The results of electron microscopy and X-ray diffraction measurements of the copolymer indicate that the stacking leads to a low-order organization. The interplanar spacing of 2.0 Å relates conceivably to the intramolecular distance between equal groups of the main chain. Apparently, the macromolecules are stretched because the growth of the stacks produces much stronger pulling together of the macromolecules in the copolymer than in the homopolymer. The strain may result in rupture of the film, if a nodule exceeds a critical size (Figure 3c).

The strain of the polymer film around the nodules seems to be a cause of formation of the nonphotochromic zones surrounding the nodules (Figure 2). This explanation is consistent with the strong effect of the local free volume and segmental mobility of a polymer on the photochromic behavior of spiropyrans.[6,7] One can explain along the same lines the structural stabilization of the merocyanine form in the stacks, revealed by the high thermal stability of the nodules, which do not lose their color even above 150 °C, while the color formed on irradiation of the films disappears above 50 °C.

Conclusion

Investigation of nodules on the polymer films disclosed new important features of zipper crystallization. The stack formation in the homopolymer proceeds faster along the macromolecular chains than expected for a random process, while in the copolymer the last process becomes efficient and leads to the low-dimensional order. The possibility of random migration can explain why the zipper crystallization occurs in the atactic polymers: Apparently, the process goes predominantly along a main chain until a structural irregularity is encountered, which can be bypassed by the transfer of stacking to a neighbor macromolecule. The stack formation leads to shrinking of the material both during zipper crystallization and during the photocontraction of a "quasi-liquid".[8] Perhaps this process is to be taken into account on consideration of the photomechanical effect reported by Smets and co-workers.[9]

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Registry No. SMA homopolymer, 57981-89-2; (SMA)·(MMA) (copolymer), 51816-58-1.

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X-ray Studies of the Structure of Liquid Crystalline Copolyesters: Treatment of an Atomic Model as a One-Dimensional Paracrystal

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ABSTRACT: X-ray fiber diagrams of wholly aromatic copolyesters contain aperiodic intensity maxima on the meridian. It is shown that the positions of these maxima are predicted by calculation of the interference function for a model in which the monomers are represented as points, separated from their neighbors by the appropriate residue lengths. Subsequently these calculations were extended to an atomic model for the chain which leads to good agreement for both position and intensity of the maxima. The easiest approach for the point model is to treat the chain as a one-dimensional paracrystal with bimodal coordination statistics. This paper shows how this procedure can be used for an atomic model for the copolymer chain. This allows the prediction of the scattering by an infinite polymer chain with a distribution of residue orientations about the chain axis and, hence, the investigation of the correlation or persistence length for the stiff chain conformation.

We are using X-ray methods to investigate the physical structure of wholly aromatic copolyesters prepared, for example, from *p*-hydroxybenzoic acid (HBA) and 2-hydroxy-6-naphthoic acid (HNA) and from HBA, 2,6-dihydroxynaphthalene (DHN), and terephthalic acid (TPA). These copolymers form liquid crystalline melts and can be processed therefrom, e.g., as high-strength fibers and novel molded plastics. Their solid-state structure is of interest because of the sensitivity of the bulk properties to relatively small changes in monomer chemistry. In particular, there is evidence for the existence of three-dimensional order, and this order increases with thermal treatment, which is often necessary to obtain optimum mechanical properties.

In previous papers from this laboratory we have shown that the X-ray diffraction data for these copolymers are consistent with a structure made up of oriented, extended chains of completely random monomer sequence. These conclusions are based on a treatment of the copolymer chains as an aperiodic one-dimensional lattice,[1] as will be summarized below. In recent work we have begun to consider the three-dimensional packing of the random

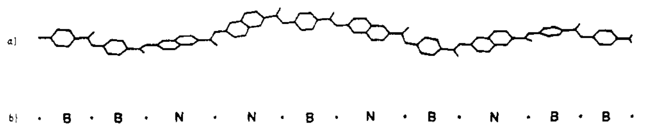

Figure 1. (a) Projection of the structure of a typical random sequence of copoly(HBA/HNA). (b) Point residue approximation of the chain in (a). HBA and HNA are further abbreviated to B and N, respectively.

copolyester sequences, and in view of the size of the necessary calculations, we have explored the different routes by which this problem can be approached. As will be shown below, we find that the most economical approach in terms of computer time is to treat the chain as a one-dimensional paracrystal. We have previously shown that a model of the chain as an aperiodic array of point residues can be treated in this manner.[2] The same approach was taken independently by Bonart[3] in an interpretation of the small-angle X-ray data for keratin, where the aperiodic X-ray maxima were analyzed in terms of a random array of helical and nonhelical chain segments. Several other treatments of this problem can be found in the literature, notably that by Hendricks and Teller[4] for distorted layer structures in inorganic materials such as clays. However, this approach has not previously been applied to linear chains of polyatomic monomer units, and this extension is the subject of this paper.

Figure 1 shows a typical random sequence of copoly(HBA/HNA). The 1,4- and 2,6-linkages of the planar aromatic and ester groups lead to an extended conformation, and this extended character is probably enhanced by the formation of liquid crystalline structure in the melt. Schematics of the X-ray diffraction patterns of copoly(HBA/HNA) for three monomer ratios are shown in Figure 2.[5] A series of meridional maxima are seen that are aperiodic, i.e., they are not orders of a simple repeat, and also shift in position with the monomer ratio. These intensities are derived from the projection of the structure onto the fiber axis (z). It can be seen in Figure 1 that the 1,4- and 2,6-linkage bonds are approximately parallel to the fiber axis. The actual conformation will depend on the aromatic–carboxyl torsion angles, but the *projection* of the extended chain onto the fiber axis will be approximately independent of these torsion angles, at least over short lengths of chain. In particular, the axial advance will be approximately constant for each HBA and for each HNA residue.

In our initial calculations we represented each monomer unit as a point placed for convenience at the ester oxygen and separated from its immediate neighbors by the approximate residue lengths (6.35 Å for HBA and 8.37 Å for HNA), as shown in Figure 1. The Fourier transform of a linear array of N points is given by

$$F_c(Z) = \sum_{j=1}^{N} \exp(2\pi i Z z_j) \tag{1}$$

where z_j is the axial coordinate of the jth point and Z is the reciprocal space coordinate in the direction corresponding to the fiber axis. For an array of parallel chains, assuming that there is no axial register (as in a nematic structure), we need to average over all n possible monomer sequences, and the meridional intensity $I(Z)$ is given by

$$I(Z) = \frac{1}{n} \sum_{c=1}^{n} p_c |F_c(Z)|^2 \tag{2}$$

where p_c is the probability of the cth sequence. For long polymer chains, determination of $I(Z)$ via eq 2 is a lengthy calculation, but this is simplified by grouping the terms when $I(Z)$ is calculated as the Fourier transform of the autocorrelation function of the average chain $Q(z)$:

$$I(Z) = \sum_{l=1}^{M} Q(z_l) \cos (2\pi Z z_l) \tag{3}$$

For the chains of point residues, $Q(z)$ is zero except at M specific values of $z = z_l$ and corresponds to the neighbor probability function for the copolymer chain. $Q(z)$ for a point model of copoly(HBA/HNA) at a 58/42 mole ratio is shown in Figure 3a.

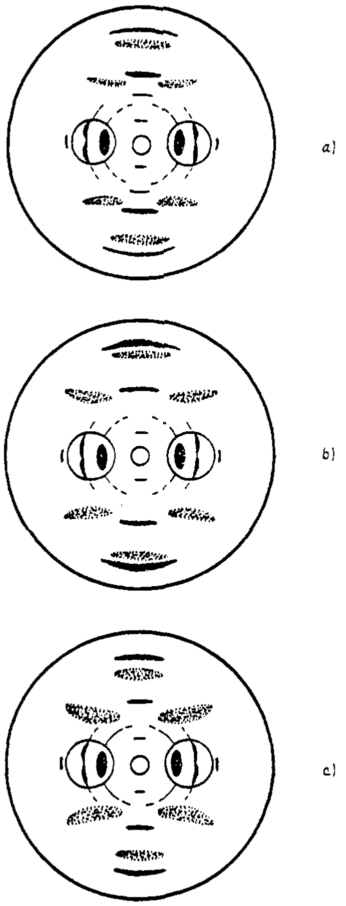

Figure 2. Schematics of X-ray fiber diffraction patterns of three HBA/HNA monomer ratios: (a) 30/70, (b) 58/42, (c) 75/25. The original patterns recorded on film are shown in ref 5.

Equation 3 can be simplified further because the summation has a closed solution. This is derived by treating the aperiodic chain as a one-dimensional paracrystal, after Hosemann.[6] In Figure 3a, $Q(z)$ for 58/42 copoly(HBA/HNA) is separated into components for the 0th, 1st, 2nd, 3rd, ... −1th, −2th, −3th, ... nearest neighbors, which are labeled $H_0, H_1, H_2, H_3, \ldots H_{-1}, H_{-2}, H_{-3}, \ldots$, respectively. It can be seen that H_2 is the self-convolution of H_1:

$$H_2 = H_1 * H_1 \tag{4}$$

and in general

$$H_n = H_{n-1} * H_1 \tag{5}$$

The Fourier transform of $Q(z)$, i.e., $I(Z)$, can then be written

$$I(Z) = \mathcal{F}[Q(z)] = \sum_{-\infty}^{+\infty} \mathcal{F}(H_m) = \sum_{-\infty}^{+\infty} F^m(Z) \tag{6}$$

where

$$F(Z) = \mathcal{F}(H_1) \tag{7}$$

Since

$$F^{-n}(Z) = F^{*n}(Z) \tag{8}$$

eq 6 can be written as

$$\begin{aligned} I(Z) &= 1 + \frac{F(Z)}{1 - F(Z)} + \frac{F^*(Z)}{1 - F^*(Z)} \\ &= \mathrm{Re}\left[\frac{1 + F(Z)}{1 - F(Z)}\right] \\ &= \frac{1 - |F(Z)|^2}{1 - 2\,\mathrm{Re}\,F(Z) + |F(Z)|^2} \end{aligned} \tag{9}$$

For a limited chain of N monomers, eq 9 becomes

$$I(Z) = \mathrm{Re}\left[\frac{1 + F(Z)}{1 - F(Z)} - \frac{2F(Z)[1 - F^N(Z)]}{N[1 - F(Z)]^2}\right] \tag{10}$$

Taking axial lengths of the residues based on stereochemically acceptable models for the monomers, the above approach leads to prediction of aperiodic intensity maxima at scattering angles that match those observed for both series of copolymers.[5] However, such a model cannot reproduce the intensities of these maxima until the effect of intraresidue interferences are included, which requires consideration of atomic models for the residue. This is achieved by separating $Q(z)$ into components:

$$Q(z) = Q(0) + \sum_{\mathrm{A}}\sum_{\mathrm{B}} Q_{\mathrm{AB}}(z) \tag{11}$$

Each $Q_{\mathrm{AB}}(z)$ term describes the probability of sequences beginning with monomer A and ending in monomer B. [N.B.: In ref 1, the origin term, $Q(0)$, is combined into $Q_{\mathrm{AA}}(z)$ and $Q_{\mathrm{BB}}(z)$.] Figure 3 shows the four $Q_{\mathrm{AB}}(z)$ components of $Q(z)$ for 58/42 copoly(HBA/HNA). $I(Z)$ for an atomic model is then given by

$$I(Z) = \sum_{\mathrm{A}}\sum_{\mathrm{B}}\sum_{l} Q_{\mathrm{AB}}(z_l) F_{\mathrm{AB}}(Z) \exp(2\pi i Z z_l) \tag{12}$$

$F_{\mathrm{AB}}(Z)$ is the Fourier transform of the cross convolution of residue A with residue B:

$$F_{\mathrm{AB}}(Z) = \sum_{j}\sum_{k} f_{j,\mathrm{A}} f_{k,\mathrm{B}} \exp(2\pi i Z(z_{k,\mathrm{B}} - z_{j,\mathrm{A}})) \tag{13}$$

where f is the atomic scattering factor and the subscripts j,A and k,B designate the jth atom of residue A and the kth atom of residue B. We have shown[7] that calculations via eq 12 lead to prediction of meridional maxima in approximately the same positions as for the point model and those observed and also give good agreement between the observed and calculated intensities.

Extension of these calculations to a three-dimensional model requires knowledge of the chain conformation and packing, and it is the aim of this work to refine such a model by trial and error to obtain the best possible agreement between the observed and calculated scattering over the whole range of the observed data. We have extended eq 12 to predict $I(R,Z)$ for the whole pattern, where R is the radial reciprocal space coordinate. So far we have predicted the scattering for an average chain in two conformations: an extended chain with random torsional orientation of the residues and a rigid chain with parallel aromatic planes, which represent extremes of the possible molecular conformations in the bulk polymer. Initial results[8] suggest that the extended/random conformation gives better agreement with the observed data, but this conclusion should be viewed with caution because the effect of chain packing has yet to be considered.

The above calculations require iteration of a routine based on eq 12 over an R,Z coordinate grid, and it is desirable to optimize this calculation via a closed form analogous to eq 9 and 10. Inspection of the $Q_{\mathrm{AB}}(z)$ components in the example in Figure 3 shows that they resemble the original $Q(z)$. For example, the positive terms of $Q_{\mathrm{AA}}(z)$ are the same as the origin and positive terms in $Q(z)$ except they are multiplied by the square of the mole fraction p_{A}^2 and shifted by $+z_{\mathrm{A}}$; the negative terms are similar except that they are shifted by $-z_{\mathrm{A}}$. Hence the Fourier transform of $Q_{\mathrm{AA}}(z)$ can be written as

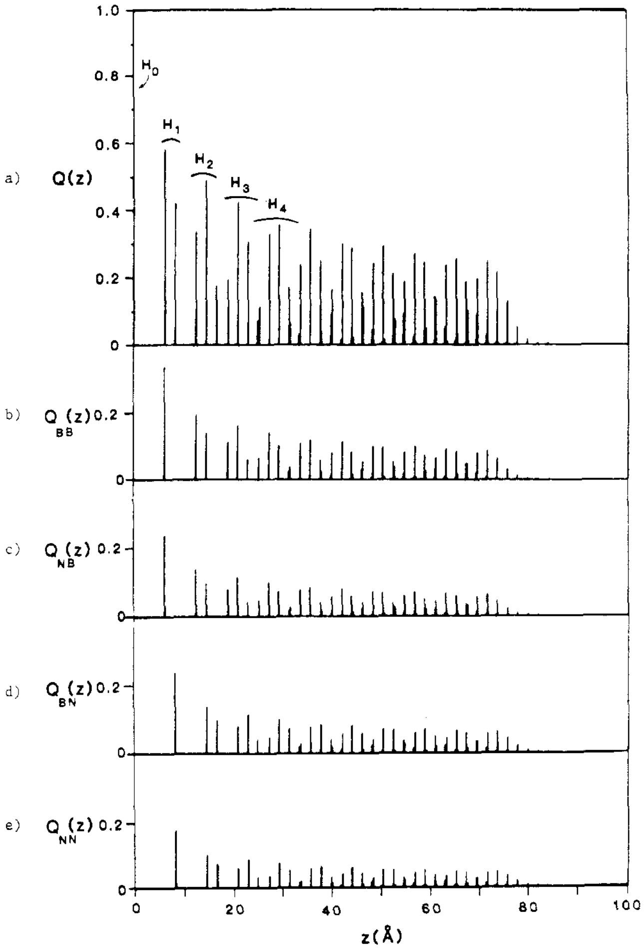

Figure 3. Neighbor probability distribution (autocorrelation) for a random chain of copoly(HBA/HNA), residue ratio 58/42, plotted out to the 10th neighbor and its components: (a) $Q(z)$, (b) $Q_{\mathrm{BB}}(z)$, (c) $Q_{\mathrm{NB}}(z)$, (d) $Q_{\mathrm{BN}}(z)$, (e) $Q_{\mathrm{NN}}(z)$. HBA and HNA abbreviated to B and N in the subscripts.

$$[Q_{\mathrm{AA}}(z)] = p_{\mathrm{A}}^2\left[\left(1 + \frac{F(Z)}{1 - F(Z)}\right)\exp(2\pi i Z(+z_{\mathrm{A}})) + \left(1 + \frac{F^*(Z)}{1 - F^*(Z)}\right)\exp(2\pi i Z(-z_{\mathrm{A}}))\right] \tag{14}$$

and similar equations can be written for the other components of $Q(z)$. The full expression for the intensity for an infinitely long random sequence of polyatomic monomers is then

$$\begin{aligned} I(Z) &= \sum_{\mathrm{A}} p_{\mathrm{A}} F_{\mathrm{AA}}(Z) + \sum_{\mathrm{A}}\sum_{\mathrm{B}} p_{\mathrm{A}} p_{\mathrm{B}} F_{\mathrm{AB}}\left[\frac{\exp(2\pi i Z z_{\mathrm{B}})}{1 - F(Z)} + \frac{\exp(2\pi i Z(-z_{\mathrm{A}}))}{1 - F^*(Z)}\right] \\ &= \sum_{\mathrm{A}} p_{\mathrm{A}} F_{\mathrm{AA}}(Z) + \sum_{\mathrm{A}}\sum_{\mathrm{B}} p_{\mathrm{A}} p_{\mathrm{B}}\left(2\,\mathrm{Re}\left[\frac{F_{\mathrm{AB}}\exp(2\pi i Z z_{\mathrm{B}})}{1 - F(Z)}\right]\right) \end{aligned} \tag{15}$$

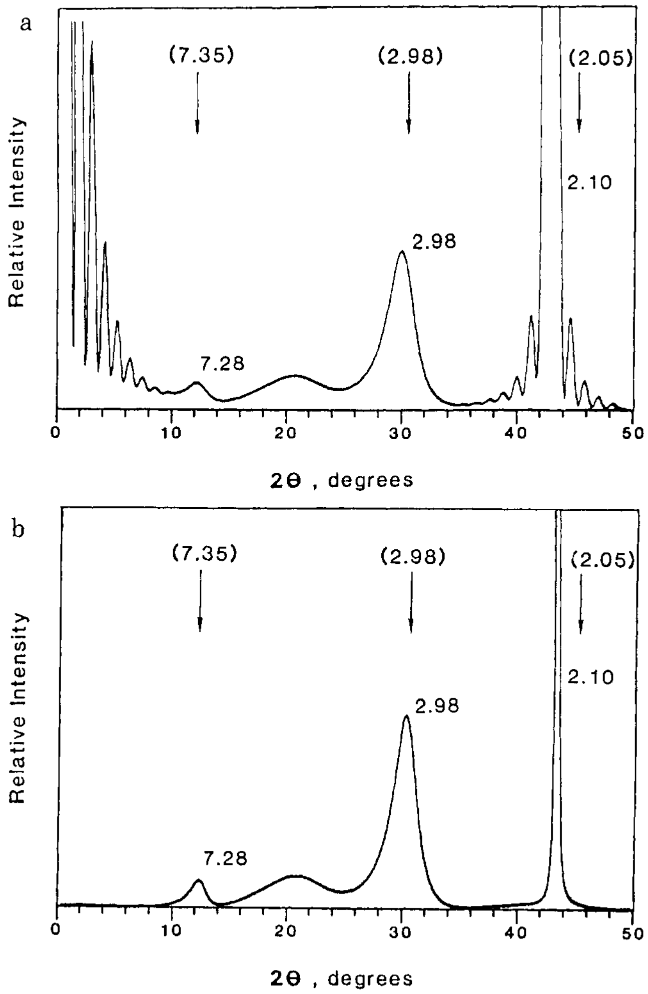

Figure 4. (a) Intensity calculated for copoly(HBA/HNA), residue ratio 58/42, by using the one-dimensional paracrystalline atomic model for a random chain of 11 residues. (b) Intensity calculated for the same copolymer for an infinite chain. (Bragg spacings of the calculated peaks are given in Å. Positions of the observed meridional maxima are indicated by arrows with the *d*-spacings in parentheses.)

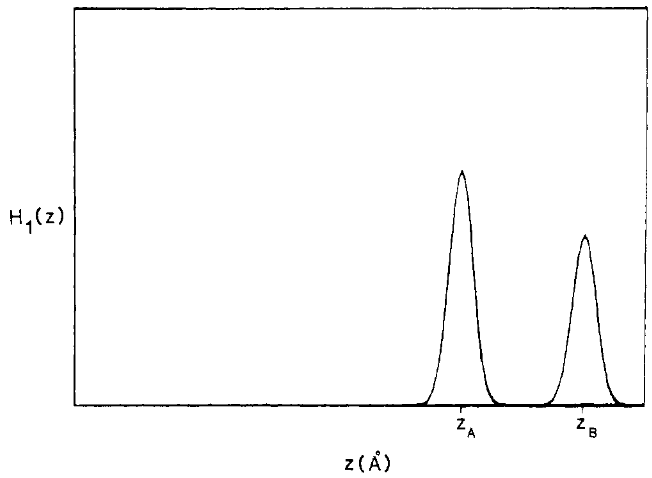

Figure 5. First neighbor probability distribution $H_1(z)$, calculated from eq 16 with $a = 13.28$, $b = 12.95$, $z_A = 6.35$ Å, and $z_B = 8.37$ Å.

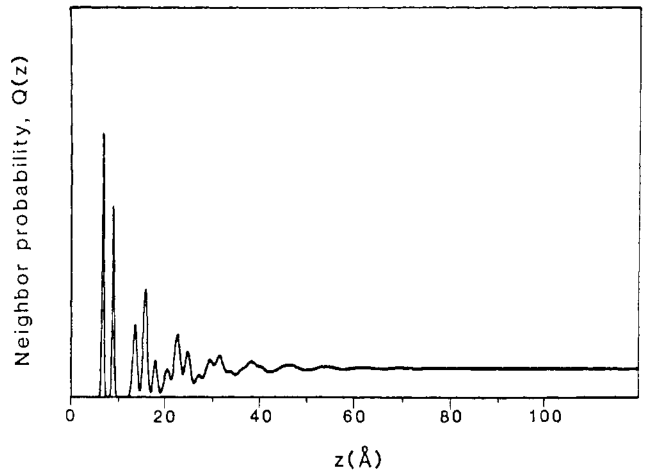

Figure 6. Neighbor probability distribution $Q(z)$ for an infinite random chain of copoly(HBA/HNA), residue ratio 58/42, using the first neighbor distribution $H_1(z)$ shown in Figure 5.

and can be adapted for a finite chain as in eq 10. Figure 4a shows $I(Z)$ calculated in this manner for chains of 11 residues for 58/42 copoly(HBA/HNA) on the basis of the atomic coordinates for the monomers given in ref 5. The results are the same as those obtained by using eq 12 and also published in ref 5, but required one-tenth of the computer time. The calculation for an infinite chain is shown in Figure 4b, for which there is a further reduction in computation time by a factor of ~3.

The ability to calculate $I(Z)$ for an infinite atomic model presents the ideal way to investigate the extent of correlations along the chain. Previously we have done this by calculations for chains of limited length: we have found that the width of the peak at a Bragg spacing of 2.1 Å decreased with chain length, and the best agreement with the observed data is found for chains of 9–13 residues, depending on the HBA/HNA ratio in the range 30/70 to 75/25.[7] The degree of polymerization for the copolymer is in the range of 150 residues, based on the reported molecular weight.[9] Hence the chain length determined from the line width corresponds to a correlation of persistence length for the stiff chain. In the above analyses we have assumed that the chains are straight, with the ester oxygen–ester oxygen vectors parallel to the chain axis. However, as can be seen in Figure 1, this is only an approximation; there is, in fact, a distribution of these vectors about the chain axis. Thus the correlation length can be thought of as the length beyond which the approximation of a perfectly straight chain breaks down. This variability in residue length can be introduced into the calculation by replacing the δ-function components of $H_1(z)$ by, e.g., exponential distributions. We have derived $H_1(z)$ from

$$H_1(z) = p_A' \exp[-a(z - z_A)^2] + p_B' \exp[-b(z - z_B)^2] \quad (16)$$

The widths of the distribution are defined by a and b. As an example, Figure 5 shows $H_1(z)$ with $a = 13.28$ and $b = 12.95$, which was set to give a width of 2.0 Å at the base $[H_1(z) = 10^{-7}]$ of each distribution. p_A' and p_B' are normalized probabilities that set the area under the two peaks to p_A and p_B. Figure 6 shows $Q(z)$ calculated for an infinite chain of the 58/42 copolymer derived from $H_1(z)$ in Figure 5. This width for the components of $H_1(z)$ was selected because it leads to a smooth $Q(z)$ at $z \simeq 80$ Å, which corresponds to a correlation length of 11 residues, but it appears reasonable in terms of the possible range of residue orientations. Figure 7 shows the calculated intensity for the point model of the infinite chain using eq 9. The width of the 2-Å peak is similar to that calculated for a chain of 11 residues with constant l_A and l_B. (Refinement of a, b, z_A, and z_B is currently in progress, based on a study of molecular models and a point by point comparison of the

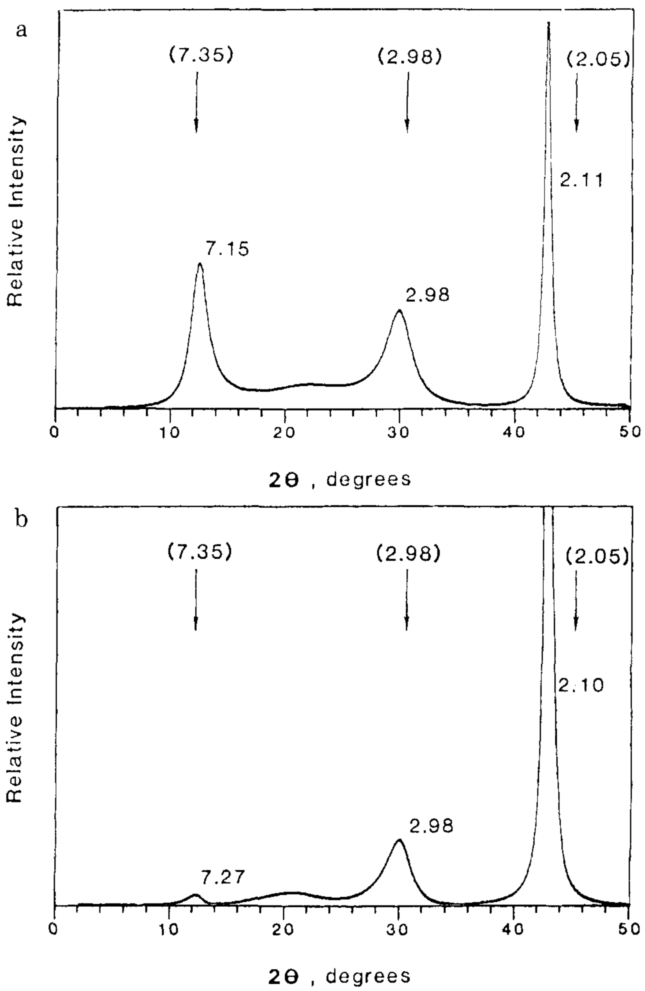

Figure 7. Intensity calculated for an infinite random chain of copoly(HBA/HNA), residue ratio 58/42, by using the neighbor probability distribution shown in Figure 6: (a) point model; (b) atomic model. (Bragg spacings of the calculated peaks are given in Å. Positions of the observed meridional maxima are indicated by arrows with the d-spacings in parentheses.)

observed and calculated intensity.)

For a model with polyatomic monomers we need to separate the $Q(z)$ and $H_1(z)$ terms in the point monomer equations into their AB components

$$I(Z) = \mathcal{F}[Q(0)] + \mathcal{F}[\sum_{A}\sum_{B} Q_{AB}(z)] \qquad (17)$$

where

$$Q_{AA}(z) = H_{AA}(z)*\sum_{0}^{\infty} H_n(z) + H_{AA}(-z)*\sum_{-\infty}^{0} H_n(z) \qquad (18)$$

and so on for the other components of $Q(z)$. $\mathcal{F}[Q(0)] = 1$ for the point monomers. As before

$$\mathcal{F}[Q_{AA}(z)] = 2\ \mathrm{Re}\left[\frac{\mathcal{F}[H_{AA}(z)]}{1 - F(Z)}\right] \qquad (19)$$

and so on. These terms now need to be adjusted for intraresidue interferences, which is complicated by the now-variable residue lengths. This essentially means that we need a different set of atomic coordinates for each residue length. However, the effect of such changes on the slowly varying $F_{AB}(Z)$ terms is minimal (see ref 7), and assumption of a constant $F_{AB}(Z)$ set at the values for the midpoint of the $H_{AB}(z)$ distribution is an acceptable approximation. Figure 7 shows the calculation for an infinite chain atomic model with variable residue lengths. The results can be seen to be comparable with those obtained previously (Figure 4) and are in good agreement with the experimental data. This procedure requires only 15 s of computer time (VAX 11/780), as against 6 min for the calculation via eq 12 for a chain of 11 residues. (The latter results contain subsidiary maxima due to finite chain length, and our procedure in ref 7 was to smooth these by averaging over different chain lengths, with a further increase in computation time.) The approaches presented above can be easily extended to the three-dimensional cylindrically averaged structure, and details of the latter calculations will be described in the near future.

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