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Effects of Annealing on the Structure Formation in a Thermotropic Liquid Crystalline Copolyester

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ABSTRACT: Structure formation in a thermotropic liquid crystalline copolyester was studied by wide-angle X-ray diffraction (WAXD) and differential scanning calorimetry (DSC). The lateral packing of molecular chains in a copolymer of *p*-hydroxybenzoic acid (HBA) and 2-hydroxy-6-naphthoic acid (HNA) was shown to be transformed from hexagonal packing to an orthorhombic one in the course of annealing above 230 °C. The lattice constants of the orthorhombic lattice of the copolymer are slightly higher than the lattice constants reported for the HBA homopolymer, suggesting that the orthorhombic lattice in the copolymer is not only formed by the sequence of the HBA homopolymer block. The WAXD intensity of the equatorial reflections was calculated at various angles of rotation of the aromatic plane in the orthorhombic lattice. From a comparison of experimental and theoretical intensities of the equatorial reflections, the aromatic plane was shown to be inclined by 6–16° and 140–156° from the 100 plane. Although the sequence distribution of the copolymer was not influenced by annealing, the repeating unit length along the fiber direction slightly increased on annealing. The experimental results are discussed in terms of interchain and intrachain correlations of molecular planes that are related to the conformational order of molecular chains.

Introduction

The structure of thermotropic liquid crystalline polyesters has been extensively studied not only for their scientific interest but also from an industrial point of view, since they can be processed as high performance materials. One of the most popular liquid crystalline polyesters is a family of random copolymers having a *p*-hydroxybenzoic acid (HBA) unit as a major constituent. From the analysis of the electron diffraction pattern, the crystal structure of the homopolymer of HBA was first proposed to be an orthorhombic unit cell with dimensions of a = 7.62 Å, b = 5.70 Å, and c = 12.56 Å (phase 1).[1-3] The unit cell was shown to consist of two molecular chains with 2/1 screw axis along the fiber direction. It was reported later that another orthorhombic modification with a = 3.77 Å, b = 11.06 Å, and c = 12.89 Å (phase 2) exists in the HBA homopolymer, particularly at low degrees of polymerization.[4] In addition, the crystal structure was shown to be transformed from an orthorhombic unit cell to a hexagonal cell when the temperature is raised above 350 °C.[2,5]

The structure of a liquid crystalline copolyester with a random sequence distribution involves the more complicated problem of fitting the regular crystal lattice with three-dimensional periodicity. The position and intensity of meridional WAXD reflections were calculated for a liquid crystalline copolyester with a random sequence distribution by Blackwell and his co-workers[6-10] and by Mitchell and Windle.[11] The calculation predicts that the meridional WAXD profile for a random copolymer is sensitive to composition, monomer repeat length, and blockiness of sequence distribution. In addition, Windle and his co-workers discussed the three-dimensional structure of a liquid crystalline polyester and proposed that nonperiodic sequences of the copolymer laterally match each other to form nonperiodic layer (NPL) crystals.[12,13] They presented experimental evidence and statistical analysis that support the presence of NPL crystals. More recently, Biswas and Blackwell predicted equatorial and off-equatorial WAXD patterns for three-dimensional assemblies of copolymer chains with random sequence distributions.[14]

On the other hand, the effects of annealing on the structure of liquid crystalline copolyesters have also been studied extensively.[11,15] In the course of annealing, not only is the lateral order of the random copolyester improved but also the random sequences crystallize into ordered crystals with higher melting temperatures.[15,16] Recently we have reported that the dynamic modulus at higher temperatures has been much improved by annealing.[17] The increase in the thermal stability on annealing is strongly related to the enhancement of structural order.

In this work, we report the effect of annealing on structure formation of a liquid crystalline copolyester and present a detailed analysis of the ordered structure developed by annealing.

Experimental Section

The copolyester studied in this work is composed of 73 mol % of the *p*-hydroxybenzoic acid (HBA) unit and 27 mol % of the 2-hydroxy-6-naphthoic acid (HNA) unit. Pellets of the copolymer were obtained from Polyplastics Co. Ltd. Oriented sheets 0.4–0.5 mm thick were prepared by extrusion molding at 290 °C. The sheets were annealed for 6 h at 180–270 °C by using a vacuum oven. Dimensions of the sheets did not change significantly in the course of annealing.

Wide-angle X-ray diffraction (WAXD) studies were carried out by using a pinhole beam of Ni-filtered Cu Kα radiation (40 kV, 20–40 mA). The WAXD diagrams were taken with a flat-film camera. WAXD profiles were recorded along the equatorial and meridional directions by using a transmission diffractometer equipped with a scintillation counter and a pulse-height analyzer.

Melting behavior was characterized with a Perkin-Elmer DSC-II differential scanning calorimeter at a heating rate of 20 K/min. Temperature was calibrated with standard samples of indium and lead.

Theoretical

The WAXD intensity of the equatorial reflection was calculated assuming that the HBA and HNA units were aligned in a common crystal lattice. The lattice constants were obtained from the experimental WAXD profile of the annealed sample. The WAXD intensity of the $hk0$ reflection, $I(h,k,0)$, is given by

$$I(h,k,0) = F(h,k,0)^{*}F(h,k,0) \qquad (1)$$

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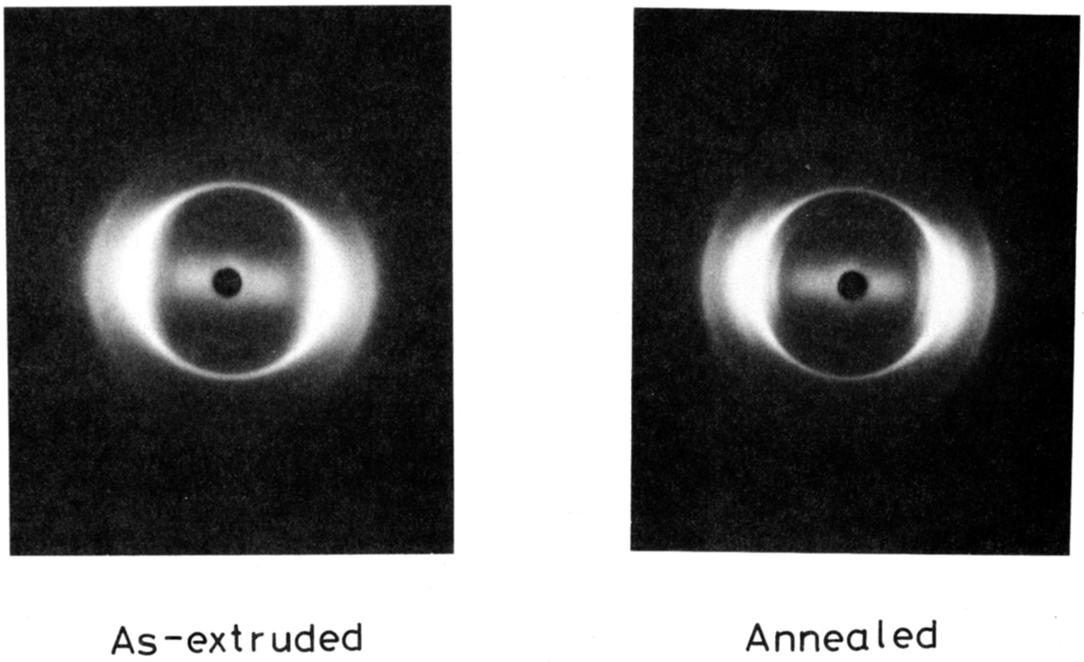

As-extruded

Annealed

Figure 1. WAXD fiber diagrams of as-extruded and annealed sheets of HBA/HNA copolyester.

$$F(h,k,0) = \sum_j f_j \exp[2\pi i(hx_j/a + ky_j/b)] \qquad (2)$$

where f_j is the atomic scattering factor of the jth atom and the sum is over all atoms in the unit cell.

In the case of a random copolymer, eq 2 should be averaged over the two monomer units

$$F(h,k,0) = P_A F_A(h,k,0) + P_B F_B(h,k,0) \qquad (3)$$

where P_A and P_B are the molar fraction of the monomer units A (HBA) and B (HNA), respectively. $F_A(h,k,0)$ and $F_B(h,k,0)$ stand for the Fourier transforms of the atomic coordinates in units A and B, respectively

$$F_A(h,k,0) = \sum_j f_j \exp[2\pi i(hx_{j,A}/a + ky_{j,A}/b)] \qquad (4)$$

where the sum is taken over all atoms in unit A. An analogous equation is obtained for the monomor unit B.

The atomic coordinates of HBA and HNA units were taken from ref 6. The torsional angle between aromatic plane and the ester linkage was set at 30°, as suggested by potential energy calculations of model compounds.[18]

Results and Discussion

Effects of Annealing of the Lattice Structure. Figure 1 shows the effects of annealing on the WAXD pattern for the HBA/HNA copolyester. A higher degree of orientation was revealed from the low degree of arcing of the equatorial and meridional reflections. Before annealing, two reflections were observed on the equator at d = 3.30 and 4.47 Å. On annealing at 270 °C, the former reflection shifts slightly to a higher Bragg angle whereas the latter moves to a lower Bragg angle. In addition, two other reflections appeared on the equator at d = 3.96 and 5.60 Å. The results showed that the lateral packing of molecular chains was changed by annealing at higher temperature.

Figure 2 shows the effects of annealing temperature (T_a) on the equatorial WAXD profile. No remarkable change was observed at T_a < 230 °C, while the reflection at d = 4.47 Å (2θ = 19.8°) shifted to a lower Bragg angle and became asymmetrically shaped at T_a = 230–240 °C. Upon further increasing the annealing temperature (T_a

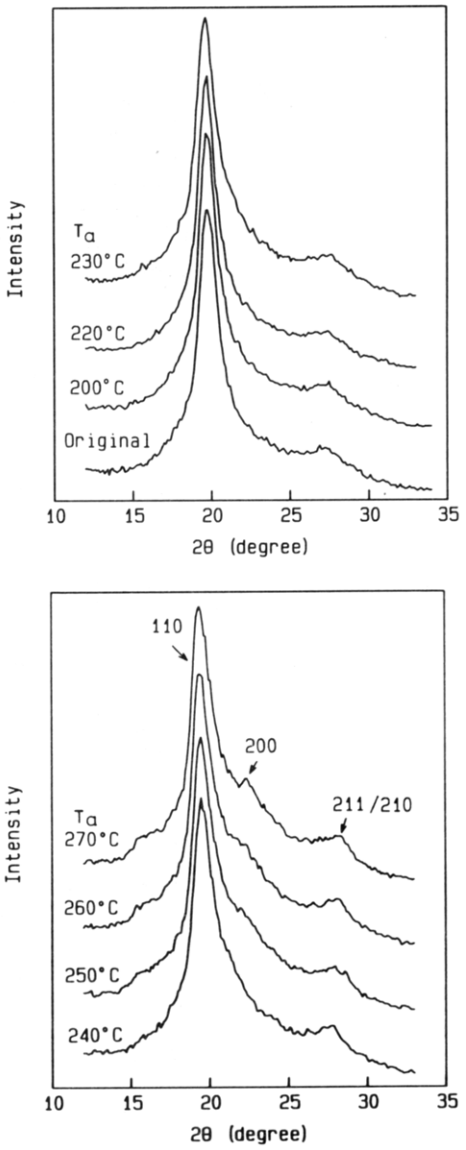

Figure 2. Effects of annealing temperature (T_a) on the equatorial WAXD profile.

Table I
Observed *d* Spacings of the HBA/HNA Copolyester

sample	*d* spacing, Å	assignment
as-extruded	4.47	110[a]
	3.30	211/210[a]
	6.5	meridional
	3.1	meridional
	2.07	meridional
annealed at 270 °C	5.59	another crystal modification
	4.55	110
	3.96	200
	3.19	211/210
	6.5	meridional
	3.1	meridional
	2.08	meridional

[a] Indexed with respect to an orthorhombic unit cell.

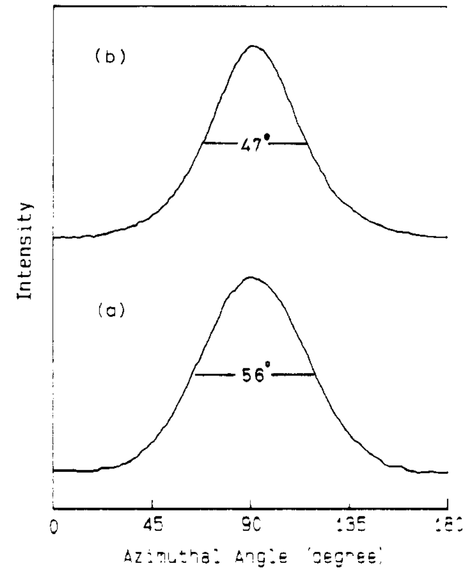

Figure 3. The azimuthal intensity profiles of WAXD in as-extruded sheet: (a) d = 3.30 Å reflection; (b) d = 4.47 Å reflection.

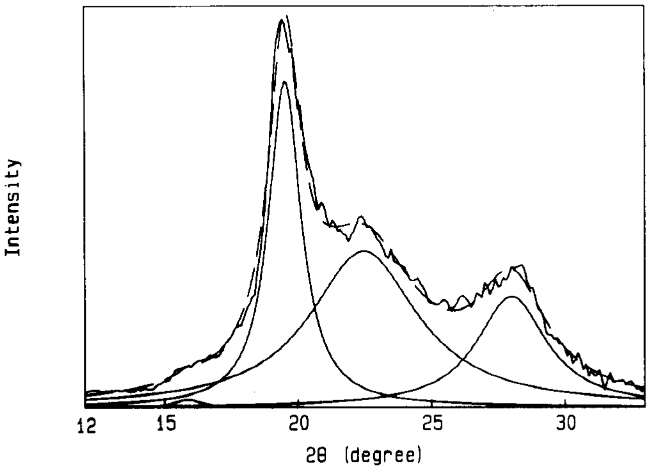

Figure 4. Curve fitting of the equatorial WAXD profile of annealed sheet (T_a = 270 °C).

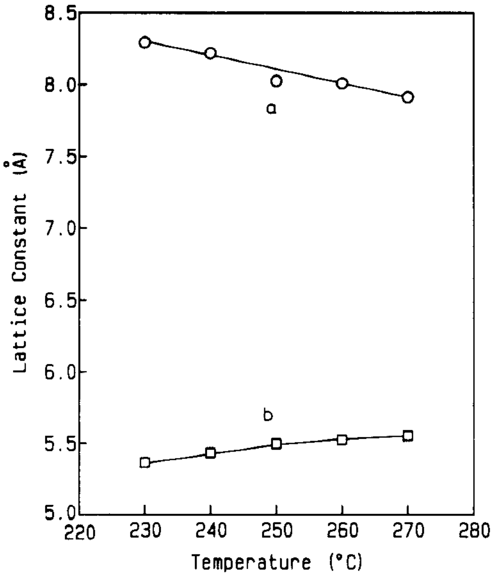

Figure 5. Effects of annealing temperature on the lattice constants.

> 240 °C), two reflections appeared at d = 3.96 (2θ = 22.5°) and 5.6 Å (2θ = 16°) as was also observed in the WAXD fiber diagram pattern. The observed values of the d spacing are summarized in Table I.

Figure 3 shows the azimuthal intensity profiles of WAXD measured at d = 4.47 and 3.30 Å. The reflection at d = 3.30 Å showed a broader intensity distribution along the azimuthal angle than the reflection at d = 4.47 Å. The results suggested that there was a contribution from the off-equatorial intensity to the former reflection and hence that there might be a certain degree of three-dimensional order with the axial register between neighboring sequences.

The WAXD results of the HBA/HNA copolymer can be interpreted by referring to the crystal structure of the HBA homopolymer.[1-5] The equatorial WAXD profile of as-extruded sheet of HBA/HNA copolyester resembles the WAXD profile of the high-temperature phase of the HBA homopolymer.[2,5] The d spacing of the as-extruded sheet is in coincidence with the hexagonal lattice with a = 5.16 Å, which corresponds to the orthorhombic lattice with a = 8.94 Å and b = 5.16 Å ($a = 3^{1/2}b$). On the other hand, the WAXD peak positions of the annealed copolyester sheets (T_a > 220 °C) are close to those of the low-temperature phase of the HBA homopolymer,[1-5] suggesting an orthorhombic packing in annealed copolyester sheets. The reflections at d = 4.55, 3.96, and 3.19 Å can be assigned to the 110, 200, and 210/211 reflections, respectively, of the orthorhombic lattice. The WAXD reflections of HBA/HNA copolyester are much broader than the corresponding reflections in the HBA homopolymer,[5] suggesting that crystals in the copolyester have a lower degree of perfection and are smaller in crystallite dimensions than those of the HBA homopolymer. The 111 reflection was observed in the WAXD profile of the low-temperature phase of the HBA homopolymer, whereas the 111 reflection in the annealed copolyester was hidden behind neighboring reflections with higher intensity. The weak shoulder at d = 5.60 Å observed in the WAXD profile of annealed copolyester originates from a small amount of another orthorhombic modification, which was found by Lieser.[4] As a result, annealing at T_a > 230 °C induces a transition from the hexagonal packing to the orthorhombic packing in extruded HBA/HNA copolyester sheet.

In order to obtain the value of peak positions, overlapping reflections were resolved by least-squares curve fitting using Lorentz functions, after the observed WAXD profiles were corrected for polarization and Lorentz factors (Figure 4). The lattice constants a and b were obtained from the d spacings of the 110 and 200 reflections. Figure 5 shows the dependence of the lattice constants on the annealing temperature. With a rise in annealing temperature, the length of the a axis monotonically decreases and that of the b axis increases. As the hexagonal lat-

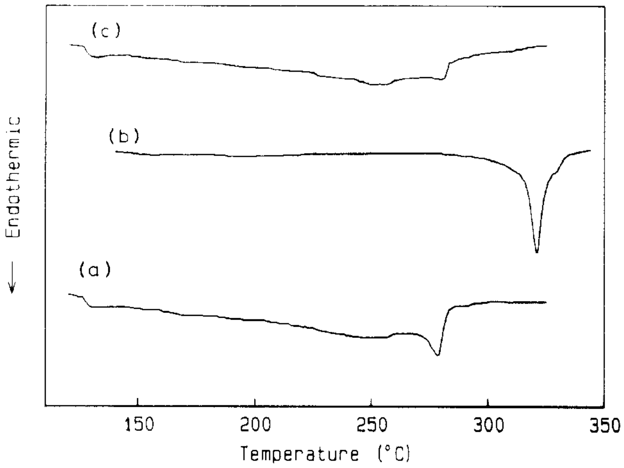

Figure 6. DSC thermograms of HBA/HNA copolyester: (a) unannealed; (b) annealed at 270 °C for 6 h; (c) second DSC heating trace of annealed sample.

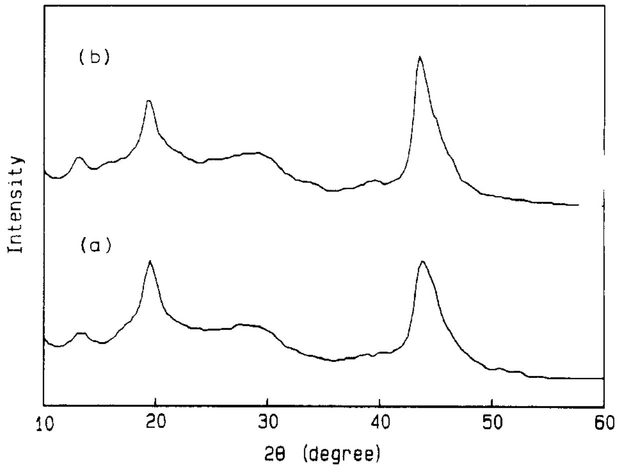

Figure 7. The meridional WAXD profiles: (a) as-extruded; (b) annealed at 270 °C for 6 h.

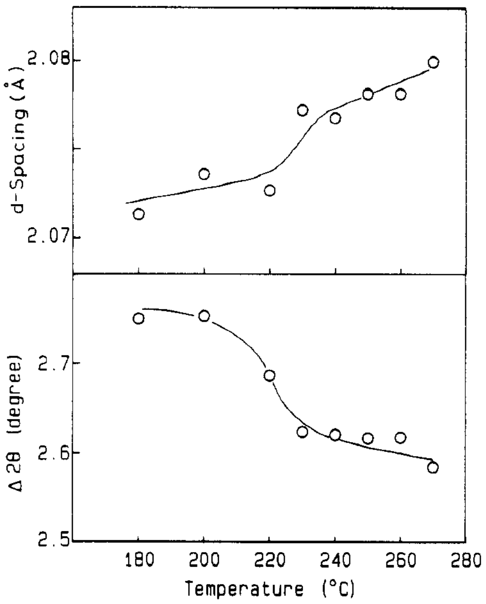

Figure 8. Effects of annealing on the *d* spacing and integrated width of d = 2.08 Å reflection.

tice corresponds to the orthorhombic cell with a = 8.94 Å and b = 5.16 Å ($a = 3^{1/2}b$), it can be said that the deviation from the hexagonal packing becomes larger with increasing annealing temperature.

The cross sectional area of the orthorhombic lattice, $a \times b$, in the annealed copolyester was slightly higher than any reported values for $a \times b$ in the orthorhombic lattice of the HBA homopolymer.[1-5] It was shown from the broadness of the WAXD reflections that orthorhombic crystals of the copolyester were less ordered than those of the HBA homopolymer. These results suggest that the orthorhombic crystals of annealed copolyester are not composed only of blocks of the HBA unit in the copolyester. It is a matter of the fact that the crystallization of homopolymer sequences is restricted in the copolyester with a random sequence distribution. It is feasible that HBA and HNA units are incorporated into the crystalline structure that gives rise to the equatorial WAXD reflections. Windle et al proposed that a random sequence in a liquid crystalline copolyester propagated laterally to form nonperiodic layer (NPL) crystals,[12,13] which might be one of the hopeful models for the crystal structure of the liquid crystalline copolyester.

Figure 6 shows effects of annealing on differential scanning calorimetry (DSC) thermograms of the liquid crystalline copolyester. The as-extruded specimen begins to melt at 220–230 °C and exhibits a broad but small endotherm in the temperature range of 240–280 °C. The mobile molecules may organize into a structure of higher order in the heating process. The premelting and reorganization process induces the hexagonal–orthorhombic transition in the course of annealing above 230 °C. The hexagonal–orthorhombic transformation hardly takes place in the heating process of a DSC scan at a heating rate of 20 K/min, suggesting that the structural transition is dependent not only on annealing temperature but also on annealing time. We varied annealing time from 3 to 48 h at a constant annealing temperature of 230 °C and confirmed that the DSC melting peak shifts to the higher temperature region with increasing annealing time. The hexagonal–orthorhombic transition is facilitated by annealing for the longer period.

On the other hand, a sharp and intense peak appears at 320 °C in the DSC curve of the annealed sheet. The orthorhombic crystal melts at higher temperature with a higher enthalpy change than the hexagonal crystal, suggesting a higher degree of structural order in the orthorhombic crystal. The second DSC heating trace of an annealed sheet (Figure 6c) is approximately the same as the DSC of the extruded sheet before annealing (Figure 6a). The orthorhombic crystal structure developed by annealing was shown to revert back to the hexagonal structure on melting and recrystallization.

Effect of Annealing on the Structure of Molecular Chains. Figure 7 shows the effects of annealing on the meridional profile of WAXD. The meridional WAXD of the annealed copolyester sheet is similar to that of the as-extruded sheet as a whole. Although the reflection at d = 2.08 Å is not affected by the changes in the structure of molecular chains, the peak positions of other meridional reflections were reported to be sensitive to the monomer sequence distribution of the stiff copolymer chains.[10,11] It was shown from the meridional WAXD profiles that the HBA/HNA copolymer has a random sequence distribution.[6-11] The similarity of the meridional WAXD reflections of the annealed sheet to that of as-extruded sheet suggests that the monomer sequence distribution of the copolymer is not affected by annealing. Although transesterification is expected in annealing of the liquid crystalline copolyester at higher temperature, it does not have a significant effect on the sequence distribution of the copolyester.

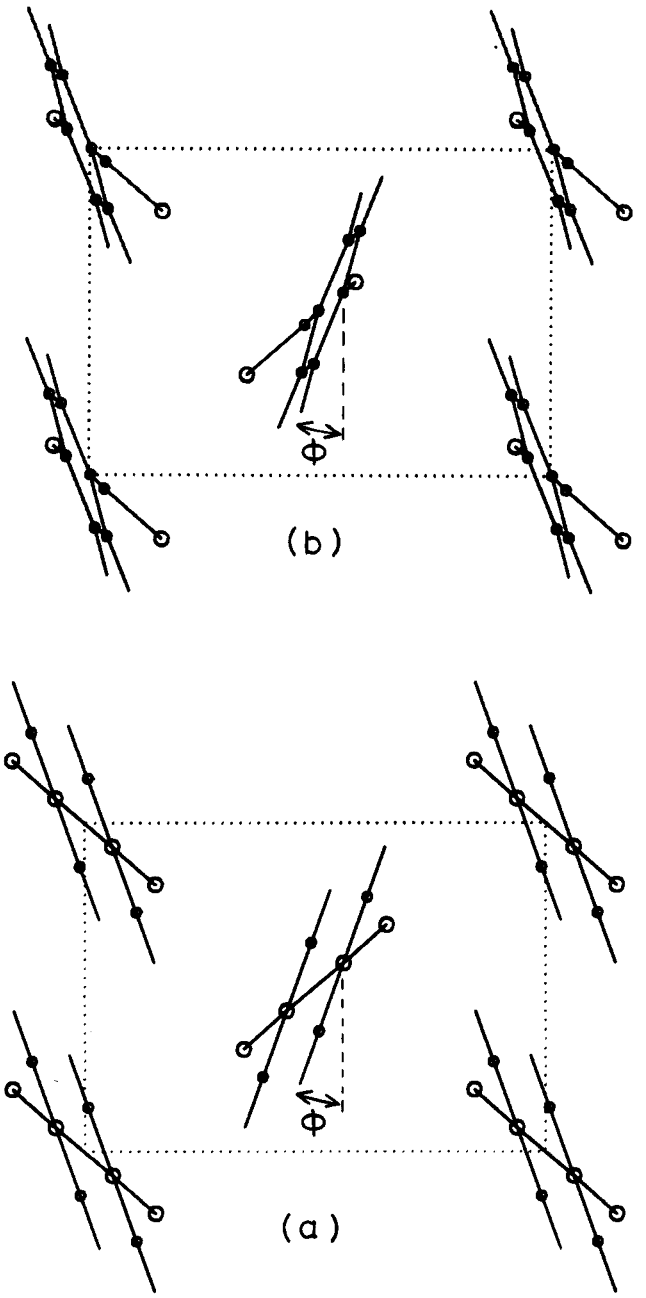

Figure 9. Structural models used for the calculation of WAXD intensity of *hk*0 reflections: (a) 2/1 helix; (b) trans zigzag conformation.

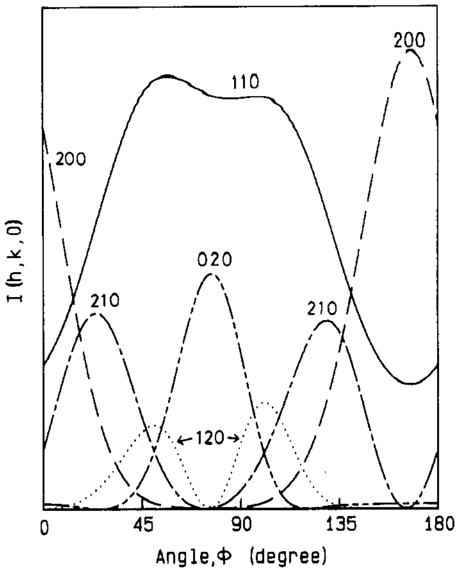

Figure 10. The WAXD intensity distribution on angle ϕ calculated for the structure in Figure 9a.

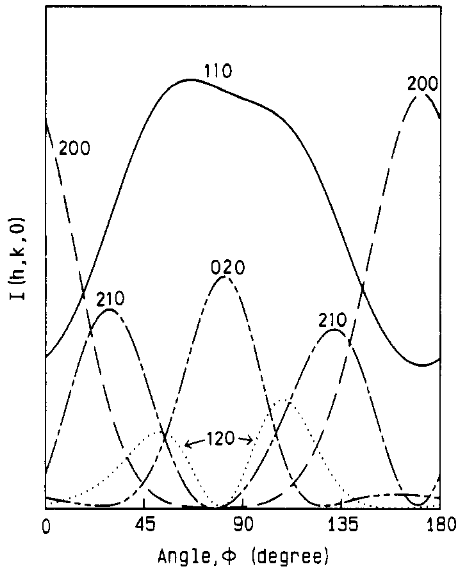

Figure 11. The WAXD intensity distribution on angle ϕ calculated for the structure in Figure 9b.

Apart from the sequence distribution, a careful examination of the WAXD meridional reflection reveals that annealing causes significant changes in the peak position and the width of the d = 2.08 Å reflection (2θ = 43.8°). Figure 8 shows the dependence of the d spacing and integrated band width of the d = 2.08 Å reflection on annealing temperature. The d = 2.08 Å reflection approximately corresponds to the 003 reflection of the HBA unit and 004 reflection of the HNA unit. The HBA and HNA units are not necessarily aligned parallel to the fiber axis, but there will be a distribution of projected repeating units depending on the conformation of aromatic ester linkage. The increase in d spacing with increasing annealing temperature suggests that the molecular chains rearrange into a more extended conformation upon annealing. On the other hand, the extent of the WAXD line broadening of the d = 2.08 Å reflection was shown to give the lower limit of the persistence length of the stiff molecular chains.[6,8,10,11] The integrated width of the d = 2.08 Å reflection slightly decreases with increasing annealing temperature, which suggests an increase in the persistence length of the molecular chains. Consequently, the observed changes in the d = 2.08 Å reflection result from extension and stiffening of the molecular chains through a change in the conformation of the aromatic ester linkage.

Structure of the Orthorhombic Lattice. In order to examine the structure of orthorhombic lattice, the intensity of equatorial reflections of WAXD was calculated as a function of the angle, ϕ between the aromatic plane and the 100 plane. The structural models used for the calculation are shown in Figure 9. Structure **a** corresponds to the 2/1 helix with the aromatic planes parallel to the fiber axis, whereas the aromatic planes are inclined from the fiber axis forming a trans zigzag conformation in structure **b**. The dependence of the WAXD intensity on the inclination angle, ϕ, of the aromatic plane is shown in Figures 10 and 11. Structures **a** and **b** gave analogous results.

The intensity of the equatorial reflections is shown to be sensitive to the orientation of the aromatic plane in the 001 plane, which makes it possible to consider a structure for the orthorhombic lattice of the copolyester. The intensity of the *hk*0 reflections shows a maximum when the aromatic plane is nearly parallel to the *hk*0 planes. The 020 reflection ($2\theta = 32.2°$) is absent from the observed equatorial profile of WAXD, which excludes the possibility of alignment of the aromatic plane in the 010 plane. The ϕ angle can be evaluated from the intensity ratio of the 110 and 200 reflections, I_{110}/I_{200}.

Although the peak height of the 110 reflection is nearly twice as high as that of the 200 reflection, the curve fitting (Figure 4) suggests that the 200 reflection is much broader than the 110 reflection and that the intensity of the 200 reflection is higher than that of the 110 reflection. Although the intensity ratio of the two reflections depends upon the details of the cruve fitting, the value of I_{110}/I_{200} lies in the range of 0.5–1. Thus the possible angle range was determined to be 6–16° and 140–156°.

From the symmetry of the hexagonal lattice, it is expected that the molecular chains have cylindrical or 3-fold symmetry when projected on the 001 plane. Since completely random rotation of aromatic planes around the fiber axis is not allowed for steric reasons, the aromatic planes are oriented in three equivalent directions in the hexagonal lattice and rotationally correlated with neighboring chains. On the other hand, the present calculation of WAXD intensity shows that only two regions are possible for a rotational angle in the orthorhombic lattice.

In the molten state, the aromatic planes might be freely distributed along the chain axis. When the extruded polymer is cooled, the molecular chains with the conformational disorder are frozen. Although a lateral interchain correlation of aromatic planes exists, the aromatic planes of one molecular chain are less correlated along the chain axis in the as-extruded sheet. This model corresponds to the condis crystal in the classification proposed by Wunderlich.[19] Molecular chains with the disordered conformation can pack in a hexagonal lattice. On annealing, the disordered conformation tends to be transformed into the energetically stable form having 2-fold symmetry, as was found in the molecular chains of the HBA homopolymer. Molecular chains with an ordered conformation can no longer stay in the hexagonal array, which induces the structural transition to the orthorhombic packing. The enhancement of conformational order by annealing is consistent with the experimental finding that the projection of monomer repeat units on the fiber axis increases with increasing annealing temperature. As a result, the hexagonal–orthorhombic transition is concerned with the increase of conformational order by annealing.

References and Notes

(1) Hay, I. Abstracts of the 39th Pittsburgh Diffraction Conference, Cleveland, OH, Nov 1981.

(2) Blackwell, J.; Lieser, G.; Gutierrez, G. A. *Macromolecules* **1983**, *16*, 1418.

(3) Geiss, G.; Volksen, W.; Tsay, J.; Economy, J. *J. Poly. Sci., Polym. Lett. Ed.* **1984**, *22*, 433.

(4) Leiser, G. *J. Polym. Sci., Polym. Phys. Ed.* **1983**, *21*, 1611.

(5) Hanna, S.; Windle, A. H. *Poly. Commun.* **1988**, *29*, 236.

(6) Chivers, R. A.; Blackwell, J.; Gutierrez, G. A. *Polymer* **1984**, *25*, 435.

(7) Blackwell, J.; Gutierrez, G. A.; Chivers, R. A. *Macromolecules* **1984**, *17*, 1219.

(8) Blackwell, J.; Biswas, A.; Bonart, R. C. *Macromolecules* **1985**, *18*, 2126.

(9) Chivers, R. A.; Blackwell, J. *Polymer* **1985**, *26*, 997.

(10) Biswas, A.; Blackwell, J. *Macromolecules* **1987**, *20*, 2997.

(11) Mitchell, G. R.; Windle, A. H. *Colloid Polym. Sci.* **1985**, *263*, 230.

(12) Windle, A. H.; Viney, C.; Golombok, R.; Donald, A. M.; Mitchell, G. R. *Faraday Discuss. Chem. Soc.* **1985**, *79*, 55.

(13) Hanna, S.; Windle, A. H. *Polymer* **1988**, *29*, 207.

(14) Biswas, A.; Blackwell, J. *Macromolecules* **1988**, *21*, 3146, 3152, 3158.

(15) Butzbach, G. D.; Wendorff, J. H.; Zimmermann, H. J. *Polymer* **1986**, *27*, 1337.

(16) Lin, Y. G.; Winter, H. H. *Macromalecules* **1988**, *21*, 2439

(17) Nakayama, K.; Kyotani, M.; Kaito, A. The proceedings of the 39th Japanese Joint Conference for the Technology of Plasticity, Yokohama, Japan, Oct 1988.

(18) Hummel, J. P.; Flory, P. J. *Macromolecules* **1980**, *13*, 479.

(19) Wunderlich, B.; Moller, M.; Grebowicz, J.; Baur, H. In *Advances in Polymer Science*; Springer-Verlag: Berlin, 1988; p 1.

Registry No. HNA, 81843-52-9.