Three-dimensional structure of copolymers of *p*-hydroxybenzoic acid and 2-hydroxy-6-naphthoic acid: A model for diffraction from a nematic structure

Robin A. Chivers and John Blackwell
Department of Macromolecular Science, Case Western Reserve University, Cleveland, Ohio 44106, USA

(Received 5 November 1984; revised 21 August 1984)

X-ray methods have been used to investigate the three-dimensional structure of copolymers of 4-hydroxybenzoic acid (HBA) and 2-hydroxy-6-naphthoic acid (HNA). X-ray patterns of melt spun fibres indicate a high degree of axial orientation of the molecules, but with poor lateral order, except in some highly ordered regions. Our previous calculations have shown that the aperiodic meridional maxima are consistent with chains of completely random monomer sequence. Extension of these calculations to the three-dimensional structure has been done by calculating the cylindrically averaged intensity transform for single chains. The results point to a distorted hexagonal array of chains which have extended but otherwise random conformations, i.e. there is a broad distribution of aromatic-carboxyl torsion angles. It is suggested that in some regions the chain packing is more regular, perhaps due to axial register of HBA-rich sequences, giving rise to the off-equatorial reflections characteristic of three-dimensional order.

(Keywords: liquid crystalline polymers; X-ray diffraction; copolyesters; conformation)

INTRODUCTION

There has been much interest in recent years in the synthesis and characterization of stiff-chain polymers[1,2]. These usually consist of rigid aromatic monomers linked such that there is relatively little conformational freedom in the polymer backbone. Amide and ester linkages have been found useful in this regard: the most successful commercial polymer of this type is poly(*p*-phenylene terephthalamide) which is processed as Kevlar fibres from liquid crystalline solutions in sulphuric acid[3]. Interest in the equivalent polyesters has focused on copolymers, generally those containing 1,4-phenylene and 2,6-naphthylene moieties. These copolymers are thermotropic, i.e. they form liquid crystalline melts, and they can be processed therefrom, e.g. as high strength melt spun fibres and novel moulded plastics.

Figure 1 shows the X-ray fibre diagrams of copolymers of 4-hydroxybenzoic acid (HBA) and 2-hydroxy-6-naphthoic acid (HNA): data are shown for the 30/70, 58/42 and 75/25 HBA/HNA mole ratios. The scattered intensity is largely along the meridian and the equator, and only a few diffraction maxima can be seen. These show relatively little arcing, which indicates a high degree of axial orientation. One Bragg reflection is detected just above and below the equator and hence there is some three-dimensional order in the structure. Otherwise the lack of intensity off the meridian and equator points to a low degree of lateral registration of the molecules. It appears that the molecules form some sort of nematic structure, except that there is some three-dimensional order giving rise to the Bragg reflections. The sharpness of the latter reflections indicates that they arise from ordered regions that have lateral widths of ~100 Å. Blundell[4] has used the intensities of the Bragg reflections to estimate the 'degree of crystallinity' as 21% in the 40/60 HBA/HNA copolymer. The absence of more extensive lateral register is not surprising in a copolymer, and contrasts with the high crystallinity seen for the homopolymer Kevlar.

In previous papers from this laboratory[5,6] we have concentrated on interpreting the meridional intensity data. These consist of three or four maxima in the range $d \leqslant 2$ Å. They are found to be aperiodic, i.e. they are not orders of a simple repeat, and vary steadily in *d*-spacing with monomer ratio across the entire composition range. We have shown that the positions and intensities of these maxima can be predicted by calculation of the theoretical diffraction patterns of copolymer chains of random monomer sequence. When block copolymer character is introduced into the calculations the match between the observed and calculated diffraction patterns is soon lost, and all but minimal deviations from fully random sequences can be ruled out. Similar results have also been obtained for a second set of copolyesters prepared from HBA, 2,6-dihydroxynaphthoic acid, and terephthalic acid[7].

The above results were based entirely on meridional intensity data. The theoretical diffraction patterns were derived from the Fourier transform of the average chain projected onto the fibre axis, assuming the absence of axial register. In order to determine the chain conformation and the three-dimensional chain packing we have to consider the entire X-ray diffraction pattern, not simply the meridional intensity data. We have approached this

0032-3861/85/070997-06$03.00

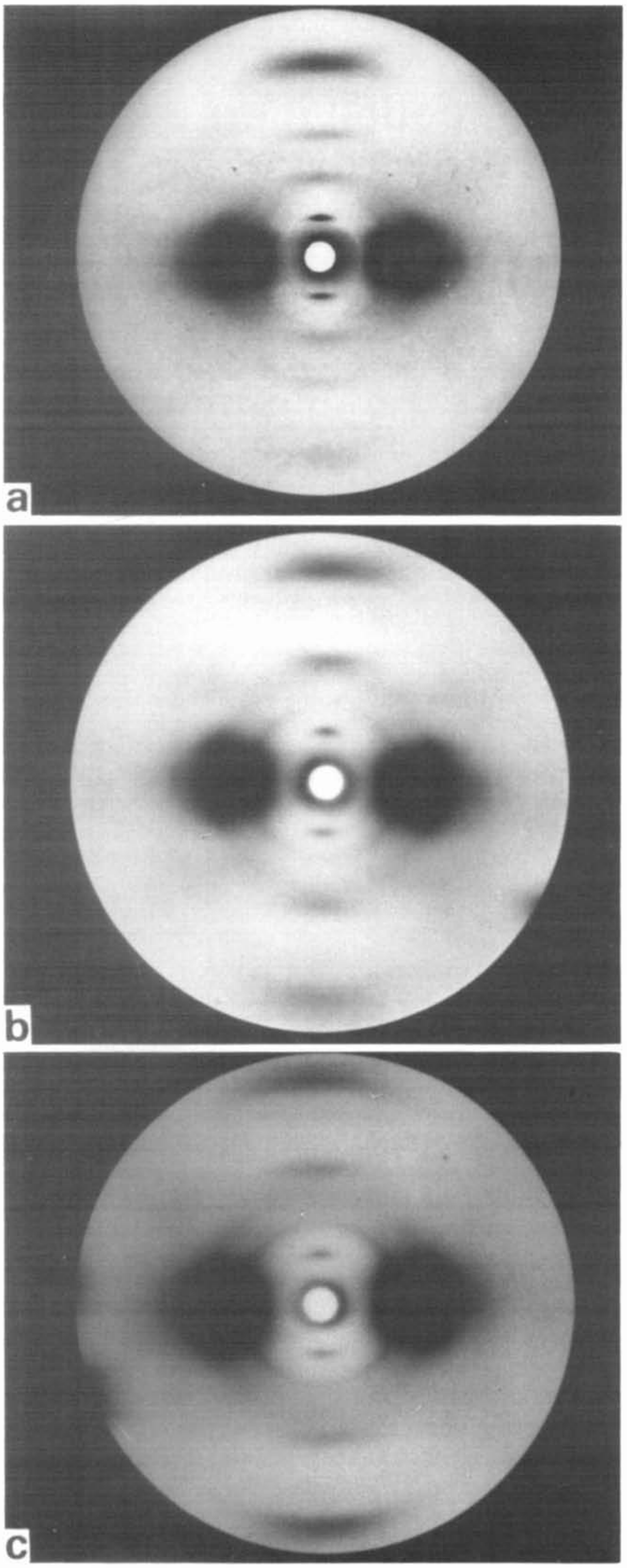

Figure 1 X-ray fibre diagrams of HBA/HNA copolyesters prepared in the following monomer ratios: (a) 30/70; (b) 58/42; (c) 75/25

problem in the manner used previously for structures such as DNA and TMV[8,9], with modifications for treatment of a random monomer sequence. Firstly we have calculated the cylindrically averaged Fourier transform for a single averaged sequence and have then considered the effects of lateral packing of the molecules in a largely nematic array. The theoretical approach and results are described below.

DIFFRACTION BY APERIODIC COPOLYESTER CHAINS

The diffraction from a three-dimensional array of N atoms is given by:

$$I(X,Y,Z) \propto |F(X,Y,Z)|^2 \tag{1}$$

where:

$$F(X,Y,Z) = \sum_{j=1}^{N} f_j \exp[2\pi i(Xx_j + Yy_j + Zz_j)] \tag{2}$$

f_j is the atomic scattering factor of the jth atom at coordinates x_j, y_j, z_j, and X, Y, Z are the coordinates in reciprocal space. Since we are considering the diffraction by fibres, it is more convenient for us to use cylindrical polar coordinates in which z corresponds to the fibre axis, and then equation (2) may be rewritten as:

$$F(R,\Psi,Z) = \sum_{j=1}^{N} f_j \exp[2\pi i\{r_j R \cos(\Psi - \phi_j) + Zz_j\}] \tag{3}$$

The atomic and reciprocal space coordinates are now r_j, ϕ_j, z_j and R, Ψ, Z, respectively.

A typical random sequence of copoly(HBA/HNA) is shown in *Figure 2*. The conformation is necessarily extended as a consequence of the 1,4-phenylene and 2,6-naphthylene linkages and the planarity of the ester groups. The chain conformation depends on the torsion angles about the aromatic–ester linkage bonds, and these bonds are approximately parallel to the chain axis. Hence the axial rise for an HBA or HNA residue is approximately independent of the local chain conformation. The meridional scattering is given by the projection of this structure on the chain (z) axis, and a series of sharp maxima arise as a consequence of the correlations along the chain.

When we consider the three-dimensional structure then the actual chain conformation becomes a critical consideration, and we are faced with two possible situations.

(a) We could have a completely random set of torsion angles, which can be treated by cylindrically averaging each monomer residue in real space in order to model all possible conformations. This would still lead to an

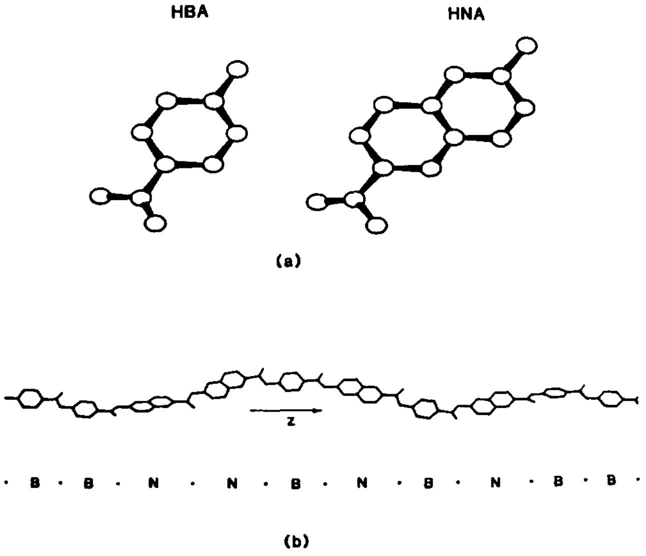

Figure 2 Projections of the structures of HBA and HNA residues

extended, rodlike conformation, which would have a cylindrical cross section. Chains of this type would probably tend to pack on a hexagonal lattice, but with complete axial and rotational freedom in a nematic structure. The observed Bragg reflections on the equator at $d = 4.6$ and 2.6 Å index as 100 and 110 for a hexagonal unit cell with $d = 5.2$ Å, and hence there is hexagonal packing for at least some of the chains. There is also non-Bragg diffuse scatter on the equator in the region of $d = 4.5$ Å as would be expected for irregular packing of the same chains.

(b) The second alternative is that the torsion angles have specific values that are repeated along the chain. (For example, the chain could have a ribbon-like conformation.) The presence of off-equatorial Bragg reflections points to the presence of some regular three-dimensional packing, which will require an ordered conformation for at least part of the structure. This case can be treated by calculation of $I(R,\Psi,Z)$ for a rigid chain followed by cylindrical averaging in reciprocal space.

The most likely structure is probably a compromise between the two. The totally rigid chain would appear to be unlikely, except in the three-dimensionally ordered regions. The completely random conformation is also unlikely since one would expect a distribution of torsion angles about preferential values governed by the potential energy at the linkages. For the present, however, we have performed calculations for the two extremes of the random and rigid conformations.

RANDOM CONFORMATION

Equation (3) is the Fourier transform of a chain of N atoms, and the intensity $I(R,\Psi,Z)$ is given by:

$$\begin{aligned} I(R,\Psi,Z) &= F(R,\Psi,Z)F^*(R,\Psi,Z) \\ &= \sum_j \sum_k f_j f_k \exp 2\pi i[r_j R \cos(\Psi - \phi_j) - r_k R \cos(\Psi - \phi_k) \\ &\quad + Z(z_j - z_k)] \end{aligned} \tag{4}$$

We need to average over all possible residue conformations, and this is indistinguishable from cylindrical averaging of a single chain, for which the predicted intensity is:

$$I(R,Z) = \sum_j \sum_k f_j f_k J_0(2\pi R r_j) J_0(2\pi R r_k) \exp[2\pi i Z(z_j - z_k)] \tag{5}$$

where $J_0(X)$ is the zeroth order Bessel function of argument X. Equation (5) is for one specific chain and must be averaged over all possible monomer sequences, which is effected in equation (6).

$$\begin{aligned} I(R,Z) = \sum_l \sum_A \sum_B Q_{AB}(z_l)[&A_{AB}(R,Z) \cos 2\pi Z z_l \\ &+ B_{AB}(R,Z) \sin 2\pi Z z_l] \end{aligned} \tag{6}$$

in which

$$\begin{aligned} A_{AB}(R,Z) = \sum_j \sum_k f_{A,j} f_{B,k} J_0(2\pi R r_{A,j}) J_0(2\pi R r_{B,k}) \\ \times \cos 2\pi Z(z_{A,j} - z_{B,k}) \end{aligned} \tag{7}$$

and $B_{AB}(R,Z)$ is the equivalent sine term.

In equation (6), $Q_{AB}(z_l)$ is the probability of finding a residue of type A at a distance $+z_l$ from a residue of type B. The first summation is for all such z_l separations and the second and third summations cover all residue pairs. This approach has been used previously to calculate the meridional scattering (i.e. for the one-dimensional structure), and further details can be found in ref. 10. Equation (7) gives the real and imaginary components of the Fourier transform of the crosss convolution of residue B with residue A when both residues are cylindrically averaged. Subscripts A,j and B,k designate the jth atom of residue A and the kth atom of residue B, respectively.

RIGID CONFORMATION

For the rigid conformation we need to average the intensity in equation (4) over all possible values of Ψ. The expression in equation (3) can be expanded as the summation of a series of Bessel functions:

$$\begin{aligned} F(R,\Psi,Z) = \sum_{j=1}^{N} \sum_{n=1}^{\infty} f_j J_n(2\pi R r_j) \exp[i\{n(\Psi + \pi/2) - n\phi_j \\ + 2\pi Z z_j\}] \end{aligned} \tag{8}$$

Taking $I(R,\Psi,Z) = F(R,\Psi,Z)F^*(R,\Psi,Z)$ and averaging over all Ψ from 0 to 2π then

$$\begin{aligned} I(R,Z) = \langle |F^2(R,Z)| \rangle_\Psi = \sum_{n=1}^{\infty} \sum_{j=1}^{N} f_j^2 J_n^{\,2}(2\pi R r_j) \\ + 2 \sum_{n=1}^{\infty} \sum_{j=1}^{N} \sum_{k=1}^{N} f_j f_k J_n(2\pi R r_j) J_n(2\pi R r_k) \\ \times \exp[i\{n(\phi_j - \phi_k) + 2\pi Z(z_j - z_k)\}] \end{aligned} \tag{9}$$

If we subdivide the chain into its constituent monomers and assign probabilities so as to average over all possible chain sequences using $Q_{AB}(z)$ as above, then equation (9) simplifies to:

$$\begin{aligned} I(R,Z) = \sum_l \sum_A \sum_B Q_{AB}(z_l)[&A'_{AB}(R,Z) \cos 2\pi Z z_l \\ &+ B'_{AB}(R,Z) \sin 2\pi Z z_l] \end{aligned} \tag{10}$$

where

$$\begin{aligned} A'_{AB}(R,Z) = \sum_n \sum_j \sum_k f_{A,j} f_{B,k} J_n(2\pi R r_{A,j}) J_n(2\pi R r_{B,k}) \\ \times \cos[n(\phi_{A,j} - \phi_{B,k}) + 2\pi Z(z_{A,j} - z_{B,k})] \end{aligned} \tag{11}$$

and $B'_{AB}(R,Z)$ is the equivalent sine term. A'_{AB} and B'_{AB} are the real and imaginary components of the cylindrically averaged Fourier transform of the cross convolution of residue B with residue A. Our molecule possesses no helical symmetry, and hence the first summation in equation (11) needs to be done over all possible values of n. In practice, however, only the low order terms make a significant contribution: we have found that calculations using the range $n = 0 - \pm 10$ are more than adequate for present purposes.

INTERCHAIN INTERFERENCE EFFECTS

The above treatment derives the scattering pattern for an isolated molecule of average sequence, with two types of cylindrical averaging. If we assume random axial stagger of the chains, these results can be compared to the observed X-ray fibre diagrams, provided that we allow for the effect of interchain interferences. As we have indicated, it appears that the chains pack on an approximately hexagonal net in part of the specimen, but the packing is less well ordered elsewhere. The array of chains can be treated as a paracrystalline hexagonal net, for which the interference function $I(R)$ can be derived following the method described by Burge[10]. For a nematic structure with random axial stagger, i.e. no chain register, $I_1(R,Z)=1$ except in the region of the equator.

EXPERIMENTAL

X-ray fibre diagrams of three copoly(HBA/HNA) preparations were recorded as described in ref. 5 and are shown in *Figure 1*. Cylindrical polar atomic coordinates for the HBA and HNA residues are given in *Table 1*, and projections of these structures are shown in *Figure 2*. The coordinates are derived from those used previously[6], and are based on standard bond lengths and angles. The residues are arranged with the ester oxygen–ester oxgen vector parallel to the chain axis.

Calculations performed for chains of average length 10 monomers were found to give reasonable agreement in terms of the widths of the meridional maxima in one-dimensional calculations[6]. A Gaussian distribution of chain lengths about 10 residues (standard deviation 1 residue) was used to smooth the subsidiary maxima that arise for the single short chain. This chain length should be viewed as the persistence length for the ordered chain rather than the degree of polymerization, which is thought to be approximately 150[12].

$I(R,Z)$ was calculated for all three monomer ratios for chains in the random and the rigid conformation, both with and without the effect of chain packing. The data were calculated on a 1681 point (R,Z) array for $d > 2.0$ Å and are presented as contours of equal intensity on a tan 2θ/tan 2θ plot for comparison with the X-ray data.

Table 1 Cylindrical polar atomic coordinates

	r	ϕ	z
HBA			
Ester oxygen	0.00	0.00	0.00
Carbonyl carbon	1.14	−1.57	0.77
Carbonyl oxygen	2.24	−1.58	0.31
Phenyl carbon 1	0.80	−1.54	2.22
Phenyl carbon 2	0.73	0.52	2.72
Phenyl carbon 3	1.80	−1.91	3.09
Phenyl carbon 4	0.88	0.79	4.09
Phenyl carbon 5	1.56	−1.97	4.47
Phenyl carbon 6	0.28	−1.57	4.97
Ester oxygen	0.00	0.00	6.35
HNA			
Ester oxygen	0.00	0.00	0.00
Carbonyl carbon	1.25	−1.57	0.56
Carbonyl oxygen	2.26	−1.54	−0.09
Naphthyl carbon 1	1.18	−1.64	2.04
Naphthyl carbon 2	2.35	−1.88	2.70
Naphthyl carbon 3	0.44	−0.24	2.78
Naphthyl carbon 4	2.38	−1.93	4.09
Naphthyl carbon 5	0.33	−0.29	4.17
Naphthyl carbon 6	1.20	−1.84	4.83
Naphthyl carbon 7	1.28	0.86	4.91
Naphthyl carbon 8	1.23	−1.94	6.22
Naphthyl carbon 9	1.22	0.94	6.31
Naphthyl carbon 10	0.11	−0.74	6.96
Ester oxygen	0.00	0.00	8.37

(N.B. Bernal chart geometry has not been used to avoid loss of the calculated meridional $I(0,Z)$ data, which are seen in the observed fibre diagrams due to imperfect orientation.)

RESULTS

Figure 3 shows $I(R,Z)$ for (a) the random and (b) the rigid conformation for the 58/42 copolymer. These data are for the isolated chain; there has been no allowance for interchain interferences. The calculated data can be compared with the observed intensity in *Figure 3c*, where the pattern in *Figure 1b* is shown as a sketch on the same tan 2θ scale. Allowance must still be made for arcing of the observed maxima due to the distributions of orientation. No Lorentz/polarization correction has been applied.

It can be seen that both models give good agreement on the meridian, as has already been described[6]. There is also intensity along the equator, which declines steadily with R. There is no sign of an equatorial maximum in the 5–4 Å region, so this observed effect must be due to interchain interferences. The layer line at $d = 2.1$ Å is much more extensive than for the other meridionals, and this matches what is observed. The major differences between the data for the two single chain models are in the extent of the 7.5 Å layer line and the diffuse non-meridional layer line at ~ 4.5 Å. In this regard the random conformation gives significantly better agreement with the observed data and must be considered preferable to the rigid chain. Similar conclusions are recorded for the 30/70 and 75/25 copolymers.

For a structure with random axial stagger, the interchain interference effects will be confined to the equatorial region. The measured density points to an average chain separation of 4.5 Å, if the array is hexagonal. *Figure 4a* shows the interference function, $I(R)$, for an array of 19 chains, i.e. two rings of successive neighbours about a central chain. This is the Fourier transform of the radial distribution function shown in *Figure 4b*, which is for the 19 chain model with paracrystalline distortions incorporated as Gaussian distributions of the intermolecular distances, where the breadth of the distribution is proportional to the distance between neighbours. Incorporation of such interference effects would modulate the transforms to produce a broad peak on the equator at $d \simeq 4.3$ Å.

Thus the major features of the X-ray pattern: the meridionals at $d = 7.5$, 3.0 and 2.1 Å, the broad equatorial at 4.5 Å, the layer line streak at 2.1 Å, and off-meridional intensity at a layer line spacing of 4.5 Å, are all reproduced by the model consisting of a nematic array of chains of random conformation. The good agreement between the observed and calculated data is apparent if one allows for the smearing of the latter due to fibre disorientation.

DISCUSSION

The above results taken together with those of our previous papers lead to the following conclusions with regard to the structure of the copolyester fibres. The chains are random sequences of the two monomers oriented parallel to the fibre axis. The chains have highly extended conformations, but otherwise the results favour random orientation of adjacent monomers with respect to the chain axis, i.e. there is a large range of possible torsion

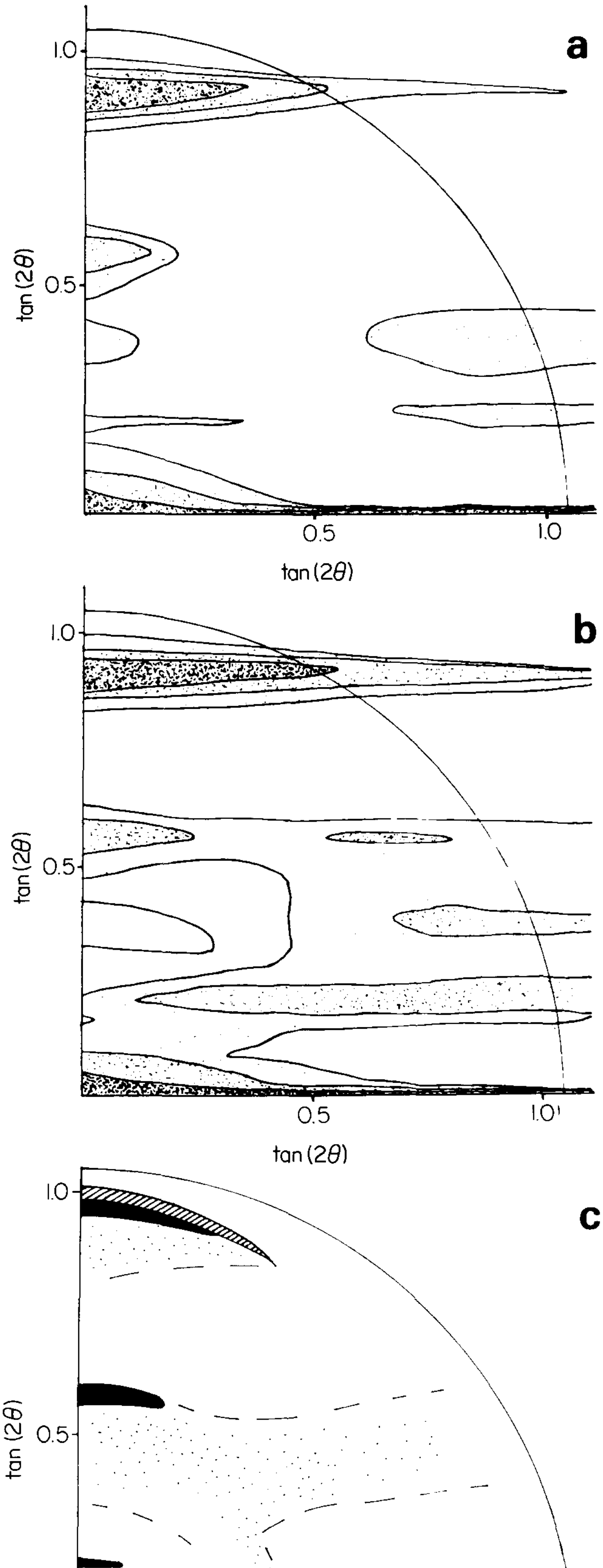

Figure 3 Contour plots of the logarithm of intensity calculated for (a) random and (b) rigid chain conformations of HBA/HNA 58/42. The arc represents the approximate boundary of the experimentally observable region. (c) A schematic representation of the diffraction pattern for HBA/HNA 58/42 shown in *Figure 1b*

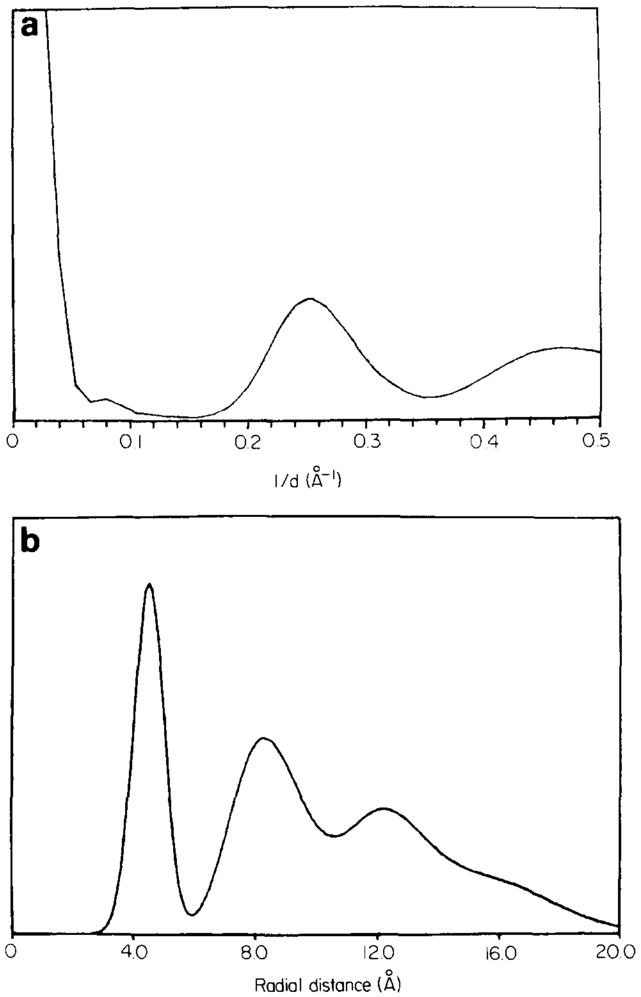

Figure 4 (a) The interchain interference function, calculated as the Fourier transform of the radial distribution shown in *Figure 4b* for a bundle of 19 chains. (b) The radial distribution in a bundle of 19 chains of mean separation 4.5 Å

angles for the aromatic–carboxyl bonds. These chains are then arranged on a distorted hexagonal network, with random axial stagger, i.e. a nematic structure for cylindrical chains.

However, the above model must be modified to take account of the Bragg reflections. These have not been considered so far because three-dimensional order has yet to be introduced into the model. It has been shown elsewhere that the diffraction characteristics of the ordered regions are very similar to those for poly(HBA) in its high temperature form[14]. It seems very likely that the Bragg reflections arise from stacking of certain chain sections, perhaps HBA rich and/or HNA rich sequences, in a manner similar to that in the HBA homopolymer. The fact that only a first layer line reflection is seen shows that these ordered regions cannot be very extensive in the axial direction.

It can be seen that there is very little intensity in the region of the 3.3 Å off-equatorial in the case of the random conformation (*Figure 3a*). However, intensity is seen in this region in the transform of the rigid chain (*Figure 3b*), and it is probable that stacking in the ordered regions requires adoption of a particular conformation for those sequences. The model used to produce *Figure 3b* is only one of a number of rigid conformations that might occur in the ordered regions. We are currently exploring methods to incorporate preferred axial register of the chain sequences into the calculations. We are also applying the same techniques to the three-dimensional structures of two other wholly aromatic copolyesters to see if they throw further light on the conformation and packing of these materials.

ACKNOWLEDGEMENTS

We acknowledge the support of NSF Grant ISI81-16103, NSF Grant DMR81-07130 (from the Polymer Program), and Celanese Research Company.

REFERENCES

1 Jin, J.-I., Antoun, S., Ober, C. and Lenz, R. W. *Br. Polym. J.* 1980, **12**, 132
2 Preston, J. *Angew. Makromol. Chem.* 1982, **109/110**, 1
3 Carter, G. B. and Schenk, V. T. J. in 'Structure and Properties of Oriented Polymers', (Ed. I. M. Ward), John Wiley and Sons, New York, 1975
4 Blundell, D. J. *Polymer* 1982, **23**, 359
5 Gutierrez, G. A., Chivers, R. A., Blackwell, J., Stamatoff, J. B. and Yoon, H. *Polymer* 1983, **24**, 937
6 Chivers, R. A., Blackwell, J. and Gutierrez, G. A. *Polymer* in press
7 Blackwell, J. and Gutierrez, G. A. *Polymer* 1982, **23**, 671
8 Franklin, R. E. and Klug, A. *Acta Crystallogr.* 1955, **8**, 777
9 Klug, A., Crick, F. H. C. and Wyckoff, H. W. *Acta Crystallogr.* 1958, **11**, 199
10 Blackwell, J., Gutierrez, G. A. and Chivers, R. A. *Macromolecules* in press
11 Burge, R. E. *Acta Crystallogr.* 1959, **12**, 285
12 Burge, R. E. *Proc. Roy. Soc.* 1961, **A260**, 558
13 Calundann, G. W. (Celanese), US Pat. 4 161 470 (1979)
14 Blackwell, J., Lieser, G. and Gutierrez, G. A. *Macromolecules* 1983, **16**, 1418