Macromolecules **1998,** *31,* 7562−7565

A Transient Liquid Crystalline Phase as a Precursor for Crystallization in Random Co-polyester Fibers

G. E. Welsh,[†] D. J. Blundell,[‡] and A. H. Windle*,[†]

Department of Materials Science and Metallurgy, University of Cambridge, Pembroke Street, Cambridge CB2 3QZ, U.K., and Wilton Materials Research Centre, ICI, PO Box 90, Wilton, Middlesbrough, Cleveland TS6 8JE, U.K.

Received April 6, 1998

Introduction. We wish to report an observation made on random copolymers of PET and PEN (polyethylene naphthalene-2,6-dicarboxylate) and present strong evidence for the formation of a transient smectic phase, which appears to be the precursor of strain induced crystallization. The intriguing fact that even 50/50 *random*-copoly(PET/PEN) can crystallize, although only on hot drawing, has recently been reported and discussed.[1,2] The initial observations reported here have been made on specimens rapidly quenched from the drawing melt, and the somewhat slower crystallization rate of the copolymers compared with the homopolymers may have aided the observation. Nevertheless, we have been able to repeat the experiment on both parent homopolymers with a similar result. The work thus serves to support and connect a number of reports in the literature[3−7] which point to some type of mesophase as part of the homopolymer drawing process. This work also points to parallels with structural observations made on thermotropic liquid crystalline co-polyesters of the HBA/HNA type.

50/50 Random Copolymers—A Smectic Phase. Figure 1 shows wide-angle X-ray transmission diffraction patterns of a series of 50/50 random copolymer fibers of PET/PEN drawn under different conditions. Parts a and b of Figure 1 are the patterns for samples drawn to extension ratios of approximately 6 and 10, respectively. Key aspects of these two patterns are the high degree of orientation, the almost complete absence of crystallization as indicated by the breadth of the equatorial peaks (the plots of Figure 1x show radial sections through these, and there is just a hint of the three major crystal peaks in the case of Figure 1b but not of Figure 1a), and the presence of a sharp meridional peak at a position equivalent to 11.5 Å. The meridional maximum (see enlarged region of patterns) indicates register between the chemical repeats of neighboring chains which is exactly orthogonal to the chain axis. The lateral half-width of this peak corresponds to a lateral extent of the correlation in excess of 70 Å. The absence of crystalline order in the interchain packing means that the quenched samples (parts a and b of Figure 1) have order which could well be classified as smectic A. Two caveats are necessary at this point. First, the liquid crystalline phase, as observed, is in the quenched "glassy" form, second the classification is not strictly "smectic" for which the lateral correlation is between the positions of the molecular ends, but a "chained" smectic,[8] where the correlation is between chemical repeat units. For the less rapidly cooled sample, Figure 1c, the crystalline peaks are becoming apparent on top of the equatorial maxima, although the meridional maximum is still clearly apparent. The initial development of nonmeridional peaks on the first layer line can also be detected. The fuller crystallization in the sample obtained on annealing (Figure 1d) causes a very pronounced weakening of the smectic A meridional maximum as its intensity spreads along the layer line and *hkl* type maxima develop on various layer lines. The fact that the random copolymer chains are aperiodic means the layer lines become more diffuse on moving to higher orders, only to sharpen up again at $l = 4$ and above. This effect has been analyzed in more detail for this system in ref 2 and for thermotropic liquid crystalline random co-polyester systems in refs 9 and 10.

We conclude that the achievement of high chain orientation in these 50/50 random copolymer samples is associated with the formation of a smectic A phase in which the chains show a well-developed longitudinal register without being packed on a crystal lattice and that the development of triclinic crystals occurs at the expense of the smectic phase, the orthogonal register being replaced by an oblique one which is nevertheless significantly faulted. The smectic phase was observed at all practicable draw temperatures between T_g and T_m (100 and 135 °C, respectively for the 50/50 composition), at a strain rate of 2 s^{-1}. In the experiment described here, the possibility remains open that the smectic phase is only formed during cooling to T_g rather than during drawing at temperature. However, the cooling rate in such thin fibers is very fast (in excess of 200° s^{-1}) and it is very unlikely that the longitudinal segregation implicit in the nematic−smectic transformation would occur during the quench or over longer periods of time at room temperature in the glassy phase which results. As a final check on this issue, the drawing experiments have been repeated in situ in the synchrotron beam, experiments which involve a wider collaboration and will be reported separately. The initial results demonstrate unequivocally that the smectic phase forms at elevated temperature during the draw.

Effect of Composition. The availability of a range of copolymer compositions has enabled this study to be extended across the full composition range to include the parent homopolymers. Parts a and b of Figure 2 show the diffraction patterns from copolymer samples rich in PET and rich in PEN, respectively, as well as the two parent homopolymers in both quenched (parts c and d of Figure 2) and annealed (parts e and f of Figure 2) states. All six samples have been drawn to a draw ratio of approximately 5 at a temperature a few degrees (<5) above T_g and quenched into iced water. The smectic A meridional maximum is apparent for all compositions across the range, although in the case of the PEN homopolymer and the random copolymer with 16% of PET repeat units, it has not been possible to quench fast enough to prevent some crystallization as detectable in the equatorial maxima and by the sampling of the other layer lines. All of the compositions will crystallize on slower cooling or after subsequent annealing, leading to a loss of the meridional smectic peak. (cf. Figure 1d) below). Figure 3 plots the meridional repeats corresponding to the meridional maxima

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[†] University of Cambridge.

[‡] ICI.

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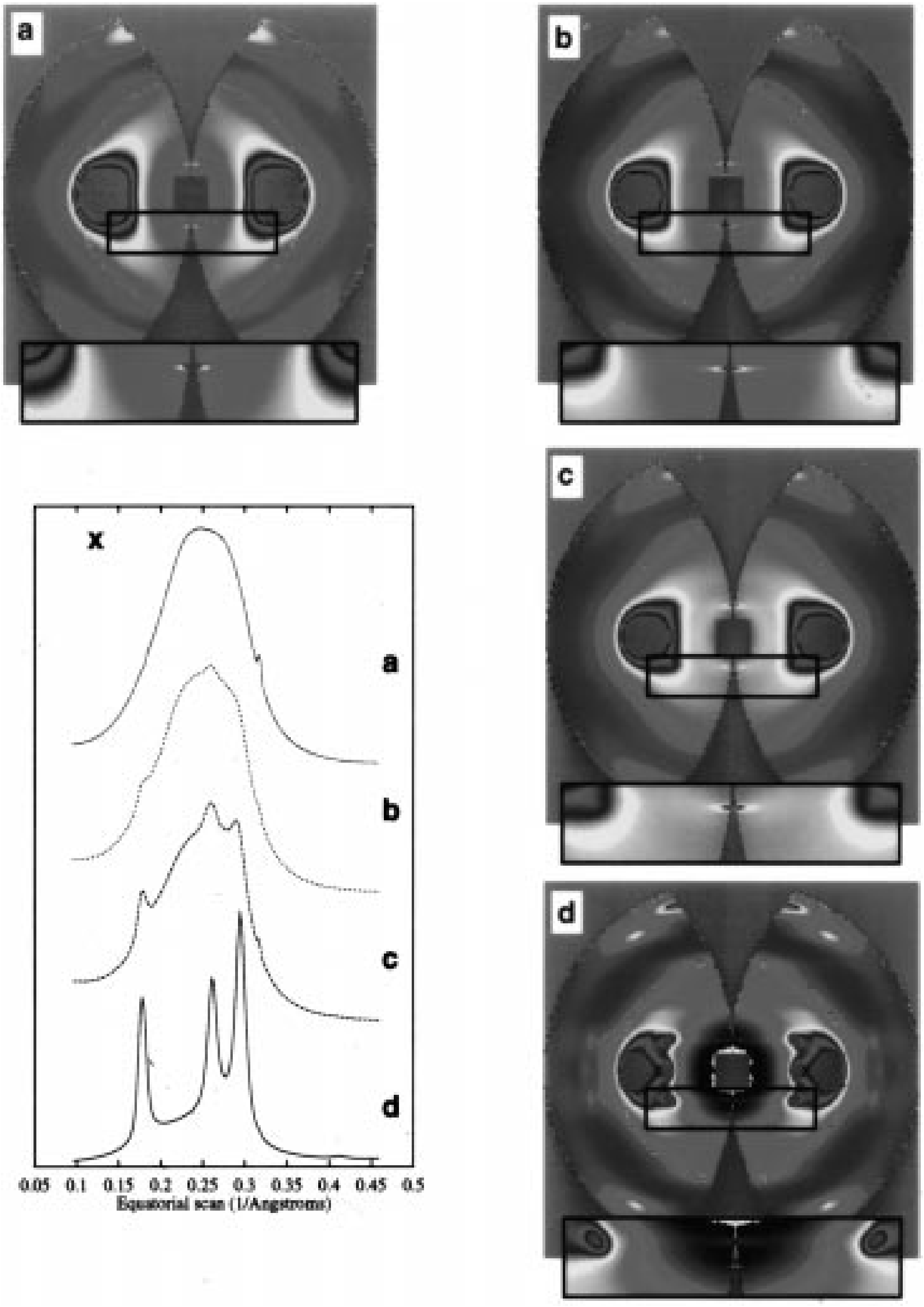

Figure 1. Series of transmission X-ray diffraction patterns from 50/50 PET/PEN fibers, geometrically corrected for distortion due to the curvature of the Ewald sphere, by mapping into reciprocal space.[14] (a) Amorphous monfilaments drawn to a DR of 6 at approximately 2s^{-1} at 100 °C in silicone oil and immediately quenched into iced water. (b) As in part a, except drawn to a DR of 10. (c) As in part b, but cooled in air to room temperature. (d) As in part c, but subsequently annealed at a fixed load for 24 h at 100 °C. Inset x: Radial scans through the equatorial reflections of samples a−d. (Each of the patterns in Figures 1 and 2 was obtained from a bundle of parallel fibers using the Daresbury SRS synchrotron source (beam line 7.2) with a Mar image plate. In all cases the fiber axis was vertical. The fibers were dusted with Si powder to give calibration rings on the diffraction patterns. Analysis of the patterns and mapping into reciprocal space was carried out using the CCP13 software suite (Denny, R. C. http://wserv1.dl.ac.uk/SRS/CCP13). The patterns shown all extend to 0.52 Å^{-1}and a color scale is used to contour the intensity. The blank area around the meridian is an inaccessible region of reciprocal space due to the curvature of the Ewald sphere.)

in the smectic phase and the position of the first layer line in the crystallized cases as a function of composition including five compositions additional to those shown in Figures 1 and 2. A significant point to be drawn from Figure 3 is that the chain “repeat” increases on crystallization of the smectic, especially for samples toward the compositional limits. In the case of the smectic phase of the PET homopolymer, the extension on crystallization is about 4% in general agreement with the data of ref 5, and the greater extension of some 6% for PEN is in good agreement with the data of ref 6. The extension for the 50/50 copolymer sample is rather smaller, on the order of 3%. The pattern from the annealed PET homopolymer, Figure 2e, shows a scatter of sharp crystalline reflections above and below the layer lines. This is due to the chain axes being tilted with respect

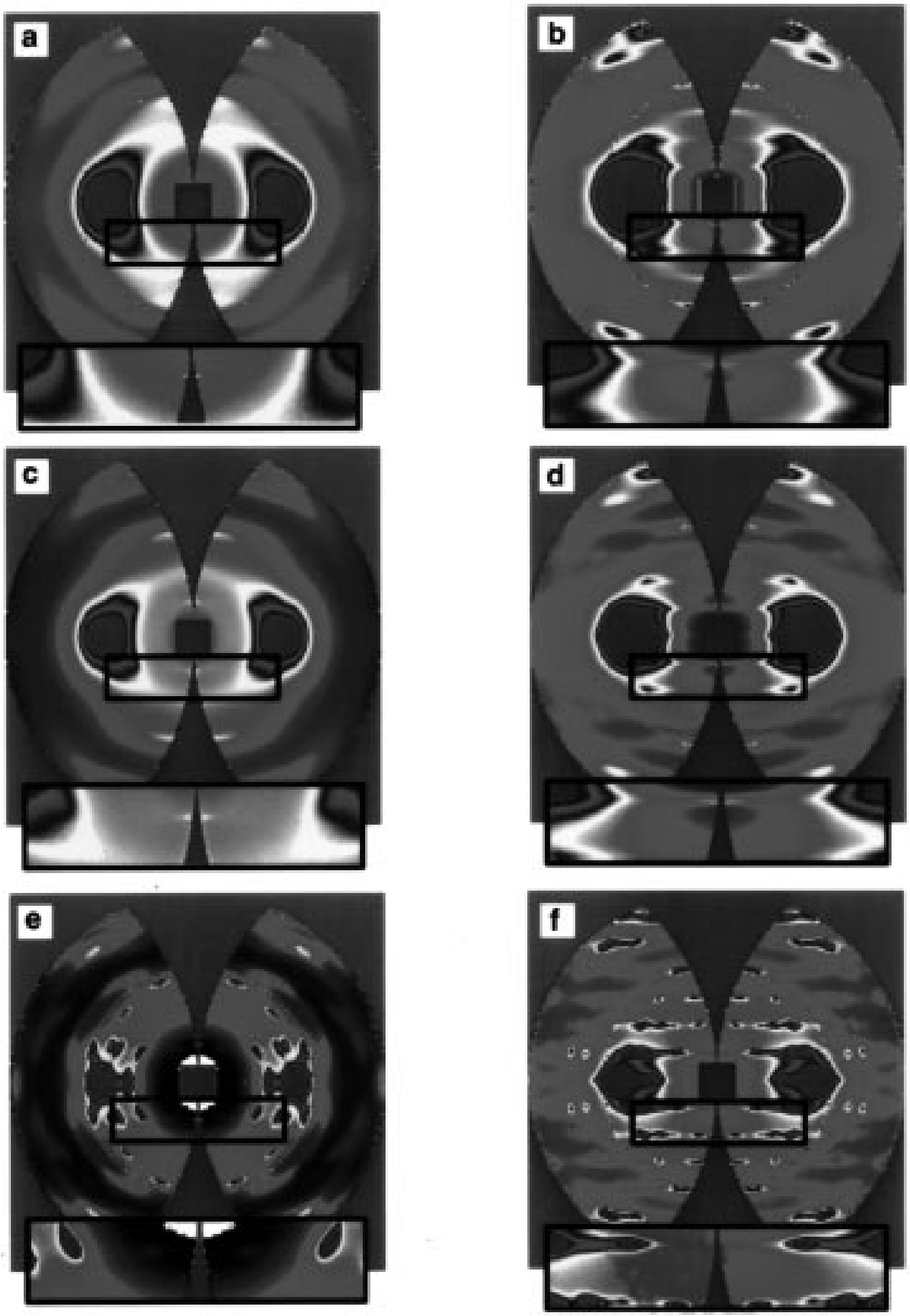

Figure 2. Series of geometrically corrected transmission X-ray diffraction patterns from PET-rich and PEN-rich PET/PEN random copolymer fibers and from the PET and PEN homopolymers. In all cases amorphous monofilaments were drawn to DR 5 at approximately 2 s^{-1} at a few degrees (<5) above T_g in silicone oil. All samples were quenched into iced water except for the annealed homopolymer samples e and f, which were quenched by room-temperature air. Key: (a) 84% PET; (b) 16% PET; (c) PET; (d) PEN; (e) PET annealed at 190 °C for 24 h at a fixed length; (f) PEN annealed at 210 °C for 24 h at a fixed length.

to the fiber axis (an effect well documented for PET[11] and seen in other triclinic polyesters.[12]) Tilt is observed in all fiber patterns from annealed PET-rich (>70% PET) PET/PEN fibers. In line with the suggestions of Bonart[4] concerning PET, we conclude that the sequential shear, on conversion from smectic A to triclinic crystal, reacts against the constraint of the surrounding polymer to produce the tilt. Finally an analogy must be drawn with intrinsically liquid crystalline thermotropic copolyesters (e.g. random copolymers of hydroxy benzoic and naphthoic acids) where under conditions of melt orientation a smectic phase is clearly apparent.[13]

Conclusion. Samples of random copolymers of ethylene terephthalate and ethylene naphthalene-2,6-dicarboxylate rapidly, quenched during drawing, show strong evidence of a transient smectic state. The distinct meridional maximum, characteristic of the smectic phase, is lost on annealing, which induces crystallization. Similar observations have been made on the parent homopolymers, PET and PEN, providing compelling confirmation of previous reports.[3–7] The observations suggest that commercial polyester fiber drawing processes may now be open to reinterpretation and further optimization.

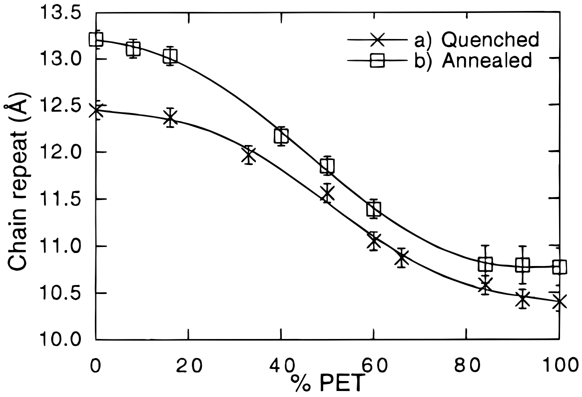

Figure 3. Variation of chain repeat with composition for (a) quenched and (b) annealed fiber samples. (a) The chain repeat obtained from the position of the first meridional maximum, initially measured from the fiber diffraction patterns and confirmed with a meridional diffractometer scan for the following PET/PEN ratios: 100%, 84%, 50%, 16%, and 0%. (b) The chain repeat obtained from the spacing of the first layer line measured from fiber diffraction data from samples annealed to induce crystallization. (Large error bars for 16% PET, 92% PET, and PET are due to the need to correct for the tilt of the crystal *c* axis away from the fiber axis.)

Acknowledgment. The polymers were synthesized by Dr. W. A. MacDonald, of ICI(Polyesters), and by Dr. X. Lu as a part of a previous study[1] in the Cambridge laboratory. We wish also to acknowledge the provision of research funding by ICI and EPSRC as a CASE award.

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MA980536T