Registry No. I, 32131-17-2; V, 110295-55-1; VI, 110295-56-2; VII, 110295-57-3; VIII, 110295-58-4; IX, 110295-59-5; XI, 110295-60-8; $H_2N(CH_2)_6NH_2$, 124-09-4; $HO(CH_2)_2OH$, 107-21-1; cyclopentanone, 120-92-3; methyl 2-oxocyclopentanecarboxylate, 10472-24-9; (adipoyl chloride)(hexamethylenediamine) (copolymer), 28502-27-4.

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X-ray Diffraction from Liquid-Crystalline Copolyesters: Matrix Methods for Intensity Calculations Using a One-Dimensional Paracrystalline Model

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ABSTRACT: X-ray fiber diagrams of wholly aromatic liquid-crystalline copolyesters contain a series of aperiodic meridional maxima at positions that depend on the monomer ratio. Previous papers from this laboratory have shown that the positions and relative intensities of these maxima are predicted by a structure consisting of parallel extended chains of completely random monomer sequence. We present here a generalized approach for studying the diffraction characteristics of polyatomic monomers in stiff-chain systems with varied chemistries and microstructures. The random chain is most conveniently treated as a one-dimensional paracrystal with multimodal coordination statistics, and the use of matrices to define the neighbor probabilities leads to an efficient calculation of the scattering by nematic arrays of finite or infinite copolymer chains. Modification of the correlation statistics allows for investigation of the sensitivity of the X-ray data to nonrandom comonomer sequence distributions. The procedures also include consideration of nonlinearity of the chains, leading to determination of the correlation or persistence length for the stiff-chain conformation from the half-widths of the invariant peaks.

Introduction

Previous papers from this laboratory have described analysis of the structure of wholly aromatic melt-processable liquid-crystalline copolyesters. The X-ray fiber diagrams of copolyesters prepared, e.g., from *p*-hydroxybenzoic acid (HBA) and 2-hydroxy-6-naphthoic acid (HNA) show features unlike those reported previously for any other group of polymers, in that the intensity distribution is aperiodic along the chain axis direction. It has been shown that these data are predicted for an array of copolymer chains of completely random sequence. The aperiodic diffraction maxima arise due to structural correlations which are inherent in extended random copolymer chains. These copolyesters have also generated commercial interest in that high strength/high modulus fibers and high performance moldings can be obtained from the ordered melts. The synthesis and properties of these polyesters are the subject of numerous papers and patents (for reviews see ref 1–3). It has been found that the bulk properties of these copolymers are very sensitive to variations in the monomer chemistry.[4] There is also evidence for changes in the three-dimensional order as a result of thermal treatment, leading to an overall improvement in the properties of these systems.[5]

Figure 1 shows the intensity distribution along the meridian, as obtained by a $\theta/2\theta$ diffractometer, for five comonomer ratios. The observed meridional maxima are aperiodic, i.e., they are not orders of a simple repeat, and also shift in position with monomer ratio. The *d*-spacings of the meridional maxima are listed in Table I.

Modeling the structure of the copolyesters as an array of parallel chains with completely random monomer sequence leads to predicted X-ray scattering patterns that are in good agreement with the observed data.[6,7] The

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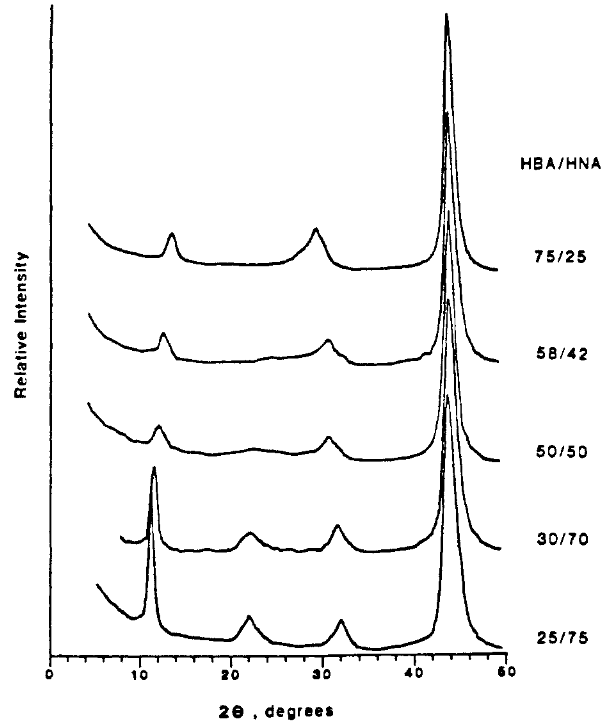

Figure 1. $\theta/2\theta$ meridional diffractometer scans of fibers of copoly(HBA/HNA) for five comonomer ratios: 75/25, 58/42, 50/50, 30/70, and 25/75.

Table I
d-Spacings of Meridional Maxima of Copoly(HBA/HNA)

molar ratio	obsd d-spacings,[a] Å	calcd d-spacings, Å point model	calcd d-spacings, Å atomic model
25/75	8.11 ± 0.07	7.94	8.00
	4.15 ± 0.02	4.17	4.19
	2.85 ± 0.02	2.84	2.84
	2.09 ± 0.0	2.10	2.10
30/70	7.89	7.88	7.88
	4.09	4.17	4.20
	2.87	2.85	2.86
	2.09	2.10	2.10
50/50	7.49	7.41	7.52
		4.12	4.26
	2.95	2.93	2.94
	2.09	2.10	2.10
58/42	7.19	7.20	7.30
		4.02	4.33
	2.96	2.98	2.98
	2.08	2.11	2.11
75/25	6.70	6.71	6.85
	3.09	3.09	3.08
	2.09	2.11	2.11

[a] Diffractometer; experimental errors are given for the 27/75 copolymer and are similar for the other compositions.

theoretical predictions are most efficiently performed by treating the chain as an aperiodic one-dimensional paracrystal,[8,9] as will be summarized below. Other treatments of the interference effects of one-dimensional aperiodic point lattices can be found in the literature, notably by Hendricks and Teller for layered structures in clays[10] and by Bonart et al. for polymeric systems.[11-13] Extension of these procedures to a chain of polyatomic monomers is described in ref 14. The present paper describes a more general approach, which streamlines the calculation by incorporating matrix descriptions of the neighbor correlations.

Theoretical Modeling

In order to derive the meridional intensity, we need to consider the projection of the structure onto the fiber axis (z). Figure 2 shows a projection of five model chains of copoly(HBA/HNA) with typical random sequences. These have been constructed by using standard bond lengths and angles and assuming rigid planarity of the aromatic and ester groups. Torsional rotations about the aromatic–carbonyl and aromatic–oxygen bonds provide the only conformational freedom for the otherwise stiff extended chain. The aromatic–ester torsion angles were set at +30° or +150° (where 0° and 180° correspond to coplanarity), which are consistent with the structures of model compounds.[15] As can be seen in Figure 2, the 1,4- and 2,6-linkage bonds are approximately parallel to the fiber axis and hence the projection of the chain onto the z axis will be approximately independent of the conformation, at least over short lengths of the chain.

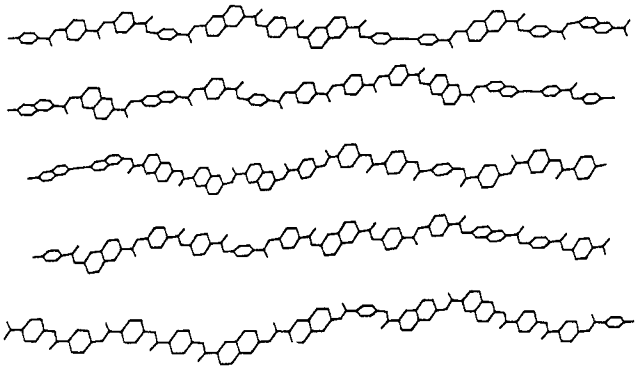

Figure 2. Projection of the structure of five model chains of copoly(HBA/HNA) with typical random sequences.

Point Model

As a first approximation, each monomer was represented by a point, placed for convenience at the ester oxygen, and separated from adjacent points by the corresponding residue lengths. Lengths of 6.35 and 8.37 Å were derived for the models of HBA and HNA residues, respectively. Monte Carlo methods were used to set up large numbers of copolymer sequences, and the meridional intensity was calculated by averaging the squared Fourier transforms.[16] This approach was successful in predicting the meridional maxima, but a more efficient and complete calculation for the meridional intensity would be to calculate the Fourier transform of the autocorrelation function of the average chain, $Q(z)$:[17]

$$I(Z) = \sum_j Q(z) \exp(2\pi i Z z_j) \qquad (1)$$

Here Z is the reciprocal coordinate in the direction corresponding to the chain axis. $Q(z)$ describes the probability distribution of the nearest-neighbor terms along the random chain and is zero except at specific values of $z = z_j$.

The summation in eq 1 has a closed solution which can be derived by treatment of the chain as a one-dimensional paracrystal, as described by Hosemann.[18] $Q(z)$ can be written as the sum of the neighbor probabilities on either side of the origin:

$$Q(z) = Q_0 + Q_1 + Q_{-1} + \cdots + Q_n + Q_{-n} + \cdots \qquad (2)$$

Since Q_2 is the self-convolution of Q_1,

$$Q_2 = Q_1 \star Q_1 \qquad (3)$$

and in general,

$$Q_n = Q_{n-1} \star Q_1 \qquad (4)$$

$I(Z)$, the Fourier transform of $Q(z)$, can then be written as[19]

$$I(Z) = \mathcal{F}[Q(z)] = 1 + 2\,\mathrm{Re}\left[\frac{H_1(Z)}{1 - H_1(Z)}\right] \qquad (5)$$

where Re signifies the real component and

$$H_1(Z) = \mathcal{F}[Q_1(z)] \qquad (6)$$

i.e., $H_1(Z)$ is the Fourier transform of the first nearest-neighbor terms in $Q(z)$. For a limited chain of N monomers, eq 5 becomes

$$I(Z) = \mathrm{Re}\left[\frac{1 + H_1(Z)}{1 - H_1(Z)} - \frac{2H_1(Z)[1 - H_1^{N}(Z)]}{N[1 - H_1(Z)]^2}\right] \qquad (7)$$

Atomic Model

Calculations for random chains of point monomers result in the prediction of the positions of the aperiodic meridional maxima. However, in order to predict the relative intensities of the meridional peaks, it is necessary to consider an atomic model for the chain, so as to allow for intra- as well as interresidue interferences. We have shown previously that this can be done by separating $Q(z)$ into its components:[20]

$$Q(z) = Q(0) + \sum_{\mathrm{R}}\sum_{\mathrm{S}} Q_{\mathrm{RS}}(z) \qquad (8)$$

and then, analogous to eq 1, deriving the intensity distribution as

$$I(Z) = \sum_{l}\sum_{\mathrm{R}}\sum_{\mathrm{S}} Q_{\mathrm{RS}}(z) F_{\mathrm{RS}}(Z) \exp(2\pi i Z z l) \qquad (9)$$

where

$$F_{\mathrm{RS}}(Z) = \sum_{j}\sum_{k} f_{\mathrm{R},j} f_{\mathrm{S},k} \exp[2\pi i Z(z_{\mathrm{S},k} - z_{\mathrm{R},j})] \qquad (10)$$

is the Fourier transform of the convolution of the monomer pair RS. f refers to the atomic scattering factors and the subscripts R,j and S,k refer to the jth atom of monomer R and the kth atom of monomer S. A closed form of eq 9, analogous to eq 5, has been derived for an atomic model.[21]

Matrix Treatment

The convolution property expressed in eq 4 holds for the HBA/HNA copolymer since either monomer can combine with itself and the other. However, this is not true for all copolymer systems, e.g., the copolyester prepared from HBA, 2,6-dihydroxynaphthalene (DHN), and terephthalic acid (TPA). In this system, only certain monomer pair combinations are allowed, but the above treatment can still be applied if we write $H_1(Z)$ as a matrix whose nonzero elements consist of the allowed monomer pair contributions. We can define $H_1(Z)$ as a product of three matrices:

$$H_1(Z) = \mathbf{P}{\cdot}\mathbf{M}{\cdot}\mathbf{X} \qquad (11)$$

where $\mathbf{P}$ is a diagonal matrix representing the monomer composition (molar ratios), $\mathbf{M}$ is the matrix defining the probabilities of forming specific monomer pairs, and $\mathbf{X}$ is another diagonal matrix consisting of the phase terms for the different monomer lengths (i.e., the monomer–monomer separations in the dimers). Specifically, each row of the matrix $\mathbf{M}$ defines the probabilities for a monomer to combine with itself and with each of the others. The sum of these probabilities on each row should thus be unity. The order of the matrices is determined by the number of unique monomers comprising the system. For example, in the case of copoly(HBA/HNA), if we further abbreviate HBA and HNA as B and N, the three matrices of second order are defined as follows:

$$\mathbf{P} = \begin{bmatrix} P_{\mathrm{B}} & 0 \\ 0 & P_{\mathrm{N}} \end{bmatrix} \quad \mathbf{M} = \begin{bmatrix} M_{\mathrm{BB}} & M_{\mathrm{BN}} \\ M_{\mathrm{NB}} & M_{\mathrm{NN}} \end{bmatrix} \quad \mathbf{X} = \begin{bmatrix} X_{\mathrm{B}} & 0 \\ 0 & X_{\mathrm{N}} \end{bmatrix}$$

where, e.g., P_{B} = molar ratio of monomer B, M_{BB} = combination probability for the monomer pair BB (=P_{B}), and X_{B} = phase term for the length of monomer B [=exp($2\pi i Z z_{\mathrm{B}}$)] Note that all of the M_{RS} terms are defined and, in the case of a completely random copolymer, are equal to the molar ratios P_{S}, which also satisfies the normalization condition for each row. A more complex example is the HBA/DHN/TPA system. The DHN and TPA residues have symmetrical structures, but there is a sense to the HBA residue and hence there are effectively four monomers: up-HBA, DHN, TPA, and down-HBA. The resulting fourth order matrices are defined as follows:

$$\mathbf{P} = \begin{bmatrix} P_{\mathrm{B}} & & & 0 \\ & P_{\mathrm{N}} & & \\ & & P_{\mathrm{P}} & \\ 0 & & & P_{\mathrm{D}} \end{bmatrix} \qquad \mathbf{X} = \begin{bmatrix} X_{\mathrm{B}} & & & 0 \\ & X_{\mathrm{N}} & & \\ & & X_{\mathrm{P}} & \\ 0 & & & X_{\mathrm{D}} \end{bmatrix}$$

$$\mathbf{M} = \begin{bmatrix} M_{\mathrm{BB}} & M_{\mathrm{BN}} & M_{\mathrm{BP}} & M_{\mathrm{BD}} \\ M_{\mathrm{NB}} & M_{\mathrm{NN}} & M_{\mathrm{NP}} & M_{\mathrm{ND}} \\ M_{\mathrm{PB}} & M_{\mathrm{PN}} & M_{\mathrm{PP}} & M_{\mathrm{PD}} \\ M_{\mathrm{DB}} & M_{\mathrm{DN}} & M_{\mathrm{DP}} & M_{\mathrm{DD}} \end{bmatrix}$$

where B, N, P, and D are further abbreviations of up-HBA, DHN, TPA, and down-HBA. In our calculations we have assumed that the up and down senses for HBA are presented in equal amounts in the random copolymer. Of the 16 possible dimers, only 8 are chemically feasible and the rest, namely, BN, BD, NN, ND, PB, PP, DB, and DP, are forbidden. The probabilities corresponding to these pairs are therefore set to zero and matrix $\mathbf{M}$ becomes

$$\mathbf{M} = \begin{bmatrix} M_{\mathrm{BB}} & 0 & M_{\mathrm{BP}} & 0 \\ M_{\mathrm{NB}} & 0 & M_{\mathrm{NP}} & 0 \\ 0 & M_{\mathrm{PN}} & 0 & M_{\mathrm{PD}} \\ 0 & M_{\mathrm{DN}} & 0 & M_{\mathrm{DD}} \end{bmatrix}$$

Normalization of each row to unity results in $M_{\mathrm{RS}} = 2P_{\mathrm{s}}$ for the completely random copolymer.

The product $\mathbf{P}{\cdot}\mathbf{M}$ defines the absolute values of the probabilities of the nearest-neighbor pairs in the autocorrelation function. Analogous to the treatment of the paracrystalline model, the Fourier transform of $Q_2(z)$ is given by

$$\mathcal{F}[Q_2(z)] = H_2(Z) = \mathbf{P}[\mathbf{M}{\cdot}\mathbf{X}]^2 \qquad (12)$$

and in general

$$H_n(Z) = \mathbf{P}[\mathbf{M}{\cdot}\mathbf{X}]^n \qquad (13)$$

If the matrix sum of the Fourier transforms of all the neighbors on the positive side of the origin is denoted by the matrix $\mathbf{T}$, where

$$\mathbf{T}(Z) = \sum_{1}^{\infty} H_n(Z) = \mathbf{P}\left[\frac{\mathbf{M}{\cdot}\mathbf{X}}{\mathbf{I} - \mathbf{M}{\cdot}\mathbf{X}}\right] \qquad (14)$$

and $\mathbf{I}$ is the unit matrix, then $\mathbf{I}(Z)$ can then be written as

$$\mathbf{I}(Z) = 1 + 2\,\mathrm{Re}\,[\sum_{\mathrm{R}}\sum_{\mathrm{S}} T_{\mathrm{RS}}] \qquad (15)$$

where T_{RS} denotes the elements of matrix T.

For the atomic model, the intensity distribution is derived by associating each $F_{\mathrm{RS}}(Z)$ term with the corresponding T_{RS} element of matrix $\mathbf{T}$ defined in eq 11 and can be written as

$$\mathbf{I}(Z) = \sum_{\mathrm{R}} p_{\mathrm{R}} F_{\mathrm{RR}}(Z) + 2\,\mathrm{Re}\,[\sum_{\mathrm{R}}\sum_{\mathrm{S}} F_{\mathrm{RS}}(Z) T_{\mathrm{RS}}(Z)] \qquad (16)$$

The results obtained from the above treatment are similar to those obtained previously.[16,17] Table I lists the

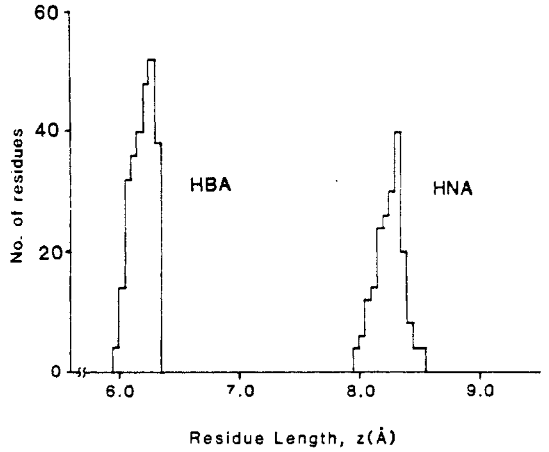

Figure 3. Typical histogram of axial residue lengths for 58/42 copoly(HBA/HNA) obtained by surveying 40 random chains with 13 monomers each. The corresponding normalized distribution is obtained by dividing by the total number of monomers.

d-spacings of the maxima calculated from the point and atomic models for five different comonomer ratios.

Stiff-Chain Persistence Lengths

The above model of the chain is highly idealized in that we have assumed all the ester oxygen–ester oxygen vectors for the residues in the chain to be colinear with the *z*-axis. This leads to a very sharp peak at $d \cong 2.1$ Å in calculations for an infinite chain, which is a consequence of the fact that the residue lengths of HBA and HNA are approximately in the ratio 3:4. We have shown elsewhere that this peak gets broader with decreasing chain length in calculations for finite chains.[22] However, a real chain cannot be linear as our model, in which all the ester oxygens are colinear. This nonlinearity means that the projected residue lengths on the fiber axis will not be constant, but rather there will be a distribution of the projected residue lengths which arises due to the offset 2,6-linkages and can be further enhanced by variation of the aromatic–ester torsion angles. The fact that we can reproduce the peak width at $d \cong 2.1$ Å with a chain of 9–13 monomers, when the actual DP for the copolyesters is approximately 150, indicates that the observed data estimate the correlation length for the extended chains, i.e. the approximation of a perfectly straight chain breaks down after about 11 monomers or ~80 Å for these copolymers.

The present method of calculating the intensity distribution provides a route to incorporate nonlinear structures into the infinite chains. As can be seen in Figure 2, nonlinearity leads to a distribution of ester oxygen–ester oxygen vectors about the mean chain direction, with a result that the axial advance per monomer is not constant for each monomer type. Figure 3 shows a histogram of axial residue lengths obtained by surveying 40 chains of 13 monomer each for 58/42 copoly(HBA/HNA). The sequences were selected by using a random number generator, taking into account the monomer ratio, with the aromatic–ester torsion angles limited to ±30° and ±150° and also selected at random. For a chain of nonlinear structures, the elements of matrix **X** are defined as the Fourier transform of the normalized distribution of monomer axial lengths. For example, if $q_R(z)$ represents the normalized axial length distribution for monomer R, then

$$\mathbf{X}_R(Z) = \int_{-\infty}^{\infty} q_R(z) \exp(2\pi i Z z)\, dz \qquad (17)$$

In practice it is easiest to define $q_R(z)$ in terms of a histogram of projected monomer lengths, as in Figure 3, in which case the integral in eq 17 is replaced by a summation:

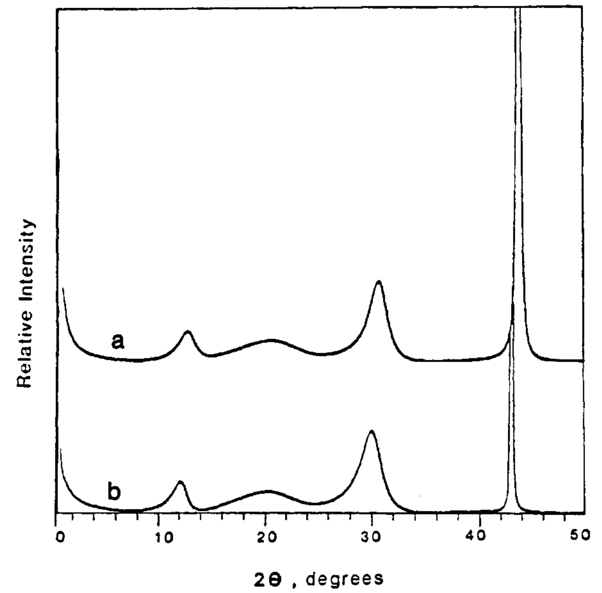

Figure 4. Calculated meridional intensity distribution for 58/42 copoly(HBA/HNA): (a) using the distribution of axial residue lengths given by Figure 3; (b) using constant axial residue lengths.

$$\mathbf{X}_R(Z) = \sum_j q_{R_j} \exp(2\pi i Z z_{R_j}) \qquad (18)$$

where q_{R_j} is the fraction of monomer R having projected length z_{R_j}.

For the atomic model, the variability of the residue axial lengths results in a further complication in that, to be exact, a different set of atomic coordinates is needed for each residue length. However, the effect of small structural changes on the slowly varying $F_{RS}(Z)$ terms is minimal and the assumption of a constant $F_{RS}(Z)$, set at the weighted average of the distribution, is an acceptable approximation. Figure 4 compares the calculated intensity distributions for 58/42 copoly(HBA/HNA) for an infinite straight chain and a chain incorporating the distribution of residue lengths. It can be seen that the results are similar except that the peak at $d \cong 2.1$ Å broadens with the introduction of the residue length distribution. There is also a general shift of the peak positions toward lower *d*-spacings (higher 2θ); this occurs because the "average" monomer is tilted away from the chain axis and hence has a projected length less than the previously assumed maximum residue length.

The concept of persistence length can also be understood by incorporating the length distribution function into the correlation function $Q(z)$ for the straight chain. This combination leads to a correlation function which describes the probabilities for nearest neighbors in chains such as those in Figure 2. A comparison of the correlation function with and without a residue length distribution is shown in Figure 5. It can be seen that the correlation function gets progressively broader as one moves away from the origin until $Q(z)$ approaches a constant value at a neighbor separation corresponding to the correlation or persistence length for the chain.

Sensitivity to Nonrandomness

The analyses so far have shown that the X-ray scattering data for the copolyester systems under study are consistent with a highly extended chain with completely random sequence. NMR studies of the microstructure of these systems have been limited due to the insolubility of the polymers and the chemical similarity of the monomer residues. The question naturally arises as to how sensitive

Table II
Calculated *d*-Spacings of Meridional Maxima of 58/42 Copoly(HBA/HNA) for Varying Degrees of Blockiness

r_H/r_C	*d*-spacings, Å						
100.0	8.34	6.33	4.19	3.18	2.79	2.11	2.09
20.0	8.34	6.33	4.19	3.18	2.79	2.11	2.09
10.0	8.34	6.33	4.19	3.18	2.79	2.11	
5.0	8.34	6.37	4.19	3.17	2.79	2.11	
4.0	8.27	6.37	4.19	3.17	2.80	2.11	
3.0	8.27	6.37	4.19	3.16	2.81	2.11	
2.0	8.00		4.20	3.14	2.86	2.11	
1.8	7.94		4.20	3.13		2.11	
1.6	7.76		4.20	3.10		2.11	
1.4	7.58		4.22	3.05		2.11	
1.2	7.41		4.24	3.00		2.11	
1.0	7.30		4.33	2.98		2.10	
obsd	7.19 ± 0.07			2.96 ± 0.02		2.08 ± 0.01	

are the X-ray data to nonrandom sequence distributions. Previous investigations on the effects of nonrandom monomer sequences for copoly(HBA/DHN/TPA) were done by modification of the individual terms in $Q(z)$. The results showed that the meridional peak positions and intensities are sensitive to sequence distribution and that all but minimal blockiness in the HBA/DHN/TPA copolymer can be ruled out.[23]

The matrix treatment of nearest-neighbor probabilities described above readily facilitates the modeling of nonrandom microstructures. In kinetic studies, blockiness in copolymers is usually considered in terms of reactivity ratios. In the case of copolyesters such as copoly(HBA/HNA), the individual monomer reactivities may be different, and the ensuing copolymer microstructure may also be affected by subsequent transesterification. The latter effect could lead toward randomness or toward a blocky structure, depending on the circumstances.[24] Whatever the final microstructure, it can be defined by modifying the terms in the matrix **M**. For example, for copoly(HBA/HNA)

$$\mathbf{M} = \begin{bmatrix} r_{BB}M_{BB} & r_{BN}M_{BN} \\ r_{NB}M_{NB} & r_{NN}M_{NN} \end{bmatrix}$$

where r_{BB}, r_{BN}, r_{NB}, and r_{NN} are the proportional changes that adjust the first-nearest-neighbor probabilities relative to their values in the completely random structure. The normalization condition requires that the following conditions be satisfied:

$$r_{BB}M_{BB} + r_{BN}M_{BN} = 1 \qquad (19)$$

$$r_{NB}M_{NB} + r_{NN}M_{NN} = 1 \qquad (20)$$

Furthermore,

$$r_{BN} = r_{NB} \qquad (21)$$

since in the infinite chain there must be equal number of HBA–HNA and HNA–HBA linkages. For convenience, we define the ratio r_H/r_C as

$$r_H/r_C = r_{BB}/r_{BN} \qquad (22)$$

i.e., the ratio for the increased preference for the formation of HBA–HBA pairs over the HBA–HNA pairs, which is a measure of blockiness.

Figure 6 shows the meridional intensity distributions for 58/42 copoly(HBA/HNA) with r_H/r_C varying from 1 to 100. The *d*-spacings of the predicted maxima are listed in Table II. The calculations are for an atomic model of an infinite chain with constant residue axial lengths. At $r_H/r_C = 100$, the presence of homopolymer blocks is clearly indicated by the fact that the predicted peaks occur at either orders of 6.35 Å (for poly(HBA)) or 8.37 Å (for poly(HNA)). As r_H/r_C decreases, the peaks get broader due to the fact that the average block length gets shorter, and shifts in the peak positions become apparent at $r_H/r_C \leq 5$. The only curve to give good agreement with the observed data is for $r_H/r_C = 1$, the completely random copolymer. All microstructures with $r_H/r_C \geq 2$ show deviations from the observed data, with significantly different peak positions along with the presence of additional peaks, such that these structures can be ruled out.

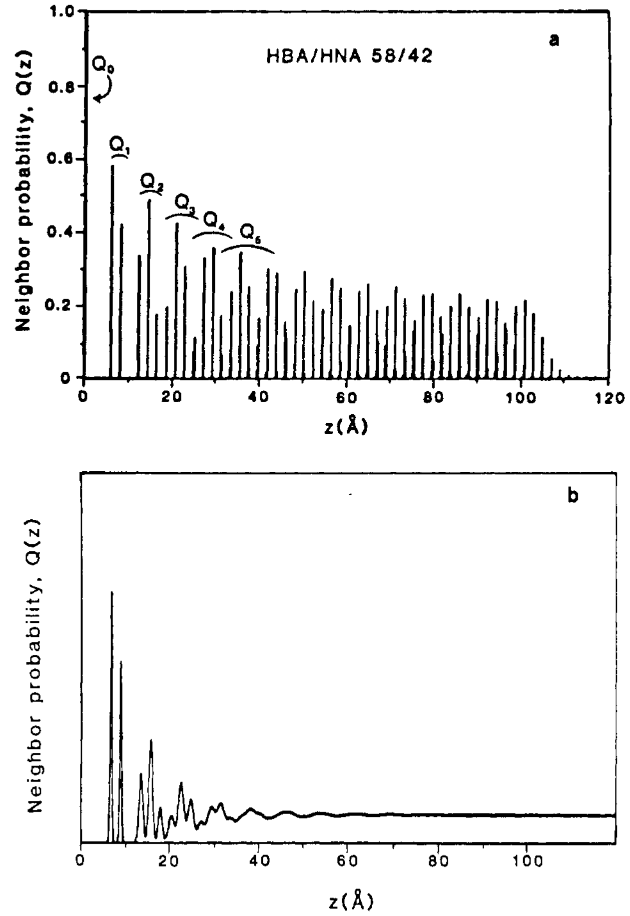

Figure 5. Autocorrelation function for 58/42 copoly(HBA/HNA): (a) for constant residue lengths, plotted out to the 14th nearest neighbor; (b) after incorporation of the axial residue length distribution.

The ratio $r_H/r_C = 2$ is nevertheless a relatively blocky structure, and it is necessary to study the data on a finer grid in the range $r_H/r_C = 2.0$–1.0. Figure 7 shows data calculated in this range for 0.2 increments of r_H/r_C, and the peak positions are listed in Table II. The best agreement is for the random copolymer, not only in the

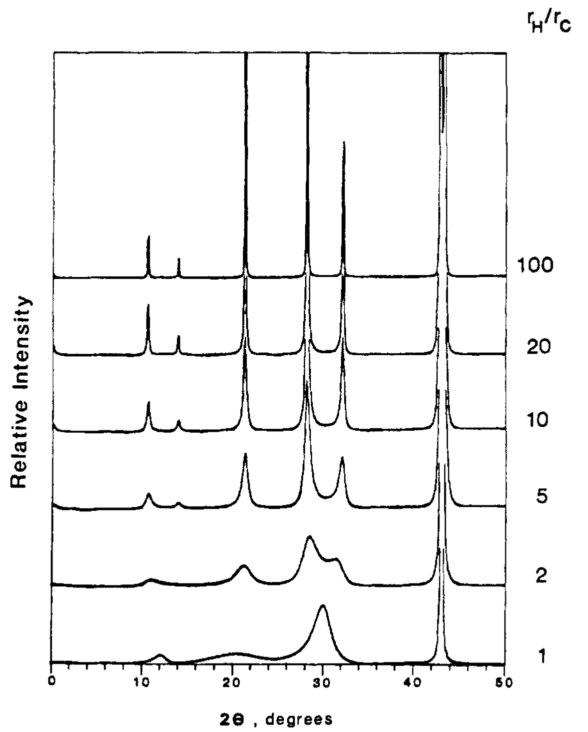

Figure 6. Calculated meridional intensities for 58/42 copoly(HBA/HNA) at varying degrees of blockiness defined by the ratio r_H/r_C. The random copolymer corresponds to $r_H/r_C = 1$.

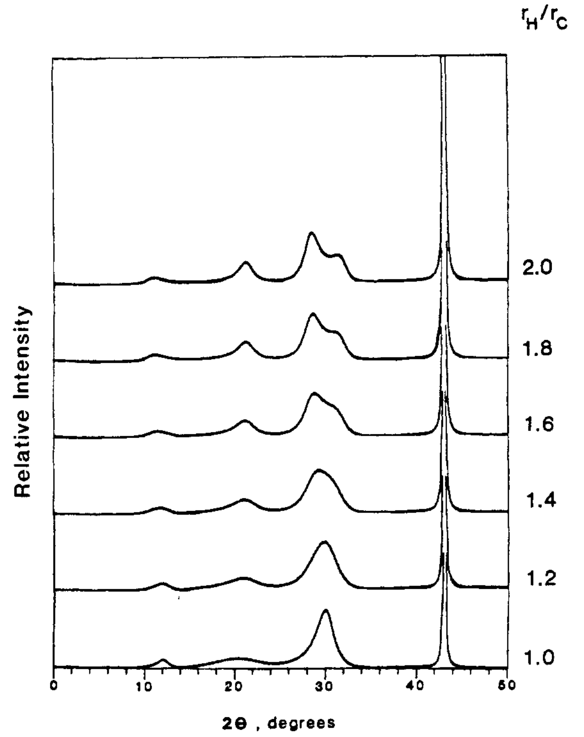

Figure 7. Calculated meridional intensities for 58/42 copoly(HBA/HNA) with r_H/r_C varying from 1.0 to 2.0 in increments of 0.2. The random copolymer ($r_H/r_C = 1$) gives the best fit with the observed data.

peak positions but also in terms of the general appearance of the observed diffractometer scan. (Note that some intensity is seen in the region of the predicted peak at 4.33 Å, but the low signal-to-noise ratio does not allow us to measure a peak position.) The most significant effect of a change in microstructure is the shift in the position of the first peak from 7.30 Å at $r_H/r_C = 1.0$ to 8.00 Å at $r_H/r_C = 2.0$. The position of the observed peak can be determined to within 0.1 Å, and thus the data are sensitive to changes at $r_H/r_C < 2.0$. It is necessary to be cautious in assigning a limit to this sensitivity because the peak positions are to some extent dependent on the structure assumed in what is still a simple idealized model for the chain. Nevertheless, an upper limit can presently be set at $r_H/r_C = 1.4$, and we may achieve better than this in the future as our modeling becomes more sophisticated. Values of $r_H/r_C < 1.0$ correspond to a preference for alternating copolymer. We have considered such structures and these can also be ruled out after small deviations from randomness. Thus we can say that for copoly(HBA/HNA), the random copolymer gives the best agreement for the meridional scattering and that all but minimal blockiness can be ruled out.

The above procedures have been successfully applied to analyze the structure of other wholly aromatic copolyester and copolyamide systems which exhibit aperiodic meridional maxima. Analyses of the three-dimensional structure are currently in progress, extending the work of Chivers et al.[25] to calculate the cylindrically averaged transforms of single chains.

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