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X-ray Analysis of the Kinetics of Transesterification in Blends of Wholly Aromatic Thermotropic Copolyesters

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ABSTRACT: The kinetics of the transesterification reaction occurring in blends of wholly aromatic copolyesters have been investigated by simulation of the changes that occur in the X-ray scattering data as a result of the interchange. The X-ray fiber diagrams of copolyesters prepared from *p*-hydroxybenzoic acid (HBA) and 2-hydroxy-6-naphthoic acid (HNA) contain nonperiodic diffraction maxima along the chain axis direction that vary in position (scattering angle) with the monomer composition and are due to the structural correlations in chains of completely random comonomer sequence. Melt blends of two different compositions initially show the scattering maxima of both components, but these shift as the specimen is held in the melt, until they merge to give the diffraction data characteristic of the intermediate composition. We have simulated the changes in these data by modeling the changes in the correlation function that occur as a result of the transesterification reaction. We find that the data are best reproduced using a completely random interchange model for a completely compatible blend. Simulations based on preferential reactivities of one or other of the monomers or partial segregation of one phase gave significantly inferior agreement with the positions of the observed diffraction maxima. The statistical modeling allows us to derive kinetic parameters for the reaction, for which we obtain an activation energy of 142 kJ/mol and a rate constant of 2.3×10^{-4} s^{-1} at 315 °C. Compared to the equivalent data for isotropic polyesters, the activation energy compares very well, but the rate constant is 1 order of magnitude lower, perhaps due to the ordering in the thermotropic melt.

Introduction

In a previous paper[1] we showed that transesterification in melt blends of thermotropic wholly aromatic copolyester can be followed by X-ray diffraction methods. Copolyesters prepared from *p*-hydroxybenzoic acid (HBA) and 2-hydroxy-6-naphthoic acid (HNA) give rise to nonperiodic diffraction maxima along the chain axis direction that occur at different scattering angles depending on the monomer ratio. We found that melt blending two preparations of copoly(HBA/HNA) with different monomer ratios leads initially to a compatible blend that shows the scattering maxima characteristic of both compositions. When this blend is maintained in the melt, i.e. above the solid state-to-nematic transition temperature (T_m), these maxima shift slowly due to the changes in the sequence distribution resulting from transesterification, until they merge to give the maxima characteristic of the intermediate random composition. This paper describes theoretical modeling of the structural changes that occur during the transesterification reaction, in order to predict the changes in the diffraction pattern as a function of time. The analysis provides a route to define the reaction kinetics.

It has been shown that transesterification in isotropic melt blends of polyesters can lead to random or blocky microstructures, depending on the conditions.[2−4] Blocky sequences can result from crystallization-induced reaction at lower temperatures, whereas randomization occurs at higher temperatures. Physical manifestations of transesterification are shifts in the thermal transitions, increased compatibility, and changes in solubility. The chemical changes have been followed by infrared[5,6] and NMR spectroscopy.[7−9] The latter techniques are most readily applied when the component monomers have significantly different chemical structures and where the initial and final products are soluble. Neutron scattering has also been used to follow the reaction between deuterated and undeuterated poly(ethylene terephthalate): the reaction led to progressively shorter deuterated blocks, until complete randomization was achieved.[10−12] The extent of transesterification was determined to be a linear function of reaction time: the data followed an Arrhenius relationship, with an activation energy of 152 kJ/mol and a rate constant of 1.87×10^{-3}.

The nonperiodic scattering maxima observed along the chain axis direction for copoly(HBA/HNA) are characteristic of extended, parallel chains of completely random comonomer sequence.[13−16] Random sequence distributions for copoly(HBA/HNA) have also been confirmed by ^{2}H-NMR analysis of diad frequencies.[8] Although nonrandom microstructures containing homopolymer or alternating copolymer blocks have been proposed[17] on the basis of DSC data for thermally annealed and other specimens with different thermal histories, such nonrandomness is not consistent with the available X-ray data, which rules out all but minimal blockiness. Similar X-ray analyses have demonstrated random microstructures in other wholly aromatic copolyesters, copolyimides and copolyamides.[18−20]

In our previous work,[1] we prepared a melt blend of 75/25 and 30/70 copoly(HBA/HNA) in the (monomer mole) ratio 2:1, such that the overall monomer composition was 60/40. The X-ray scattering by fibers drawn from the blend immediately after preparation is shown in Figure 1 (curve a). We observe maxima at $d = 7.91$, 4.12, and 2.88 Å due to the 30/70 copolymer and at $d = 6.70$ and 3.08 Å due to the 75/25 copolymer; the intense peak at $d = 2.08$ Å is given by both compositions. T_m for the melt blend was 227 °C, compared to 288 and 303 °C for the two components, respectively, suggesting that a substantially homogeneous, compatible blend had been achieved. Specimens of this blend were main-

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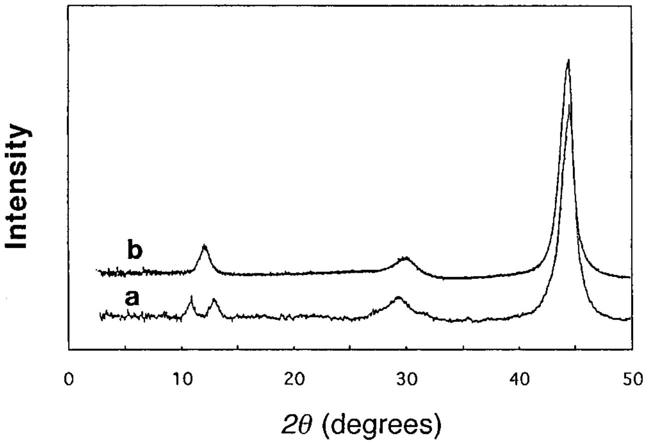

Figure 1. $\theta/2\theta$ wide angle X-ray diffractometer scans along the fiber axis direction for melt-spun fibers of a melt blend of 30/70 and 75/25 copoly(HBA/HNA): (a) immediately after melt blending; (b) after compression molding at 315 °C for 60 min. The overall monomer mole ratio was 60/40 (data from ref 1).

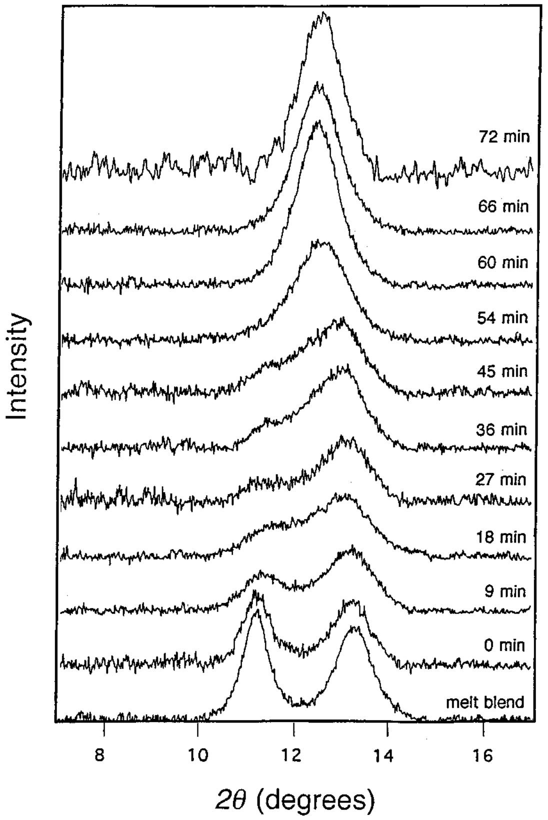

Figure 2. $\theta/2\theta$ diffractometer scans of the $2\theta = 7-17°$ region for the melt blend of 30/70 and 75/25 copoly(HBA/HNA) after compression molding at 315°C for different reaction times, as indicated on each curve (data from reference 1).

Table 1. *z*-Axis Atomic Coordinates for HBA and HNA Residues

HBA		HNA		
			z (Å)	
atom	z (Å)	atom	*cis*	*trans*
O1 (ester)	0.0000	O1 (ester)	0.0000	0.0000
C1	1.3814	C1	1.4127	1.3563
C2	1.8874	C2	2.0907	2.3519
C3	2.2522	C3	2.1340	1.7105
C4	3.2643	C4	3.4902	3.7017
C5	3.6290	C5	3.5333	3.0602
C6	4.1351	C6	4.1682	4.6972
C7 (carbonyl)	5.5838	C7	4.2115	4.0558
O2 (carbonyl)	6.0501	C8	5.5677	6.0471
O3 (ester)	6.3486	C9	5.6108	5.4055
		C10	6.2889	6.4012
		C11(carbonyl)	7.7747	7.8123
		O2 (carbonyl)	8.4617	8.1228
		O3 (ester)	8.3048	8.7439

tained at 315 °C for different lengths of time, after which fibers were drawn and X-ray data were recorded. After such heating for 60 min, we obtained the axial scattering data shown in Figure 1 (curve b). Three maxima are observed at $d = 7.12$, 2.96, and 2.08 Å, which are the same as those seen for a 60/40 random copolymer prepared by melt acetolysis of the monomers. The axial scattering data in the $d = 9-6$ Å region ($2\theta = 7-17°$) for specimens of the blend held in the melt for different times are shown in Figure 2. The maxima at $d = 7.91$ and 6.70 Å characteristic of the starting copolymers shift steadily toward one another, until they coalesce at $d = 7.12$ Å. T_m for these preparations also shifts steadily over this 60 min period from 227 to 248 °C, which again is characteristic of the 60/40 random copolymer.

In the work described below, we have simulated the diffraction effects due to transesterification in the blend of the 30/70 and 75/25 random copolymers. To do this, we have extended the analyses of the scattering by nonperiodic chains[21] to include the changes in sequence that result from interchange reaction between chains of different composition. It will be seen that we are able to reproduce the observed X-ray data in Figures 1 and 2, which can then be used to investigate the reaction kinetics.

Experimental Section

Molecular Models. The atomic coordinates for HBA and HNA were based on X-ray data for low molecular weight model compounds.[22-25] The HBA coordinates were identical to those used previously.[21] For HNA, we used two sets of coordinates corresponding to the *cis* and *trans* conformations of the monomer, with the planes of the naphthylyl and ester groups inclined at 10°. The coordinates of the *z*-axis projections of HBA and *cis*- and *trans*-HNA are given in Table 1. Analyses of the mechanical properties of HBA/HNA fibers[26] suggest that *cis*-HNA is the predominant conformation in these copolymers. The *cis:trans* ratio for HNA was refined to obtain the best agreement between the observed and calculated *d*-spacings for each comonomer composition, and ratios of 100:0, 81:19, and 68:32 were used for the 75/25, 60/40, and 30/70 copolymers, respectively. These ratios are consistent with the theoretical calculations of Troughton *et al.*[26] and were assumed to be unchanged during the course of the reaction. The atomic coordinates given in Table 1 are for models in which the ester oxygens linking successive monomers are collinear. Nonlinearity of the extended chains was modeled by incorporating a truncated Gaussian distribution of lengths for each monomer, centered on a average length that was 0.12 Å less than the distance between the ester oxygens, as has been described previously.[21] In principle the slit-collimated diffractometer data should be desmeared, but the effects on the peak positions would be very small, and we have not done this. Matching the observed and calculated peak positions would then require very minor changes (refinement) in the atomic coordinates for the average HBA and HNA monomers, and this would not affect the conclusions on the transesterification kinetics described below.

Scattering by Extended Aperiodic Copolymer Chains. The X-ray scattering along the chain axis direction, $I(Z)$, is calculated from the z-axis projection of the structure, where Z is the reciprocal space coordinate and z is the distance along the chain axis. For a nematic structure, $I(Z)$ can be calculated[18] for an isolated infinite chain of random sequence:

$$I(Z) = \sum_j p_j F_{jj}(Z) = 2\mathrm{Re}\sum_j \sum_k p_j F_{jk}(Z) \frac{M_{jk} \exp 2\pi i Z z_k(Z)}{1 - M_{jk} \exp 2\pi i Z z_k(Z)} \qquad (1)$$

p_j is the monomer mole fraction of monomer j, and z_k is the length of monomer k projected along the chain axis. Each M_{jk} term consists of the product of the monomer proportion p_j and the combinatorial probability, r_{jk}:

$$M_{jk} = \frac{r_{jk} p_k}{\sum_j r_{jk} p_j} \qquad (2)$$

When $r_{jk} = 0$, monomer j cannot be followed by monomer k, whereas random chain statistics occur when $r_{jk} = 1$; values of r_{jk} between 0 and 1 correspond to varying degrees of homopolymer blockiness. Normalization by the denominator in eq 2 is necessary to maintain chain continuity. $F_{jk}(Z)$ is the Fourier transform of the cross-convolution of monomer j with monomer k:

$$F_{jk}(Z) = \sum_u \sum_v f_{j,u} f_{k,v} \exp(2\pi i Z(z_{k,v} - z_{j,u})) \qquad (3)$$

f is the atomic scattering factor, and z is the atomic coordinate along the chain axis direction; where j, u and k, v designate the uth atom of monomer j and vth atom of monomer k, respectively.

Random Transesterification. For the blends, we will use B′/N′ and B″/N″ to designate the monomers of the 30/70 and 75/25 copolymers, respectively, so that effectively we consider four independent monomers. The mole fractions of the two copolymers are w and $1 - w$, respectively. Initially, we consider a model in which there is homogeneous mixing of the molecules, and interchange reaction between chains is random; i.e. there is no preference for reaction at a particular region of the chain or at a given type of monomer. We define a cross reaction parameter, r, which increases from 0 (no reaction) to 1 (complete randomization) during the reaction. Note that we only model detectable reactions, which are those between monomers originating from different starting copolymers (B′ or N′ reacting with B″ or N″, or vice versa), thereby altering the overall composition of a given chain. Reactions between 75/25 chains, for example, do not affect the sequence statistics.

At the start of the reaction ($r = 0$), the M_{jk} terms of eq 1 form a 4 × 4 matrix:

$$\begin{matrix} p_{B'} & p_{N'} & 0 & 0 \\ p_{B'} & p_{N'} & 0 & 0 \\ 0 & 0 & p_{B''} & p_{N''} \\ 0 & 0 & p_{B''} & p_{N''} \end{matrix} \qquad (4)$$

Here the zeros indicate there has been no cross reaction. When transesterification is complete ($r = 1$), there is equal probability for a given monomer to be followed by a monomer originating from the same or different type of copolymer (weighted by the starting amounts of each copolymer). After complete transesterification, the structure is described by the following M_{jk} matrix:

$$\begin{matrix} wp_{B'} & wp_{N'} & (1-w)p_{B''} & (1-w)p_{N''} \\ wp_{B'} & wp_{N'} & (1-w)p_{B''} & (1-w)p_{N''} \\ wp_{B'} & wp_{N'} & (1-w)p_{B''} & (1-w)p_{N''} \\ wp_{B'} & wp_{N'} & (1-w)p_{B''} & (1-w)p_{N''} \end{matrix} \qquad (5)$$

which leads to $I(Z)$ for the random copolymer of intermediate composition.

Over the course of the transesterification reaction, the intermediate copolymers must be nonrandom. They can be thought of as block copolymers composed of alternating segments of the two starting copolymers, the lengths of which decrease progressively until complete randomization is achieved. The matrix of M_{jk} terms becomes

$$1/L \quad \begin{matrix} wp_{B'} & wp_{N'} & r(1-w)p_{B''} & r(1-w)p_{N''} \\ wp_{B'} & wp_{N'} & r(1-w)p_{B''} & r(1-w)p_{N''} \\ rwp_{B'} & rwp_{N'} & R(1-w)p_{B''} & R(1-w)p_{N''} \\ rwp_{B'} & rwp_{N'} & R(1-w)p_{B''} & R(1-w)p_{N''} \end{matrix} \qquad (6)$$

where L is the matrix normalization factor and R is the normalized reaction probability factor:

$$L = w + r(1 - w) \qquad (7)$$

$$R = L[(1 - rw/L)/(1 - w)] \qquad (8)$$

Nonrandom Transesterification. It is possible that nonrandom sequence distribution in the intermediates may also be due in part to unequal *rates* of interchange at the different monomers. The combinatorial probabilities can be altered by weighting each M_{jk} term by a kinetic factor that depends on the monomers involved. As an example, consider the case in which the ester linkages following HBA monomers transesterify more readily. Initially, the proportions of B′B′ and B′N′ pairs would decrease more rapidly than N′B′ and N′N′ pairs in the B′/N′ copolymer. Correspondingly, the number of newly formed B′B″ and B′N″ pairs would increase more rapidly than N′B″ and N′N″ pairs. We define this using a parameter s, where $0 < s < 1$ and larger values of s correspond to higher rates of reaction for ester linkages following HBA monomers. The matrix of M_{jk} terms is now

$$1/L \quad \begin{matrix} wp_{B'}(1-s) & \mathrm{w}p_{N'}(1-s) & r(1+g)(1-w)p_{B''} & \mathrm{r}(1+g)(1-w)p_{N''} \\ wp_{B'} & wp_{N'} & r(1-w)p_{B''} & r(1-w)p_{N''} \\ r(1+g')wp_{B'} & r(1+g')wp_{N'} & \mathrm{R}(1-s')(1-w)p_{B''} & R(1-s')(1-w)p_{N''} \\ r\mathrm{w}p_{B'} & r\mathrm{w}p_{N'} & R(1-w)p_{B''} & R(1-w)p_{N''} \end{matrix} \qquad (9)$$

where

$$g = [w/r(1 - w)]\, s \qquad (10)$$

$$R = [w(1 - r) + r(1 - w)]/(1 - w) \qquad (11)$$

$$g' = p_B/p_B{}'\, g \qquad (12)$$

$$s' = \{wr/[w(1 - r) + r(1 - w)]\}g' \qquad (13)$$

For a given set of p_B, $p_{B'}$, and w, the only independent parameters are the extent of transesterification, r, and the monomer transesterification rate parameter, s. The latter may be a constant or may be allowed to vary with the extent of the reaction. The case where transesterification is kinetically favored *before* rather than *after* a given monomer, i.e. at the "hydroxyl" rather than the "carboxylic acid" end, can be modeled by reversing the sense of the atomic coordinates used to calculate the $F_{jk}(Z)$ terms.

Unreactive Domains. A further complexity is the possible existence of domains of, e.g., the minor component in a continuous matrix of the major component, due to incomplete mixing or complete or partial phase separation. As a result, a fraction of one or other of the polymers would be unavailable for reaction with the other. The X-ray studies of transesterification in blends of these copolyesters by DeMeuse and Jaffe[27] showed much slower changes than were seen in our work,[1] and we have suggested that the differences were due to less than complete mixing in their specimens. Rheological experiments suggest that domains exist even in melts of the unblended copolymers,[28,29] for which unsheared samples show a yield stress. This effect can be reduced or eliminated by holding the sample at high temperature or by preshearing and is probably due to residual order that persists for some time above T_m. Such ordering may inhibit mixing during melt blending, although the thermal properties of the blends argue against the existence of extensive unmixed domains.

To model the effect of unreactive domains, we define q as the fraction of the component that forms domains; $1 - q$ is the fraction of that component that is dispersed (or at the edges of the domains) and capable of random transesterification with the second component. q decreases as a function of r, i.e., the reaction time:

$$q = q_0(1 - r) \tag{14}$$

where q_0 is the initial fraction forming domains, since the domains would get progressively smaller due to reaction at the edges and vanish when $r = 1$. Effectively the blend has three components, but otherwise the treatment is the same as before.

Transesterification Kinetics. If x represents the number of transesterification events in a polymer with n ester linkages, the probability of reaction, P, at any given site is

$$P = 1 - (1 - 1/n)^x \tag{15}$$

The number of transesterification events per monomer is $\nu = x/n$, and as $n \rightarrow \infty$

$$P = 1 - e^{-N} \tag{16}$$

Assuming all ester bonds are equally accessible, the first reaction at a given site alters the chain statistics by altering first nearest neighbor probabilities. (Subsequent reactions at the *same* site have no effect on the overall statistics.[30]) For the component of mole fraction w in a blend of two copolyesters with different monomer ratio, the probabilities of the same or different pairwise combinations as a result of the reaction with the other copolymer species are

$$P_{\text{same}} = w[1 - P(1 - w)] \tag{17a}$$

$$P_{\text{other}} = w[P(1 - w)] \tag{17b}$$

The ratio $P_{\text{same}}/P_{\text{other}}$ can also be derived from the starting monomer ratios and the combinatorial probabilities in matrix (6):

$$P_{\text{same}}/P_{\text{other}} = w/r(1 - w) \tag{18}$$

Hence

$$r = wP_t/[1 - P_t(1 - w)] \tag{19}$$

and

$$\nu = \ln(1 + r/[w(1 - r)]) \tag{20}$$

Figure 3 shows a plot of ν versus r for the present blend of 30/70 and 75/25 copoly(HBA/HNA), for which $w = 0.342$. It can be seen that ν is an approximately linear function of r for $r < 0.5$. Thus, if we can determine r at different times during the reaction by matching the observed and calculated d-spacings of the nonperiodic scattering maxima, we can then obtain ν as a function of time and hence determine the kinetics for the transesterification reaction.

Results

Random Transesterification. Calculated $I(Z)$ data in the region of the first nonperiodic maxima derived using the random transesterification model for different values of r are shown in Figure 4. As r increases from 0 (no reaction), the peaks originally at $d = 6.70$ and 7.88 Å shift toward each other at $r = 0.1$ and merge into a single peak at $d = 7.16$ Å when $r = 0.20$. This peak then becomes progressively narrower, until the width becomes constant at $r \geq 0.40$. By definition, randomization is not complete until $r = 1$, but the breadth of the peaks predicted for random copolymers and their relatively close proximity means that for $r \geq 0.40$ we cannot distinguish the transesterification product from the completely random 60/40 copolymer.

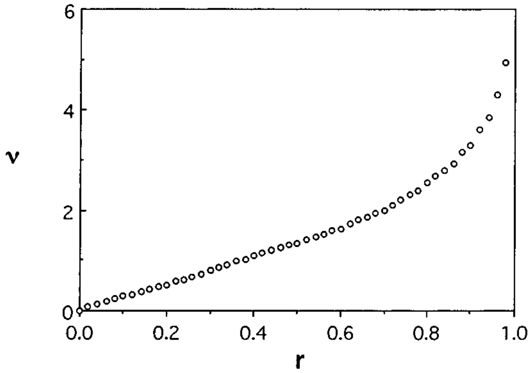

Figure 3. Plot of ν versus r for the relationship $\nu = \ln(1 + r/w(1 - r))$ for the bend of 75/25 and 30/70 copoly(HBA/HNA) with $w = 0.342$. ν is the number of transesterifications per monomer, r is the cross reaction parameter, and w is the initial mole fraction of the 30/70 copolymer.

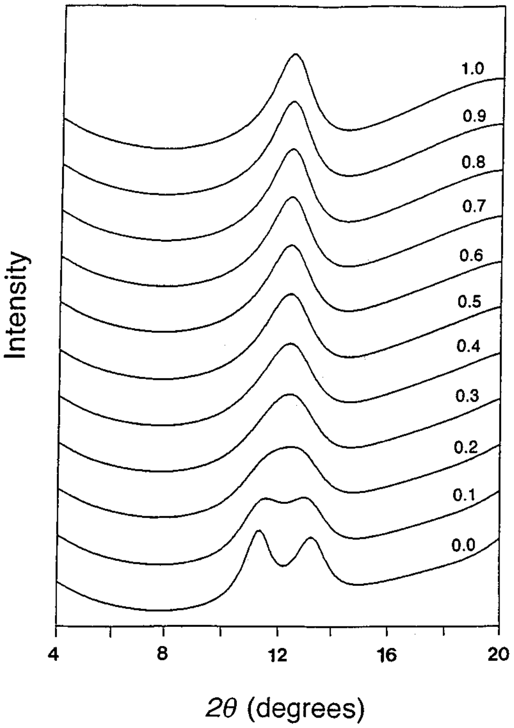

Figure 4. Predicted X-ray scattering along the chain axis direction for transesterified blends of 30/70 and 75/25 copoly(HBA/HNA) in the range $r = 0-1.0$ in increments of 0.1.

In order to explore further the sensitivity of the scattering data to r, we simulated the changes in the diffraction patterns that would occur during transesterification if the two homopolymers, poly(HBA) and poly(HNA), were combined in a 60:40 mole ratio, as shown in Figure 5. The first maxima for the original homopolymers shift toward one another and also broaden, until they merge at $r \cong 0.70$, and become indistinguishable from the peak at $d = 7.16$ Å for the random copolymer at $r \cong 0.85$. This modeling creates a 60/40 copolymer containing homopolymer blocks that get progressively shorter until randomization is achieved. Such blockiness was considered previously for the 58/42 copolymer by Biswas and Blackwell.[21] Converting

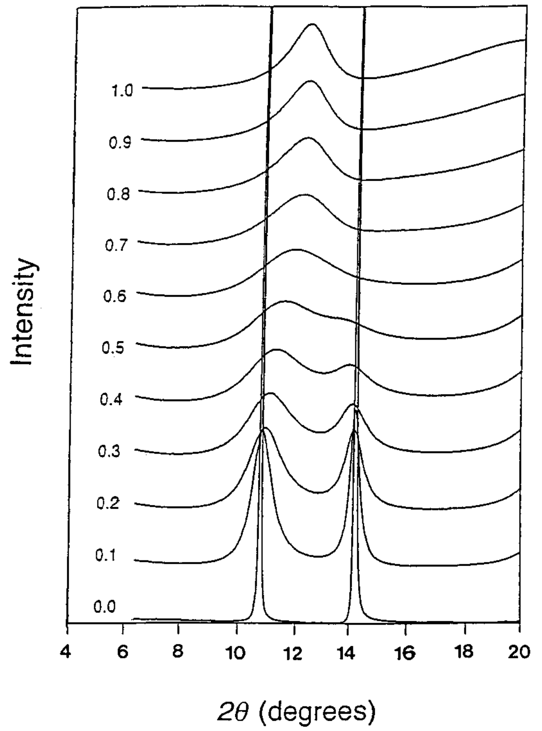

Figure 5. Predicted X-ray scattering along the chain axis direction for transesterified blends of the two homopolymers, poly(HBA) and poly(HNA), combined in a 60:40 mole ratio.

their statistical parameters to the presently defined r convention, they found that the predicted Z-axis maxima were essentially indistinguishable for $0.85 < r < 1.00$ but that two peaks were resolved at $r < 0.71$.

The differences between the predicted data for the blends of the copolymers and homopolymers are to be understood in terms of the changes in proportions of monomer pairs over the course of the reaction, as shown in Figure 6. For the blend of the 30/70 and 75/25 copolymers, at $r = 0.40$ the monomer pairs probabilities are $p_{BB} = 0.375$, $p_{BN} = p_{NB} = 0.225$, and $p_{NN} = 0.175$. These data are very similar to those for the random 60/40 copolymer, where $p_{BB} = 0.360$, $p_{BN} = p_{NB} = 0.240$, and $p_{NN} = 0.160$, and consequently, further monitoring of the transesterification reaction is beyond the limits of experimental error. For the homopolymer blend, the starting sequence distribution is much further from that for the 60/40 random copolymer, and a comparable situation is not reached until $r = 0.90$, with a result that the separate peaks would be resolved in the X-ray data over a much wider range of r.

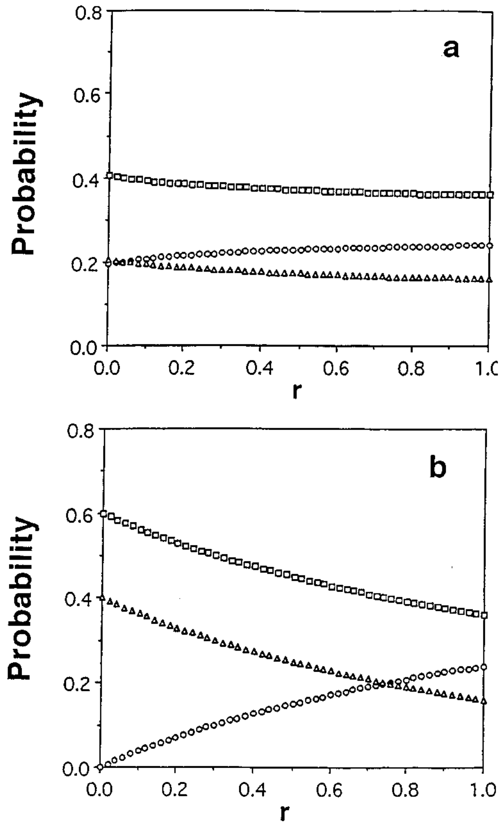

Figure 6. Proportions of monomer pairs present in transesterified blends of (a) 30/70 and 75/25 copoly(HBA/HNA) and (b) 3:2 blends of the homopolymers, poly(HBA) and poly(HNA), plotted as functions of r. Pair probabilities: (□) BB, (△) NN, (○) BN = NB.

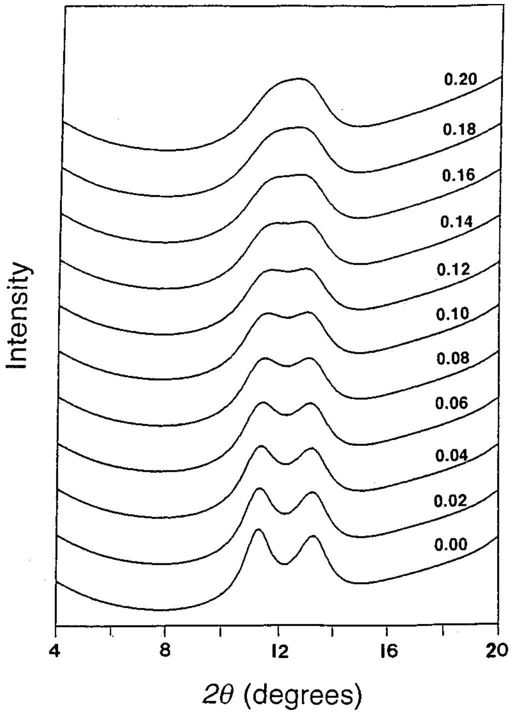

Figure 7. Predicted X-ray scattering along the chain axis direction for random transesterification in the blend of 30/70 and 75/25 copoly(HBA/HNA) for 0.02 increments of r in the range $r = 0.00-0.20$. (These data would fall in the region of the lowest three curves in Figure 4.)

Figure 7 shows the predicted scattering for blends of the 30/70 and 75/25 copolymers for $r = 0-0.20$, in increments of 0.02. These data were resolved into two component peaks using a Gaussian–Lorentzian peak fitting program, in the same way as was done for the observed data. The d-spacings derived from the peak positions are compared with those observed in Figure 8: the observed d-spacings are plotted against reaction time in Figure 8a; the d-spacings in the predicted data are plotted against r in Figure 8b. It can be seen that the calculated peak positions follow the observed data closely if we assign the data recorded after 60 min in the melt to $r = 0.40$. If we assume that the reaction proceeds linearly with time, as has been reported for other polyesters,[10–12] then the reaction is complete after 150 min, i.e. reaction time $t = 9 \times 10^3 r$ s. Thus, for each value of r, we can calculate ν, the number of transesterification events per monomer, using eq 20, and the observed and calculated d-spacings are plotted against ν in Figure 8c. The monomeric transesterifi-

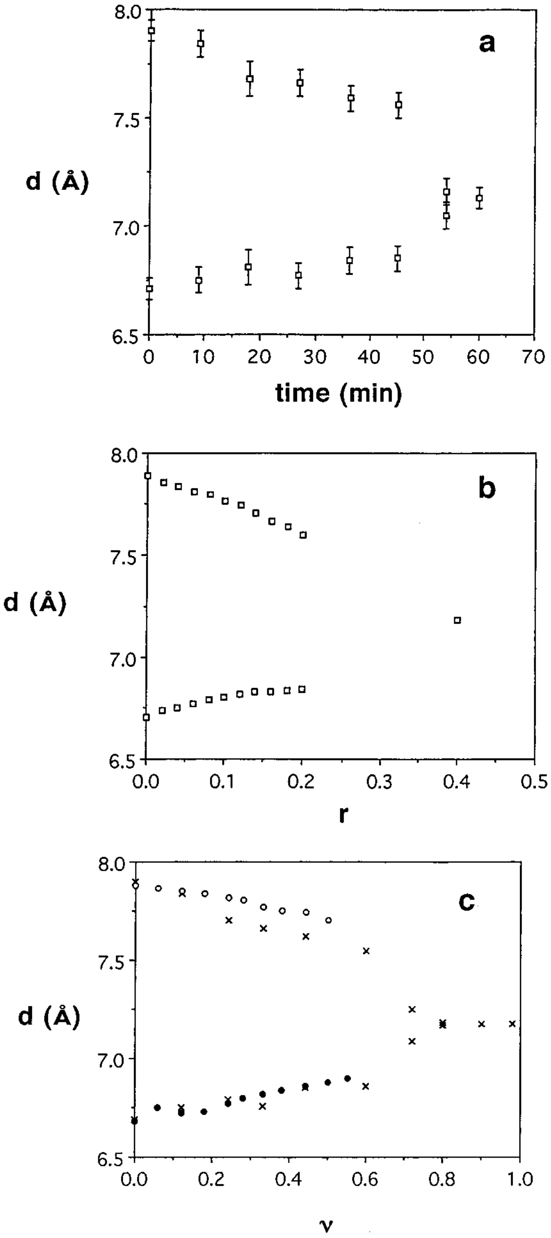

Figure 8. (a) Observed *d*-spacings (from Figure 2) plotted against time for the X-ray scattering peaks along the chain axis direction. (b) Predicted *d*-spacings (from Figures 4 and 7) plotted against *r*. (c) Observed (×) and calculated *d*-spacings (○ and ●) plotted against *ν*.

cation rate constant, *k*, is given by $\nu = kt$, and ν is plotted against *t* in Figure 9. The upper straight line is for the experimental data in Figure 8 and leads to $k_{315°C} = 2.3 \times 10^{-4}$ s^{-1}. The lower plot is for the analogous data obtained for blends held in the melt for different times at 295 °C,[1] and yields $k_{295°C} = 0.83 \times 10^{-4}$ s^{-1}. Assuming an Arrhenius relationship, we estimate an activation energy of 142 kJ/mol, in good agreement with the values of 152 kJ/mol for PET[10] and 142−173 kJ/mol for a wholly aromatic copolyester.[11] The rate constants are 1 order of magnitude smaller than the value of $k_{280°C} = 1.87 \times 10^{-3}$ s^{-1} measured for PET, but this may reflect the nematic structure and higher melt viscosity of copoly(HBA/HNA), i.e., a lower molecular mobility.

Close comparison of Figures 2 and 7 shows some discrepancies in the match of intensities and peak profiles. The intensities observed for the peaks at $d = 7.91$ and 6.67 Å (relative to that at $d = 2.08$ Å) are less that those for the unblended components. In general, the relative intensities for the first meridional maximum for fibers of copoly(HBA/HNA) are underestimated in predictions based on a single chain, which cannot simulate the intensification due to ordered packing in the solid state. However, the first two meridional maxima observed for the transesterification intermediates, particularly the one associated initially with the minor component, are lower than predicted by simple addition of the observed data for the pure solid state components and more closely approximate those predicted for the isolated chains. As transesterification nears completion, the chain compositions become increasingly similar and once again the meridional intensity increases above the calculated value. This phenomenon can be attributed to the greater diversity of individual chain compositions during the initial stages of transesterification, which restricts the development of three-dimensional order. Poorer chain packing in the unreacted blend (as compared to the situation in the unblended components) is also consistent with the decrease in T_m and the broadening of the melt transition,[1] and with the increased free volume detected by positron annihilation spectroscopy.[31]

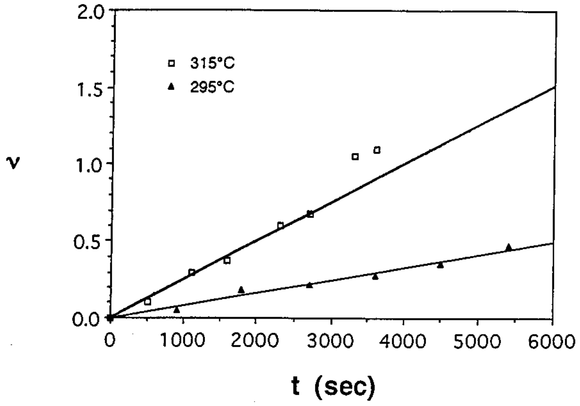

Figure 9. Number of reactions per monomer, *ν*, plotted against reaction time, *t*, at 315 °C (□) and 295 °C (▲).

A second discrepancy is that the widths of the calculated peaks are broader than those of the observed peaks, especially for the first peak which derives originally from the minor component of the blend. This may result from our use of a mixed *cis*/*trans* conformation for HNA in the 30/70 component, which matches the position of the peak at the expense of a certain increase in the width. Finally, the first observed peak deviates more from the calculated positions than does the stronger second peak. (Note, however, that the more rapid decrease in intensity for the first peak and the increasing asymmetry tend to increase the uncertainty in the derivation of its position by curve fitting. In the calculated data, determination of *d* for the first peak becomes extremely difficult for $r \geq 0.20$, where curve-fitting preferentially detected a single peak.[1])

Nonrandom Transesterification. The possibility that random transesterification may not accurately describe the process occurring was explored by altering the model to include kinetic effects or incomplete molecular mixing. The effects on the predicted scattering due to nonrandomness arising from differences in monomer reactivities are shown in Figure 10, for preferential reaction at the HBA units. Here $s = 0.3$, meaning that reaction after HBA is favored by 1.43 to 1 over reaction after HNA. This change has the effect that the first diffraction peak is predicted to shift

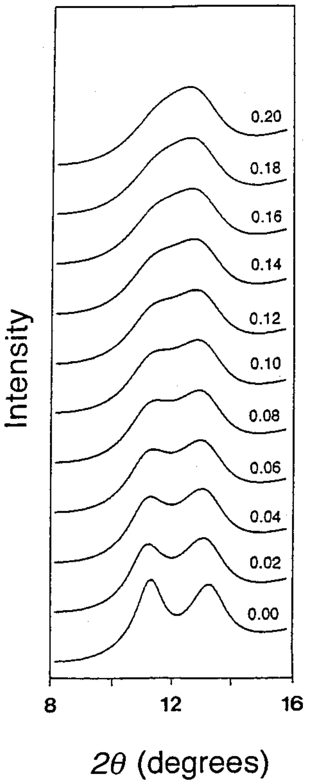

Figure 10. Predicted X-ray scattering along the chain axis direction for nonrandom transesterification in the blend of 30/70 and 75/25 copoly(HBA/HNA). Reaction after HBA units is favored by 1.43:1 over reaction after HNA units. The data are for 0.02 increments of r in the range $r = 0.00-0.20$.

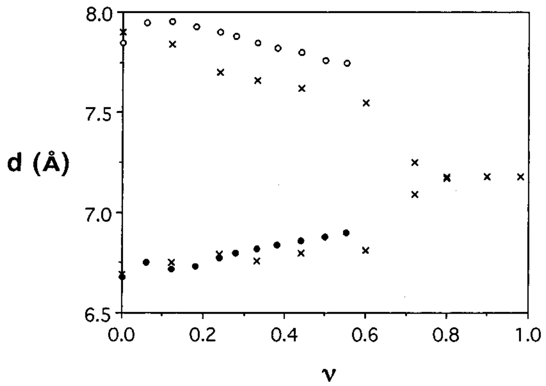

Figure 11. Comparison of the observed d-spacings (×; from Figure 2) and those predicted (○ and ● from Figure 10) for nonrandom transesterification where reaction after HBA is favored. The data are plotted as functions of ν.

outward more slowly and the second peak to shift inward more rapidly than occurs using the completely random model. This results in higher d-spacings for both peaks that do not match the observed data, as seen in the plots of d versus ν in Figure 11. The match continues to be unacceptable when we allow s, the preference for reaction at the HBA units, to vary as a function of r. The opposite trend is observed when HNA reacts more rapidly: both peaks initially shift to lower d-spacings Changing the reactive end of the monomer from the "acid" to the "phenol" group has very little effect on the results. We can conclude that models based on preferential reactivity for one of the two monomers lead to poorer agreement than does the completely random exchange model.

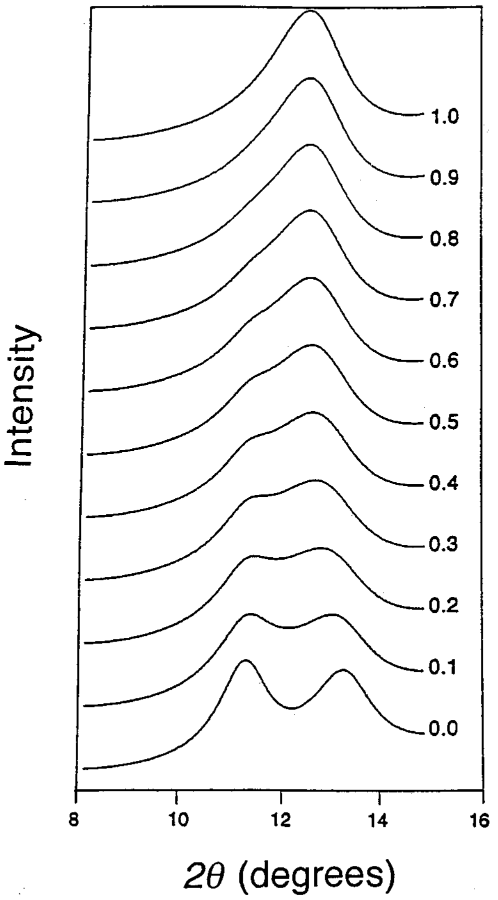

Figure 12. Predicted X-ray scattering along the chain axis direction for transesterification in 2:1 blends of 75/25 and 30/70 copoly(HBA/HNA) in which 50% of the 30/70 component is initially phase separated. The data are for 0.1 increments of r in the range $r = 0-1.0$.

Next we considered a domain model in which the 30/70 copolymer is not completely dispersed. Figure 12 shows the predicted scattering for a model in which 50% of the 30/70 copolymer is initially inaccessible to the 75/25 copolymer, but becomes linearly more accessible as r increases, until the domains vanish at $r = 1.0$. The effects are similar to those predicted above for a model in which the exchange reaction occurs preferentially at the HBA units, since the relative proportion of HNA available for reaction is reduced: the first peak becomes broader and slowly shifts outward, while the second peak shifts inward more rapidly and becomes sharper. Overall, the d-spacings are larger than those for the fully random model and do not fit the observed data, as seen in Figure 13. Similarly, results for a 75/25 HBA/HNA domain model resemble those for a nonrandom reaction model in which HNA is more reactive, and the agreement is inferior to that for the random model.[30]

The existence of domains also leads to significant differences in the predicted overall kinetics, since incomplete dispersion means that fewer reactions are productive. Consequently, the original scattering maxima in Figure 12 move toward each other more slowly and merge into a single peak at $r \approx 0.80$, compared to $r \approx 0.40$ for the random transesterification model. The predicted rate constant increases by a factor of ~2.5. However, 50% segregation of the minor phase is necessary to get even this close to the observed rate constant. It is unlikely that so much of this component is segregated, because in this case we would expect to detect two T_m peaks in the unreacted blend, rather than the single observed peak at 227 °C.

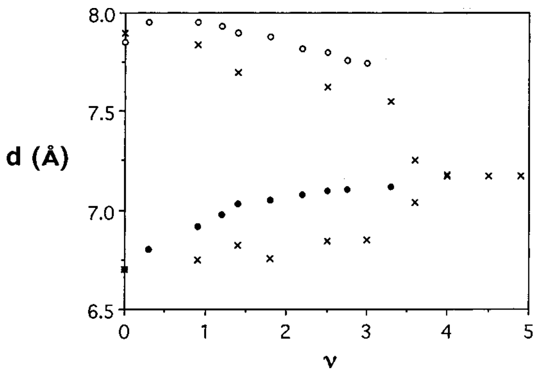

Figure 13. Comparison of the observed *d*-spacings (×; from Figure 2) and those predicted (○ and ● from Figure 12) for transesterification when there is 50% initial phase separation of the 30/70 minor component. The data are plotted as functions of *ν*.

Conclusions

The positions of the nonperiodic meridional scattering maxima observed for the transesterification intermediates of the blend of 30/70 and 75/25 copoly(HBA/HNA) can be modeled by assuming complete molecular dispersion and random reaction between chains. Significant preferential reactivity of the ester groups associated with one or other of the two monomers can be ruled out, as this causes unacceptable shifts in the calculated *d*-spacings. Incomplete mixing, i.e., domain formation, also results in unacceptable shifts in the *d*-spacings predicted for the intermediates. The activation energy derived for the completely random reaction is very similar to those reported by other groups in neutron diffraction studies of transesterification of nonliquid crystalline polyesters. However, the rate constants are 1 order of magnitude lower than for the latter systems, which may reflect the differences in melt viscosity and mobility in the LC and isotropic states.

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