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Three-Dimensional Structure of Main-Chain Liquid-Crystalline Copolymers. 2. Interchain Interference Effects

Amit Biswas and John Blackwell*

Department of Macromolecular Science, Case Western Reserve University, Cleveland, Ohio 44106-2699. *Received December 7, 1987*

ABSTRACT: Previous analyses of the X-ray fiber diagrams of wholly aromatic copolyesters have shown that these systems consist of oriented arrays of chains with completely random comonomer sequence. Nevertheless, these copolymers exhibit sharp equatorial and off-equatorial Bragg maxima that are indicative of three-dimensional crystallinity. This paper shows that these diffraction characteristics are predicted when limited register occurs between adjacent chains. This is achieved when one monomer on each chain of the array comes into register in a plane perpendicular to the fiber (chain) axis. As such, this requires a small shift for each chain (~4 Å at the most) from the arrangement in a nematic structure. Analyses are developed to predict the interference effects for three-dimensional arrays of copolymer chains, with or without chain register. The results show that in as-spun fibers even the limited register described above exceeds that necessary to generate the observed diffraction effects. Rather, there is a normal distribution of chain origins about the registry plane, with a standard deviation of ~2 Å, which corresponds to only a small preference for registration.

Introduction

The X-ray data for thermotropic wholly aromatic copolyesters are very intriguing because these polymers exhibit substantial three-dimensional crystallinity despite the fact that they have a random comonomer sequence. The latter fact has been established by X-ray analyses in this and other laboratories over the last few years.[1-4] The X-ray fiber diagrams contain a series of aperiodic meridional maxima, and it has been shown that these are reproduced in position and approximate intensity in theoretical calculations for nematic arrays of extended chains of completely random sequence.[5,6] When nonrandom sequence distributions are considered by variation of nearest-neighbor statistics, the agreement between the observed and calculated meridional data becomes unacceptable for all but minimal blockiness.[7,8]

The evidence for three-dimensional order comes from the presence of sharp equatorial and off-equatorial Bragg reflections in the fiber diagrams. Three-dimensional register is required by the presence of a sharp off-equatorial at $d \cong 3.3$ Å, which occurs at a layer line spacing of 12–15 Å, depending on the chemical composition. Thermal annealing of these copolymers can result in a sharpening of these reflections corresponding to an increase in crystallite size,[9] and there can be the generation of additional maxima, some of which may be due to development of an additional polymorphic structure.[10] Application of the Scherrer equation to the equatorial maxima yields crystallite widths of 70–190 Å,[11] depending on the thermal history, which indicates large ordered regions consisting of ~200–1500 chains. In addition, degrees of crystallinity as high as 80% have been reported,[12] based on division of the diffraction data into "crystalline" and "amorphous" components. Typical values for quenched specimens are in the range 30–50%, which increases on annealing.[13] It should be noted that annealing does not lead to changes in the positions of the meridional maxima; i.e., there is no evidence for any departure from a random sequence distribution.[10]

Our previous analyses of the structure addressed a one-dimensional problem, since the diffraction along the meridian is derived from the projection of the "average" chain onto the fiber axis. In view of the approximate linearity of the chain, this projection is approximately independent of conformation. However, when we attempt to derive a three-dimensional structure from the entire diffraction pattern, it is necessary to consider the actual chain conformation. Our first step in analyzing the structure was to calculate the cylindrically averaged transform for individual chains of average sequence. The original approach described by Chivers and Blackwell[14] for the copolyester of *p*-hydroxybenzoic acid (HBA) and 2-hydroxy-6-naphthoic acid (HNA) has been generalized for other chemical structures and applied to different conformations.[15] The main conclusion is that the chains have a pseudo "dimer repeat", with the successive ester groups pointed to opposite sides of the chain, analogous to the dimer repeats observed for homopoly(HBA)[16] and poly(*p*-phenyleneterephthalamide).[17] This pseudo dimer repeat is necessary, since correlations between successive monomers in the dimer are responsible for the generation of the layer line on which the off-equatorial maximum lies.

The present paper considers the interference effects that occur when these chains are packed with their origins on a two-dimensional network. If the origin atoms are coplanar but there is no radial correlation for the chain position, i.e., there is cylindrical averaging of the chains independent of the two-dimensional lattice, then the effect of interference is to sample the cylindrically averaged transform for the chain at the lattice points. The fact that layer line reflections are observed in the fiber diagrams means that we must have some sort of chain register. Such register is likely to involve stacking of aromatic groups or dipole–dipole interaction of the carboxyl groups, and hence there will be a spatial correlation between certain monomers on adjacent chains.

The first possibility for chain register that comes to mind is the lateral alignment of homopolymer sequences, some

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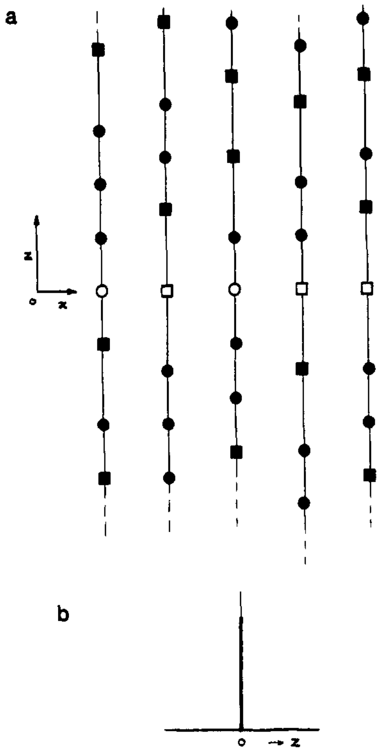

Figure 1. (a) Two-dimensional arrangement of chains with the origin monomers (unshaded) lying on the x-axis. ● and ■ denote the two types of monomers. (b) Distribution of origin monomers about the x-axis.

of which occur even in completely random copolymers. It is easily apparent, however, that there would be too few of these sequences to account for the high degree of order, even if it were possible to segregate them during crystallization of the melt. Windle and co-workers[18,19] have proposed a less stringent requirement in which there is alignment of short identical copolymer sequences. They have used computer-generated random sequences and shifted the chains along their axes so as to optimize the overlap between adjacent chains. This approach is interesting but still requires extensive rearrangement of the chains from the random nematic structure; even then it cannot generate the high degrees of crystallinity (up to 80%) and large crystallite sizes (up to 180 Å) that are seen for these copolymers.

Our approach to the above problem has been to require chain register at one point only in a sequence. The simplest definition of register is where one monomer on each chain is in the same horizontal plane, as shown in two dimensions in Figure 1. Here each chain is depicted as a linear sequence of point monomers. Our definition of register takes no account of the differences between monomers or of the possibility of different chain sense (up or down). We can think of this register as when one ester oxygen of each chain lies in the register plane. The crystal would then be relatively perfect on the register plane, and the perfection would deteriorate progressively as the random sequences proceed above and below that plane.

Scattering by Arrays of Aperiodic Chains

We have shown previously that $I_a(Z)$, the scattering in the chain (Z) axis direction by a nematic array of chains of point monomers, is given by[20]

$$I_a(Z) = \mathrm{Re}\left[\frac{1 + H(Z)}{1 - H(Z)}\right] \tag{1}$$

where Re designates the real component and $H(Z)$ is the Fourier transform of the first nearest-neighbor probability distribution along the z (fiber axis) direction. In the case of finite chains, each of N monomers, eq 1 becomes

$$I_a(Z) = N\,\mathrm{Re}\left[\frac{1 + H(Z)}{1 - H(Z)} - \frac{2H(Z)[1 - H^N(Z)]}{N[1 - H(Z)]^2}\right] \tag{2}$$

Consider now the two-dimensional array of points in Figure 1, representing M chains, each of N monomers. The chains are sections of random sequences of two monomers A and B of lengths z_A and z_B, and the overall molar proportions of the monomers are p_A and p_B. The separation between chains in the X direction is a. The total scattering intensity can be separated into intra- (1) and intermolecular (2) components

$$I(X,Z) = I_1(X,Z) + I_2(X,Z) \tag{3}$$

The intramolecular component I_1 is simply M times $I_a(Z)$ calculated in eq 2. $I_2(X,Z)$ can be written as a sum over the interferences between the first, second, etc., nearest-neighbor chains.

$$I_2(X,Z) = \sum_{m=1}^{M-1}(M - m)I_2^m(X,Z) \tag{4}$$

Here the $I_2^m(X,Z)$ terms define the interferences between the mth nearest-neighbor chains, i.e., the ith and the $i+m$th chain (which are separated by a distance ma), and there will be $M - m$ such interactions. $I_2^m(X,Z)$ is further defined in terms of interferences between the monomers in the ith and the $i+m$th chain as

$$I_2^m(X,Z) = \sum_{j=0}^{N-1}\sum_{k=0}^{N-1} C_{i,i+m}^{j,k}(X,Z) \tag{5}$$

$C_{i,i+m}^{j,k}(X,Z)$ is the contribution due to interference between the scattering between the jth monomer on chain i and the kth monomer on chain $i + m$. $C_{i,i+m}^{j,k}(X,Z)$ can be expressed as

$$C_{i,i+m}^{j,k}(X,Z) = 2\cos(2\pi Xma)\, C_i^j(Z)\, C_{i+m}^{k*}(Z) \tag{6}$$

$$C_i^j(Z) = \sum p_{i,j} \exp(2\pi i Z z_{ij}) \tag{7}$$

where * represents the complex conjugate and the sum is over all possible positions for the jth monomer of the ith chain. In general this monomer is at a distance $z_{i,j}$ along the ith chain, and the associated probability for each such occurrence is $p_{i,j}$. For a chain of random comonomer sequence, $p_{i,j}$ is the product of j terms of p_A or p_B, and $z_{i,j}$ is the sum of j monomer lengths, i.e., z_A or z_B.

It is convenient to express the double summation of eq 5 as a single summation over the difference variable n defined as $|j - k|$

$$I_2^m(X,Z) = \sum_{n=0}^{N-1} D_{i,i+m}^n(X,Z); \qquad n = |j - k| \tag{8}$$

In this equation, the first term, $D_{i,i+m}^0(X,Z)$, for example, is the sum over the terms $C_{i,i+m}^{0,0}(X,X)$, $C_{i,i+m}^{1,1}(X,Z)$, ..., $C_{i,i+m}^{n,n}(X,Z)$, etc. In terms of the composition, p_A and p_B, and the monomer lengths, z_A and z_B,

$$\begin{aligned} C_{i,i+m}^{0,0}(X,Z) &= 2\cos(2\pi Xma)[(p_A + p_B)(p_A + p_B)] \\ &= 2\cos(2\pi Xma) \end{aligned} \tag{9}$$

$$\begin{aligned} C_{i,i+m}^{1,1}(X,Z) = {} & 2\cos(2\pi Xma) \times \\ & [(p_A \exp(2\pi i Z z_A) + p_B \exp(2\pi i Z z_B)) \times \\ & (p_A \exp(-2\pi i Z z_A) + p_B \exp(-2\pi i Z z_B))] \\ = {} & 2\cos(2\pi Xma)\, K(Z) \end{aligned} \tag{10}$$

where

$$K(Z) = H(Z)\,H^*(Z) \tag{11}$$

Similarly

$$C^{2,2}_{i,i+m}(X,Z) = 2\cos(2\pi Xma)K^2(Z) \tag{12}$$

and in general

$$C^{n,n}_{i,i+m}(X,Z) = 2\cos(2\pi Xma)\,K^n(Z) \tag{13}$$

$D^0_{i,i+m}(X,Z)$ can now be written as

$$\begin{aligned} D^0_{i,i+m}(X,Z) &= 2\cos(2\pi Xma)[1 + K(Z) + K^2(Z) + \ldots + K^n(Z) + \ldots + K^{N-1}(Z)] \\ &= 2\cos(2\pi Xma)\left[\frac{1 - K^N(Z)}{1 - K(Z)}\right] \end{aligned} \tag{14}$$

Similarly

$$D^1_{i,i+m}(X,Z) = 2\cos(2\pi Xma)2\,\mathrm{Re}\left[\frac{1 - K^{N-1}(Z)}{1 - K(Z)}H(Z)\right] \tag{15}$$

The $N - 1$ power in the numerator reflects the fact that there are $N - 1$ first-nearest-neighbor terms, compared to N zero-order terms. The final $H(Z)$ component takes account of the phase shift between the first nearest neighbors. This extends to the general case

$$D^n_{i,i+m}(X,Z) = 2\cos(2\pi Xma)2\,\mathrm{Re}\left[\frac{1 - K^{N-n}(Z)}{1 - K(Z)}H^n(Z)\right] \tag{16}$$

and thus

$$I^m_2(X,Z) = 2\cos(2\pi Xma)\left[\frac{1 - K^N(Z)}{1 - K(Z)} + 2\,\mathrm{Re}\sum_{n=1}^{N-1}\left(\frac{1 - K^{N-n}(Z)}{1 - K(Z)}H^n(Z)\right)\right] \tag{17}$$

which will be abbreviated to

$$I^m_2(X,Z) = 2\cos(2\pi Xma)\,I_b(Z) \tag{18}$$

where

$$I_b(Z) = \frac{1 - K^N(Z)}{1 - K(Z)} + 2\,\mathrm{Re}\left[\frac{H(Z)}{K(Z) - H(Z)}\left(\frac{1 - K^N(Z)}{1 - K(Z)} - \frac{1 - H^N(Z)}{1 - H(Z)}\right)\right] \tag{19}$$

The total interference function (eq 3) can therefore be written as

$$I(X,Z) = MI_a(Z) + I_b(Z)\,I_c(X) \tag{20}$$

where

$$I_c(X) = 2\sum_{m=1}^{M-1}(M - m)\cos(2\pi Xma) \tag{21}$$

Note that I_a and I_b are functions of Z only. It is readily shown that the above question becomes a Laue function when the chains are periodic. The above derivation is for chains of N point monomers in which register is defined by setting the first monomer in each chain in a plane. Analogous expressions for the situation where the central monomer of each chain defines the register plane have also been derived, and its diffraction characteristics have been found to be similar to that described here.

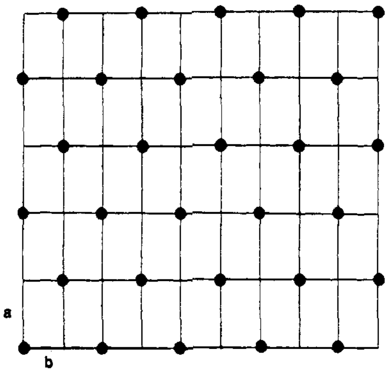

Figure 2. Hexagonal lattice represented as an orthogonal arrangement of points with unoccupied lattice sites.

For a three-dimensional $M_1 \times M_2$ array of chains separated by a along the x-axis and b along the y-axis in an orthorhombic lattice

$$I(X,Y,Z) = M_1M_2I_a(Z) + I_b(Z)\,I_c(X,Y) \tag{22}$$

where

$$I_c(X,Y) = 4\sum_{m_1=0}^{M_1-1}{}'\sum_{m_2=0}^{M_2-1}{}'(M_1 - m_1) \times (M_2 - m_2)\cos(2\pi Xm_1a)\cos(2\pi Ym_2b) \tag{23}$$

The primes on the summation signs indicate that the term $m_1 = m_2 = 0$ is omitted from the summation and that the terms $m_1 = 0$, $m_2 \neq 0$, $m_1 \neq 0$, and $m_2 = 0$ are given half-weight only.[21] $I_c(X,Y)$ for a hexagonal lattice can be derived as a special case of the orthorhombic lattice, as shown in Figure 2, where a and b are in the ratio $3^{1/2}$:1 and half the lattice points are unoccupied (the vacancies occur at $m_1a + m_2b$ when $m_1 + m_2$ is odd). The separation between adjacent points is $2b$, and the total number of lattice points decreases from M_1M_2 to $M_1M_2/2$ such that

$$I_c(X,Y) = 2\sum_{m_1=0}^{M_1-1}{}'\sum_{\substack{m_2=0 \\ m_1+m_2=\text{even}}}^{M_2-1}(M_1 - m_1) \times (M_2 - m_2)\cdot\cos(2\pi Xm_1a)\cos(2\pi Ym_2b) \tag{24}$$

In the case of fiber symmetry, eq 24 can be cylindrically averaged and expressed as

$$I_c(R) = 2\sum_{m_1=0}^{m_1-1}{}'\sum_{m_2=0}^{m_2-1}{}'(M_1 - m_1)(M_2 - m_2)J_0[2\pi R(m_1^2a^2 + m_2^2b^2)^{1/2}] \tag{25}$$

where J_0 is the zeroth-order Bessel function.

Imperfect Axial Register

The condition of perfect register, defined by setting the first monomer in each chain in a plane, can be relaxed by introduction of a distribution function to describe the probability that an origin monomer will be in the reference plane (see Figure 3). We have used a normal distribution $G(z)$ with standard deviation σ to describe this probability

$$G(z) = \frac{1}{(2\pi)^{1/2}\sigma}\exp(-z^2/2\sigma^2) \tag{26}$$

The Fourier transform of $G(z)$ is $A(Z)$, where

$$A(Z) = F(G(z)) = \exp(-2\pi^2Z^2\sigma^2) \tag{27}$$

Such deviations from register will only affect the intermolecular interference terms and are incorporated via the convolution theorem:

$$I(R,Z) = MI_a(Z) + A(Z)\,I_b(Z)\,I_c(R) \tag{28}$$

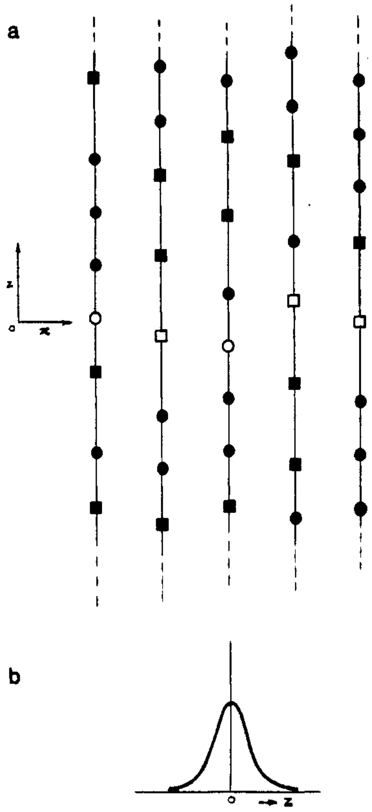

Figure 3. (a) Two-dimensional arrangement of chains with the origin monomers (unshaded) distributed about the x-axis. (b) Gaussian distribution defining the position of origin monomers about the x-axis.

Atomic Monomers

In the above derivations, we have represented the individual monomers by points. If we are to allow for intramonomer interference effects, it is necessary to use atomic models for the monomers, which requires us to consider the chain conformation. In paper 1 of the series in this issue[15] we derived the intensity transforms for chains in two extremes of the conformation: a rigid extended chain in which all the monomer rotations are fixed with respect to each other and a random extended conformation in which successive monomers (or dimers) can have every possible orientation about the z axis such that there is no correlation between the torsional rotation of successive monomers (or dimers). Calculations of single-chain transforms showed slightly better agreement for the extended random conformation, and this option has been used here. However, this choice is not critical at this stage, and the actual conformation of the chain will be considered in more detail in paper 3 of this series.

With a transfer from Cartesian to cylindrical polar coordinates, the monomer residues are composed of atoms with coordinates r_j,ϕ_j,z_j and scattering factor f_j. The coordinates in reciprocal space are R,Φ,Z. Cylindrical averaging of the structure requires calculation of

$$I(R,Z) = MI_a(R,Z) + A(Z)\, I_b(R,Z)\, I_c(R) \tag{29}$$

for an array of M chains. The intra- and interchain components, $I_a(R,Z)$ and $I_b(R,Z)$, are

$$I_a(R,Z) = N(\sum_{A} p_A F_{AA}(R,Z) + 2\,\mathrm{Re} \sum_{A}\sum_{B} F_{AB}(R,Z)\; T_{AB}(Z)] \tag{30}$$

$$I_b(R,Z) = \mathrm{Re} \sum_{A}\sum_{B} F_{AB}(R,Z)[U_{AB}(Z) + 2V_{AB}(Z)] \tag{31}$$

where

$$F_{AB}(R,Z) = \sum_{j}\sum_{k} f_{A,j} f_{B,k} J_0(2\pi R r_{A,j})\; J_0(2\pi R r_{B,k})\, \exp[2\pi i Z(z_{B,k} - z_{A,j})] \tag{32}$$

The terms $T_{AB}(Z)$, $U_{AB}(Z)$, and $V_{AB}(Z)$ are terms in the **T**, **U**, and **V** matrices, respectively, which are defined as follows:

$$\mathbf{T}(Z) = \mathbf{P}\left[\frac{\mathbf{H}(Z)}{\mathbf{I} - \mathbf{H}(Z)} - \frac{\mathbf{H}(Z)[\mathbf{I} - \mathbf{H}^N(Z)]}{N[\mathbf{I} - \mathbf{H}(Z)]^2}\right] \tag{33}$$

Here **I** is the unity matrix and $H(Z)$ is defined as

$$\mathbf{H}(Z) = \mathbf{MX}(Z) \tag{34}$$

The matrices **P**, **M**, and **X** have been defined in paper 1[15] as

$$\mathbf{P} = \begin{bmatrix} p_A & 0 \\ 0 & p_B \end{bmatrix}$$

$$\mathbf{M} = \begin{bmatrix} p_A & p_B \\ p_A & p_B \end{bmatrix}$$

$$\mathbf{X} = \begin{bmatrix} \exp(2\pi i Z z_A) & 0 \\ 0 & \exp(2\pi i Z z_B) \end{bmatrix}$$

For the definition of **U** and **V**, it is necessary to define three additional matrices, $\mathbf{C}_0$, **C**, and **S**:

$$\mathbf{C}_0 = \begin{bmatrix} p_A p_A & p_A p_B \\ p_B p_A & p_B p_B \end{bmatrix} \qquad \mathbf{S} = \begin{bmatrix} K(Z) & 0 \\ 0 & K(Z) \end{bmatrix}$$

$$\mathbf{C} = \begin{bmatrix} p_A p_A & p_A p_B \exp[2\pi i Z(z_B - z_A)] \\ p_B p_A \exp[2\pi i Z(z_A - z_B)] & p_B p_B \end{bmatrix}$$

Using these matrices, $U(Z)$ and $V(Z)$ are defined as

$$\mathbf{U}(Z) = \mathbf{C}_0 + \mathbf{C}(Z)\left[\frac{\mathbf{I} - \mathbf{S}^N(Z)}{\mathbf{I} - \mathbf{S}(Z)}\right] \tag{35}$$

$$\mathbf{V}(Z) = \mathbf{C}_0\mathbf{H}(Z)\left(\frac{\mathbf{I} - \mathbf{H}^{N-1}(Z)}{\mathbf{I} - \mathbf{H}(Z)} + \frac{\mathbf{C}(Z)\;\mathbf{H}(Z)}{\mathbf{S}(Z) - \mathbf{H}(Z)}\left[\frac{\mathbf{I} - \mathbf{S}^{N-1}(Z)}{\mathbf{I} - \mathbf{S}(Z)} - \frac{\mathbf{I} - \mathbf{H}^{N-1}(Z)}{\mathbf{I} - \mathbf{H}(Z)}\right]\right) \tag{36}$$

Experimental Section

Fiber diffraction patterns of as-drawn samples of the liquid-crystalline copolymer, HBA/HNA, in a 30/70 molar ratio were obtained by procedures described elsewhere.[22] These samples were provided to us by the Celanese Research Co., Summit, NJ.

Theoretical model calculations for a three-dimensional structure of 30/70 copoly(HBA/HNA) were done by using the expressions derived above; 200 "average" chains, each of 15 dimers, were considered for the calculation. The chains were arranged on a lattice, as shown in Figure 2, with an interchain chain spacing of a = 5.3 Å. The choice of such an ensemble was based on the following: (a) The observed equatorial maxima at $d \cong$ 4.6, 2.6, and 2.3 Å index as the 100, 110, and 200 reflections for a hexagonal net with $a \cong$ 5.3 Å. The arrangement of chains on the lattice shown in Figure 2 with an interchain spacing of 5.3 Å would account for these observations. (b) The lateral crystallite width measured from the half-width of the equatorial maximum at $d \cong$ 4.5 Å, using the Scherrer equation, is approximately 100 Å. An arrangement of 200 chains on the lattice defined above, with an interchain spacing of 5.3 Å, leads to a diagonal width of ~110 Å.

In paper 1 we have used the so-called "random dimer" model of an average chain in which the copolymer chain is treated as a random array of the four possible dimers with fixed confor-

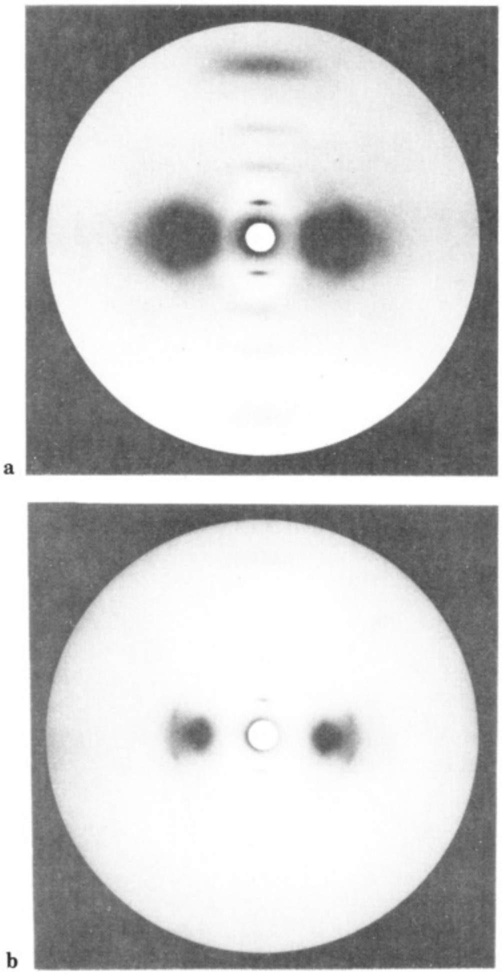

Figure 4. Fiber diffraction patterns from melt-drawn samples of 30/70 copoly(HBA/HNA) at (a) high and (b) low exposure times.

mations but with no rotational correlations between successive dimers. Two conformations were considered for the four possible dimers: a pseudo 2_1 helical structure with parallel aromatic planes or one with inclined aromatic planes, analogous to the conformation adopted by poly(*p*-phenyleneterephthalamide) in the solid state. These will be referred to as the parallel aromatic and inclined aromatic conformation, respectively. Spatial correlations in the basal plane between residues in different chains are assumed to be absent. (The effects of these correlations will be addressed in paper 3). Hence the transform of the average chain is sampled by the interference function of the lattice of 200 chains, taking account of the fact that all 200 chains have their origins in register. The perfection of the axial register was modified by varying σ in eq 26 in 0.5-Å increments from 0 to 5.0 Å. Random axial stagger as in a nematic array was simulated by using a large value for the standard deviation, i.e., σ = 10 Å.

The theoretical intensities, $I(R,Z)$, normalized to the scattering by one "average" residue, were calculated on a 201 × 201 grid along the positive R and Z axes for scattering angles of $2\theta \leqslant 50°$ ($\theta = \sin^{-1}[\lambda/(R^2 + Z^2)^{1/2}]$). No Lorentz/polarization corrections were applied to the data. For display purposes, the high intensities close to the origin ($(R^2 + Z^2)^{1/2} = 0.05$ Å^{-1}) were set at 0. Elsewhere, intensities between 0 and 30.0 (per average residue) were put on a linear scale of 256 shades of gray (white = 0, black = 255). Intensities higher than 30.0 were set at black. This amounts to truncation of the high intensities so that the weaker intensities can be seen. All four quadrants were then displayed on a 401 × 401 grid on an AED 512 terminal.

Results and Discussion

The X-ray diffraction pattern of as-spun fibers of 30/70 copoly(HBA/HNA) is shown in Figure 4. A high degree of molecular orientation parallel to the fiber axis is apparent. The meridional maxima are aperiodic as discussed above. The data for the other comonomer ratios are similar except for the positions of the layer lines. The 30/70 copolymer gives a very strong equatorial at $d \cong 4.6$ Å, followed by weaker maxima at 2.6 and 2.3 Å. These index as the 100, 110, and 200 reflections for a two-dimensional hexagonal lattice, with dimension $a \cong 5.3$ Å. The presence of an off-equatorial with $d \cong 3.3$ Å at $R,Z = 0.294, 0.067$ Å^{-1} is an indication of three-dimensional order. The R coordinate requires a doubling of the unit cell to the orthorhombic option with $a \cong 9.18$ and $b \cong 5.3$ Å, such that the off-equatorial is on the $21Z$ row line. For the present, we will use the simpler hexagonal unit cell, which contains one copolymer chain. The packing of the chains in the orthorhombic two-chain unit cell will be addressed in paper 3.

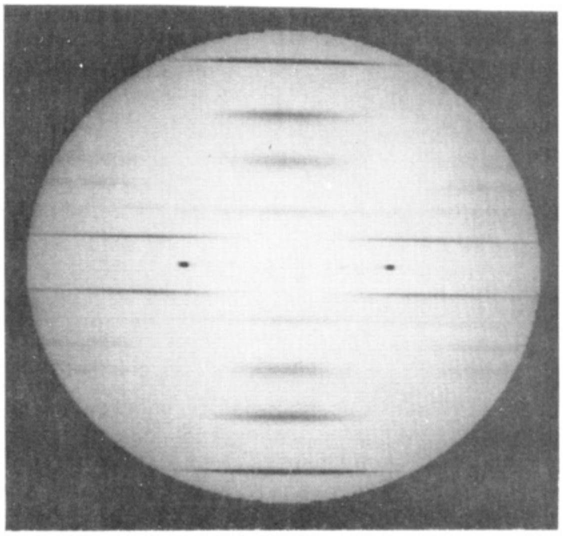

Figure 5. Calculated diffraction pattern for 200 hexagonally packed chains of 30/70 copoly(HBA/HNA) with completely random axial stagger simulated by σ = 10.0 Å.

Figure 5 shows the calculated diffraction pattern for a nematic array of chains packed on a hexagonal network with a = 5.3 Å. The chains are constructed of pseudo 2_1 dimers, and there is no rotational correlation between successive dimers; i.e., each dimer is cylindrically averaged. Random axial stagger is simulated by setting σ = 10.0 Å in eq 26, although the results are largely indistinguishable for $\sigma > 5.0$ Å. As is to be expected, Bragg maxima at d = 4.6, 2.6, 2.3 Å, etc., are generated on the equator, but the layer lines are continuous since there is no axial register.

The effect of introducing a register plane containing the origin atom (an ester oxygen) on each chain is shown in Figure 6 and corresponds to σ = 0.0 Å. The same equatorial maxima are generated as for the nematic case, but we now also obtain sharp maxima (sampling) on the layer lines. The most obvious of these are on the first layer and the strong layer line containing the meridional at d = 2.1 Å, which is outermost in Figure 6. Maxima are predicted on the other layer lines, but these are too weak to be resolved in Figure 6. This sampling by the interchain interference function is also responsible for the sharpening (in the R direction) of the meridional maxima. It is clear therefore that the relatively minimal registration proposed is sufficient to generate Bragg maxima on the layer lines. Indeed, with registration as defined, we have more extensive ordering than is indicated by the observed data, at least for the as-spun fibers; i.e., we predict sharp maxima on all layer lines whereas they are only observed on the first layer. We need to reduce the order imposed on the

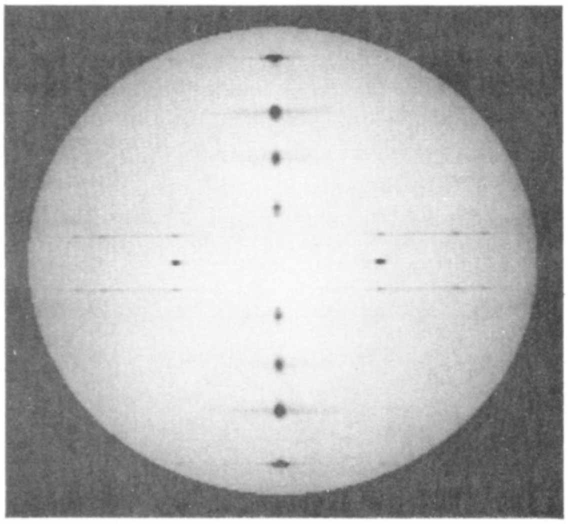

Figure 6. Calculated diffraction pattern for 200 hexagonally packed chains of 30/70 copoly(HBA/HNA) with perfect axial register (see Figure 1). The value of σ is 0.0 Å.

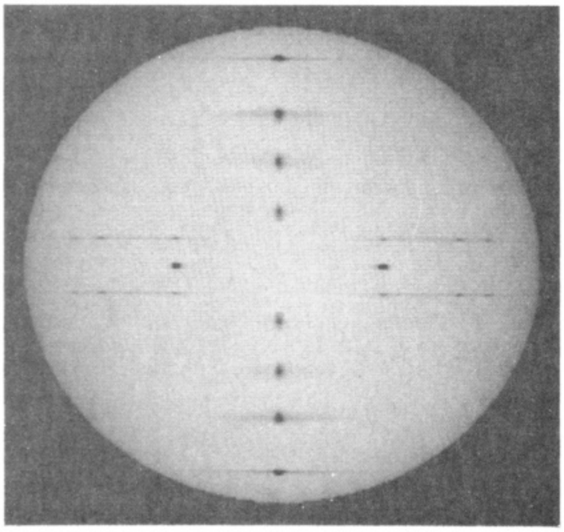

Figure 7. Calculated diffraction pattern for 200 chains of 30/70 copoly(HBA/HNA) in a hexagonal arrangement with $\sigma = 0.5$ Å.

model, which can be done by relaxing the requirement that the origin atom *must* lie on the register plane so as to consider the situation where this registration is *probably* the case, as defined by the $G(z)$ normal distribution.

Figures 7–9 show the predicted diffraction patterns for structures in which the registration is relaxed by setting σ at 0.5, 1.0, and 2.0 Å, corresponding to progressively wider distributions of the chain origins about the register plane. It can be seen that layer line sampling ceases to occur at progressively lower layer lines as σ increases.

The results in Figure 9 for $\sigma = 2.0$ Å compare favorably with the observed data for the as-spun fibers, for which off-equatorial Bragg reflections occur only on the first layer line. In addition, the sharpening of the calculated meridional at $d = 7.88$ Å leads to an intensification at small values of R. We have reported previously that in our calculated meridional intensities for nematic structures the first meridional maximum is often weaker than in the observed data, and thus the introduction of chain register improves the overall agreement in this area. The calculated Bragg reflections on the first layer line are on row lines; i.e., they are directly above the equatorials, which is expected for the one-chain unit cell. Modification of the structure to use a two-chain unit cell followed by refinement of the chain conformation and chain stagger leads to better match in terms of the sampling positions, as will be described in paper 3. There is no sampling on the higher layer lines, which are continuous streaks similar to those in Figure 5 for the unregistered structure.

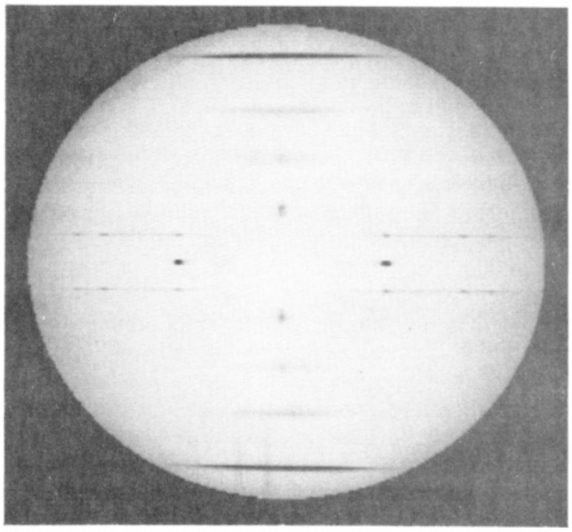

Figure 8. Calculated diffraction pattern for 200 chains of 30/70 copoly(HBA/HNA) is a hexagonal arrangement with $\sigma = 1.0$ Å.

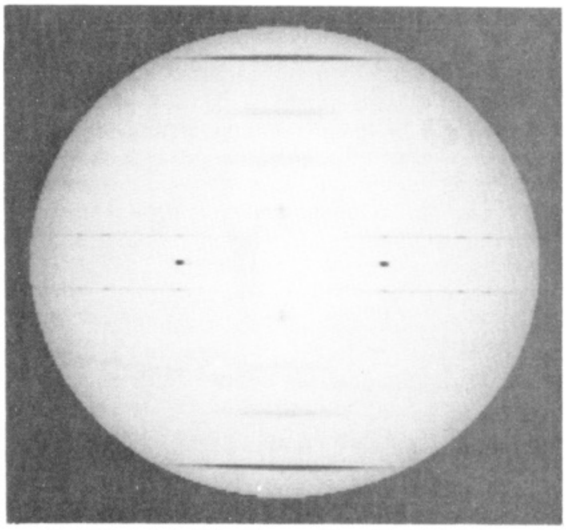

Figure 9. Calculated diffraction pattern for 200 chains of 30/70 copoly(HBA/HNA) in a hexagonal arrangement with $\sigma = 2.0$ Å.

Thus we have demonstrated that the diffraction characteristics that we associate with crystallinity are generated by these random copolymers with the introduction of minimal register. All that is necessary is that an origin atom on each chain of an array should be preferentially in a reference plane perpendicular to the chain axis. Structural correlations exist along the chains, since the structure is a random array of a small number of rigid monomers (two in this case), and hence the Fourier transform of the average chain consists of a series of aperiodic layer lines. If we set the chains on a lattice and bring their origins into register, then structural correlations will exist not only along and perpendicular to the chains but also at oblique angles, giving rise to sampling of the layer lines as in Figure 6.

It should be noted that although we require only registration at one point on each chain (i.e., in the register plane), considerably more register is inherent in the structure. In the case of copoly(HBA/HNA), the axial advance for each monomer should be approximately equal to the residue lengths, which are 6.35 and 8.37 Å for HBA and HNA, respectively. The ratio of these lengths is very close to 3:4 and accounts for the compositionally invariant peak at $d \cong 2.1$ Å, which is the third order of 6.35 Å and the fourth order of 8.37 Å. Consequently, when two chains are in register at one point, there is between a 1 in 3 and a 1 in 4 chance (depending on the monomer ratio) that the ester oxygens of other individual monomers on the two chains will be in register. The 3:4 ratio is not exact, but there is some flexibility in the chain, and the energy gains due to stacking of the aromatic units and better chain packing will probably serve as a driving force to optimize the registration as defined here. The strong $d \cong 2.1$ Å meridional is a common feature of the aromatic copolyesters and copolyamides that we have examined, and this type of registration is probably also present in systems with more than two types of monomers.

A further point is that even limited register with one monomer of each chain in a plane exceeds what is necessary to generate the characteristics of order in the observed data. Better agreement is obtained when the origin monomer has a normal distribution about the register plane, with a standard deviation of $\sigma = 2.0$ Å. To put this in perspective, the difference in monomer lengths is 2.02 Å, and the maximum possible origin shift is ~4 Å (i.e., approximately half the average monomer length) since anything more than this brings a neighboring residue closer to the register plane. The normal distribution means that 68% of the origins must be within ±2.0 Å of the register plane. In the completely nematic structure 50% of the chain origins (51.5% for the 30/70 copolymer treated here) would occur over this distance. Hence although we clearly have some requirement for register, the requirement is not great and can be achieved with a very small shift of the chain along the axis. There is no need to invoke large shifts of the chains that optimize the alignment of identical sequences, which in any case would be insufficient to account for the observed crystallinity and crystallite size. Nucleation of the crystals may well involve alignment of a few short homopolymer sequences or identical copolymer sequences, but thereafter, register is envisaged in the limited way defined above.

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Registry No. (HBA)(HNA) (copolymer), 81843-52-9.

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Three-Dimensional Structure of Main-Chain Liquid-Crystalline Copolymers. 3. Chain Packing in the Solid State

Amit Biswas and John Blackwell*

Department of Macromolecular Science, Case Western Reserve University, Cleveland, Ohio 44106-2699. *Received December 15, 1987*

ABSTRACT: This paper describes the three-dimensional structure for the ordered packing of wholly aromatic thermotropic copolyesters. Previous work has established that copolyesters prepared, e.g., from *p*-hydroxybenzoic acid (HBA) and 2-hydroxy-6-naphthoic acid (HNA) are random copolymers, based on the observed aperiodicity of the meridional diffraction maxima. However, the presence of sharp equatorial and off-equatorial Bragg maxima is indicative of three-dimensional order akin to crystallinity. In the as-spun fibers, there is orthorhombic (pseudohexagonal) packing of the chains, with a base plane unit cell with dimensions $a = 9.18$ Å and $b = 5.30$ Å. Paper 1 of the series in this issue established that in order to generate the first layer line the chains must have a pseudodimer repeat; i.e., there are conformational correlations between adjacent monomers along the chain. Paper 2 showed that the off-equatorial Bragg maxima are generated by limited axial register between adjacent random sequences. In the present paper, we consider the actual conformation and packing of the chains. Analyses are developed to predict the diffraction patterns of assemblies of random sequences, with varying degrees of rotational correlations between dimer units on adjacent chains. The results show a preference for a chain conformation in which aromatic planes along the chain are mutually inclined at ~60°, in a structure analogous to that of poly(*p*-phenyleneterephthalamide). The conformational correlations of the dimers along adjacent chains are quite limited; i.e., the three-dimensional "crystallinity" corresponds to regions of local order that probably arise due to the anisotropic cross sections of the monomer units.

Introduction

This paper extends our previous X-ray analyses of the structure of wholly aromatic copolyesters to look at the chain conformation and packing in the solid state. At the present time, there is considerable interest in the structure–property relationships of copolyesters prepared from,

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