A Flow-Orientation Transition in a Thermotropic Random Copolyester

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Introduction. This paper reports some preliminary results of a study of flow-induced orientation in a series of liquid crystalline polymers based on hydroxybenzoic acid (HBA) and hydroxynaphthoic acid (HNA) units. Previous, *in situ* studies of orientation in flowing liquid crystalline polymers of this type have shown the development of significant chain orientation in the direction of shear,[1] as well as the tendency for shear-induced crystallinity at temperatures close to the melting point.[2] A recent series of measurements, covering a range of molecular weights, shear temperatures, and strain rates, have shown a striking orientational transition for samples of lower molecular weight at temperatures only slightly above the crystal melting point.

Experimental Section. The polymer which forms the main basis of this report is a random copolymer of composition 75/25 HBA/HNA and molecular weight 8600 supplied by Hoechst Celanese Corp. The molecular weight was stabilized at this value by the addition of a small amount of terephthalic acid at polymerization and measured by viscometry. The crystallinity of this polymer is 20% at room temperature,[3] and the crystal melting point is 275 °C by DSC.

The X-ray measurements of orientation were carried out in a shear cell designed by Mackley and described elsewhere.[2] The cell permits control of temperature to within ±1 °C, while the shear conditions can be programmed. In the experiment described in this paper, the diffraction patterns were recorded on film and subsequently digitized for analysis.

Results. Figure 1 shows diffraction patterns of the shearing melt of the $M_w = 8600$ polymer at two different shear rates at 285 °C: (a) 100 and (b) 5 s^{-1}. While at the higher strain rate the orientation is typical of a flowing thermotropic polymer melt with the chain axes aligning parallel with the shear direction (as shown by the main equatorial reflections lying on the axis normal to the chain axis on the diffraction pattern), at the lower strain rate the chain axes orient orthogonal to the shear axis although they still lie in the shear plane. Subsequent three-dimensional analysis of a sample quenched during shear confirms this orientation.

Figure 2 plots a series of azimuthal intensity scans (around the equatorial circle) for different strain rates at 285 °C. At strain rates of 10 s^{-1} and below, the equatorial reflections concentrate on the shear axis of the diffraction pattern, indicating the orthogonal orientation of the chains to the shear. At the transition strain rate, which is 80 s^{-1} at this temperature, very little preferred orientation can be seen at all, while at higher strain rates it develops again, but now with the chains parallel to the shear axis.

As the temperature is increased, $\dot{\gamma}_c$, the critical strain rate for the orientation transition, decreases. At 295 °C, for example, it has dropped to around 10 s^{-1}. Figure 3 is a plot of $\dot{\gamma}_c$ against the temperature of shear. Above 300 °C it was not possible to obtain transverse orientation, even at the lowest strain rates available.

It is well-known[4-6] that the crystal melting point of this type of polymer can be increased by annealing in the solid state and that this effect is associated with the transition of the pseudohexagonal crystal structure to the more stable orthorhombic form.[3,7] One consequence of the annealing effects is that it was necessary for the sample to be heated at rates of at least 20 °C/min in the cell in order to obtain a shearable "melt" phase.

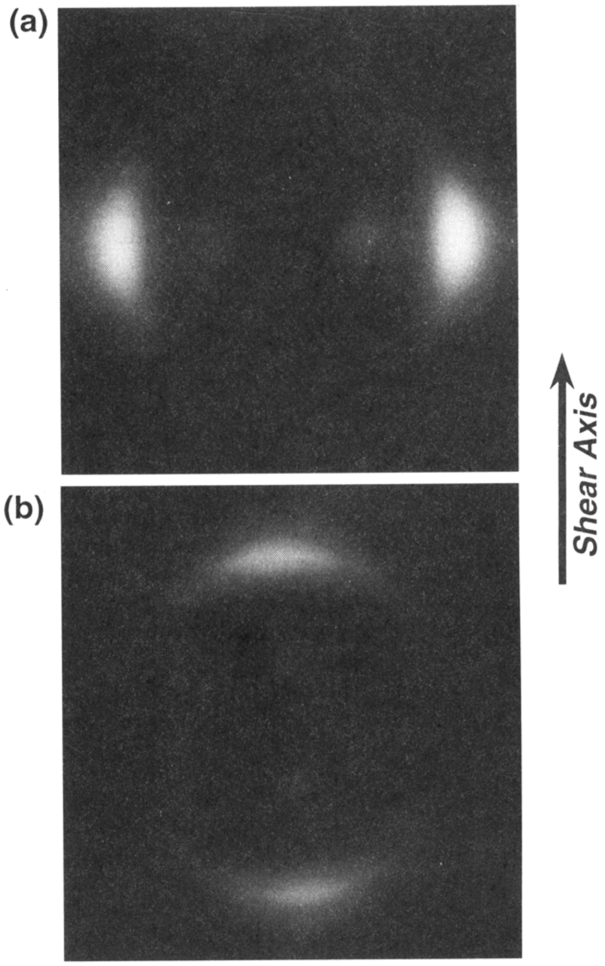

Figure 1. Flat-plate X-ray diffraction patterns of 75/25 copoly-(HBA/HNA), $M_w = 8600$, at 285 °C while shearing at (a) 100 and (b) 5 s^{-1}. Note the concentration of the equatorial reflections at $2\theta = 18.4°$ into arcs which indicate that the chain molecules are orientating parallel and orthogonal to the shear flow, respectively. Ni-filtered Cu Kα radiation was used.

Once in the melt, there were no observable time effects. The orientation obtained under a given set of condtions was unchanged with time under shear up to several hours.

It is important to note that the transverse orientation is only observed relatively close to the crystal melting point which itself is not very clearly defined.

Furthermore, the diffraction patterns which show the transverse orientation, such as Figure 1b, also show evidence of some crystallinity in the form of a superimposed, but narrow (in 2θ), equatorial arc. It is apparent that the alignment of the chains transverse to the shear axis is associated with the presence of a low level of crystallinity, possibly induced by the shear itself.

The orientational phenomena summarized in Figure 3 appear to be largely thermoreversible. A sample sheared at 285 °C under conditions to produce the transverse orientation ($\dot{\gamma}_c = 10$ s^{-1}) was cycled in temperature up to 300 °C and back to 285 °C in the absence of shear, and the shear experiment was repeated. The transverse orientation was again reestablished, although its quality was degraded to some extent. However, after a similar

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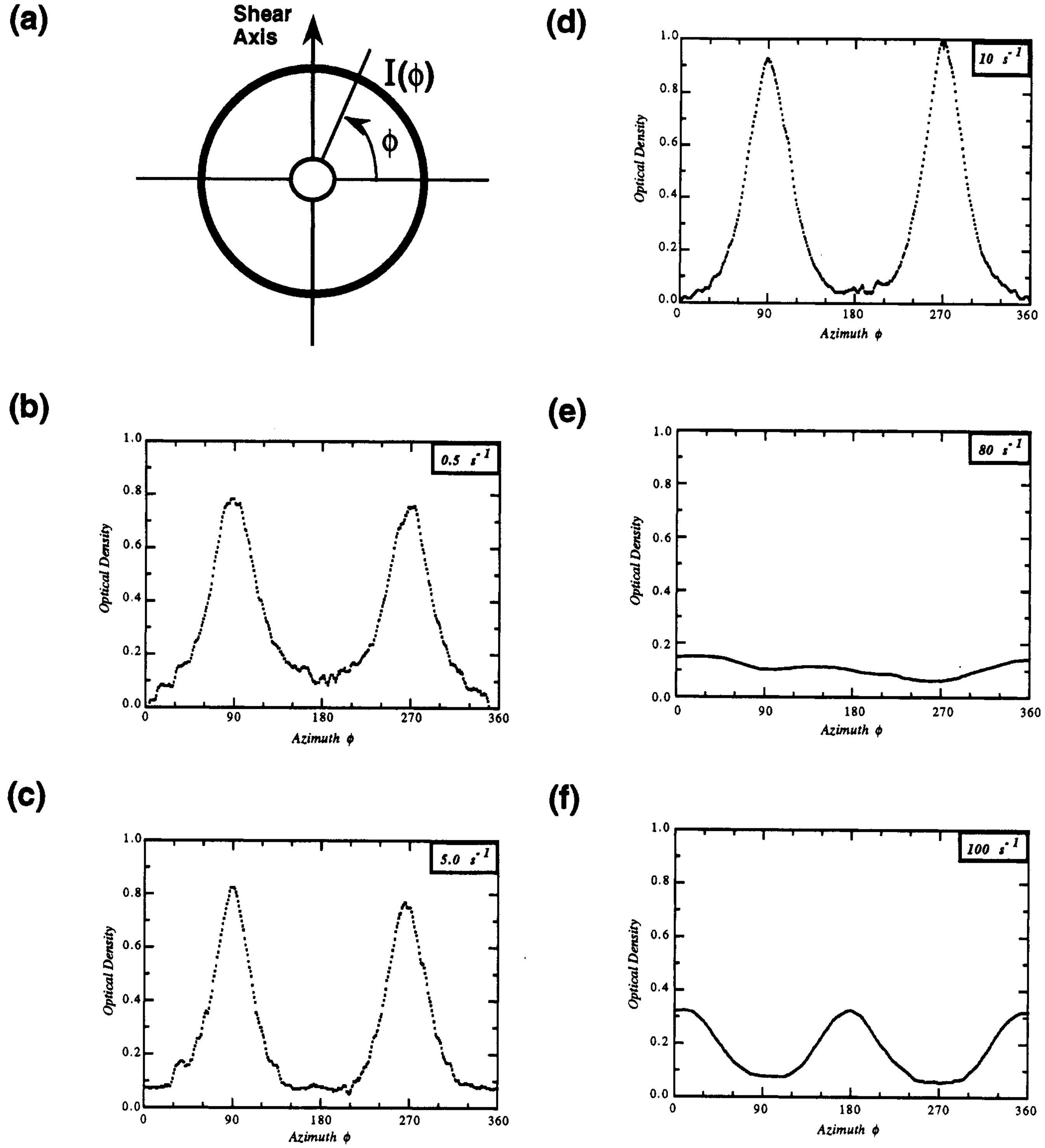

Figure 2. (a) Definition of the azimuthal angle ϕ. (b–f) Normalized azimuthal variation of the 110 intensity reflection of 75/25 copoly(HBA/HNA), M_w = 8600, at 285 °C while shearing at the strain rates indicated on the plots.

cycle to 315 °C the transverse orientation only gradually re-formed at 285 °C.

Discussion. The striking observations require explanation on two levels. First, an explanation for the transverse orientation itself is necessary. While there have been observations of transversely oriented crystal populations in semicrystalline polymers, the bases of their explanations (*a*–*c* epitaxial growth in the case of polypropylene[8] and different modes of attachment into a gel network in the case of PVC[9]) are inappropriate for the case of liquid crystalline melt shear considered here, as the effect is seen for all of the polymer, not just the crystalline component, even if it is present at all. At a deeper level the understanding will have to embrace the complex temperature, molecular weight, and strain rate criteria which are observed.

It appears that the transverse orientation is associated with a low level of crystallinity in the shearing melt (<5%). The crystals do not prevent continuous, stable shear over periods on the order of several hours, and it is possible that they are continually re-forming during the flow. While crystallinity has been seen during shear of the high molecular weight, Vectra-type, material,[2] we have not been able to obtain a transverse orientation regime for molecular weights above 14 000. However, it should be noted that the (axial) orientation of the few percent of crystalline phase in the Vectra polymer was observed to be poor compared with that of the liquid crystalline phase.[2]

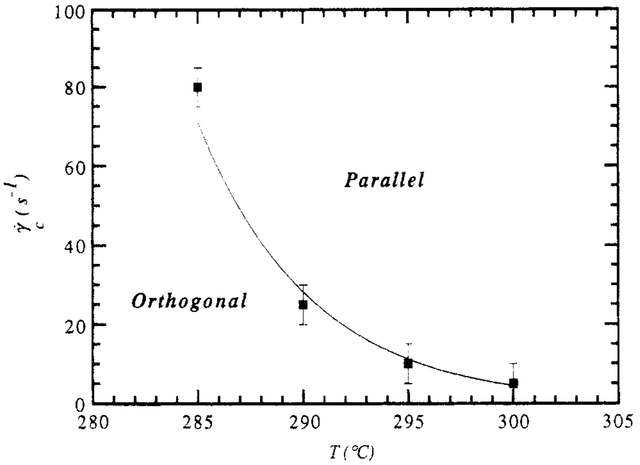

Figure 3. Critical shear rate γ_c as a function of temperature T. This plot defines the temperture–strain rate parameters for stabilization of either orthogonal or parallel orientation. The line corresponds to an exponential fit of the data.

We suggest that the thin platelet crystals themselves are capable of undergoing shear in the melt but that they only shear in a direction normal to their chain axes. Such shear would be compatible with the view that the crystals are associated with the segregation of short, similar sequences in the otherwise random copolymer chains,[10,11] as it would not necessarily lead to the loss of the special longitudinal register intrinsic to their formation. A further indication comes from measurements of the room temperature deformation of highly oriented samples of the high molecular weight polymer.[12] The deformation mode observed in samples compressed at different angles to their orientation axes was compatible with shear normal to, rather than parallel to, the chain axes.

For the low molecular weight material containing some crystallinity, it would follow that the shear of the crystals would be the dominant factor controlling flow and that the easy mode of crystal shear dictates the overall deformation of the chains, which can be viewed as a stack of parallel rods rolling over each other. Such a mechanism will be compromised if there is any entanglement of the otherwise parallel chains, and it would appear that the reason for the absence of transverse orientation in the higher molecular weight material may be the greater probability of "crossovers" in the longer chains. In this context it is interesting to note that Almdal et al.[13] have observed an orientation in a sheared poly(ethylenepropylene)–poly(ethylethylene) (PEP–PEE) diblock copolymer containing 65% by volume PEP in which the layers contain the shear axis but are normal to the shear plane.

The involvement of crystallites in flow processes would be expected to leave its imprint on the rheology of the melt. While measurements on the lower molecular weight material have yet to be made, it is significant to mention the results of Wissbrun et al.[14] on the high molecular weight, Vectra-type polymer. These showed a transition in the activation energy of the flow process and were interpreted in terms of a change in the crystalline structure.

More detailed explanations, and in particular a rational basis for the strain rate transition, await a full characterization of orientation within the molecular weight–temperature–strain rate domain.

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