Flow induced crystallization of polyethylene melts

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Longitudinal velocity gradients in a flowing system are known to extend molecules appreciably and have been found to be responsible for the fibrous crystallization of polyethylene from solution. In this paper the preliminary optical observations are given of the effect this type of velocity gradient has on flowing crystallizable polymer melts. By flowing molten polymer into two mutually opposed orifices a longitudinal velocity gradient is generated specifically along the symmetry axis of the system. It was found that fibrous crystallization of polyethylene melt appeared to occur preferentially along this axis, implying that longitudinal velocity gradients play an important part in the production of this fibrous crystallization. The structural implications of the resulting extrudates and filaments obtained are discussed. Additional observations of the effect a fine gauze has on the crystallization of polymer melts is also presented.

For crystalline polymers to approach their theoretical maximum stiffness two physical conditions must be satisfied. The molecular chains must crystallize in a manner such that they are highly aligned; and, equally important, the chains must possess appreciable continuity along the fibre direction[1].

By cold drawing most crystalline polymers it is possible to obtain a high degree of molecular alignment; but the existence of chain discontinuities along the draw axis prevents a high modulus material being achieved.

Obviously the finite length of the molecules is one limiting factor on the degree of chain continuity that can be obtained; however, a very much larger contribution to chain discontinuities along the fibre axis can be expected to come from the existence of chain folding where the molecules fold back and forth a larger number of times. If a high modulus fibre is to be achieved an oriented extended chain type crystal structure relatively free from folds must be obtained[1].

A possible way of producing oriented extended chain material is to align the molecules before crystallization by hydrodynamic means, and then allow the molecules to crystallize whilst in the extended configuration.

Previous experimental[2,3] and theoretical[4,5] studies have shown that in solution large polymer molecules can be readily stretched to their extended chain configuration in a longitudinal velocity gradient, whereas in the more common transverse velocity gradient the rotational nature of the flow severely restricts the extension of the molecules.

It was estimated that in solution[3] a longitudinal velocity gradient of magnitude about $10^3 sec^{-1}$ was required to extend a significant proportion of the molecules. If it is assumed that in the melt longitudinal velocity gradients are also necessary to extend molecules, the magnitude necessary to obtain appreciable molecular extension would be reduced somewhat because of the anticipated increase in relaxation times of molecules in the melt. However, a conventional fibre-spinning type apparatus can only supply a longitudinal velocity gradient at a maximum rate of about $20 sec^{-1}$ which is a factor of 50 less than that estimated to be necessary in solution. Frank suggested a system of mutually opposed jets as a possible method of producing sufficiently high longitudinal velocity gradients[2]. A longitudinal velocity gradient would by symmetry be specifically generated along the symmetry plane and axis of the system. Regions away from these areas would not necessarily contain pure longitudinal velocity gradients and in all probability would be areas containing transverse velocity gradients.

Experiments carried out using a solution of polyethylene in xylene at low supercooling, where normally no crystallization would take place, resulted in a crystal deposit being obtained between the jets[2]. This deposit has a 'shish kebab' morphology of the type first studied by Pennings[6,7]. The 'shish kebab' consists essentially of a fibrous extended chain core onto which chain folded platelets are attached[8,9].

The crystal deposit produced between the jets had little mechanical strength, presumably because of the weak compacting of the individual fibrils to form the crystal aggregate. In addition the fibre could not be produced as a continuous filament.

This paper reports the preliminary observations and their implications, made from similar experiments carried out in the melt.

In extending the work to the melt it was necessary to design a new apparatus capable of withstanding the larger pressures involved due to the increase in viscosity of the polymer melt. Details of the apparatus are given in the provisional patent specification for the system[10]. It is basically the suck jet experiment of ref. 2 except
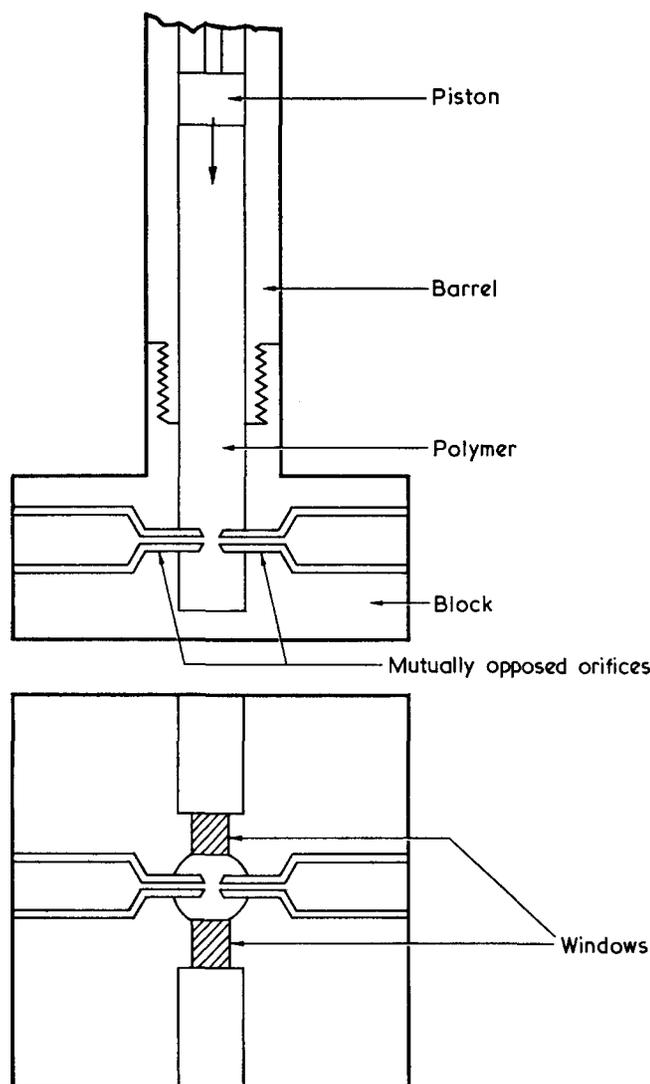
Figure 1 Apparatus used for flowing molten polymer into two mutually opposed orifices

that the polymer is forced through the jets not by suction applied to the jets but by pressure applied to the surrounding melt. The essential features of the apparatus shown in *Figure 1* involve a barrel which is charged with polymer which is then melted. A piston forces the polymer down the barrel into a lower chamber where the melt is then forced out of two mutually opposed orifices. The barrel and chamber can be maintained at any chosen temperature. Optical windows are provided in the system to enable *in situ* observations of the crystallization to be made in the region of the jet orifices.

From the selected rate of advance of the piston and the known dimensions of both piston and jet orifices, the volumetric velocity, V, into the jets can be determined. It has been shown by tracer particle experiments[3] that the velocity at the centre of symmetry of the opposed orifice type of system, is essentially zero; thus the longitudinal velocity gradient $\dot{\gamma}$ along the symmetry axis can be estimated to a first approximation simply by:

$$\dot{\gamma} = \frac{V}{d}$$

where d is the half distance between the jet orifices.

It is only possible to specify the longitudinal velocity gradient along the symmetry axis. Away from the symmetry axis predictions of the type and magnitude of the velocity gradients present cannot be specified in this precise manner.

The preliminary observed phenomena are best described with reference to *Figure 2*.

High density polyethylene Marlex 6002 was used as a sample polymer. All photographs were taken for a velocity gradient of $50\,\text{sec}^{-1}$ using jets of internal diameter $1\cdot0\,\text{mm}$.

At a temperature of 150°C the observed cross-polar and bright field flow patterns are shown in *Figures 2a* and *2b* respectively. In *Figure 2a* with the polars crossed in the 45° position a highly symmetrical birefringence pattern is seen indicating molecular orientation in this region. Absolute determination of the magnitude of the birefringence would be difficult because the observed pattern is a result of varying optical paths through material where both the direction and magnitude of the birefringence are a function of position. A rough estimation of the overall birefringence can be made by dividing the observed retardation by a mean radius of the localized birefringence: an estimation of the maximum retardation being obtained by counting the number of interference fringes from outside the birefringent area to the symmetry axis, and knowing that each fringe corresponds to one wavelength retardation. In this manner an estimated birefringence of $7\cdot2 \times 10^{-3}$ is calculated. This is a factor of $8\cdot0$ below that calculated for the theoretical birefringence[11] expected for perfectly aligned polyethylene.

A point of immediate interest seen in *Figure 2a* is the beginning of cusping of the fringes as they approach the symmetry axis of the system. This strongly suggests that there is increased molecular orientation along the symmetry axis. The bright field photograph (*Figure 2b*) is included to contrast with later pictures; only the profile of the jets and slight contamination in the melt are visible in the photograph taken during flow.

Figures 2c and *2d* show the cross-polar and bright field situation respectively for a temperature of 140°C. In addition to the features seen at 150°C, when either viewed between crossed polars or in bright field a discrete scattering line of about $0\cdot1\,\text{mm}$ diameter is seen along the symmetry axis of the jet geometry. This axial line was highly suggestive of a crystalline fibre being continuously produced along the symmetry axis with the ends of the fibre entering the jet nozzles along the jet axis. After flow the birefringence disappeared; however, the central line was seen to persist for up to 30 min after the cessation of flow.

Additional evidence to support the view that this discrete scattering line is a stable crystal form is shown in *Figure 3*. In this case the cross-polar photograph was taken when flow has terminated and the piston had been retracted slightly. In this way the pressure in the melt was returned to atmospheric pressure and some polymer 'sucked back' through the orifices. The picture shows clearly the discrete nature of the core. It also shows that the core extends into the orifices and that the core appears stable even at atmospheric pressure.

In *Figure 2c* the cusping of the interference bands is more enhanced than in *Figure 2a* indicating greater orientation along and near the symmetry axis. An estimation of the increase in birefringence along the
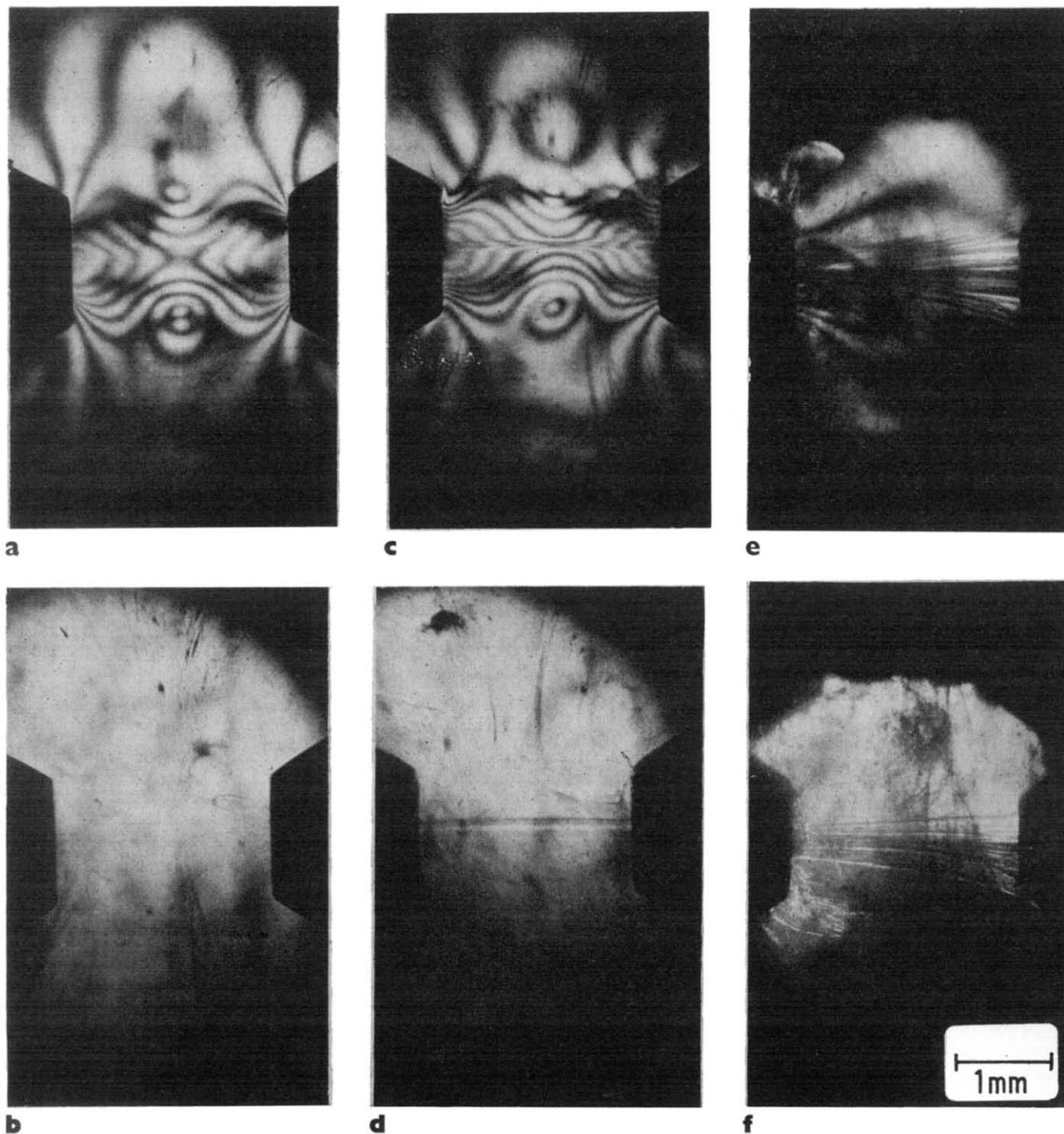
Figure 2 Photographs taken during flow of region between opposed orifices. (a) Polars crossed in 45° position, T=150°C; (b) bright field, T=150°C; (c) polars crossed in 45° position, T=140°C; (d) bright field, T=140°C; (e) polars crossed in 45° position, T=134°C; (f) bright field, T=134°C

symmetry axis can be made by dividing the increase in retardation seen near the symmetry axis by the thickness of the central thread. This gives a value of about $1\cdot7\times10^{-2}$ which is a factor of 2·4 greater than the estimated overall birefringence seen in *Figure 2a*. This makes the total birefringence along the central line only a factor of 2·5 below the theoretical value for fully aligned molecules.

Typical operating pressures for these experiments were 200 bar [1 bar = 10^5 N/m²]. For the above conditions, the polymer extruded through either of the jets could be removed as a plug or alternatively as a filament if slight tension was maintained on the extrudate as it left the exit side of the orifice. Both plug and filament showed a

similar form of X-ray pattern. *Figure 4* shows an X-ray pattern from a filament. This consists of highly oriented equatorial arcs superimposed on arcs of much larger angular spread. The pattern obtained suggests molecular orientation of a two phase nature, one phase being more highly oriented than the other.

The likely interpretation of the phenomena described above is that the core fibre is produced within the melt by the crystallization of longitudinally aligned extended chain molecules. As the molecules are aligned in this highly oriented manner along the symmetry axis the polymer crystallizes as a fibre in an extended chain form and would be expected to have a higher melting point than the mass of surrounding material. This

Figure 3 Crossed polar photograph showing discrete nature of core, seen when piston had been retracted after flow
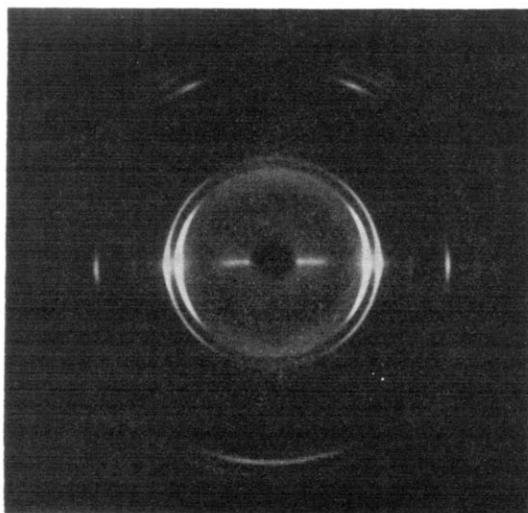

Figure 4 X-ray picture of filament, illustrating its two-phase nature

filament is continuously produced as the ends move outwardly along the high longitudinal velocity gradient centrally through the jet orifices. The polymer extruded around the core as it enters the orifices is obviously molten at this stage and acts as a 'lubricant' preventing the system from blocking. This molten material can be expected to crystallize onto the core at a later stage when the filament or plug leaves the heated region of the block, where the supercooling is sufficiently great to allow conventional chain-folded crystallization to take place.

This two-stage crystallization process offers an attractive explanation of the two-phase X-ray photograph obtained from the extrudate: the highly oriented phase corresponding to the crystalline core seen to form between the orifices and the less strongly oriented phase corresponding to the outer sheath of molten material which crystallizes onto the core in a conven-

tional manner when the extrudate has left the heated block.

Returning to the optical photographs, *Figures 2e* and *2f* show the cross-polar and bright field photographs respectively taken when flow had terminated after a run at a lower temperature of 134°C.

In this case further fibrils are seen to develop on or near the symmetry axis. As the amount of visible crystalline material was seen to increase the pressure within the melt rapidly increased until the maximum permissible pressure was reached where either one or both jets blocked. In this respect the experiment has similarities to observations of van der Vegt and Smit[12] and Porter and Southern[13] where they observe sudden increases in pressure resulting in total blockage when extruding polyethylene through tapered capillaries. They attributed this increase in pressure and blockage to the onset of crystallization. Using the apparatus described in this paper it is possible to confirm this type of phenomenon. The optical observations of the development of individual crystalline fibrils can be directly seen to be related to the increase in pressure of the system resulting in total blockage.

In an attempt to remove particle contamination from the melt a fine stainless-steel gauze supported on a rigid coarse gauze was placed in the polymer melt supply extending across the junction between the barrel and the bottom chamber. With the melt temperature in the barrel of 160°C the extrusion followed the same pattern described previously for this temperature. At a critical lower temperature of about 140°C where in the previous example a crystalline fibre was thought to be continuously produced; an additional part of the whole volume shown in *Figure 5* was filled with a number of fine crystalline fibrils each one appearing to originate from a single hole in the fine gauze. With the further development of the fibrils the system tended to block with a corresponding rise in pressure.
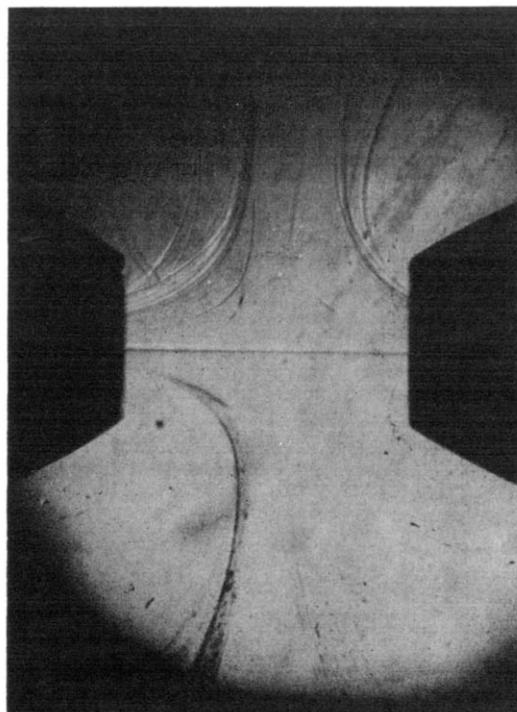

Figure 5 Photograph showing additional fibrous crystalization induced by putting gauze in polymer melt supply. $T=140$°C

It is apparent from the last example that fibrous crystallization can be induced through an array of fine holes in a gauze, presumably because of the longitudinal velocity gradient generated along the centre line of each hole. This observation may be relevant to the filtering of polymer melts in technical fibre spinning machines and to the origin of blockages which may occur.

In conclusion, it can be seen from the mutually opposed orifice experiment that longitudinal velocity gradients play a major part in inducing fibrous crystallization in the melt. Also there are sufficient indications from these preliminary observations to believe that continuous oriented filaments and/or fibril reinforced materials can be achieved effectively by careful design and control of hydrodynamic and thermodynamic parameters. Finally the experimental technique adopted in this paper of direct *in situ* optical observation of the flow and crystallization phenomena commends itself for studies of this kind.

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