Shear-induced crystallization in a liquid crystalline random copolyester

T. M. Nicholson, M. R. Mackley and A. H. Windle*

Department of Chemical Engineering and Department of Materials Science and Metallurgy, University of Cambridge, Pembroke Street, Cambridge, UK

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X-ray observations have been made during high temperature shear of a liquid crystalline copolyester. Whilst being sheared above the polymer melting point, a sharp crystallite diffraction peak develops. This peak grows in intensity as the shear rate increases and disappears on cessation of shear. It is associated with the shear stabilization of crystallites, presumably of the non-periodic-layer type.

(Keywords: liquid crystal polymer; shear; crystallization; X-ray diffraction)

Introduction

Para linked aromatic random copolyesters based on hydroxybenzoic acid (HBA) and hydroxynaphthoic acid (HNA) form liquid crystalline melts. The random nature of the copolymer reduces the crystallite melting point to ~300°C compared with a value of the order of 450°C for the homopolymer[1,2]. The level of crystallinity is also reduced to ~20%[3]. The mechanism of crystallization of random copolymers based on units of different lengths has already been addressed elsewhere[3,4]; and there is now evidence that the crystallites are platelet entities oriented normal to the polymer chain axis.

Thermotropic liquid crystal polymer melts exhibit a similar macroscopic rheology to conventional melts[5], although they orient much more readily in shear and extensional flows[6–8], and exhibit anomalous rheological behaviour in the temperature range immediately above the melting point[9,10].

This communication reports the development of crystallites during shear flow of these liquid crystalline polymers, and is part of an ongoing programme to investigate the high temperature shear behaviour of such materials.

Experimental

A high temperature micro shear cell has been developed to enable the shear of liquid crystal polymer samples to be performed under controlled temperature and deformation conditions. The sample, a 29 mm disc of hot-pressed polymer, 1 mm thick, is held between two parallel discs of mica and sheared by rotating one of these discs with respect to the other. Observations are made through a circular port towards the circumference of the discs, where the shear is closely linear. Foil heaters are employed to keep the polymer at a uniform temperature, and a microcomputer-controlled stepper motor used to generate accurately known shear rates.

Using the high intensity of the synchrotron radiation source at the SERC Daresbury Laboratory, X-ray diffraction patterns from shearing polymer samples may be collected in a matter of minutes using an area detector. The data are processed to take into account the absorption of X-rays by air and the mica windows, the changes in the intensity of the X-ray source between experiments and the variation in response of the detector. A slice through the equatorial reflection is taken to produce a plot of intensity against diffraction angle (2θ). This is then deconvoluted to remove the effect of the finite depth of the area detector.

Results and discussion

Figure 1 shows a series of diffraction curves obtained as described above for a single polymer sample of HBA–HNA (73:27%) at a temperature of 320°C, ~20°C above the polymer's melting point. The first curve (A) was taken after the sample had been brought up to temperature but before it had been sheared. The next two curves (B and C) illustrate increasing shear rates. Finally a further curve (D), measured with the polymer at rest ~2 min after cessation of rapid shear, is included.

By way of comparison, *Figure 2* illustrates powder diffraction curves measured from the same polymer (in the quiescent state) on a Siemens D500 θ–θ reflection diffractometer using a Braun position-sensitive detector. Curve A was taken at room temperature, and shows a broad crystal diffraction peak at a diffraction angle of

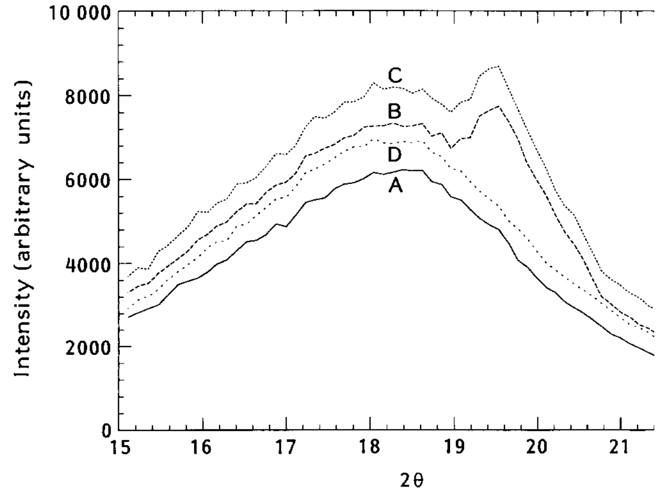

Figure 1 Diffraction data for a sample of HBA–HNA at 320°C, obtained in the shear cell; (A) polymer at rest; (B) shear rate 2 s^{-1}; (C) shear rate 20 s^{-1}; (D) polymer at rest 2 min after cessation of shear

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* To whom correspondence should be addressed

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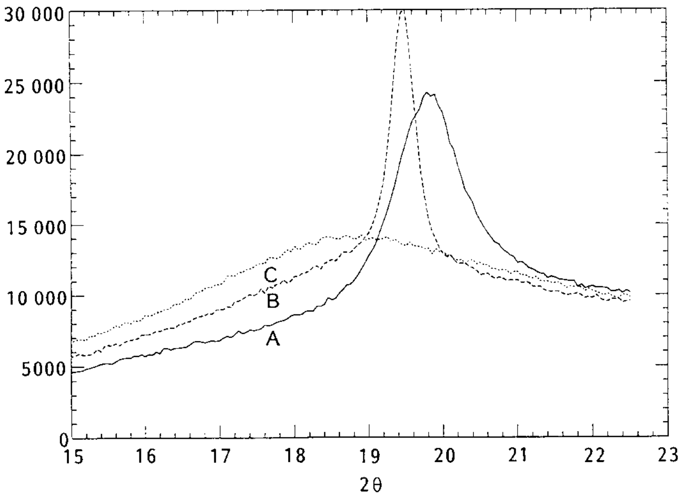

Figure 2 Equivalent scan of a non-sheared sample of the same polymer at: (A) room temperature; (B) 243°C; (C) molten at 316°C

20°. As the polymer is heated (curve B, 243°C), the crystal peak becomes sharper and, because of thermal expansion, moves to a lower angle of 19.5°. When the polymer melts (curve C, 316°C), the crystallite peak disappears and only the broad liquid crystalline diffraction halo remains.

The stationary molten liquid crystalline polymer diffraction pattern (*Figure 1A*) consists of a strong diffuse maximum consistent with that obtained by powder diffraction, as is to be expected. However, as the sample is sheared (*Figure 1B*), an additional sharp reflection begins to develop at an angle that corresponds to the 2θ angle of the crystalline diffraction when observed just below the melting point. As the shear rate is increased (*Figure 1C*) the diffuse diffraction peak increases in intensity. This may be attributed to a reduction in its azimuthal spread due to further development in the orientation of the molten polymer at the higher shear rate. In contrast the superimposed sharp reflection shows a much lower degree of orientation which changes little at higher shear rates. When shear ceases (*Figure 1D*) the sharp diffraction peak disappears, leaving the orientation of the diffuse pattern to decay more gradually.

The action of the shear thus appears to induce the formation of crystallites in the polymer sample at temperatures above their normal melting point. Their diffraction is broader than that seen for crystallization below the melting point in the absence of shear, which may suggest that the crystallites are not as well formed.

Crystallite formation in these polymers is thought to result from similar sequences of monomer units on adjacent chains lining up, thus forming non-periodic-layer (NPL) crystals. During shear, polymer chains will move with respect to one another and thus favourable sequences for the formation of these NPL crystallites are more likely to be brought into register. It is possible that the crystals are continually forming and melting within the shear field.

The presence of these crystallites at temperatures above the polymer melting point during shear may play an important role in determining the optical and rheological behaviour observed in this region.

Detailed textural analysis as well as more comprehensive studies of the influence of shear rate and temperature on flow-induced crystallization are in progress and will be reported in due course.

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