to extrusion through the spinnerette. It may be noticed that an increase in shear during extrusion of the fibres from the spinnerette, other conditions being equivalent, gives fibres of increased tenacity. Shear in the capillary can be considered as a process parameter which can be varied relatively easily, while the previous shear history may be only partially diminished in the process.

1.4.4 Degree of Extension

During the filament extension, some kind of molecular displacement or rearrangement must take place. Such displacements are certainly not without influence on the intermolecular relations of the chain entanglements. Intuitively, its seems quite obvious that the fibre's semi-crystalline morphology, which is so strongly responsible for the final polymer properties, must depend to a large extent on the chain morphology which existed prior to the onset of crystallization.

1.4.5 Effective Time of Crystallization

The time span during which a polymer is able to crystallize presents rather a complex problem. It depends on several factors, such as distance between the spinnerette and the point of neck-drawing, the velocity of the filament, and the temperature range within which the rate of crystallization, at a given strain rate, assumes significance.

1.4.6 Rate of Crystallization

Basically, the rate of crystallization depends on temperature and strain. The preparation of the polymer for crystallization, in terms of previous shear experience and resulting chain orientation, seems to have an influence on the rate. Thus, the three parameters: (1) chain orientation, resulting from the sum of shear and thermal treatments and degree of extension, (2) effective time of crystallization, and (3) effective rate of crystallization, are the main factors which determine the extent to which the polymer can crystallize in the quench zone.

1.4.7 Effective Temperature of Crystallization

Filament temperature normally decreases with increasing distance from the spinnerette, so at some point it becomes low enough for crystallization to begin. At the same time, the morphology and structure depend on the actual temperature of crystallization. All of these influences result in some kind of function relating crystalline fraction to the actual temperature of growth of the crystalline domains.

1.4.8 Draw Ratio

Neck-drawing is the step which develops the final fibre structure. The outcome of neck-drawing is very strongly dependent on the structure which exists just prior to the drawing step. It may even be said with full justification that the structure of as-spun fibres dictates the draw ratio which should be applied to it. Thus, the spin draw ratio is the ratio of take-up velocity to the velocity of extrudate exiting from the capillary [31].

1.4.9 Rate of Drawing

The maximum draw ratio possible before the fibre ruptures, as well as the qualitative result of drawing, depends on the rate of drawing. It is rather difficult to ascertain whether the influence of the drawing rate is the same as its influence on all non-equilibrium processes, or whether it results from changes of actual temperature in the neck. The high heat of drawing dissipates less easily in cases where the process proceeds faster. It seems most probable that both effects are responsible for the observable influence of drawing rate on the outcome of the operation. The observation of these two effects represents an enormous task. As a rule, an increase in drawing rate results in a decrease in maximum draw ratio.

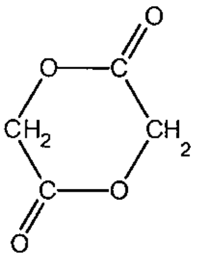
1.4.10 Actual Drawing Temperature

In most processes, heat is delivered to the fibre at the point of neck drawing, at least to initiate and localize the neck formation. At the same rate of drawing, the temperature range at which the necking is observable runs from somewhat below the actual melting point all the way down to the glass transition temperature of the polymer. The balance between the crystalline and non-crystalline fractions in the fibre structure before drawing strongly affects the temperature range within which the neck may occur. There seems to be qualitative evidence to suggest that the actual drawing temperature is higher than that indicated by the amount of heat delivered. However, the small size of the neck does not permit easy and accurate temperature measurements. Investigations of fibre properties and analyses of fibre structure show that the same as-spun fibre drawn at the same rate but at different temperatures is converted into a product of different quality. All fibre properties, particularly mechanical and thermal, are affected.

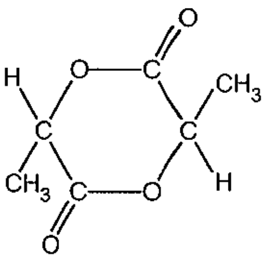
1.5 Aims of this Study

At the conclusion of this introductory chapter, it is considered both useful and convenient for the reader for the author to describe briefly what the main aims of this study were, as seen at its outset. However, as is the case with all PhD research projects, these initial aims were subject to change depending upon how the work progressed. Initially, the main aims of this study were seen to be:

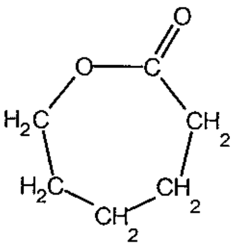
(1) To synthesize and characterize both random and segmented triblock copolymers and terpolymers based on the following 3 cyclic ester monomers:



glycolide

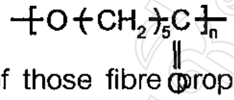


L-lactide



ε-caprolactone

(2) To study co- and the terpolymers fibre-forming (monofilament) properties via the melt spinning process. This would be preceded by melt spinning trials on a commercially available aliphatic polyester, poly(ε-caprolactone), in order to understand more clearly the effects of some of the processing variables involved and the extents to which they could be manipulated and controlled using the small-scale melt spinning equipment to be used in this work.



$$-\!\!\left[\mathrm{O}\!-\!(\mathrm{CH_2})_5\!-\!\underset{\displaystyle\mathrm{O}}{\underset{\|}{\mathrm{C}}}\right]_n\!\!-$$

poly(ε-caprolactone)

(3) To test some of those fibre properties which are most relevant to the intended application as absorbable surgical sutures, for example:
   - (a) physical properties (fibre dimensions, semi-crystalline morphology)
   - (b) thermal properties (temperature transitions, thermal stability)
   - (c) mechanical properties (tensile strength, extensibility, modulus)

This part of the work would also include studying the effects of post-spinning fibre treatments, such as drawing and annealing, on the above properties. This project is part of a much wider study on developing new materials for use as absorbable surgical sutures which is currently being carried out in Chiang Mai's Biomedical Polymers Research Unit.