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POLYMER PROCESSING

The physics of stretching chains

M R Mackley

Recent developments in the physical understanding and the achievement of high chain extension in polymeric material could lead to significant advances in existing and new areas of polymer processing technology

The development of our understanding of the physical behaviour of polymer chains is an area of physics which, over the last twenty years, has received considerable attention in both industrial and academic institutions. In addition, during this time, the growing sophistication of polymer manufacturers and processors has led to major developments in the nature, performance and applications of polymeric materials. A situation has now been reached where dramatic changes in certain physical properties can be achieved by controlling, manipulating and modifying polymeric structures.

An area which has received extensive technological and academic attention is that of stiff and strong polymeric materials. The technologist is interested in this field for several reasons; in particular, polymeric materials could have exceptionally high strength/weight and stiffness/weight ratios producing materials which could compete with, and surpass, other engineering materials such as metals. Applications for these new materials could involve load-bearing elements (where weight is a very important factor), composite materials, textiles, wires, films, tyre cord and ropes.

Put in its simplest terms the physical objective is to stretch the polymer chains uniaxially to a very high degree of alignment. In this way a material can be produced which is highly anisotropic with great stiffness and strength along the direction of the stretched chains. In addition to determining the mechanisms for achieving this high orientation, the oriented end-product will probably represent the most ordered physical state of the polymeric

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material. This state is of considerable interest as it can reveal unique chemical and physical information about the material, since physicists are usually able to deal most readily with either highly ordered or completely disordered systems, intermediate partially ordered or disordered states being difficult to interpret.

One of the intriguing aspects of the problem of high chain orientation has been the different approaches adopted to achieve similar objectives. The path that will be considered in greatest detail here will be that involved in achieving high melt or solution orientation; however, to put the subject in perspective, the elements of one of the other methods will also be described.

Characteristics of polymers

The aim is to persuade the polymer chains to align parallel to one another. A convenient point to start looking at this problem is to consider the normal conformation of polymer chains in dilute solution and the melt. A polymer chain is built up from a large number of chemical repeat units, for example the repeat unit of polyethylene is $-(\text{CH}_2-\text{CH}_2)_n-$. The chain can be characterised by the length of the repeat unit (a) and the number of repeat units in the chain (n). In dilute solution a polyethylene chain will take up a conformation close to that of a random coil; it does this in an attempt to maximise its conformational entropy and consequently minimise its free energy.

A convenient measure of the chain's overall dimensions is then given by the root-mean-square (RMS) end-to-end distance of the polymer chain (l_0). From random statistical theory this can be approximately expressed as $l_0 = an^{1/2}$. Typically for a polyethylene chain with $a = 0.15 \text{ nm}$ and $n = 10^4$, the RMS end-to-end distance l_0 is about 15 nm. The situation for a concentrated polyethylene solution or melt becomes more complex and uncertain as entanglements of molecules take place. However, recent neutron diffraction evidence does suggest that the random-coil model is a reasonable approximation even in the highly entangled melt. We may consider the 'diameter' of the polymer chain to be about 1 nm.

The molecular conformation of polymers in the solid state can be much more subtle; here there are two important distinctions between glassy polymers and crystalline polymers. The structure of *glassy* polymers may be thought of as a frozen polymer melt where the random coils are 'locked' into a fixed position, rather than their conformation continually fluctuating by thermal motion as in the molten state. The structure of crystalline polymers such as polyethylene has fascinated physicists for many years and great advances in understanding have been made during that period. It is difficult to generalise and be precise about the crystalline polymer structure; the situation can most readily be seen in dilute solution crystallisation. Here thin platelet crystals are formed,

as shown in figure 1, where the molecular chains run perpendicular to the large faces of the crystal. The important point is to realise that the thickness of these lamella crystal plates is only about 10 nm; this and other evidence strongly suggests that the polymer chains take up a folded conformation of the form shown schematically in figure 2.

The situation in the bulk crystallised material is complex; however a reasonable approximation would be to consider that crystal nucleation from the melt takes place from points in the material and that there is subsequent radial crystal growth from these points to form crystal spherulites of typical diameters ranging from 1–50 μm . The building blocks of these spherulites appear to be lamellar crystals of similar form to the dilute-solution single crystals. The final spherulite, figure 3, will contain perhaps 75% crystalline material and 25% noncrystalline material, the latter predominantly existing between adjacent lamella blocks.

The situation for solutions, melts and isotropic

Figure 1 Electron micrograph of polyethylene single crystals crystallised from a solution of polyethylene in xylene

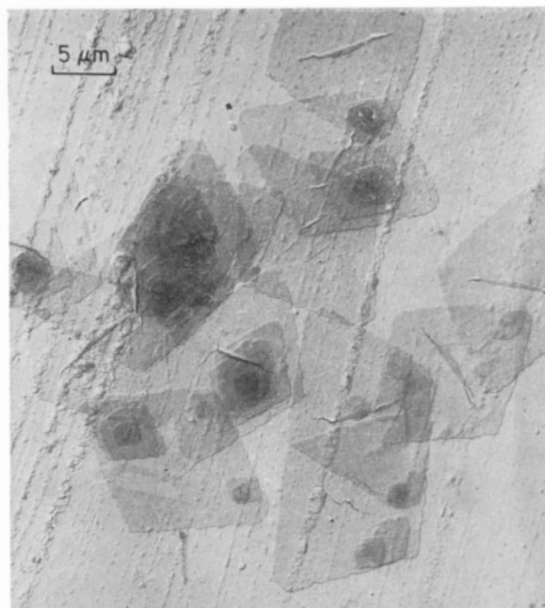
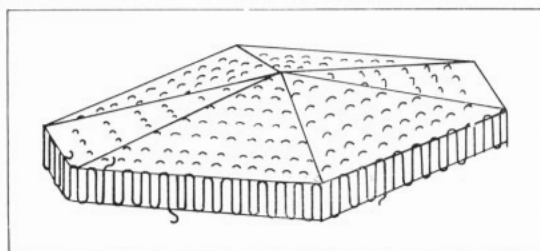


Figure 2 Schematic diagram of an idealised chain-folded configuration for a polymer single crystal



glassy solids is schematically shown in figure 4. We are now interested in looking at ways of aligning the polymer chains to form a structure such as that shown in figure 4c. A very important point to note is that the random-coil end-to-end distance of the chain in the melt was typically 15 nm; if the chain was fully extended, its extended length given by $l_e = na$, would be, say, 1.5 μm . Thus in order to stretch the random coil fully a strain l_e/l_0 of order 10^2 would be necessary.

Solid-state deformation

There are four principal methods of deforming polymers in the solid or semi-solid form and these are schematically shown in figure 5. Simple drawing constitutes the most important of these and forms the heart of most current fibre-spinning processes. Fibre-forming polymers such as polypropylene, polyamides and polyethylene can be drawn by means of a rather sharp neck. For a given set of drawing conditions such as rate of drawing, temperature of drawing and (for a given polymer)

molecular weight distribution, the material will draw to a characteristic draw ratio conveniently defined by the ratio of the starting cross sectional area A_0 divided by the area after necking A_1 . The draw ratio, $DR = A_0/A_1$, is also a measure of the total strain that is applied to the sample, high draw ratios corresponding to high strains and high chain alignment. Normally draw ratios of less than ten are achieved in most commercial drawing operations; however recent work pioneered by Professor Ward's group at the University of Leeds has led to much higher draw ratios being achieved for polyethylene. This was accomplished by significantly changing drawing conditions – in particular increasing the temperature and rate of drawing simultaneously with decreasing the molecular weight distribution of the material. The influence of an increase in the draw ratio on physical properties of polyethylene is remarkable. The undrawn material has a 'typical' polymer stiffness which is low and excludes it from many engineering applications, while the material with a draw ratio

Figure 3 Optical micrograph taken between crossed Polaroids of a thin film of melt-crystallised polyethylene, showing the typical spherulitic structure of an isotropic crystalline polymer

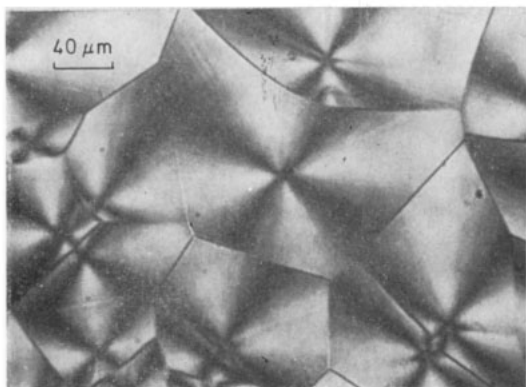


Figure 4 Schematic diagram of idealised polymeric configuration in (a) dilute polymer solution, (b) polymer melt or isotropic glassy solid, (c) uniaxially aligned polymeric chains

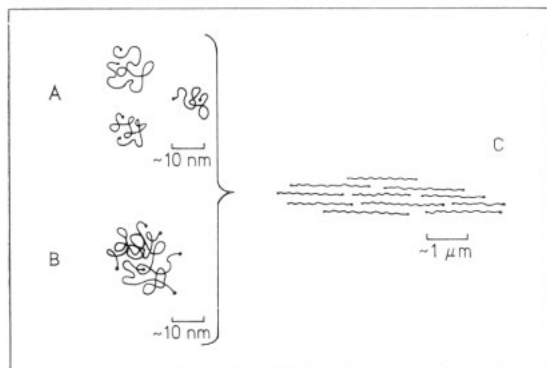
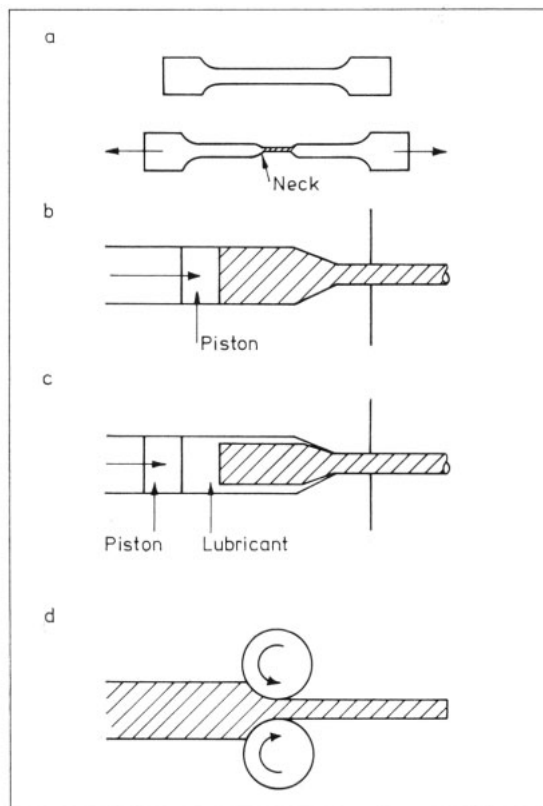


Figure 5 Schematic diagram of solid-state deformation processes. a—simple drawing, b—direct ram extrusion, c—hydrostatic extrusion, d—rolling



of 30 has a stiffness comparable to steel and a specific stiffness (defined as stiffness/density) which is four times greater than steel.

Melt and solution orientation

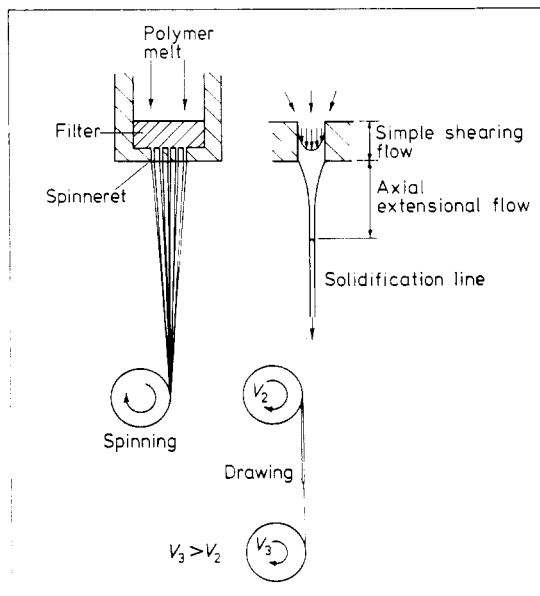
It is of value to first examine the principles of a conventional synthetic fibre-spinning plant. The chip of solid polymer is fed into a hopper and melted. The polymer melt, which has a viscosity comparable to thick treacle, is forced through various filters and fed into the spinneret, which is essentially a large array of small holes. The molten polymer is extruded through the spinneret holes and then drawn down on to a take-up spool as shown schematically in figure 6. The velocity of wind-up is greater than the melt exit velocity from the spinneret and consequently the polymer melt draws down from the original cross-sectional area of the spinneret hole. The polymer also starts to cool as soon as it leaves the spinneret and will solidify before it reaches the take-up spool.

The fibre that is formed by this method is essentially isotropic with little or no preferred orientation. As such the fibre is of little practical use and subsequent cold or warm solid-state drawing of the fibre has to be carried out as a separate process in order to produce some chain alignment and improve the stiffness and strength. Conventional fibre spinning is thus a two-stage process. This is true of most polymer processing that involves orientation; the polymer is first melted then formed into the desired geometry of fibre or film and then subsequently oriented in the solid or semi-solid state. If the chain orientation could be induced in the liquid state the prospect of a single-stage process would be possible.

In order to stretch chains in the melt or solution certain conditions must be satisfied. Several parameters are important, namely the nature and magnitude of the velocity field, the nature of the polymer and the time the material is in the velocity field. The type of velocity field is crucial. The essential point here is that the familiar simple shearing flow as experienced in normal laminar pipe flow is not, in general, satisfactory for stretching chains. Simple shearing flow contains a significant rotational component and as such the long molecules can rotate in the flow rather than deform. From this argument we would not generally expect to find high chain orientation in the capillary section of the spinneret as this will be dominantly simple shearing flow. Flows whose deformational component is greater than their rotational component may be defined as persistently extensional flows. Within this class of flows, rotation-free flows are the most efficient 'chain stretchers', of which axial extension is an example. This flow is present between the bottom of the spinneret and where the melt solidifies.

To obtain high chain extension the rate of change of longitudinal velocity V , defined by the velocity gradient $S = \delta V_x / \delta x$ for rotation-free flows, must have a magnitude sufficiently large to overcome the

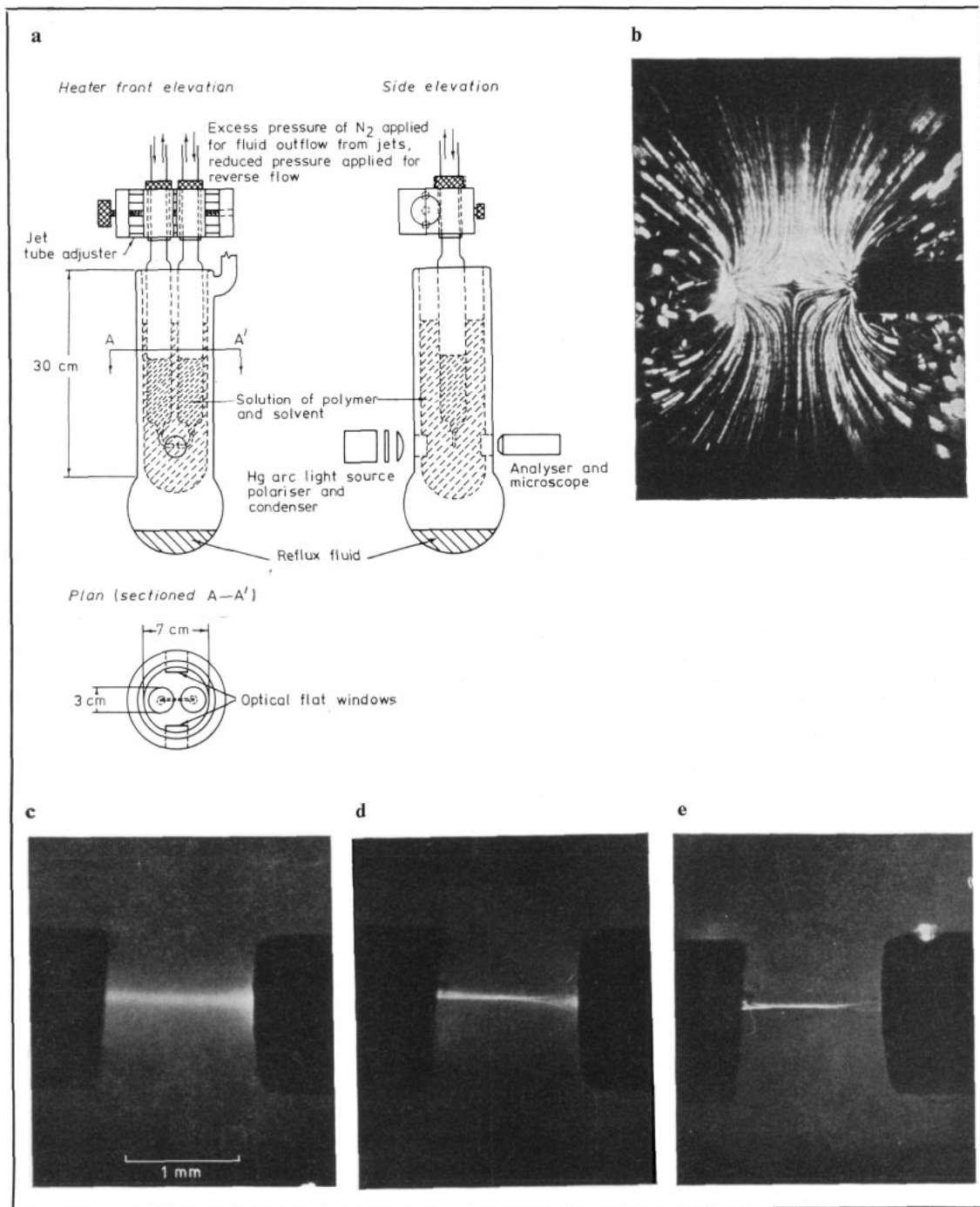
Figure 6 Schematic diagram showing the elements of conventional fibre spinning



randomising tendency of the polymer chain. This property of the molecular randomisation can be characterised by a relaxation time τ of the chain. This relaxation time is a measure of the time the chain would take to return to its random conformation from an initially extended conformation. In general τ increases with increasing molecular weight. To stretch the chain the condition $S\tau > 1$ must be satisfied; typically τ is about 10^{-3} s, thus for chain stretching $S > 10^3 \text{ s}^{-1}$ is necessary. The final requirement for chain stretching is that the molecules must be stretched for a sufficient time in order that the molecules become extended. This condition may be written as $St \gg 1$; it is this condition that traditional fibre spinning does not satisfy and is why, in general, high melt orientation cannot be achieved in this way.

Starting in 1970 at the H H Wills Physics Laboratory, Bristol, several flow devices were developed in an attempt to satisfy all the conditions necessary to produce high chain extension in polymer solutions. An example is shown in figure 7; this apparatus consists simply of two jets immersed in a sea of polymer fluid. Fluid is sucked into the jets and an axial extension velocity gradient of 10^4 s^{-1} can be produced between the jets. The degree of chain alignment can be monitored using flow birefringence techniques, in which the region in question is viewed between crossed polaroids. When the molecules become aligned there is an overall refractive index difference along and transverse to the chains and this is manifest as a birefringence on a black background. Under certain conditions it was found that very high degrees of chain orientation could be achieved; however it was also discovered that this

Figure 7 a—Schematic diagram of double-jet apparatus,
b—Streamline photograph of flow into opposed jets producing axial extensional flow between the jets,
c—Flow birefringence photograph taken between jets for axial extensional flow, 3% polyethylene xylene solution. $T=124^{\circ}\text{C}$, $S\sim 10^3\text{ s}^{-1}$. Localised chain extension can be observed near symmetry axis,
d—Flow birefringence photograph showing in situ crystal formation during flow. Details as figure 7c at $T=110^{\circ}\text{C}$,
e—Birefringence photograph taken after flow in figure 7d, showing stationary polymer fibres bridging jets. (Figures from Phil. Trans. R. Soc. (1975) 278 29–66)



chain alignment was limited to a very local region of the flow field. The reason for this localisation is quite simple – to stretch a chain from its random to stretched conformation the molecule must be strained by $l_e/l_0 \sim 10^2-10^3$. Because of the geometric nature of the flow these strains will only be achieved on or near the outgoing symmetry axis of the flow for the double jet shown in figure 7; it is only in this region of the flow that the molecules have been stretched for sufficient time and the condition $St \gg 1$ satisfied.

Having achieved high chain extension in solution the next objective is to ‘lock in’ the orientation to form a highly oriented material from a single-stage process. This was attempted by *in situ* crystallisation; the procedure was to operate at a temperature above the normal crystallisation temperature but below the dissolution or melting temperature. In this way, when the chains became aligned, the aligned molecules crystallised in preference to the unoriented ones. Using this method for polyethylene, shish-kebab type crystals were produced similar to those shown in figure 8. (This particular example has been produced by other means.) The shish-kebab structure is an exceptionally interesting fibre and resembles, in dimensional hierarchy, cellulose and asbestos fibres. The material of the backbone of the fibres is of great interest; here the molecules are aligned parallel to one another and are essentially

in an extended conformation. The regular platelets growing epitaxially onto the side faces of the fibre closely resemble chain-folded single crystals.

In terms of mechanical properties one would ideally have liked purely extended backbone material without the platelets. The reason for the existence of the platelet crystals on the backbones is not entirely clear; however subsequent experiments by Dr Pennings’ group at the Netherlands State University at Groningen led to rapid technical developments and understanding in this field.

The first key experiment was where Pennings’ group established a method for growing continuous lengths of shish-kebab fibres. This system consists of placing a piece of ‘seed’ shish-kebab crystal on the end of a fine thread. The seed is then suspended in a capillary flow as shown in figure 9. If the temperature and flow rate are correct a fibre is seen to grow from the seed and this fibre can then be wound up as a continuous thread at the same rate as it is growing. An important scientific point about this experiment was the recognition by the Bristol group that once a crystal has been formed or introduced into the flow, the subsequent flow field experienced will be significantly different. In particular, in this situation the flow near the tip of the fibre will be as shown in figure 9. Downstream of the fibre tip an essentially rotation-free extensional velocity gradient will exist; also the

Figure 8 Shish-kebab crystals of polyethylene showing predominantly extended chain backbone fibres with regularly spaced platelet crystals attached to side surfaces

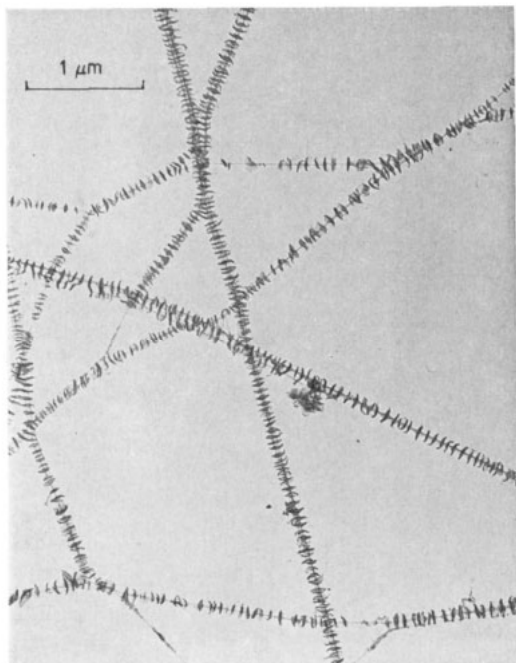
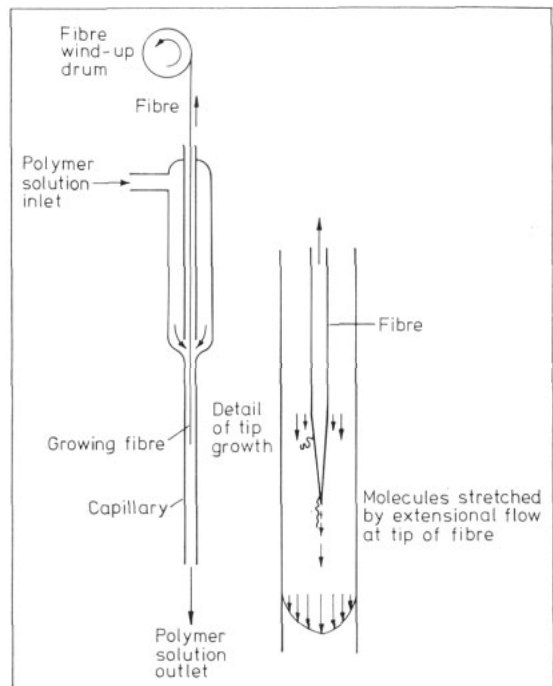


Figure 9 Schematic diagram of the Pennings’ experiment used to grow continuous fibrous crystals in a capillary flow

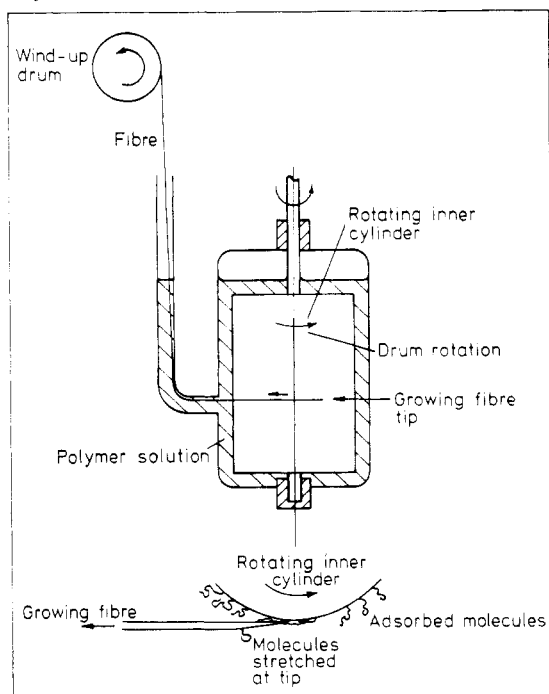


magnitude of the velocity gradient has been estimated to be of the order 10^2 – 10^6 s⁻¹, which is exceptionally high, and the situation is visualised where molecules in the region of the fibre tip are stretched by the flow and subsequently crystallised into the shish-kebab backbone configuration. Lateral growth of the fibre is limited, possibly because of the simple shearing component of flow on the side surfaces of the fibre. Examination of the fibres produced by this single-stage process reveals that they still contain the shish-kebab crystals as observed before.

The second important experiment by Pennings' group was the recent discovery that fibres could be grown at much higher temperatures than before by positioning the tip of the growing fibre near a rotating surface. The experimental system is shown schematically in figure 10. The inner cylinder rotates and the fibre growing adjacent to the surface is wound off from the side outlet pipe. A seed crystal is again required to start the process. Electron microscopic examination of these fibres reveals little or no platelet material and this is reflected in the enhanced mechanical properties. The stiffness of this material is 10^{11} N m⁻² compared to 10^9 N m⁻² for unoriented polyethylene. This experiment reveals a new single-stage way of producing very stiff oriented synthetic fibres.

The physics behind this development is not completely clear at this stage. It would appear that

Figure 10 Schematic diagram of the Pennings' experiment used to grow continuous fibrous crystals where the tip of the fibre grows close to a rotating surface



surface absorption of polymer molecules is an important factor; a mechanism can be visualised where chains from the fibre are caught by molecules absorbed onto the surface of the roller. Subsequent movement of the roller stretches the chain which is 'held at both ends' and the stretched chains subsequently crystallise to form an aggregate of backbone fibres. The dimensions of the fibres produced by the Pennings technique are directly equivalent to the fibres produced by conventional fibre-spinning techniques and as such the technological potential is obviously considerable. The technique has been shown to work for polyethylene; however there are still many unanswered questions concerning the extension to other polymeric materials and the detailed physical mechanisms involved.

Conclusions

Recent developments in flow orientation and solid-state deformation have now produced highly anisotropic materials with high stiffness and strength. Both systems could be of great technological importance and the physical principles behind the developments could be successfully used in other areas of polymer processing technology. In addition to these two techniques, alternative technological ways of producing high chain stretching exist. These are (i) carbon fibres, where an initially poorly oriented polymer is oxidised and subsequently carbonised to form a highly oriented fibre and (ii) the Du Pont Kevlar fibre, where high orientation is obtained by solution spinning of an initially stiff polymeric chain. Viewed as a whole, the ingenuity of the physicist, chemist and technologist seems impressive. However, in view of the diversity and subtle behaviour of some of nature's own anisotropic polymeric materials we still have much to learn.

Further reading

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