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Direct experimental evidence for flow induced fibrous polymer crystallisation occurring at a solid/melt interface

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We report experimental observations on the way that flowing polyethylene melts can crystallise within a processing channel geometry. Using a recently developed Multipass Rheometer (MPR), we present rheological, rheo-optic and coupled X-ray data that follow the evolution of crystallisation, as molten polyethylene flows into a slit geometry. Optical observations show that fibrous crystallisation occurs initially at the walls of the slit and not, as expected, in the entrance region to the slit. The coupled X-ray, rheology and rheo-optic data lead us to speculate that a coil-stretch transition of the polymer chains occurs at the wall of the slit and this acts as the primary cause of fibrous X-ray nucleation. At high wall shear rates we identify evidence to suggest that slip occurs between the flowing polymer and the solid wall and this in turn causes the onset of fibrous crystallisation to be surpressed. The experimental observations are generally consistent with certain theoretical predictions made by Brochard and de Gennes. © *2000 Kluwer Academic Publishers*

1. Introduction

The physical understanding of the flow induced crystallisation of polymer melts involves an appreciation of the way in which polymer chain configuration is influenced by flow and also how chain configuration can affect both the crystal nucleation and growth process. The molecular chain configuration behaviour of flowing polymer melt is central to an understanding of polymer melt rheology and as such has been extensively studied both from an experimental and theoretical point of view (see, for example, Doi & Edwards [1], Dealy, & Wissbrun, [2] McLeish [3]). The effect of flow on polymer melt crystallisation has not been elucidated to the same level; reviews by Doufas *et al.* [4], and Eder *et al.* [5] are representative summaries of current understanding.

Following early pioneering work by amongst others Peterlin [6] & Ziabicki & Kedzierska [7], it was recognised that for dilute polymer solutions, the chain stretching ability of an extensional flow was more efficient at stretching polymer chains than simple shearing flow, and a so called "coil-stretch transition" could be expected for polymer chains in extensional flow when, $\dot{\gamma}\lambda \geq 1$, where $\dot{\gamma}$ is the extensional strain rate, and λ the longest relaxation time of the chain. The chain extension enhancing ability of extensional flows has also been applied to polymer melt flow. Enhanced flow induced fibrous crystallisation for polyethylene melt has often been attributed to the extensional flow in capillary entrances, (Kolnaar & Keller [8] Mackley & Keller [9]).

In this paper we present direct experimental evidence that reveals the precise way in which flow induced crystallisation of polyethylene melt occurs. Using one apparatus, we correlate rheological, rheo-optic and rheo-X-ray data, to build up a picture of what is happening when polyethylene crystallises during flow.

2. Experimentation configuration

All experiments described in this paper were carried out in a recently developed MultiPass Rheometer (MPR). This apparatus was originally built for rheological processing measurements (Mackley *et al.* [10]); however it has subsequently been extended to provide Rheo-optic and Rheo-X-ray information (Saquet *et al.* [11]). A schematic diagram of the apparatus is given in Fig. 1, which illustrates the two piston configuration of the MPR. Either a capillary or slit test section is positioned between the two pistons. After loading, molten polymer can be forced through a test section by moving the two servo hydraulically driven pistons with the same control signal. Precise control of flow, temperature and pressure are possible using the apparatus.

We report experimental results for one grade of high density polyethylene, HDPE (type Dow 96003E). This material is a typical extrusion grade HDPE with $\bar{M}_n = 22\,900$, kg/kmol and $\bar{M}_w = 180\,000$ kg/kmol.

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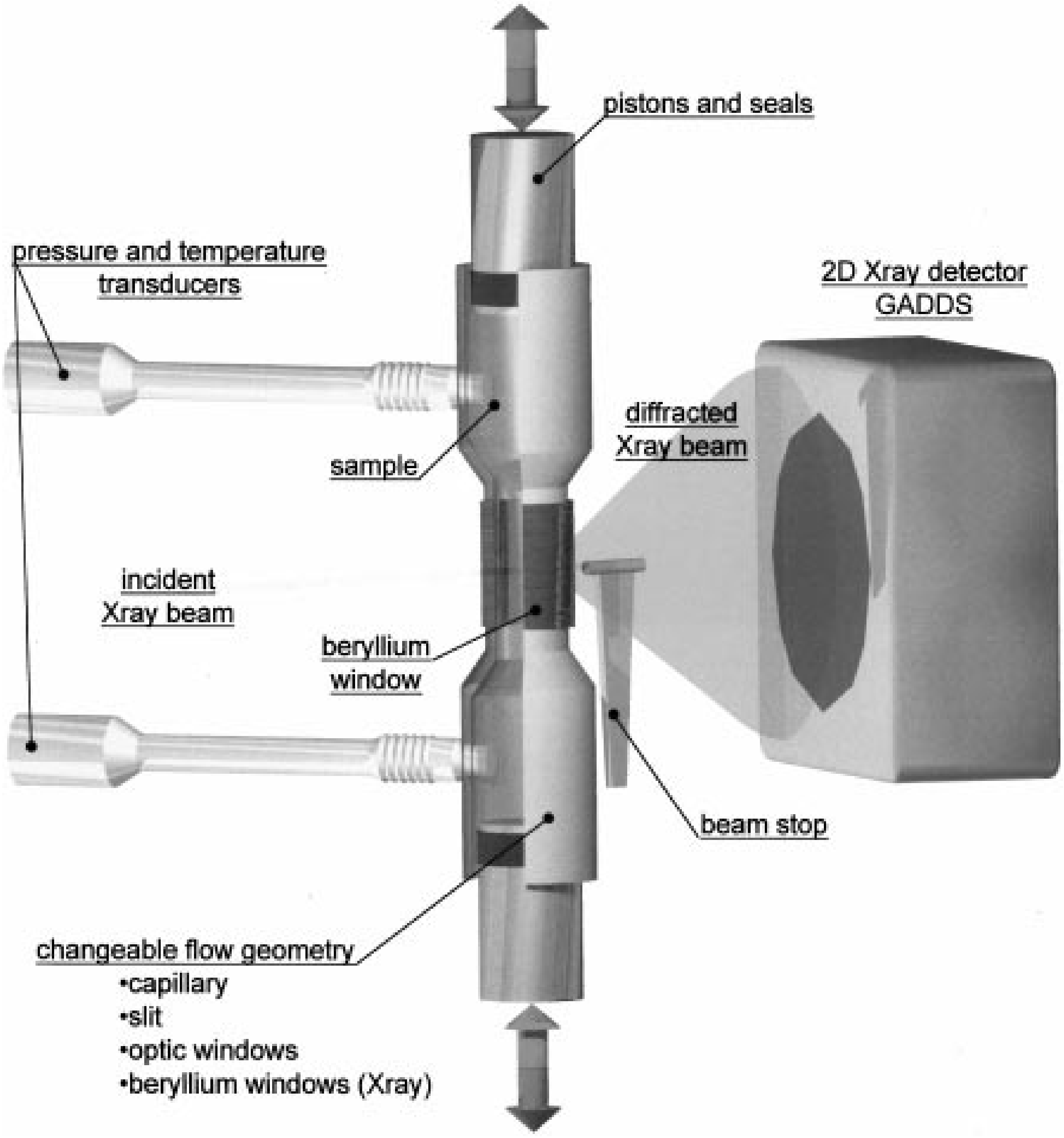

Figure 1 Schematic diagram of multiPass rheometer showing two piston rheometer and X-ray configuration.

The polyethylene was loaded into the MPR and melted initially at a temperature of 175 °C. Subsequent experiments were performed at $T = 145\,^{\circ}\mathrm{C}$ and $T = 135\,^{\circ}\mathrm{C}$. The peak melting point of this PE occurs at close to $T = 135\,^{\circ}\mathrm{C}$ and crystallisation from the melt under quiescent conditions would not normally occur at this temperature.

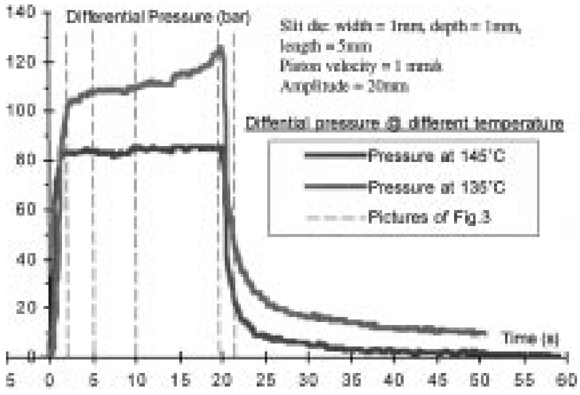

Figure 2 Pressure profiles for HDPE at 145°C and 135°C. Constant piston velocity movement of 1 mm/s from 0–20 s.

2.1. Rheology

The pressure difference across a slit configuration for two temperatures is shown in Fig. 2 for a single pass of the top and bottom piston moving together. Flow is into a slit of 1mm width, 1 mm depth and 5 mm length. The figure shows data at two temperatures. At 145 °C the constant velocity movement of the piston results in an increase in pressure difference, until a steady value of 82 bar is reached. On cessation of piston movement, pressure relaxation is observed in a similar manner to that previously reported by Ranganathan *et al*. [12]. At 135 °C a more unusual pressure trace is observed. At this lower temperature there is a steady pressure build up during the whole piston movement and this type of "pressure blockage" has been reported by a number of authors, including Van der Vegt & Smith [13], all of whom have associated the effect with flow induced crystallisation either within or upstream of the capillary.

2.2. Rheo-optics

rheo-optic experiments were performed under the same conditions as Fig. 2 and the data are shown in Fig. 3. The data shows two rheo-optic sequences, one at 145 °C and the other at 135 °C. The flow birefringence experimental apparatus used for each set is described by Saquet *et al.* [11]. The sequence at $T = 145\,^{\circ}\mathrm{C}$ shows the time evolution of the observed optical retardation bands during a single pass sequence under similar conditions to the earlier rheological data. As the overall pressure difference increases, the internal stress distribution within

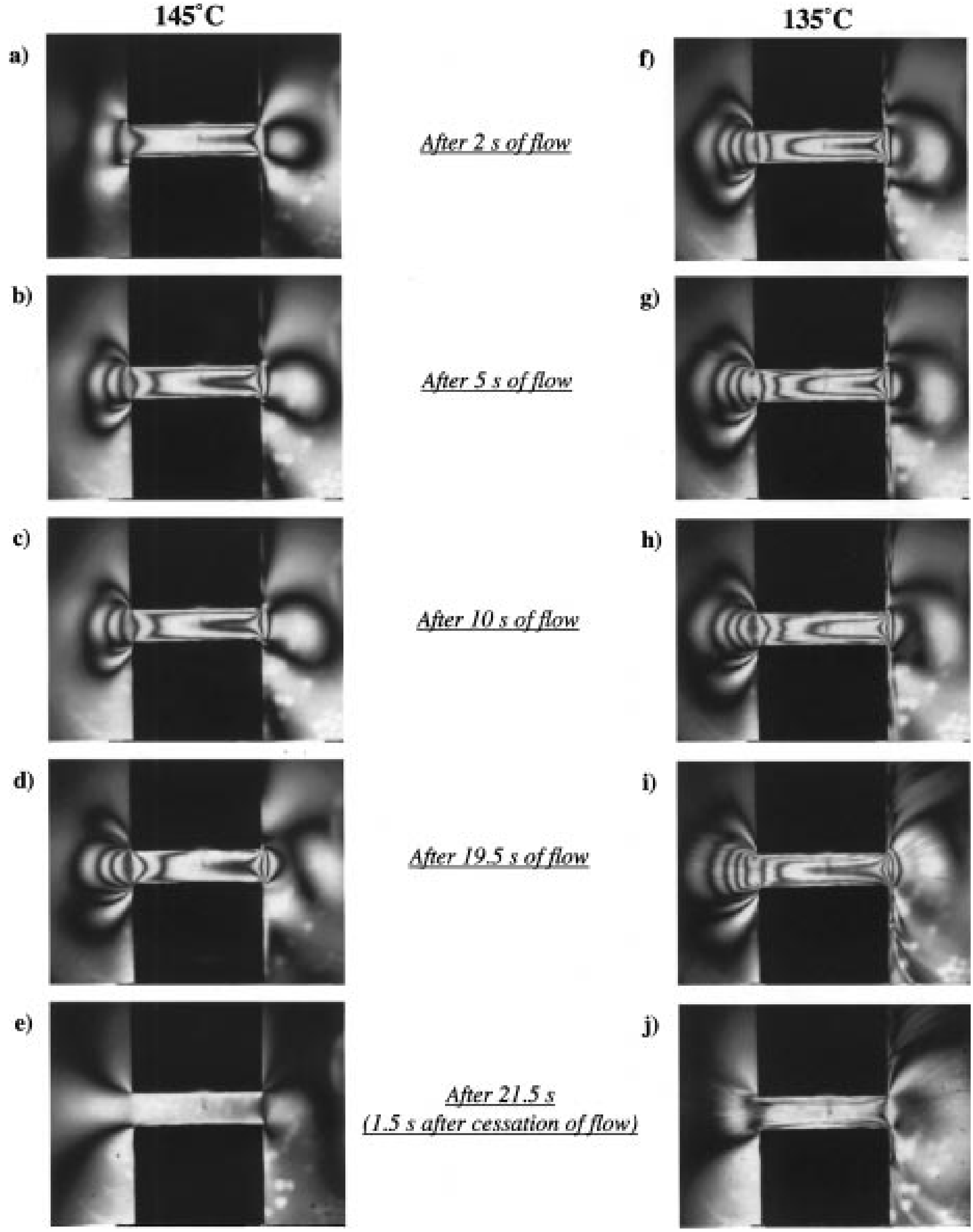

Figure 3 Observation of flow of HDPE at 145°C and 135°C under the conditions described in Fig. 2. Flow is from left to right in both cases. Polars are crossed at 45 degrees to the horizontal.

the polymer melt develops, by the emergence of integral retardation bands that correspond to certain stress levels within the melt. Weak molecular orientation within the melt gives rise to optical anisotropy which in turn can be linked to stress levels by using the well known stress optical law (Wales [14], Fuller [15]).

The birefringence patterns show the development of extensional stress within the entrance region of the slit and also the emergence of an essentially constant shear stress at the wall of the slit. From the flow birefringence it can be established that the levels of extensional stress and wall shear stress are comparable for this particular flow.

At 145 °C, the flow birefringence patterns are consistent with the earlier pressure trace and both are consistent with expectations for flowing polymer melt. At 135 °C however, an additional feature is observed. During flow, the emergence of fibres is seen to occur from the wall of the slit region and these fibres are visible in Fig 3h–j. This was a surprising result as our initial expectation had been that nucleation would occur in the upstream extensional flow region. The onset of fibrous crystallisation can be seen with greater clarity if a higher magnification is used with bright field illumination. In addition the molten polymer was subject to a number of reversing "multipasses" in order to build up an assembly of fibres. Fig. 4 shows the progressive accumulation of fibres which all emanate from the region of the wall.

2.3. Rheo-X-ray

Complementary experiments were carried out using our recently developed Rheo-X-ray facility. In this case a 2 mm internal diameter beryllium capillary was used in order to allow the X-ray beam to penetrate the walls of the capillary and pass through the central parallel section of the capillary (Saquet *et al*. [11]). The X-ray facility, which includes a 2D, (GADDS Bruker) detector provides a powerful method for establishing the presence of both orientation and crystallisation of the polymer melt during flow.

Fig. 5 shows a key series of two 2D wide angle transmission X-ray patterns together with the integrated profiles of intensity as a function of scattering angle. The data illustrate three important features.

Fig. 5a shows the X-ray data for molten polyethylene at $T = 145\,^{\circ}\mathrm{C}$. This set of data was obtained "during flow" when the pistons were being moved backwards and forwards at a constant velocity with a 0.1 second

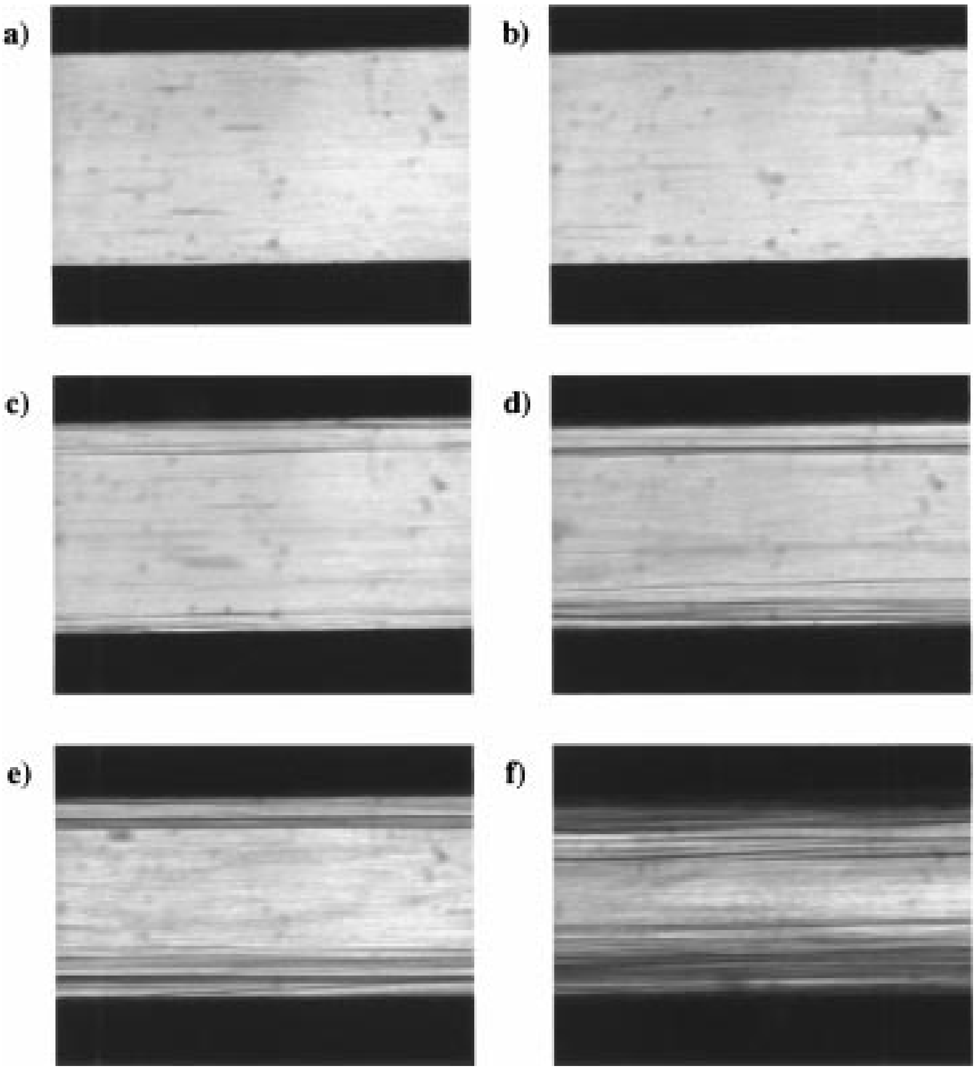

Figure 4 Onset of fibrous crystallisation at higher magnification during reversing multipasses (slit width = 1 mm).

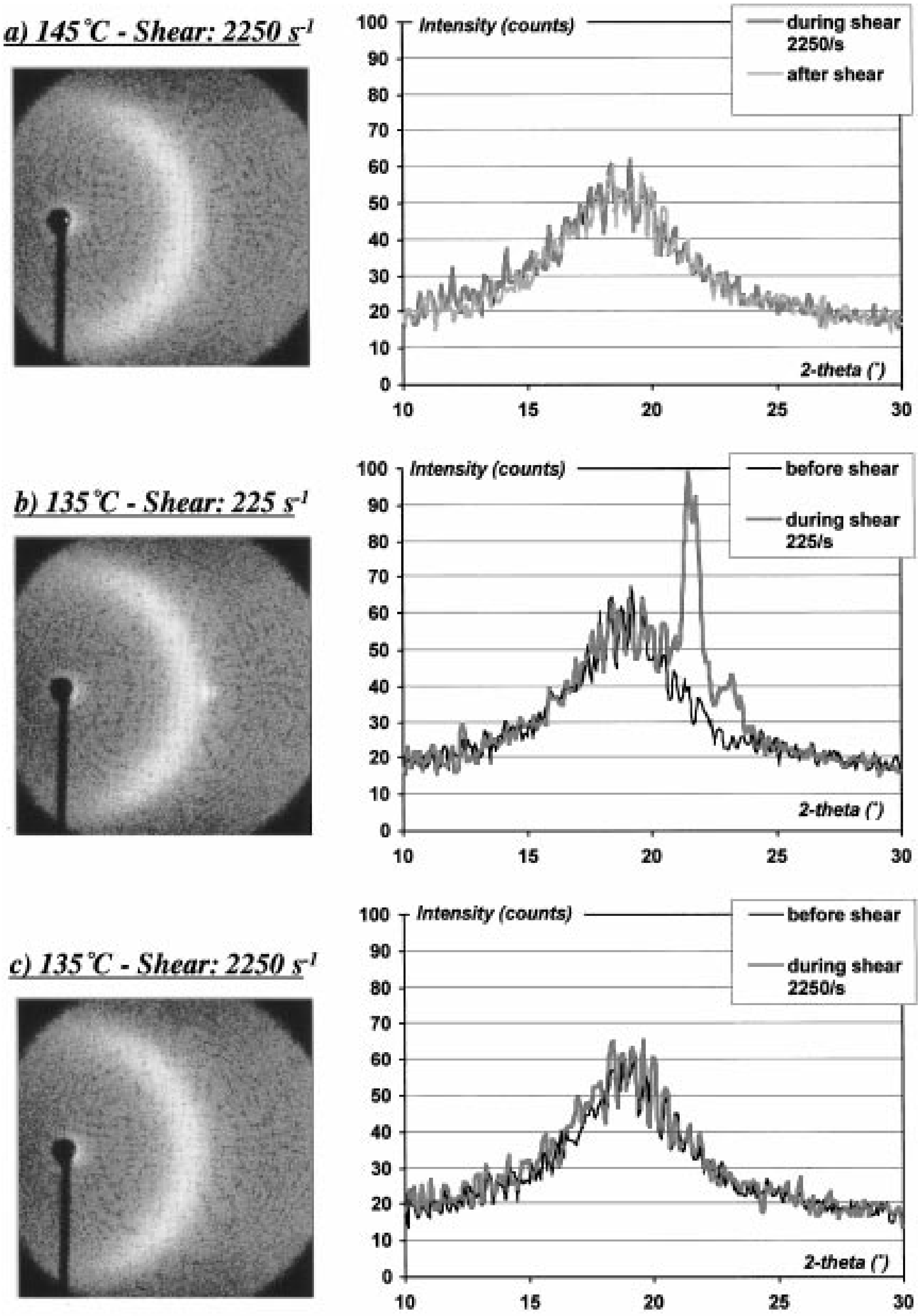

Figure 5 X-ray characterisation of HDPE at 145 °C and 135 °C during flow (capillary $D = 2$ mm $L = 10$ mm, apparent wall shear rate = 225/s and 2250/s).

delay time between each direction of piston movement. The Newtonian apparent wall shear rate for this data set was 2 250 s^{-1} and although this shear rate is moderately high there is no evidence from the X-ray data to indicate significant orientation. In addition both “at rest” and “during flow” data sets appear equivalent and consistent with an isotropic and essentially unorientated polymer melt.

Fig. 5b shows a corresponding set of data obtained after cooling to a temperature of $T = 135$ °C for an apparent wall shear rate of 225 s^{-1}. Initially the X-ray data indicated an isotropic polymer melt; however, during shear, oriented crystalline peaks appeared. On the cessation of flow these crystalline peaks were observed to remain stable for a period of at least thirty minutes.

These observations are entirely consistent with the rheo-optic observations of fibres forming at the wall during flow at this temperature. The X-ray results unambiguously identify the optical fibres as highly oriented crystalline polyethylene.

A further series of X-ray experiments were carried out at $T = 135\,^{\circ}\mathrm{C}$ but at a higher wall shear rate than previously. The polymer was remelted at $T = 150\,^{\circ}\mathrm{C}$ and then cooled to 135 °C. In this way the polyethylene started as an isotropic melt. The X-ray pattern shown in Fig. 5c was obtained "during shear" for a wall shear rate of 2 250 s^{-1} and showed no oriented crystallisation and the X-ray pattern was left essentially unchanged. The experiment was repeated a number of times and we conclude that at $T = 135\,^{\circ}\mathrm{C}$ the onset of fibrous crystallisation occurs at an apparent wall shear rate of 225 s^{-1} but not at a higher shear rate of 2 250 s^{-1}.

3. Interpretation of experimental results

Our X-ray data show that at $T = 145\,^{\circ}\mathrm{C}$ there is no detectable orientation within the resolution of our detectors. Some level of orientation must be present as flow birefringence is seen; however this orientation is undetectable by conventional X-ray techniques and if quantified would indicate very weak orientation levels.

At the lower temperature of $T = 135\,^{\circ}\mathrm{C}$, optical observations showed clearly that flow induced fibrous crystallisation occurred first at the walls of the slit and not in the bulk or extensional flow region. This unexpected result can however be explained using ideas developed by Brochard and de Gennes [16]. If polymer chains are tethered to a surface, Brochard and de Gennes hypothesised that a coil-stretch transition could occur in a shear flow at the wall. Once this is realised, preferential chain extension can be identified as occurring at the surface, thereby producing a site for flow induced nucleation to occur. A similar earlier idea for surface growth was postulated by Zwijnenburg & Pennings [17] for flow induced crystallisation of polyethylene from a polymer solution. Our moderate shear rate X-ray data therefore support the Brochard and de Gennes idea of a coil stretch transition occurring preferentially at the wall rather than in the extensional flow region of the capillary.

The high shear rate X-ray data, at 135 °C, showed no preferential crystallisation and for a possible explanation we again refer to the work of Brochard and de Gennes, together with related "slippage" experiments of Yang *et al.* [18, 19], and our own rheological data. Fig. 6 shows the steady shear flow curve of the polyethylene tested using the MPR as a capillary rheometer. The data are plotted in a similar fashion to those of Wang [18] with the apparent viscosity plotted as a function of wall shear stress. The data show a small low shear stress Newtonian plateau viscous region, followed by an intermediate stress, power law region. Finally the viscosity curve appears, at high shear stress, to asymptote to a limiting shear stress. This final region of the flow curve has been identified as a regime of wall slippage by Wang *et al.* [18]. Our 225 s^{-1} wall shear rate data correspond to a shear stress of 2.5 10^5 Pa which is within the Power law region of the flow curve. The 2 225 s^{-1} shear rate data correspond to a wall shear stress of 4 10^5 Pa where, according to Wang *et al.* [19], significant wall slipppage is believed to occur. It is also our belief that in our own high shear rate X-ray experiments wall slippage is also occurring. When wall slippage is occurring, the chains are no longer tethered to the surface, and consequently the coil stretch transition cannot occur at the walls and preferential flow induced fibrous crystallisation does not happen.

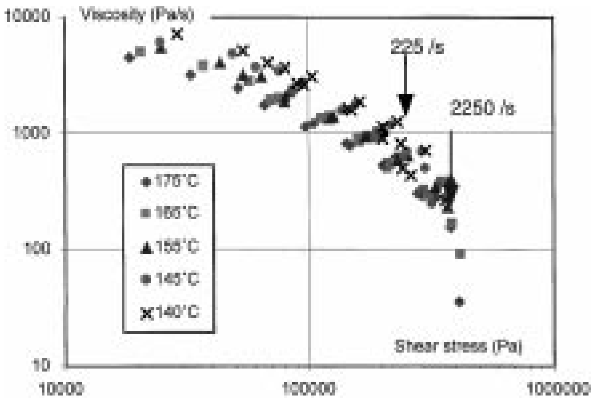

Figure 6 Apparent viscosity vs. shear stress for HDPE as a function of the melt temperature (after Bagley and Rabinowitsch corrections).

We therefore conjecture from our experimental findings that tethered chains, when subject to modest flow at a solid/melt interface, can undergo a coil stretch transition and thus nucleate fibrous crystallisation. If however significant slip exists, the coil stretch transition does not occur and enhanced fibrous crystallisation also does not happen.

In previous work on chain extension of polymer chains in extensional flows it has been recognised that not only does the coil stretch transition condition of $\dot{\gamma}\lambda \geq 1$ have to be satisfied, but also there must have been adequate strain to highly stretch the chains, (Crowley *et al.* [20] Carrington & Odell [21]). This is equivalent to stating that the chain must exist in a flow field for an adequate length of time. The entrance region of a contraction flow is extensional and the condition of $\dot{\gamma}\lambda \geq 1$ would have been satisfied for at least some of the longer chains in the molecular mass distribution for the experimental flow conditions described in this paper. The applied extensional strain in the contraction flow is however modest when compared with that required for full chain extension, because the chains spend a relatively short time passing through the contraction region of the flow. Chains tethered to a wall, however, spend a much longer time in the flowing stream and therefore have time to become significantly extended provided the appropriate coil stretch condition is $\dot{\gamma}\lambda \geq 1$ obeyed. It is therefore quite plausible that this "residence time requirement" is an important factor that has led to preferential fibrous nucleation at the wall rather than in the extensional contraction flow region.

4. Conclusion

It appears from the experiments we have described, that the onset of flow induced fibrous crystallisation provides a potentially very sensitive way of probing an essentially molecular event; namely the coil stretch transition of polymer chains, and as such the technique can usefully be used to explore aspects of chain extension itself. We have discovered that certain near wall conditions have been found to be more favourable than entry extensional flows for causing the nucleation of fibrous crystallisation. Our experimental findings relating to the polymer coil stretch behaviour and slip at the wall have also been shown to be generally consistent with the theoretical predictions of Brochard and de Gennes [16]. These results may have significance in relation to understanding and modelling the flow and processing behaviour of polymer melts.

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