

## ***In-situ* time-resolving wide-angle X-ray scattering study of crystallization from sheared polyethylene melts**

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The effect of simple shear flow on molten polyethylene is studied using *in situ* time-resolving wide-angle X-ray scattering procedures. A small degree of global molecular orientation is observed under shear flow which is linearly related to the logarithm of the shear rate. The system rapidly relaxes to an isotropic state upon cessation of shear flow. A sharp temperature drop coupled with the cessation of shear flow leads to the development of crystallinity, and it is found that the shear flow prior to crystallization has a strong effect on the degree of orientation in the recrystallized state. In fact, above a critical prior shear rate, the recrystallized state changes from globally isotropic to globally anisotropic. Copyright © 1996 Elsevier Science Ltd.

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### *Introduction*

It is well known that the introduction of anisotropy into a polymer melt can lead, on cooling, to the development of a high degree of global alignment of the crystals that form. Surprisingly, little is known quantitatively about this process. Blundell *et al.* have noted the development of an oriented crystalline state developing above  $T_g$  from amorphous poly(aryl ether ether ketone) (PEEK) samples which have been previously stretched at ambient temperature, although, again, quantitative measures of the degree of global orientation realized are not given<sup>1</sup>.

In particular, few studies have been performed *in situ* to enable the complex time and temperature dependent processes of chain alignment, relaxation and crystallization to be followed continuously. As part of a larger programme, we have set out to develop the experimental tools to enable such studies<sup>2-4</sup>. We have selected wide-angle X-ray scattering (WAXS) as the probe since this provides unambiguous values of orientation and crystallinity in addition to more general structural information. It is self-evident that X-ray scattering offers particular advantages for optically opaque or translucent samples in comparison with optical probes. The ability to probe the structure of a flowing polyethylene (PE) melt *in situ* allows the structure of the polymer to be investigated in the conditions in which it is commonly processed.

This paper presents quantitative assessment of the development of the global molecular order parameter  $\langle P_2 \rangle$  in the melt under various shear rates and the subsequent relaxation of orientation upon removal of the shear field. In addition, we shall follow the complete path of shear flow, temperature jump and crystallization, to

show that there is a critical shear rate which must be exceeded in order to develop macroscopic alignment of the semi-crystalline structure which forms.

### *Experimental*

We have utilized a similar X-ray scattering system to that employed previously<sup>2-4</sup>, apart from the rheometer to generate the shear flow field which has been produced by Linkam<sup>5</sup>. The rheometer is a parallel plate system in which the sample is contained between two steel plates, each of which is in close thermal contact with a silver block heater. An aperture in the fixed plate and a series of slots in the rotating plate, which are covered with 25  $\mu\text{m}$  Kapton windows, allow transmission of the X-ray beam for a rotation range of  $\sim 340$  degrees. The gap between the plates is controlled by four micrometer screws, and was set at  $\sim 100 \mu\text{m}$  for these experiments. The available temperature range of the rheometer is between ambient and 400°C, with available shear rates ranging between 0.05 s<sup>-1</sup> and 100 s<sup>-1</sup> without wall slippage against the polymer.

We have utilized two sources of X-rays. For the steady-state measurements we have used X-radiation generated in the laboratory using a Philips sealed tube with a copper anode target, mounted on a Hiltonbrooks DG2 X-ray generator operating at 1.6 kW driving a 40 mA current. A Huber plane model 151 graphite crystal monochromator and pinhole collimation are employed to produce a beam ( $\lambda = 1.542 \text{ \AA}$ ) of  $\sim 1 \text{ mm}$  diameter. The time-resolving measurements presented here were performed on beam-line 16.1 at the Synchrotron Radiation Source at Daresbury (Cheshire, UK), using a beam ( $\lambda = 1.488 \text{ \AA}$ ) of  $\sim 0.4 \text{ mm}$  diameter.

X-ray scattering data were collected using the Area X-ray Imaging System (AXIS) developed at the University of Reading<sup>6,7</sup>. The principal component of the detection

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system is a 50 mm diameter area X-ray camera based on an intensified CCD architecture, designed and manufactured by Photonic Science. The video signal is passed to a frame grabber, where incoming frames are co-added to provide a more intense image with reduced statistical fluctuations. The frame grabbing device employed is a DT2867 integrated image processor manufactured by Data Translation, which is mounted inside the control PC of the AXIS system. Integration times for the diffraction patterns were 4 min for the laboratory source and 10 s at the synchrotron source. The AXIS system is highly automated and the user can program complete sequences of events to provide X-ray scattering data synchronized with changes to the sample environment<sup>6-7</sup>.

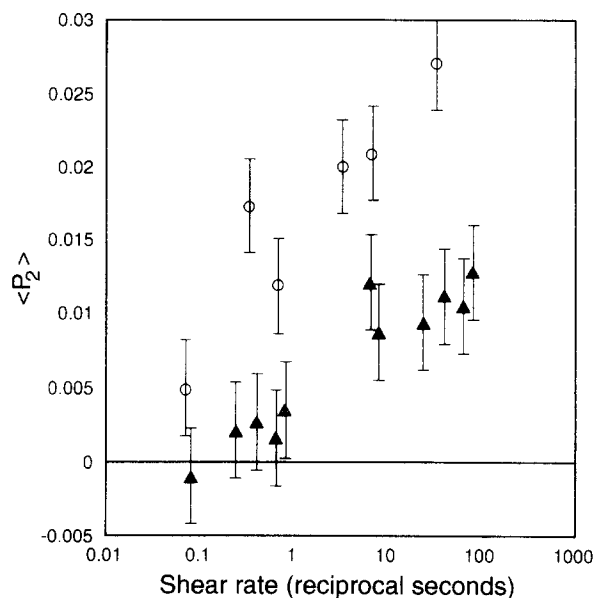
### Results and discussion

**X-ray scattering analysis.** WAXS procedures probe the polyethylene structure on a scale of 1–100 Å, revealing information about the local chain conformation, the nature of the packing and the orientation distribution of molecular segments<sup>8</sup>. The degree of segmental orientation within a polymer melt is of particular interest in this study. The area of the sample exposed by the incident beam is large in relation to such molecular units ( $\sim 1 \text{ mm}^2$ ), and therefore the orientation data obtained from the diffraction patterns are in the form of global averages. This anisotropy is described for a uniaxial system by means of a distribution function  $D_{(\alpha)}$  which denotes the probability of finding a structural unit, in this case a segment of the polymer chain or a crystal plane, at an angle  $\alpha$  to a prescribed axis, in this work the shear flow axis. It is common practice to describe the orientation distribution function through the coefficients of its spherical harmonic components  $\langle P_{2n(\cos \alpha)} \rangle$ , of which only even-order coefficients are non-zero for a uniaxial system. These coefficients may be extracted directly from the X-ray scattering, using the azimuthal distribution of the intensity function as a fixed value of the magnitude of the scattering vector and a model for the scattering of a perfectly aligned system<sup>9,10</sup>:

$$\langle P_2 \rangle = \frac{\langle P_2 \rangle_1}{\langle P_2 \rangle^m} \quad (1)$$

where  $\langle P_2 \rangle_1$  is the normalized coefficient calculated from the observed X-ray scattering and  $P_2^m$  is the coefficient calculated from the model. In situations where the scattering is most intense in a direction normal to the structural axis,  $P_2^m = -0.5$ . For other systems these coefficients may be calculated in a straightforward manner<sup>9,10</sup>.

The dynamics of a linear polymer melt under applied deformation are approached by the reptation model<sup>11-13</sup>, which has been refined through the consideration of tube renewal<sup>14,15</sup> and time dependent diffusion<sup>16,17</sup>. By the use of such theories, the degrees of orientation anticipated in sheared PE melts are expected to be very small:  $10^{-5} \leq \langle P_2 \rangle \leq 10^{-2}$ <sup>18,19</sup>, and are expected to arise from the orientation of the longest molecules within the molecular weight fraction. These molecules are highly extended and thus, upon recrystallization, bear the majority of the stress field and act as crystallization nuclei<sup>20</sup>. The shorter molecules are therefore permitted to relax considerably, and crystallize in overgrowth lamellae perpendicular to the extended core, yielding a shish kebab structure<sup>21-23</sup>.



**Figure 1** Shear-induced global molecular orientation parameters  $\langle P_2 \rangle$  in molten polyethylene obtained in steady-state simple shear for a number of shear rates at 170°C (▲) and 200°C (○)

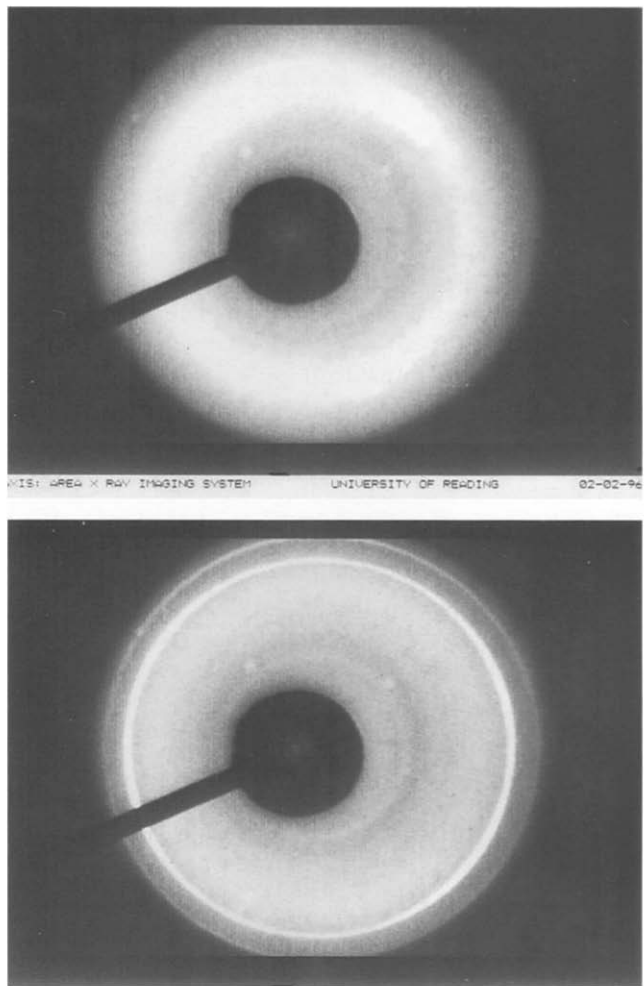
**Shear-induced molecular orientation and relaxation.** A 100  $\mu\text{m}$  thick disc of a linear polyethylene ( $M_n = 19\,600$ ,  $M_w = 325\,000$ ) was heated in the rheometer to 170°C, during which time the principal crystalline diffraction rings of the (110) and (200) planes were seen to evolve into a single amorphous halo at  $|s| \simeq 1.3 \text{ \AA}^{-1}$ . Upon application of shear, a small degree of orientation in the amorphous halo was seen to be induced (Figure 1), which increases with increasing shear rate and whose axis is concomitant with the direction of shear. For each shear rate studied, a steady-state level of orientation was reached within a single data collection cycle of 10 s. It is noted that the degree of orientation is not observed to reach a limiting value in the range of shear rates investigated, as was observed, for example, in the case of liquid crystal phases<sup>2,4</sup>. Higher strain rates are not accessible from this rheometer: careful study indicates that wall slippage at the interface predominates at shear rates above  $100 \text{ s}^{-1}$ . The magnitude of orientation observed is in good agreement with the expectations outlined above.

At the higher temperature of 200°C a greater degree of orientation was observed for the same shear rates (Figure 1). This temperature was chosen as it mimics the commonly applied industrial processing temperature for this polymer. Increasing the temperature still further to 230°C did not yield higher  $\langle P_2 \rangle$  values.

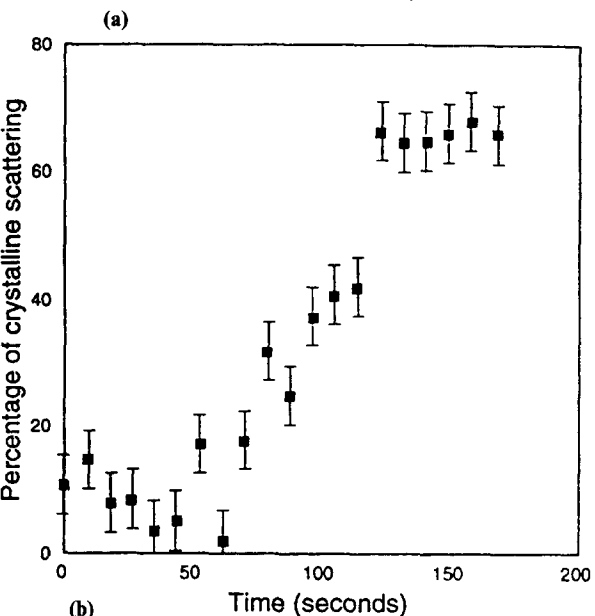
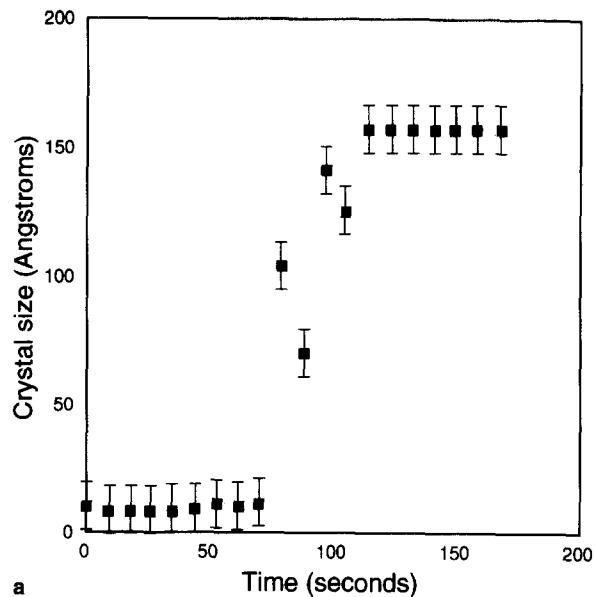
Upon cessation of the shear flow, the oriented structure was noted to relax rapidly to an isotropic state, within the 10 s time resolution used in these experiments. For the highest shear rate,  $80 \text{ s}^{-1}$ , there was evidence to suggest that the structure relaxed to a system which retained some level of orientation even after 500 s.

**Crystallization.** We performed a number of experiments in which the sample was subjected to a

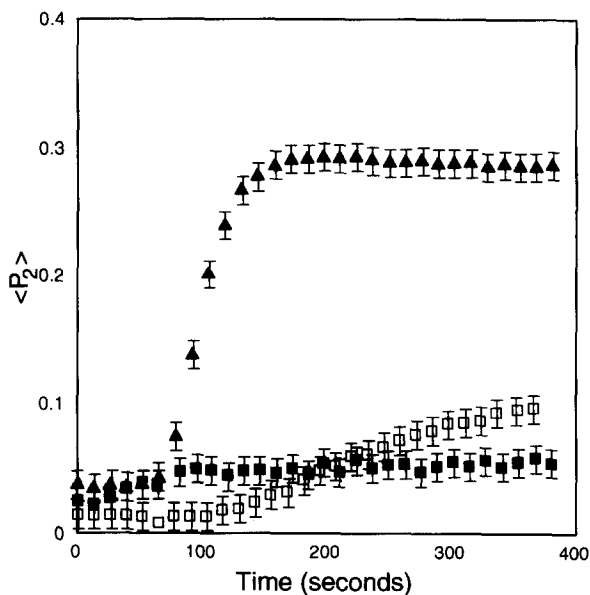
\*  $|s| = (4\pi \sin \Theta) / \lambda$ , where  $2\Theta$  is the scattering angle and  $\lambda$  denotes the incident beam wavelength



**Figure 2** Above: WAXS pattern of a 100 μm thick polyethylene sample at 170°C in simple shear at 8 s<sup>-1</sup>. Below: Crystallized at 120°C; the highlighted ring corresponds to diffraction from the (110) crystal plane



**Figure 4** (a) A plot of crystal size and (b) level of crystallinity which parallels the orientation data shown in *Figure 2* for a prior shear rate of 8 s<sup>-1</sup>



**Figure 3** A plot of the anisotropy (see text) which develops as a function of time following the cessation of shear flow and coincident temperature drop from 170°C to 120°C ( $t = 0$ ). Data are shown for three prior shear rates: 0.08 s<sup>-1</sup> (■), 0.8 s<sup>-1</sup> (□) and 8 s<sup>-1</sup> (▲)

series of shear flow rates at 170°C for 60 s. Each of these samples was then crystallized. In order to induce crystallization, the temperature of the sample stage was changed rapidly ( $dT/dt \sim 20^\circ\text{C min}^{-1}$ ) to 120°C at the same time as the shearing was halted. From the X-ray scattering patterns we were able to monitor, in real time, the global orientation, the level of crystallinity and the size of the crystals formed, in each case using the (110) crystal reflection.

An example of the 2D WAXS pattern from the sheared PE melt and subsequently crystallized state is given in *Figure 2*. *Figure 3* depicts the degree of orientation which was realized in a sample sheared at 170°C when it was recrystallized at 120°C. The orientation parameters shown in *Figure 3* relate to both the crystalline and the non-crystalline components. By separating the contributions from the amorphous and the crystalline components of the scattering pattern for the most anisotropic sample, it is calculated

that the crystalline units are oriented to a degree of  $\langle P_2 \rangle = 0.56$ , and the amorphous units much less so:  $\langle P_2 \rangle = 0.04$ . These time-resolving data were collected at the synchrotron source and indicate some important features.

Firstly, it is apparent that considerably higher degrees of orientation are achievable in the recrystallized state than can be induced in the melt. Global molecular order parameter values of  $\langle P_2 \rangle \approx 0.3$  are seen in Figures 2 and 3 for the recrystallized sheared polymer after an applied shear rate which yielded an order parameter of only  $\langle P_2 \rangle \approx 0.005$  in the molten state.

It is important to remember that in this system, as indicated by the experimental data, the global level of orientation in the melt will be approaching zero by the time crystallization occurs, as the flow field has stopped.

Secondly, it is clear that these higher levels of orientation are only reached when the previous shear rate is greater than some critical value, i.e.  $\sim 1 \text{ s}^{-1}$ . We performed a number of experiments to determine the extent to which the total shear strain, rather than the shear rate, was important and there was no significant contribution. The differences between the high level of anisotropy and the low level of anisotropy of the crystalline morphologies arise directly from the different prior shear rates.

These results are in line with expectation of the formation of shish kebab structures. We can rationalize the formation of high levels of crystalline orientation from a melt with effectively zero orientation, by the fact that only a few aligned molecules are necessary to nucleate an anisotropic system. The shear deformation aligns to a high degree the longest molecules in the molecular weight fraction (whilst the overall measure of melt orientation remains small by reason of the polydispersity of the system). Upon cessation of shear flow the majority of the aligned molecules relax; nevertheless, a suitable number remain to act as row structure crystallization nuclei. The anticipated morphology of the final state is therefore proposed to be a shish kebab structure, in which the elongated nucleus chain is surrounded by epitaxial overgrowth of smaller crystalline units. This would account for the four (110) spots observed in the crystalline diffraction pattern, which arise from the overgrowth lamellae canted at chevron angles to the linearly extended core. The fact that there is a critical shear rate, between  $0.8 \text{ s}^{-1}$  and  $8 \text{ s}^{-1}$ , over which the sample must be deformed before achieving this relatively high degree of crystalline order is related to the number of aligned nuclei in comparison to nucleation sites which will lead to an isotropic morphology. As the shear rate increases, an increasing fraction of molecules are aligned; unfortunately these will have increasingly shorter lengths and will therefore relax more rapidly when the shear flow is stopped. In short, increasingly higher shear rates become less and less effective. The particular value of the critical shear rate will depend both upon the material constants and upon the precise dynamics imposed on the sample by the sudden change in temperature.

A comparison of the time dependence of the orientation parameter (Figure 3), fraction of crystallinity and crystal size (Figure 4) indicates that the orientation develops most rapidly. In other words, the later stages of

crystallization do not involve higher levels of orientation as would be expected for a shish kebab morphology. Similar comments may be made with respect to the crystal size.

### Conclusions

The use of the *in situ* X-ray scattering procedures has been successful in enabling us to continuously monitor the development of macroscopic orientation with the imposition of shear flow and the subsequent crystallization processes. Despite the very small degrees of orientation developed in linear PE melts ( $P_2 \approx 0.005$ ), we have been able to measure these reliably and they are found to increase with increasing strain rate and to be of the order predicted by theoretical expectation. The steady-state level of orientation is observed to increase with increasing melt temperature to a limiting value of  $200^\circ\text{C}$ . Relaxation of the induced order is also found to take place on a time-scale of  $< 10 \text{ s}$ .

Higher degrees of orientational order ( $P_2 \approx 0.6$ ) are observed in the recrystallized state subsequent to shear, which is characterized by a four-spot diffraction pattern. It is believed that these patterns are related to shish kebab morphologies, where the elongated nucleus chain of high molecular weight is surrounded by epitaxial overgrowth of smaller crystalline units. We find that a critical shear rate of the order of  $1 \text{ s}^{-1}$  in the melt is required to instigate the development of a globally anisotropic crystalline structure following the cessation of shear flow.

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### References

- Blundell, D. J., Mahendrasingam, A., McKerron, D., Turner, A., Rule, R., Oldman, R. J. and Fuller, W. *Polymer* 1994, **35**, 3875
- Keates, P., Mitchell, G. R., Peuvrel-Disdier, E. and Navard, P. *Polym. Commun.* 1993, **34**, 1316
- Keates, P., Mitchell, G. R., Peuvrel-Disdier, E., Riti, J. B. and Navard, P. *J. Non-Newt. Fl. Mech.* 1994, **52**, 197
- Keates, P., Mitchell, G. R., Peuvrel-Disdier, E. and Navard, P. *Polymer* 1996, **37**, 443
- Chai, C. K., Dixon, N. M., Gerrard, D. L. and Reed, W. *Polymer* 1995, **36**, 661
- Pople, J. A., Mitchell, G. R. and Chai, C. K. *Adv. X-ray Anal.* 1995, **38**, 531
- Keates, P., Pople, J. A. and Mitchell, G. R. *Int. J. Polym. Anal. Char.* submitted
- Mitchell, G. R. in 'Comprehensive Polymer Science' (Eds. G. Allen and J. Bevington), Vol. 1, Pergamon, Oxford, 1989, Ch. 31
- Lovell, R. and Mitchell, G. R. *Acta Cryst.* 1981, **A37**, 135
- Pople, J. A., Mitchell, G. R. and Chai, C. K. 1996 (in preparation)
- Edwards, S. F. *J. Phys. A: Gen. Phys.* 1968, **1**, 15
- de Gennes, P. G. *J. Chem. Phys.* 1971, **55**, 572
- Doi, M. and Edwards, S. F. *J. Chem. Soc. Faraday Trans. 2* 1978, **74**, 1789
- Klein, J. *Macromolecules* 1978, **11**, 852
- Graessley, W. W. *Adv. Polym. Sci.* 1982, **47**, 67
- des Cloizeaux, J. *Macromolecules* 1990, **23**, 4678
- O'Connor, N. P. T. and Ball, R. C. *Macromolecules* 1992, **25**, 5677
- Bird, R. B., Armstrong, R. C. and Hassager, O. 'Dynamics of

- Polymeric Liquids', Vol. 1, Wiley-Interscience, New York, 1987
- 19 Nakatani, A. I., Poliks, M. D. and Samulski, E. T. *Macromolecules* 1990, **23**, 2686
- 20 Peterlin, A. in 'Flow-Induced Crystallization in Polymer Systems', Midland Macromolecular Monographs (Ed. R. L. Miller), Gordon and Breach Science Publishers, New York, 1979, Vol. 6, Ch. 1
- 21 Keller, A. and Machin, M. J. *J. Macromol. Sci. Phys. Ed. (B)* 1967, **1**, 41
- 22 Hay, I. L. and Keller, A. *J. Mater. Sci.* 1967, **2**, 538
- 23 Peterlin, A. *Pure Appl. Chem.: Macromol. Chem.* 1973, **8**, 277