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Transesterification in Blends of Wholly Aromatic Thermotropic Copolyesters

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ABSTRACT: The X-ray diffraction data for the copolyesters prepared from *p*-hydroxybenzoic acid (HBA) and 2-hydroxy-6-naphthoic acid (HNA) give nonperiodic layer lines that indicate a completely random monomer sequence distribution and also provide analytical information on the monomer proportions. Hence, these data provide a unique method to study transesterification between copolyesters with different monomer ratios. Immediately after melt blending, mixtures of the 30/70 and 75/25 copolymers exhibit a single solid–nematic transition at a temperature well below either the transitions of the starting copolymers or those of intermediate compositions. However, the meridional maxima for both starting copolymers can be resolved in the fiber diffraction patterns, which indicates the formation of a compatible blend. Compression molding of the melt-blended samples at 315 °C results in transesterification, leading to a random copolymer of intermediate composition after 1 h. The progress of this reaction is followed by monitoring the shift in position of the first meridional maxima as a function of time, until they merge to give a single maximum at the *d*-spacing characteristic of the random copolymer of intermediate composition. During this process, the temperature of the solid–nematic transition slowly rises until it reaches the value for the intermediate composition.

Introduction

Copolyesters of *p*-hydroxybenzoic acid (HBA) and 2-hydroxy-6-naphthoic acid (HNA) form nematic melts as a result of their highly extended conformations. X-ray diffraction patterns of melt-spun fibers of these copolymers contain nonperiodic layer lines that can be reproduced with high accuracy for models consisting of arrays of parallel chains of completely random sequence.[1-3] Three-dimensional models incorporating a pseudodimer repeat and limited axial register between chains reproduce the sharp equatorial and off-equatorial reflections that are observed in fiber diagrams[4-6] and also predict a sharpening of the meridional reflections as a result of chain packing. These nonperiodic diffraction data also provide analytical information, in that the *d*-spacings of the meridional maxima are specific for the HBA/HNA monomer composition. The first meridional maximum varies from 6.64 to 8.08 Å as the HBA content decreases from 80 to 20% (Figure 1). The maximum corresponds approximately to the average advance per monomer unit along the fiber axis, which is 6.35 and 8.37 Å for HBA and HNA, respectively, and within experimental error allows the monomer ratio to be determined to within ±1% in the intermediate composition range. These data present an ideal way to investigate possible nonrandomness in monomer sequence, although to date there have been no reports of anything other than random statistics. Consequently, the data can be expected to be very sensitive to changes in sequence distribution resulting from transesterification in melt blends of copolyesters of different monomer ratios, which is the subject of this paper.

As described previously,[1-3] the nonperiodic layer lines in the fiber pattern of poly(HBA/HNA) can be predicted as the Fourier transform of the monomer nearest-neighbor correlation function, $Q(z)$, along the chain axis, z. Modification of $Q(z)$ enables us to consider both random and nonrandom sequence statistics, and the results obtained have consistently pointed to completely random sequences. $I(Z)$, the calculated intensity scattered along the chain axis direction, is for a nematic structure, with random axial staggering of adjacent chains. In the solid state there is some degree of registration of the chains: we have proposed that there is approximate registration of short sections of the chains at their centers;[4-6] Windle and coworkers suggest that identical sequences segregate to form ordered nonperiodic lattices.[7,8] The effect of registration is to modify the intensities along the individual layer lines, and this is the likely explanation for the sharpness of the first observed meridional maxima. However, the positions of the layer lines, i.e., their Z coordinates, are unaffected by the mode of chain packing.

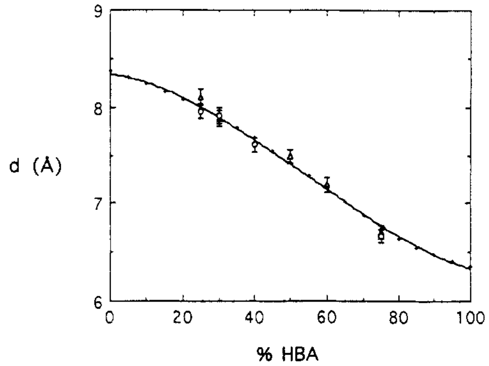

Figure 1. First meridional *d*-spacing as a function of the HBA content in HBA/HNA random copolyesters.

A consequence of the above is that the diffraction pattern of a mixture of two random copolymers will be different from that of a simple random copolyester of average composition. As a simple example, consider a mixture of a 75/25 and a 25/75 copolymer of monomers A and B in equimolar proportions to give an overall 50/50 monomer ratio. $Q(z)$ for the mixture is the sum of the $Q(z)$ terms for the two copolymers, which is different from $Q(z)$ for the 50/50 polymer. For example, the concentrations of the four constituent dimers are equal for the random 50/50 copolymer ($[AA] = [AB] = [BA] = [BB] = {}^1/_4$) whereas for the mixture the AA and BB dimers are more abundant ($[AA] = [BB] = {}^5/_{16}$; $[AB] = [BA] = {}^3/_{16}$) and similarly for the higher terms. Thus the layer lines predicted for the mixture are a combination of those predicted for the

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two components treated separately. The layer line intensities will also depend on the chain packing and will probably be different depending on whether or not we have a compatible or incompatible blend, but the layer line positions will stay the same. If transesterification occurs, then the statistics of both copolymers will change, causing shifts in the positions of the layer lines. Ultimately we will obtain the completely randomized copolymer, which will have the layer lines characteristic of the intermediate composition.

Transesterification of melt-blended polyesters in the isotropic state has been studied extensively,[9] but there has been less attention to blends of liquid crystalline polyesters. Mühlebach *et al.*[10] report the rapid transesterification of mixed powders of poly(HBA) and poly(HNA) under pressure at 450 °C. The homopolymers are infusible but can be sintered above a thermal transition in the 330–350 °C range. Application of heat and pressure to a 50/50 mole ratio mixture of the homopolymers resulted in a copolymer with a solid–nematic transition at approximately 254 °C, pointing to the formation of the random copolymer via transesterification. Changes in nearest-neighbor statistics were verified by ^{14}C-NMR. Economy *et al.*[11] have also suggested that sequence changes may occur when copoly(HBA/HNA) is annealed just below the solid to nematic transition, but this could not be confirmed by NMR. Lenz *et al.*[12] describe sequence changes due to transesterification under certain conditions, suggesting that nonrandom sequence distributions can result due to preference for homopolymer crystallization.

Transesterification between isotropic polyesters has been investigated by using small-angle neutron scattering to follow changes in the apparent molecular weight in blends of deuterated and undeuterated polymers.[13] Random scission and recombination of chains resulted in progressively smaller blocks of the deuterated component. The Arrhenius plot for poly(ethylene terephthalate) yielded an activation energy of 152 kJ/mol for the transesterification reaction. A similar value was obtained for a more rigid wholly aromatic copolyester,[14] and differences in rate constants for different molecular weight polymers suggested an activated end-group mechanism. Mühlebach *et al.*[10] have also reported a reduction in the rate of transesterification between poly(HBA) and poly(HNA) for higher molecular weight polymers, which they attributed to either the decreased number of end groups or a higher melt viscosity. However, studies of a mesomorphic polyester[15] indicated that transesterification is independent of molecular weight in the isotropic melt.

The problem of transesterification of a blend of two preparations of poly(HBA/HNA) of different compositions has been addressed previously by DeMeuse and Jaffe.[16] They combined the 30/70 and 75/25 copolymers in the melt and found that the first meridional maxima merged to give a single broad peak, at intermediate *d*-spacing. DSC data suggested the existence of a compatible blend in the solidified sample. They argued that there had been no transesterification in the specimen used for X-ray work and that the observed broad first meridional maximum is made up of the unresolved maxima for the two components. However, closer examination of their data suggests partial randomization, as will be discussed below. In the work described here we have used X-ray methods to reexamine the transesterification of copoly(HBA/HNA) blends in an analytical manner.

Experimental Section

Specimens of 75/25, 30/70, and 58/42 copoly(HBA/HNA) were generously provided by Hoechst Celanese Co., Summit, NJ, in the form of melt-extruded pellets. Fibers of these copolyesters or blends thereof were drawn by hand from the nematic melt on a hot plate. The melt blend of 30/70 and 75/25 copoly(HBA/HNA) was obtained by first weighing either chopped fibers or pellets of the two copolymers in proportion to give an overall monomer mole ratio of 60/40. The mixture was melted at 310 °C and stirred thoroughly by hand using a metal spatula for 5 min. Fibers were drawn from the nematic melt using tweezers, and these were aligned parallel to each other in bundles for mounting in an X-ray camera or on a diffractometer.

Compression molding of chopped fibers was performed using a Carver Laboratory Press. The platens were preheated to 315 °C, after which the sample was inserted and allowed to equilibrate without the application of pressure for 10 min. Specimens were subjected to 1800 psi of pressure of 315 °C for specified lengths of time ranging from 0 to 72 min and then cooled to room temperature within 20 min. The samples were then remelted, and fibers were drawn as described above.

X-ray fiber diagrams were recorded on Kodak "No-Screen" film using Ni-filtered Cu Kα radiation and toroidal collimation. The *d*-spacings of the maxima along the meridian (fiber axis direction) were calibrated using CaF$_2$.

$\theta/2\theta$ diffractometer scans along the fiber axis direction were obtained using either a Philips P3100 diffractometer or Rigaku Rotaflex diffractometer in transmission mode, with the incident and detector slits set at 0.15°. Scans over 2θ = 3–50° were performed at 0.01° increments using 10-s counting intervals. Higher resolution scans of the 2θ = 7–17° region utilized a 0.02° increment and a 160-s counting interval. Resolution of the component peaks was accomplished using a Gaussian–Lorentzian curve-fitting program.

Differential scanning calorimetry (DSC) scans were obtained using a Perkin-Elmer DSC-7. Data were recorded in the temperature range of 150–350 °C, with a heating/cooling rate of 20 °C/min. The temperature of the solid–nematic transition, T_m, was determined from the second heating scan.

The transesterification reaction was monitored by obtaining X-ray and DSC data for the following specimens, all in the form of melt-spun fibers:

(1) The initial specimens of 75/25, 58/42, and 30/70 copoly(HBA/HNA).

(2) A physical mixture of 75/25 and 30/70 copoly(HBA/HNA) fibers. These fibers were weighed in a proportion such that the overall monomer ratio was 60/40.

(3) A compression-molded mixture of 75/25 and 30/70 copoly(HBA/HNA). A physical mixture as described in (2) was chopped finely and thoroughly mixed. This sample was then compression molded for 1 h.

(4) A melt blend of 75/25 and 30/70 copoly(HBA/HNA) with an overall 60/40 HBA/HNA mole ratio.

(5) Compression-molded melt blends of 75/25 and 30/70 copoly(HBA/HNA). Finely chopped fibers of the melt blend described in (4) were divided into 80-mg portions and compression molded at 315 °C for times ranging from 0 to 72 min.

Results

Diffractometer scans of 75/25, 58/42, and 30/70 copoly(HBA/HNA) are shown in Figure 2. The *d*-spacings of the observed maxima are given in Table 1. The greatest sensitivity to monomer composition is seen in the first maximum, which occurs at *d* = 6.67, 7.15, and 7.90 Å for these three copolymers, respectively. Thermal analysis of these copolymers indicates a single solid–nematic transition occurring at T_m = 288, 248, and 303 °C, respectively. All of these data are consistent with previously reported literature values.[17] The 58/42 specimen was the closest to 60/40 that was available. The 2% difference in the monomer ratio would shift the first maximum from *d* = 7.18 Å to *d* = 7.14 Å, based on predictions for the diffraction pattern for the 60/40 copolymer (following ref 4). T_m for the 58/42 and 60/40 copolymers are approximately the same.[18]

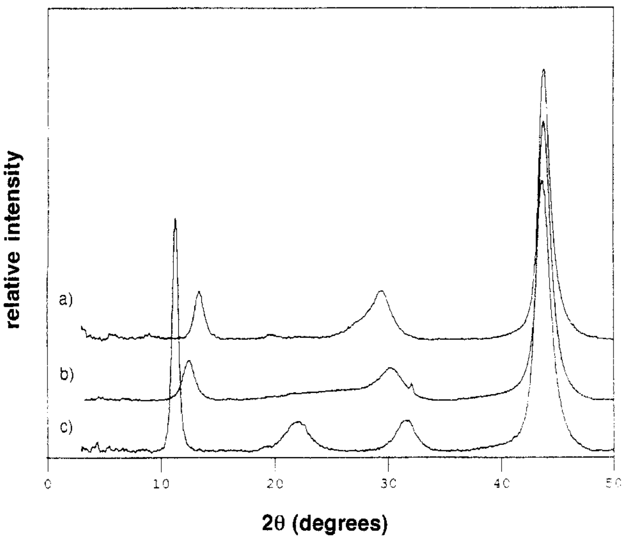

Figure 2. $\theta/2\theta$ diffractometer scans along the fiber axis direction for melt-spun fibers of (a) 75/25, (b) 58/42, and (c) 30/70 copoly(HBA/HNA).

Table 1. *d*-Spacings (Å) for Observed Meridional Maxima of Copoly(HBA/HNA) Specimens from Film Measurements

58/42	30/70	75/25	physical mixture[a]	molded mixture[b]	melt blend[c]	molded blend[d]
	7.90		7.90	7.92	7.91	
7.15 ± 0.07						7.12
		6.67	6.67	6.76	6.70	
	4.08		4.06		4.12	
		3.06	3.04	3.00	3.08	
2.96 ± 0.03						2.96
	2.87		2.89		2.88	
2.08 ± 0.01	2.08	2.07	2.07	2.08	2.08	2.08

[a] Mixture of fibers of 75/25 and 30/70 copoly(HBA/HNA); overall monomer mole ratio 60/40. [b] Specimen in *a* after compression molding at 315 °C for 30 min. [c] Melt blend of 75/25 and 30/70 copoly(HBA/HNA); overall monomer mole ratio 60/40. [d] Specimen in *c* after compression molding at 315 °C for 60 min.

The diffractometer scan of a physical mixture of 75/25 and 30/70 copolymer fibers is shown in Figure 3, curve a. These data are essentially identical to those obtained by combining the scans of the component copolymers from Figure 2 according to the weight ratio in the mixture, as is shown is Figure 3, curve b. A DSC scan of the physical mixture is shown in Figure 3, curve a. Thermal transitions occur at 303 and 287 °C corresponding to the component copolymers. A specimen held at 350 °C for 30 min exhibits transitions at 304 and 282 °C, as shown in Figure 3, curve b. The lowering of the latter transition is within the spread of T_m reported for these specimens depending on thermal history. It is possible that this shift may be due to diffusion of one copolymer into the other while in the nematic melt or to minor transesterification, but the absence of more major changes suggests that the specimen still contains separate domains of the starting copolymers.

The compression-molded physical mixture gave the meridional *d*-spacings as determined from film measurements reported in Table 1. Table 1 compares the observed *d*-spacings with those for the untreated physical mixture. The first maximum at d = 7.92 Å is within experimental error that observed for the 30/70 copolymer. The second maximum at d = 6.76 Å is somewhat shifted from the value of d = 6.67 Å for the 75/25 copolymer. Similarly, the maximum at d = 3.00 Å differs from the value of d = 3.06 Å for the 75/25 copolymer. This and the general broadening of the peaks suggest that some transesterification has occurred during compression molding of the physical mixture, but the extent of reaction is minimal.

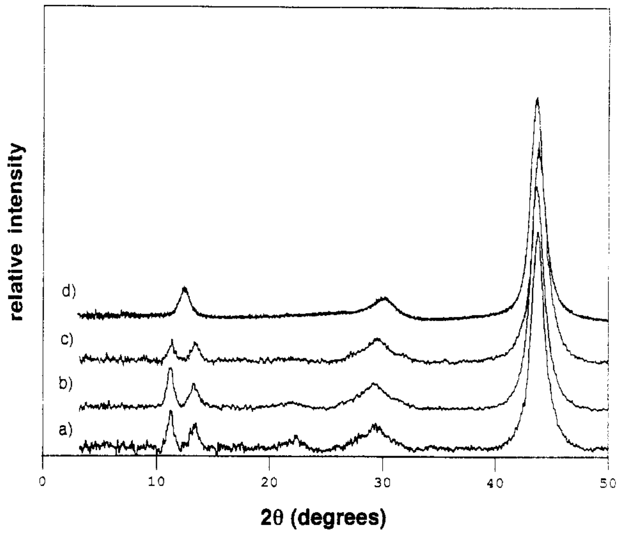

Figure 3. (a) $\theta/2\theta$ scans along the fiber axis direction for a physical mixture of melt-spun fibers of 75/25 and 30/70 copoly(HBA/HNA). The overall monomer mole ratio was 60/40. (b) Addition of $\theta/2\theta$ diffractometer scans for 75/25 and 30/70 copoly(HBA/HNA) (Figure 1, curves a and c) in weight proportion to give a 60/40 monomer mole ratio. (c) Diffractometer scan for melt-blended 75/25 and 30/70 copoly(HBA/HNA). (d) Diffractometer scan for melt-blended 75/25 and 30/70 copoly(HBA/HNA) after compression molding at 315 °C for 60 min.

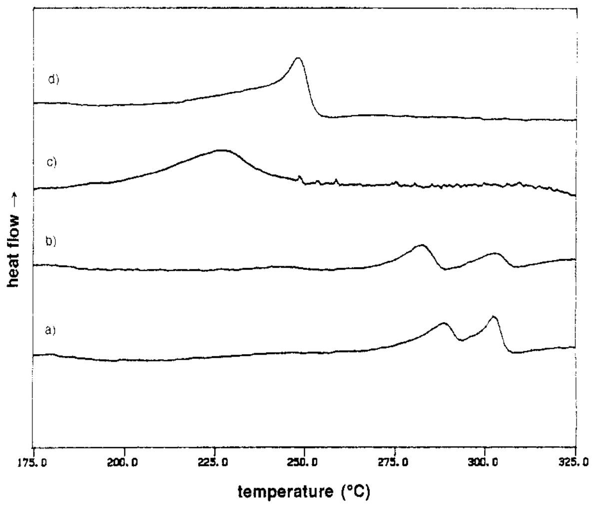

Figure 4. DSC second heating scans of (a) a physical mixture of 75/25 and 30/70 copoly(HBA/HNA), (b) the same physical mixture after thermal treatment at 350 °C for 30 min, (c) a melt blend of 75/25 and 30/70 copoly(HBA/HNA), and (d) the same melt blend after compression molding at 315 °C for 60 min.

The DSC data for the compression-molded physical mixture show a transition for the 30/70 copolymer at 302 °C, but the lower transition (if any) is broad and weak. The fact that the 75/25 copolymer has a lower T_m and hence a lower viscosity at 315 °C may allow for more extensive diffusion of the 30/70 copolymer into this phase, rather than vice versa, resulting in a broadening of the melting transition.

Figure 3, curve c, shows the diffractometer scan for the initial melt-blended specimen. The *d*-spacings of the observed maxima are given in Table 1 and are within experimental error the same as those for the physical mixture. The decrease in certain peak heights, particularly at 7.91 Å, may be due to poorer three-dimensional packing of the 30/70 copolymer and an overall reduction of crystallinity in the melt blend. Figure 4, curve c, shows the DSC scan for the same specimen with a single T_m at 227 °C, well below that of the 58/42 copolymer (248 °C) and those of the component 30/70 and 75/25 copolymers.

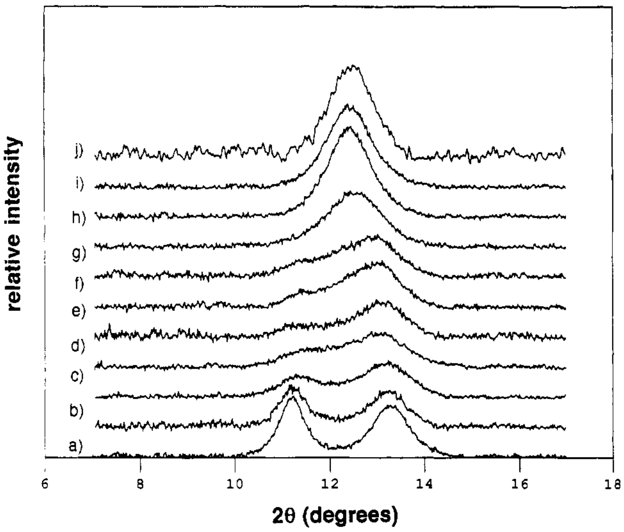

Figure 5. $\theta/2\theta$ meridional diffractometer scans of the 2θ = 7–17° region for the melt blend of 75/25 and 30/70 copoly(HBA/HNA) after compression molding at 315 °C for (a) 0, (b) 9, (c) 18, (d) 27, (e) 36, (f) 45, (g) 54, (h) 60, (i) 66, and (j) 72 min.

It appears that melt blending has resulted in the formation of a compatible blend, i.e., an intimate mixture at the molecular level, but there has not been significant transesterification during this process. Figure 3, curve d, is the diffractometer scan of the melt-blended specimen that had been compression molded at 315 °C for 60 min. The *d*-spacings of the observed maxima are given in Table 1 and are within experimental error those of the random 60/40 copolymer. Figure 4, curve d, shows the DSC data for the same specimen, with a single T_m at 248 °C which matches the value for the random 58/42 copolymer and indicates a random copolymer of similar composition. There are no further changes in the meridional diffraction pattern or T_m after compression molding for times up to 72 min. We can conclude that transesterification is complete in this specimen and has resulted in complete sequence randomization.

Figure 5 shows meridional X-ray diffractometer scans of the 2θ = 7–17° region for melt-blended specimens subjected to compression molding at 315 °C for times ranging between 0 and 72 min. The maxima characteristic of the starting copolymers are seen to shift slowly toward each other as the molding time increases. The two component peaks were resolved using a Gaussian–Lorentzian curve-fitting program. Figure 6 shows typical curve-fitting data. It should be noted that the first meridional peaks for the starting copolymers are not Gaussian nor Lorentzian but are asymmetrical, being broader on the higher 2θ side of the peaks. However, fitting the peaks with a symmetrical function does not affect the position of maximum intensity within experimental error. Table 2 lists the *d*-spacings determined from the resolved peaks. These data are plotted against molding time in Figure 7. It is seen that there is a steady but nonlinear change in *d*-spacings until the two peaks converge after 60 min. DSC scans of the same specimens are shown in Figure 8, where it is observed that T_m shifts slowly from 227 to 248 °C. T_m is plotted against compression-molding time in Figure 7, where we see an approximately linear correlation.

Discussion

From the above results it is clear that melt blending the 30/70 and 75/25 copolymers results first in the formation of a compatible blend, based on the single melt transition

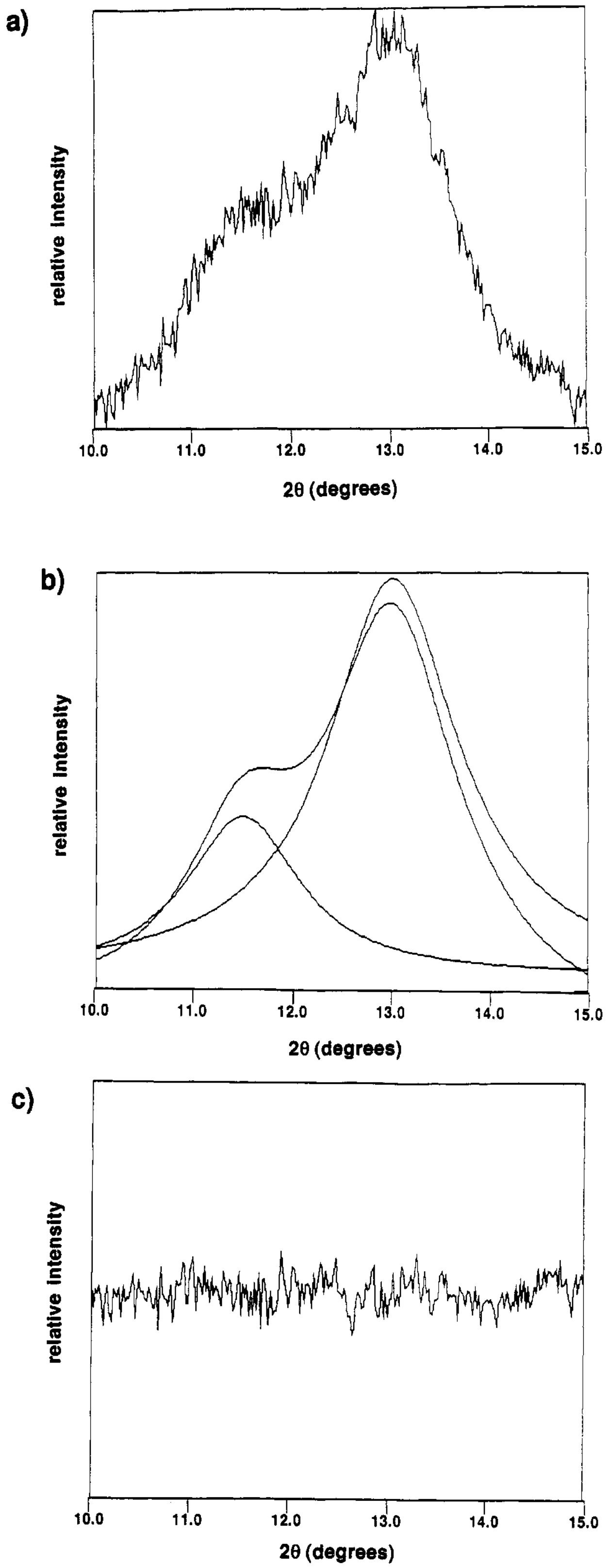

Figure 6. Curve-fitting data for Figure 5, curve d: (a) initial data; (b) best fit using two Gaussian–Lorentzian functions; (c) subtraction of the best fit curve from observed data.

observed by DSC measurements. Although at present we have no quantitative viscosity data, melt blending results in significant decrease in melt viscosity to the extent that the melt becomes much easier to stir on the hot plate. DeMeuse and Jaffe also report a negative deviation from the rule of mixtures for the viscosities of melt blends of 30/70 and 75/25 HBA/HNA.[16] The X-ray data for the initial melt blend indicates that the specimen has the same copolymerization statistics as the physical blend, but the

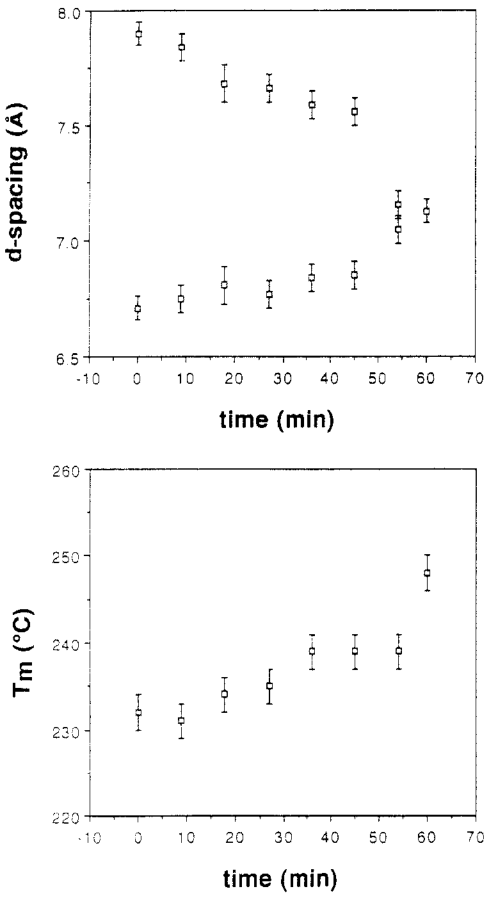

Figure 7. (a) Plots of *d*-spacing(s) vs compression-molding time for the first and second meridional intensity maxima for the compression-molded melt blend of 75/25 and 30/70 copoly(HBA/HNA). (b) Plot of T_m vs compression-molding time for the same specimens.

Table 2. First Meridional *d*-Spacing(s) of Melt-Blended 75/25 and 30/70 Copoly(HBA/HNA) after Compression Molding at 315 °C

molding time (min)	*d*-spacings (Å)	
0	6.71 ± 0.05	7.90 ± 0.05
9	6.75 ± 0.06	7.84 ± 0.06
18	6.81 ± 0.08	7.68 ± 0.08
27	6.77 ± 0.06	7.66 ± 0.06
36	6.84 ± 0.06	7.59 ± 0.06
45	6.85 ± 0.06	7.56 ± 0.06
54	7.05 ± 0.06	7.16 ± 0.06
60	7.13 ± 0.05	

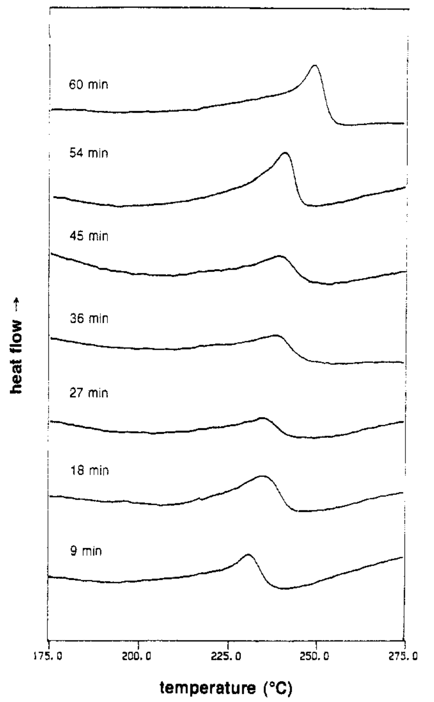

Figure 8. DSC second heating scans of the melt blend of 75/25 and 30/70 copoly(HBA/HNA) after compression molding at 315 °C for different times.

single T_m at lower temperature points to the formation of a solution of one copolymer in the other. Further evidence comes from the time-dependent changes in the X-ray data for the compression-molded melt blend. Transesterification leading to changes in sequence distribution of an incompatible blend would occur preferentially at the edges of the domains, resulting in copolymers of intermediate compositions in those regions. The diffraction maxima of these copolymers would occur between those of the initial copolymers, and the resulting pattern would show a filling in of the region between the two initial peaks, as the latter gradually decreased in intensity. Overall, one would expect to obtain one broad peak in the region d = 8.5–6.3 Å, which would gradually sharpen and become a more narrow peak at d = 7.13 Å when the copolymer fully randomized throughout the blend. This probably explains the broadening of the diffraction maxima for the compression-molded physical blend, and it seems reasonable that with increased compression-molding time or at higher temperatures this specimen would also eventually undergo complete randomization.

Our data indicate that X-ray diffraction can be used relatively easily to follow the transesterification reaction in the HBA/HNA copolymers. It can be seen that the changes in *d*-spacings are not linear but proceed slowly in the initial stages of reaction and more rapidly later in the reaction. Early in the reaction, the compatible blend will be converted into block copolymers consisting of relatively long blocks of the 30/70 and 75/25 copolymers. At this stage, the nearest-neighbor monomer statistics are virtually indistinguishable from those of the unreacted blend. As the reaction progresses, the block lengths shorten and the increasing number of crossovers from 30/70 to 75/25 statistics leads to shifts in the meridional peaks. The position of the first maximum for a single random copolymer is defined largely by the correlations within chain segments of about five monomers, i.e., consideration of segments of six or more monomers in length does not significantly affect the position of this maximum. This may explain why the effects of transesterification on the *d*-spacing of the first maximum are more appreciable toward the end of the reaction. During the reaction, the copolymer structure changes from a mixture of two random copolymers to intermediate copolymers with nonrandom statistics and finally to a random copolymer of intermediate composition. This process can be addressed theoretically by methods described previously and allows us to investigate the mechanism and kinetics of the conversion in more detail, as will be described in a second paper.

Examination of the X-ray data of DeMeuse and Jaffe[16] for the melt blend of the 30/70 and 75/25 copolymers shows a single broad meridional peak in the d = 8.5–6.3 Å range, intermediate between those observed for the two original components. These authors suggest that the observed peak is the sum of the peaks for the two unreacted components, but in fact it is too narrow for this interpretation and is more similar to our data for a partially randomized specimen, e.g., curve f in Figure 5. In our work, we saw very little evidence for transesterification at 315 °C on the time scale of 1 h without the application of pressure. The application of pressure may bring neighboring chains into closer contact, making it possible for the transesterification reaction to occur more readily. Nevertheless some reaction is to be expected at atmospheric pressure, especially at higher temperatures and over longer times. The reported activation energies of transesterification of isotropic polyesters indicate that randomization should be complete within 30 min at 315 °C. For our system, the reaction is complete after 60 min, which suggests that the nematic structure does not have a large effect on the reaction.

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