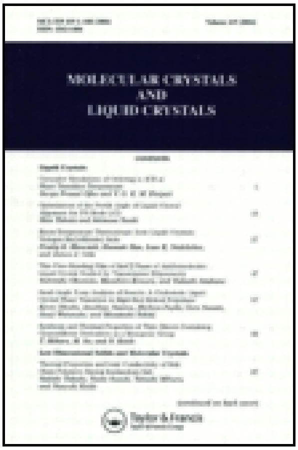

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X-Ray Diffraction Studies of Liquid Crystalline Polymers

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X-RAY DIFFRACTION STUDIES OF LIQUID CRYSTALLINE POLYMERS

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Thermotropic liquid crystalline copolyesters display an ordered fluid phase at elevated temperatures which permits the development of unusually high orientation at ambient temperatures. The transition which occurs upon cooling the high temperature nematic liquid crystalline phase very rapidly (e.g. fiber spinning) results in a polymeric glass with nematic structural order. Annealing increases structural order from the nematic glass toward ideal three dimensional crystalline order. Precision X-ray diffractometry has been used to directly observe changes in structural correlations which occur with annealing. Structural transitions range in character in these copolyesters from no change upon annealing to a transition from fully two dimensional to fully three dimensional structural order. Increased three dimensional order also results in substantially increased first order character of the high temperature phase transition. The chemical structure of co-monomers determines, in part, the final degree of dimensionality.

1. INTRODUCTION

Thermotropic main chain liquid crystalline polymers (LCP's) display a range of structural order. All of these polymers share a nematic high temperture phase. Upon fiber spinning, the polymer rapidly cools forming an oriented polymeric glass (i.e. a frozen structure which is presumably similar to the instantaneous or static structure of the high temperature nematic phase).[1] Drawn LCP fibers consist of parallel polymer chains for which the orientational order parameter is nearly unity. The fibers are uniaxial so that all structure is angularly averaged about the fiber axis of symmetry.

X-ray diffractometry may be used to examine the specific types of structural order existing in these fibers both in the neat (i.e. spun with no thermal post treatment) and annealed states. Certain polymer structures are fully two dimensionally crystalline showing a regular arrangement of monomers along the chain axis, a regular arrangement of polymer molecules on a plane perpendicular to the fiber (or molecular) axis, but no correlation of the monomer chain axis repeat between neighboring molecules. Other polymer structures are fully three dimensionally crystalline showing not only a regular arrangement of monomers along the chain axis and of polymers in a plane perpendicular to the chain axis, but also a regular arrangement of monomers between neighboring polymer molecules. These three dimensionally crystalline structures display intermolecular registration due to the synchronization of the monomer repeat between polymer molecules along the molecular axis.

2. MATERIALS AND METHODS

Three different LCP polymer fibers were examined using standard flat plate wide angle X-ray diffraction photographic methods and CuK_α radiation. The first, poly (p-phenylene benzbisthiazole)(PBZT), a lyotropic LCP, has been previously examined in detail[2]. The second is a copolymer of 1,4-hydroxybenzoic acid and 2,6-hydroxynapthoic acid[3] (BN) which has previously been shown to be a random copolymer[4,5]. The third is an alternating copolymer of 2-phenylhydroquinone and terephthalic acid (ØHT).

Extensive diffractometry studies were conducted for the BN polymer fiber. A precision two circle Huber diffractometer was used for these experiments. The diffractometer defines the incident X-ray beam with a curved graphite monochromator which focuses on the vertical plane. The sample fiber bundle is mounted in the horizontal plane on the theta circle which has a angular precision of 5 x 10^{-3} degrees. Diffracted X-rays are detected using the two theta circle in the horizontal plane with the same angular precision and a flat graphite analyzer crystal. The angular resolution of the incident and diffracted beams is determined by the choice of monochromator and analyzer crystals (ca. 0.3° for graphite). Pairs of x-y slits on both the incident and diffracted beam lines serve to reduce stray scattering. NaI scintillation detectors are used to detect diffracted X-rays and monitor the incident X-ray beam. Diffractometer scans were performed using independent computer control of each circle permitting linear scans between any two points in the reciprocal space plane containing the meridional (or S_x) axis and equatorial (or S_y) axis.

The BN fiber system was also examined using differential scanning calorimetry (DSC). For this a Dupont 1090 Thermal Analyzer with a 910 DSC module was used. Samples were heated under N_2 at 15°C/min.

Monte Carlo simulations of diffracted intensity was computed for the BN polymer using a VAX 11/780 computer. For all calculations, 10,000 monomers were considered arranged in 100 polymers. Because all polymers are of equal length the computed intensity distribution contains high frequency truncation ripples. These were reduced by smoothing computed distribution using a 5 point centered averaging window over the entire 500 point distribution.

3. Results

Figure 1 shows neat and annealed fiber diffraction patterns for all three fibers. Annealed patterns show continuous layer lines for PBZT (as previously observed)[2], shortened layer lines for BN and, an array of spots for ØHT.

Figure 2 shows a diffractometry scan along the meridian (S_x axis) for neat and annealed 25B/75N BN copolymer. Several aperiodic peaks are observed. For each peak, scans were performed at that S_x level as a function of S_y (i.e. parallel to the equator). Figure 3 shows two scans along S_y for neat and annealed 25/75BN polymer at S_x=0.125A^{-1}. Figure 4 shows the same two scans at S_x=0.479 A^{-1}. Clearly annealing causes the layer line length to decrease at small S_x whereas at higher S_x levels there is little change. Similar results for other compositions are given in the table.

Finally, figure 5 shows DSC results for neat and annealed 25/75 BN fibers. The neat fiber shows a very weak, broad, and almost indiscernable transition whereas the annealed fiber shows a first order peak.

4. Monte Carlo Calculations

Monte Carlo calculations of the intensity distribution along the S_x (meridional) axis have been previously computed and compared with observed diffractometer scans for neat BN fibers over a range of compositions[4,5]. These calculations establish that the BN copolymer is random. Results for a similar calculation are shown in figure 6. All of these calculations allow for atomic coordinates but do not consider effects due to intermolecular registration.

Figure 7 and 8 show Monte Carlo calculations of intensity distributions along different layer levels. For these calculations 100 polymer molecules are arranged on an hexagonal lattice (a=9A) and intermolecular interference is allowed. The Z axis (fiber axis) starting position of each polymer is allowed to vary randomly over an 8.5A interval (ca. the monomer length).

5. Discussion

The diffraction patterns shown in figure 1 demonstrate that annealing LCP's results in changes in the degree of intermolecular registration. PBZT remains two dimensional, BN shows a small change, and ØHT develops a high degree of three dimensional order. For PBZT, molecular rigidity probably prohibits registration which would require cooperative translation of long intervals of many monomers. ØHT is an alternating copolymer so that three dimensional long range order is possible.

However, BN is a random copolymer so that three dimensional long range order is not possible.

Monte Carlo calculations for BN demonstrate that different layer line widths are reasonable even for random copolymers placed on a regular lattice in a plane perpendicular to the molecular axis with random starting points along the fiber axis. Changes in the experimentally observed layer line widths suggest that, irrespective of the random sequence, intermolecular registration does improve upon annealing. In particular larger structural features (e.g. phenyl rings) giving rise to the smaller S_x level peak along the meridional axis develops more lateral correlation than smaller structural features (e.g. C-C bonds) giving rise to the larger S_x level meridional peak. Similar decreases in layer line widths at smaller S_x levels occur throughout the compositional range suggesting the very limited development of three dimensional long range order.

Annealing BN fibers also reduces the width of reflections on the equator (S_y axis). In particular, the strong ca. 4.5A equatorial peak (see figure 1b) sharpens substantially demonstrating improved order of the polymer lattice on a plane perpendicular to the molecular axis. The observed layer line widths (figures 3 and 4) are such that the width along

S_y is much smaller than the S_x level. Thus, the source of broadening is much more highly weighted toward lack of intermolecular registration than disorder of the polymer lattice perpendicular to the molecular axis. Futhermore, the equatorial peaks at large S_y values are substantially narrower than layer line widths at small S_x suggesting that registration is the dominant source of disorder.

Improved intermolecular registration also results in a first order thermal transition. Although neat BN polymer shows a strong equatorial diffraction peak, DSC results indicate a weak and broad transition. It is likely that the transition is really a very weak, broad first order peak rather than a specific heat discontinuity expected for a second order transition. Independent of the nature of the neat fiber to nematic transition, the thermal event is very small. Upon annealing (and the development of limited three dimensional order) a definitive small first order DSC peak occurs which is substantially sharper than the DSC transition observed for the neat fiber.

6. Conclusion

The detailed molecular structure of LCP's determines the final degree of dimensionality which is developed upon annealing. Certain

LCP's develop long range three dimensional order whereas others remain two dimensional. Annealing BN copolymer which has a random sequence distribution does not result in a two dimensional or a three dimensional structure. Rather, this copolymer develops limited three dimensional long range order and simultaneously a small DSC first order peak. The random sequence of the BN polymer prevents extensive development of three dimensional long range order but does not prohibit improved intermolecular registration.

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TABLE I Layer line widths for BN copolymer

Composition[1]	State	S_x Level (A^{-1})	Width [2] (A^{-1})
25/75	Neat	0.125	0.0262
	Annealed	0.124	0.0109
	Neat	0.480	0.1339
	Annealed	0.477	0.1465
50/50	Neat	0.135	0.0314
	Annealed	0.133	0.0109
	Neat	0.479	0.1407
	Annealed	0.479	0.1420
75/25	Neat	0.151	0.0320
	Annealed	0.152	0.0204
	Neat	0.480	0.1145
	Annealed	0.480	0.1034

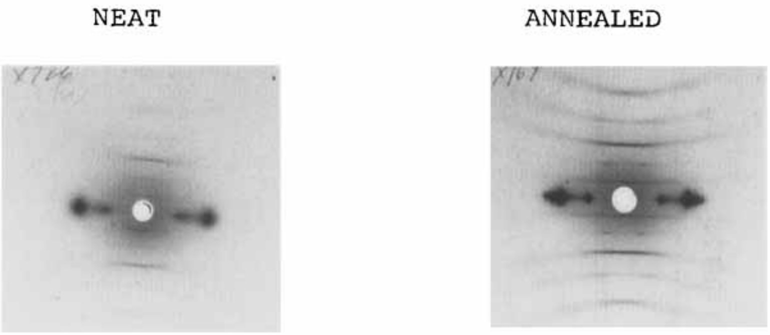
1. Composition is given as the % 1,4-hydroxybenzoic acid/%2,6-hydroxynaphthoic acid.
2. Full width at one half integral intensity of the layer line along the Sy axis.

FIGURE CAPTIONS

1. Wide angle X-ray diffraction patterns of LCP fibers in the neat and annealed states. The fiber axis is vertical.
a) Poly (p-phenylene benzbisthiazole) (PBZT). Layer lines are observed.
b) 25% 1,4-hydroxybenzoic acid/75% 2-6 hydroxynaphthoic acid. (BN). Little meridional diffraction is observed due to shortened layer lines for this highly oriented fiber.
c) 2-phenylhydroquinone/terephthalic acid (0HT). A set of Bragg spots is observed.
2. Meridional diffractometer scan of 25/75 BN copolymer fiber in the neat and annealed states. The scan is along the S_x axis (parallel to the fiber axis). $1/S_x$ gives the equivalent Bragg spacing in Angstroms along this axis. The intensities have not been normalized.
3. Layer line diffractometer scans of 25/75 BN copolymer :
a) Neat fiber $S_x = 0.125$ A^{-1}.
b) Annealed fiber $S_x = 0.124A^{-1}$.
Intensities have been normalized and show differences in the layer line widths.
4. Layer line diffractometer scans of 25/75 BN copolymer:
    a) Neat fiber $S_x = 0.480A^{-1}$.
    b) Annealed fiber $S_x = 0.477A^{-1}$.
Intensities have been normalized. Little difference is found in the layer line width.
5. DSC curves for neat and annealed 25/75 BN fiber. Neat fiber shows essentially a weak, broad transition whereas annealed fiber shows a sharp first order peak.
6. Monte Carlo calculation of meridional intensities along the fiber (S_x) axis. Intensities were computed for 100 polymer molecules each containing 100 monomers. 2500 monomers of 1,4-hydroxybenzoic acid and 7500 monomers of 2,6-hydroxynapthoic

acid were randomly distributed along the polymer chains. Intensities for each of the 100 polymers were averaged to produce the final intensity distribution. Intermolecular interferences were not considered. The intensity distribution has been smoothed to eliminate truncation effects. The distribution has been corrected by the Lorentz polarization factor.

7. Monte Carlo calculation of intensity along a layer line parallel to the equatorial (S_y) axis. The S_x level is 0.125A^{-1}. The composition is the same as used for figure 6. Each polymer molecule is separated from next molecule by 9A on a line perpendicular to the fiber axis. The Z axis starting point parallel to the fiber axis is random over an 8.5A interval (ca. one Monomer length). Intermolecular interference is allowed.
8. Monte Carlo calculation of intensity along a layer line. The S_x level is 0.476A^{-1}. All other parameters are the same as used for figure 7.



(a) PBZT

(b) 25/75 BN

(c) ØHT

FIGURE 1

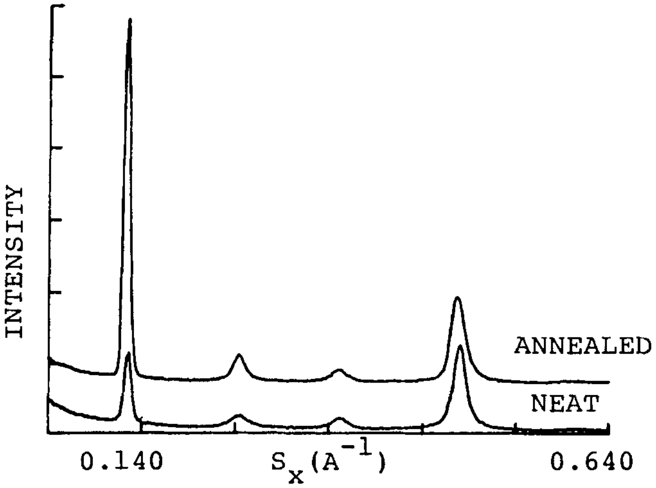
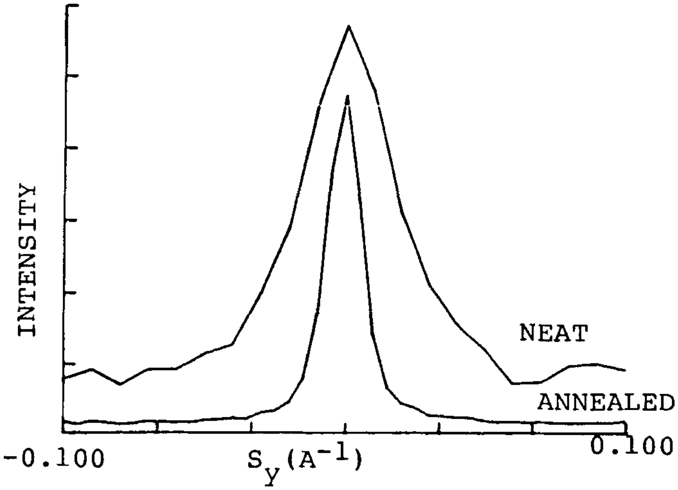


FIGURE 2



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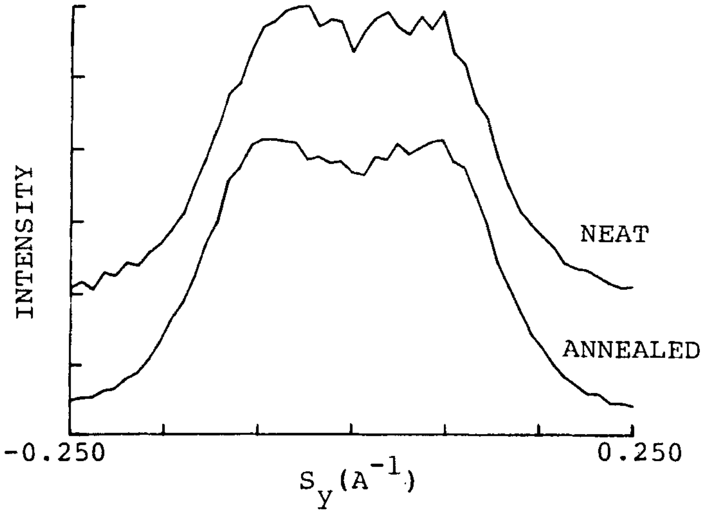

FIGURE 4

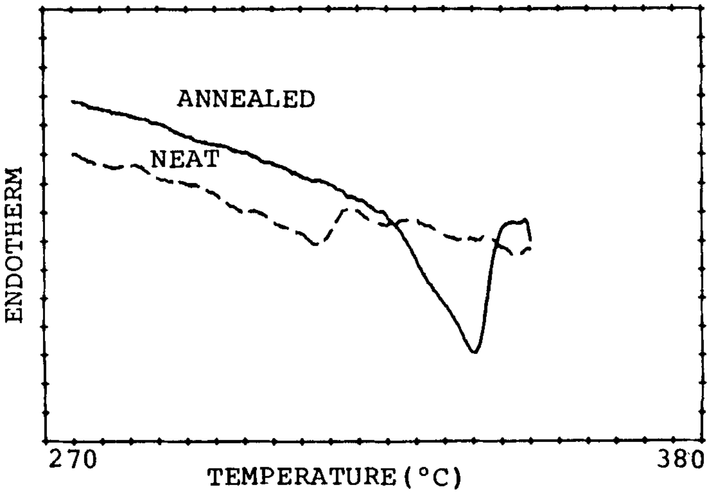

FIGURE 5

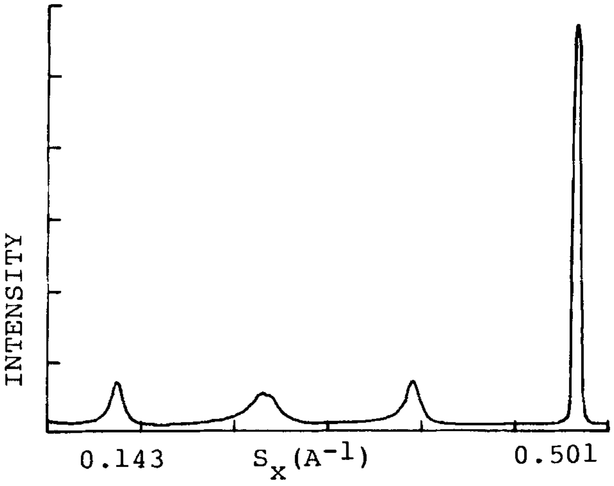

FIGURE 6

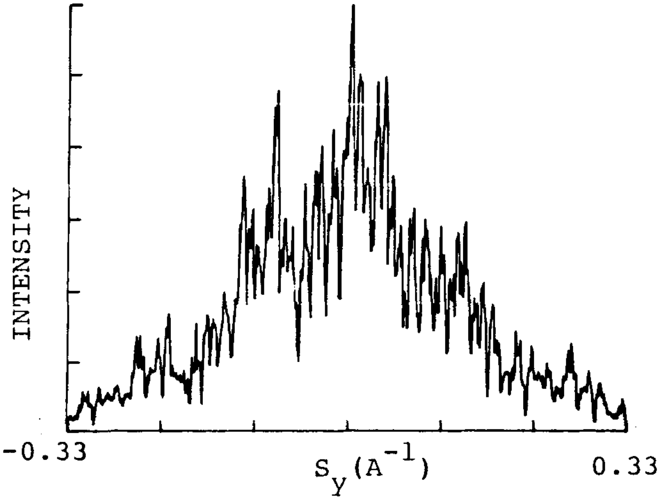

FIGURE 7

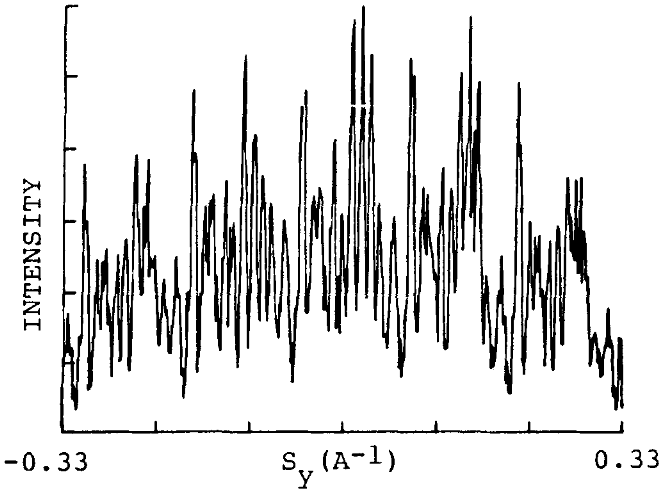

FIGURE 8