polymer papers

The structure of liquid crystalline aromatic copolyesters prepared from 4-hydroxybenzoic acid and 2-hydroxy-6-naphthoic acid

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X-ray methods have been used to investigate the structure of liquid crystalline copolyesters prepared from 4-hydroxybenzoic acid (HBA) and 2-hydroxy-6-naphthoic acid (HNA). Fibre diagrams and meridional diffractometer scans have been obtained for melt-spun specimens of five HBA/HNA ratios: 25/75, 30/70, 50/50, 58/42 and 75/25. The data indicate a high degree of axial orientation. The lateral packing is more irregular but the observation of some equatorial and off-equatorial Bragg reflections indicates the presence of some three-dimensional order. The patterns differ in the number and position of the meridional maxima, and these can be predicted accurately by a point model for aperiodic chains of totally random sequence. The sensitivity of the data to monomer ratio is illustrated by calculations across the range of composition from 100% HBA to 100% HNA.

Keywords X-ray diffraction; liquid crystalline polymer; aromatic copolyester; thermotropic; computer modelling; structure determination

INTRODUCTION

This paper describes our X-ray work on the structure of wholly aromatic copolyesters prepared from 4-hydroxybenzoic acid (HBA) and 2-hydroxy-6-naphthoic acid (HNA). These copolymers are part of a family of aromatic copolyesters that give rise to liquid crystalline melts as a result of their stiff, extended chain conformations (for review see ref. 1), and these properties can be utilized, for example, to produce high-strength fibres. We have previously reported studies of the structure of copolyesters prepared from 4-hydroxybenzoic acid, 2,6-dihydroxynaphthalene and terephthalic acid[2]. Fibre diagrams of the latter polymers are indicative of a high degree of axial orientation. With regard to the lateral packing of the molecules, intense non-Bragg equatorial scatter indicates that the chains are packed irregularly, except that the presence of some sharp equatorials and off-equatorials requires a degree of three-dimensional order. Probably the most interesting data are found on the meridian of the X-ray photographs, where the *d*-spacings of the intensity maxima are not orders of each other, and also vary depending on the monomer ratios. We have shown that the positions of these reflections can be predicted by an aperiodic point model for a random sequence of monomers, and that the data are compatible with a structure consisting of highly oriented chains of totally random sequence. In a second paper[3] we have shown that the predicted meridional data are highly sensitive to block copolymer character, by varying the reactivities of the monomers when generating the chain sequences. The meridional transforms are significantly different from the observed data if the HBA–HBA reactivity is 1.5 or more, compared to 1.0 for the other reactions, which effectively rules out extensive blockiness.

We have now extended these calculations to an analysis of the diffraction patterns of this second aromatic copolyester and the results are presented below. X-ray data on a copolymer of 4-hydroxybenzoic acid and 2-hydroxy-6-naphthoic acid were reported earlier by Blundell[4], who observed that part of the structure was ordered. Using the usual methods for estimating the degree of crystallinity, Blundell argued that approximately 21% of the 40/60 polymer has lateral order. Optical microscopy and electron diffraction studies of oriented films of the 70/30 copolymer by Donald *et al.*[5] showed the presence of extensive ordering, with a sinusoidal variation of the chain orientation along the direction of draw, reminiscent of what has been seen previously for Kevlar fibres[6].

EXPERIMENTAL

Specimens of copolyesters of 4-hydroxybenzoic acid (HBA) and 2-hydroxy-6-naphthoic acid (HNA) were synthesized following the method described by Calundann[7]. Five HBA/HNA ratios were prepared: 25/75, 30/70, 50/50, 58/42 and 75/25. The molecular weights are believed to be approximately 20000, corresponding to approximately 140 residues per chain. Melt-spun fibres were arranged in parallel bundles to serve as X-ray specimens. The X-ray fibre diagrams were recorded on Kodak No-screen X-ray film using a Searle toroidal focusing camera and Ni-filtered Cu Kα radiation from a Rigaku Denki rotating anode. The *d*-spacings were determined from linear densitometer scans of the films,

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and were calibrated using calcium fluoride. Meridional *d*-spacings were also determined from $\theta/2\theta$ scans obtained using a Philips D-76 diffractometer equipped with a curved quartz crystal monochromator. The *d*-spacings were calculated from the positions of intensity maxima (the peaks were not always symmetrical) with an accuracy of $\pm 0.1°$ in 2θ. Aluminium was used for calibration.

In this paper we will be concerned with the prediction of the positions of the intensities on the meridian of the X-ray photograph, based on a random sequence of monomers, using the same method as was used in previous work[2] on the copolymers of HBA, 2,6-dihydroxynaphthalene (DHN) and terephthalic acid (TPA). The intensity of the meridian derives from the squared Fourier transform of the structure projected onto the fibre axis. The geometry of the aromatic and carboxyl groups inevitably leads to a stiff extended chain. The 1,4-phenylene and 2,6-naphthalene linkages are approximately colinear with the chain axis, and thus the projection of a chain onto the fibre axis is approximately independent of the chain conformation, i.e. of the aromatic–carboxyl torsion angles. We have used a point model for the chain, in which each residue is approximated by a single point, placed for convenience at the ester oxygen. A random number generator is used to generate HBA/HNA sequences, and the separation between successive points along the chains is 6.35 Å for HBA and 8.52 Å for HNA, based on single-crystal X-ray structures of model compounds[8–10]. The Fourier transform, $F(Z)$, of a linear array of n points is

$$F(Z)=\sum_{1}^{n}\exp(2\pi i Z z_j)$$

where Z is the coordinate in reciprocal space, along the axis corresponding to the meridian of the X-ray photograph, and z_j is the coordinate of the jth point in the chain in real space. The squared transform $|F(Z)|^2$ is then averaged over a number of chains. In the data presented below the calculations were performed for 200 chains of 15 residues generated by a random number generation from a single batch of 3000 residues with the desired HBA/HNA ratio. $|F(Z)|^2$ was determined at 667 increments of 0.001 Å^{-1} between $Z=0$ and 1–1.5 Å^{-1}.

RESULTS AND DISCUSSION

The X-ray fibre diagrams for fibre preparations of 30/70, 58/42 and 75/25 copolymers are shown in *Figure 1*, and schematics that indicate the positions of all the observed intensity maxima are shown in *Figure 2*. The *d*-spacings for the meridional maxima determined from the film fibre diagrams and $\theta/2\theta$ diffractometer scans for all five preparations are given in *Table 1*. In view of the scattering geometry, the diffractometer data obtained for the moving fibres should be more accurate than those from film fibre diagrams of stationary fibres, but the latter technique is more sensitive for the weak reflections.

The X-ray data can be summarized as follows.

(1) All five monomer ratios give two relatively sharp equatorial reflections at $d \simeq 4.5$ and 2.6 Å and an off-equatorial at $d \simeq 3.3$ Å. Owing to imperfect orientation, the 4.5 and 3.3 Å reflections are arced, and the ends of the arcs intersect the meridian.

(2) There is non-Bragg scatter in the equatorial regions in the range of $d=6$–3 Å.

(3) The patterns differ in the number and positions of the meridional maxima: there are three for the 75/25, 58/42 and 50/50 ratios and four for the 30/70 and 25/75 ratios in the range out to 2 Å (not counting the arced equatorial and off-equatorial).

(4) There is weak diffuse intensity above and below the equatorial maxima. In addition, extremely weak diffuse intensity occurs on or close to the meridian at $d \simeq 2.3$ Å.

These data are reminiscent of those reported for the HBA/DHN/TPA copolymers[2] and for copolymers of HBA and ethylene terephthalate[11]. The chains in the specimen are oriented along the direction of draw. A fraction of the specimen has relatively ordered lateral packing, giving rise to the sharp equatorial and off-equatorial reflections. These reflections are at approximately the same *d*-spacings as those for HBA/DHN/TPA and HBA/ethylene terephthalate copolymers, and it is likely that there are features common to the ordered packing in all of these copolymers of HBA. The non-Bragg equatorial scatter indicates that there is imperfect lateral packing of the aligned chains in order regions of the specimen. Further discussion of the lateral packing will be given in a later paper.

The variability of the *d*-spacings of the meridional maxima and the fact that they are not orders of one another suggests an aperiodic chain structure. *Figure 3* shows the computed meridional transforms for random point models for HBA/HNA ratios in 10% increments from 100/0 to 0/100. The positions of the predicted maxima are listed in *Table 2*. At the extremes of the series are the homopolymers, which show primary maxima at orders of 6.36 Å for poly-HBA and 8.52 Å for poly-HNA. The calculations are done for chains of 15 residues, and so the subsidiary maxima are seen, but these would be smoothed away in any real structure due to variations in the persistence length. A *highly* blocky copolymer would be expected to show both sets of maxima. Both homopolymers give a maximum at ~2.1 Å, which corresponds fortuitously to the third order of HBA and the fourth order of HNA.

The transforms change progressively across the series, with the change from three to four maxima occurring in the region of 50/50. The *d*-spacings of the maxima (*Table 2*) are predicted to be very sensitive to the monomer ratio: the *d*-spacing of the first reflection changes from 8.52 Å to 6.36 Å and the increments between successive 10% changes in composition generally exceed the experimental error for the observed data. It should be noted here that the calculations are subject to the usual statistical limitations in the assumption of randomness in the model. The calculated *d*-spacings are reproducible to approximately 0.001 Å^{-1} (the *Z*-sampling increment) in these calculations based on 3000 monomers. This effect is most appreciable at higher *d*-spacings: the position of the peak at 7–8 Å is predicted to within ± 0.06 Å. These variations could be reduced by the use of a larger number of monomers, but do not affect the general conclusions about the trends across the series of monomer compositions.

Figure 4 shows the computed meridional transforms for the five HBA/HNA ratios. The positions of the observed maxima are indicated by arrows; the *d*-spacings of the calculated peaks are compared with the observed *d*-spacings in *Table 1*. In these calculations only the *positions* of the maxima are important. Before we can compare the

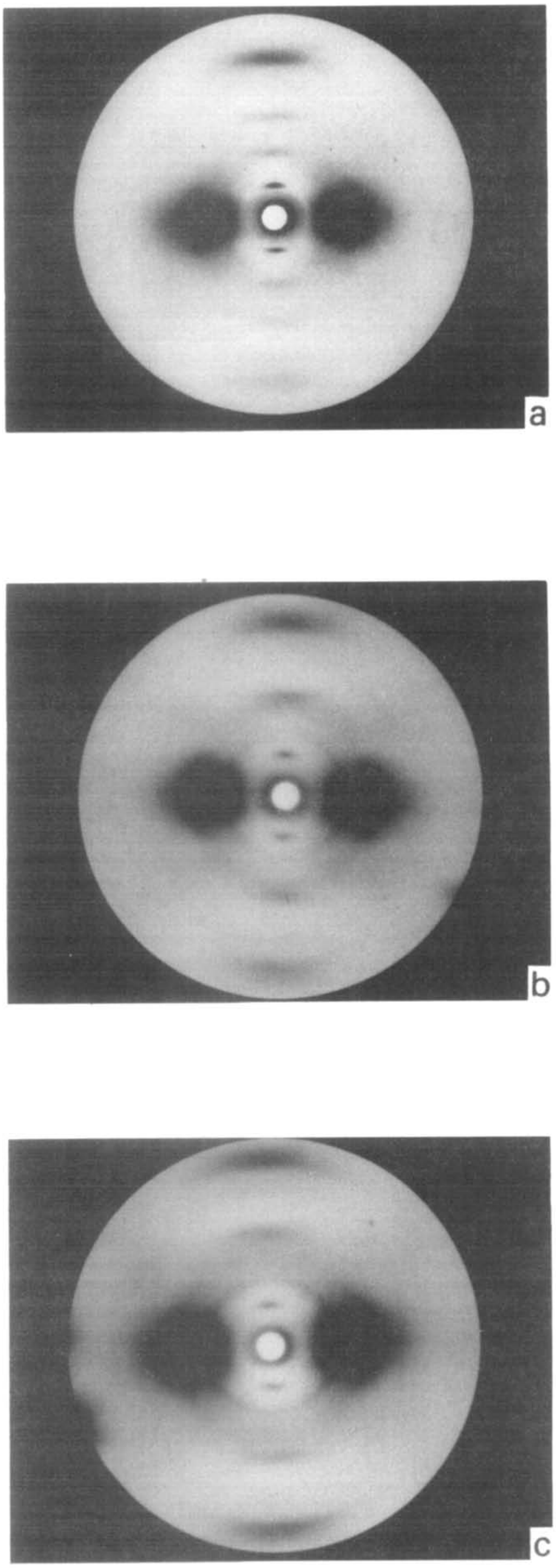


Figure 1 X-ray fibre diagrams of melt-drawn fibres of HBA/HNA copolyesters for three monomer ratios: (a) 30/70, (b) 58/42, (c) 75/25

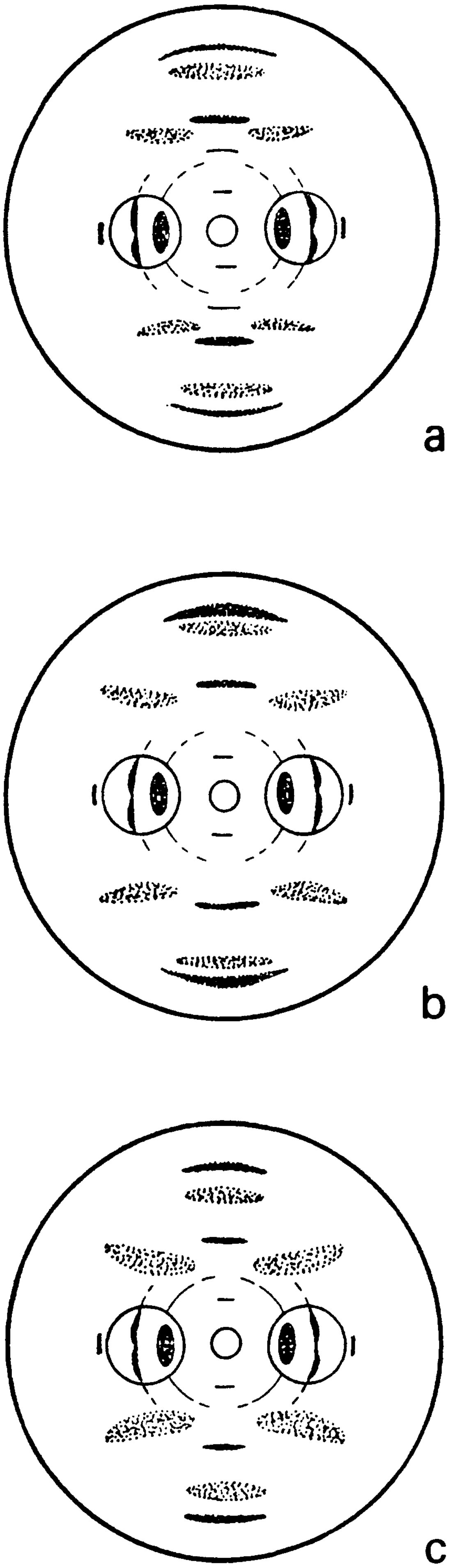
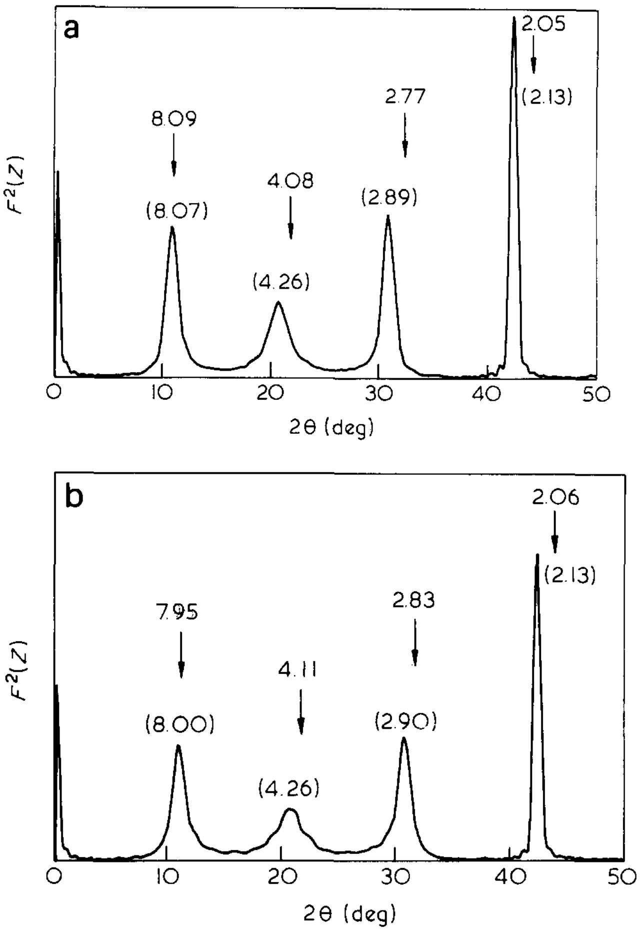


Figure 2 Schematics of the three X-ray patterns shown in *Figure 1*. HBA/HNA ratios: (a) 30/70, (b) 58/42, (c) 75/25



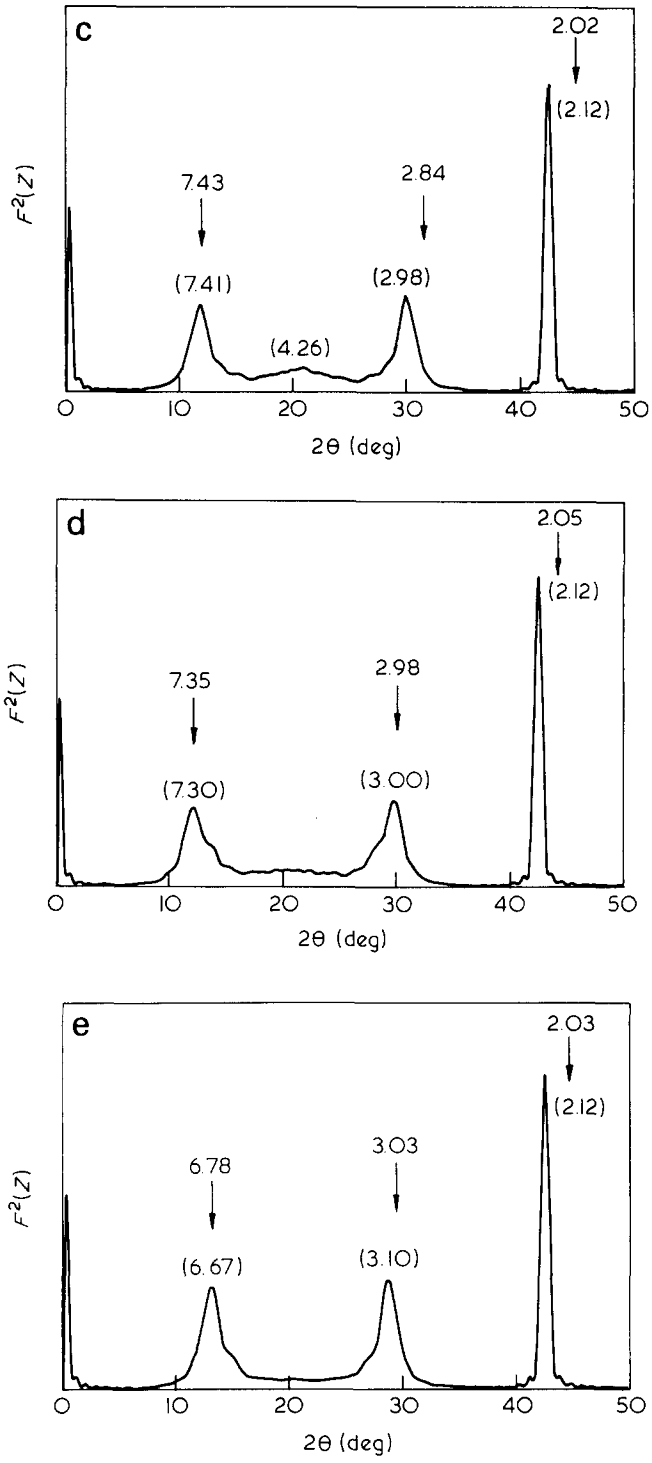


Figure 3 Squared averaged Fourier transforms of point models for random HBA/HNA sequences for the following monomer ratios: (a) 25/75, (b) 30/70, (c) 50/50, (d) 58/42, (e) 75/25. The positions of the observed meridional maxima (film data) are shown by arrows; the observed *d*-spacings are shown (in Å) above the arrows; the *d*-spacings of the calculated peaks are in parentheses

Table 1 Observed and calculated meridional *d*-spacings

	d-spacings (Å)		
	Observed		Calculated
Composition, HBA/HNA	Diffractometer	Film	
25/75	8.11 ± 0.07*	8.09 ± 0.07	8.07 ± 0.06
	4.15 ± 0.02	4.08 ± 0.04	4.26 ± 0.04
	2.85 ± 0.01	2.77 ± 0.03	2.86 ± 0.02
	2.09 ± 0.01	2.05 ± 0.03	2.13 ± 0.02
30/70	7.89	7.95	8.00
	4.09	4.11	4.26
	2.87	2.83	2.90
	2.09	2.06	2.13
50/50	7.49	7.43	7.41
			4.26
	2.95	2.84	2.98
	2.09	2.02	2.12
58/42	7.19	7.35	7.30
	2.96	2.98	3.00
	2.08	2.05	2.12
75/25	6.70	6.78	6.67
	3.09	3.03	3.10
	2.09	2.03	2.12

* Experimental errors in the measured *d*-spacings and approximate ranges of the calculated *d*-spacings due to statistical fluctuations are indicated for the 25/75 composition, and are similar for the other preparations

Table 2 *d*-spacings of predicted meridional maxima for HBA/HNA copolymers at different monomer ratios

Monomer ratio, HBA/HNA	Predicted *d*-spacings (Å)				
0/100	8.52		4.26	2.84	2.13
10/90	8.34		4.26	2.86	2.13
20/80	8.20		4.26	2.86	2.13
30/70	8.00		4.26	2.90	2.13
40/60	7.89		4.26	2.92	2.12
50/50	7.41		4.26	2.98	2.12
60/40		7.15		3.01	2.12
70/30		6.90		3.07	2.12
80/20		6.54		3.13	2.12
90/10		6.50		3.15	2.12
100/0		6.36		3.17	2.12

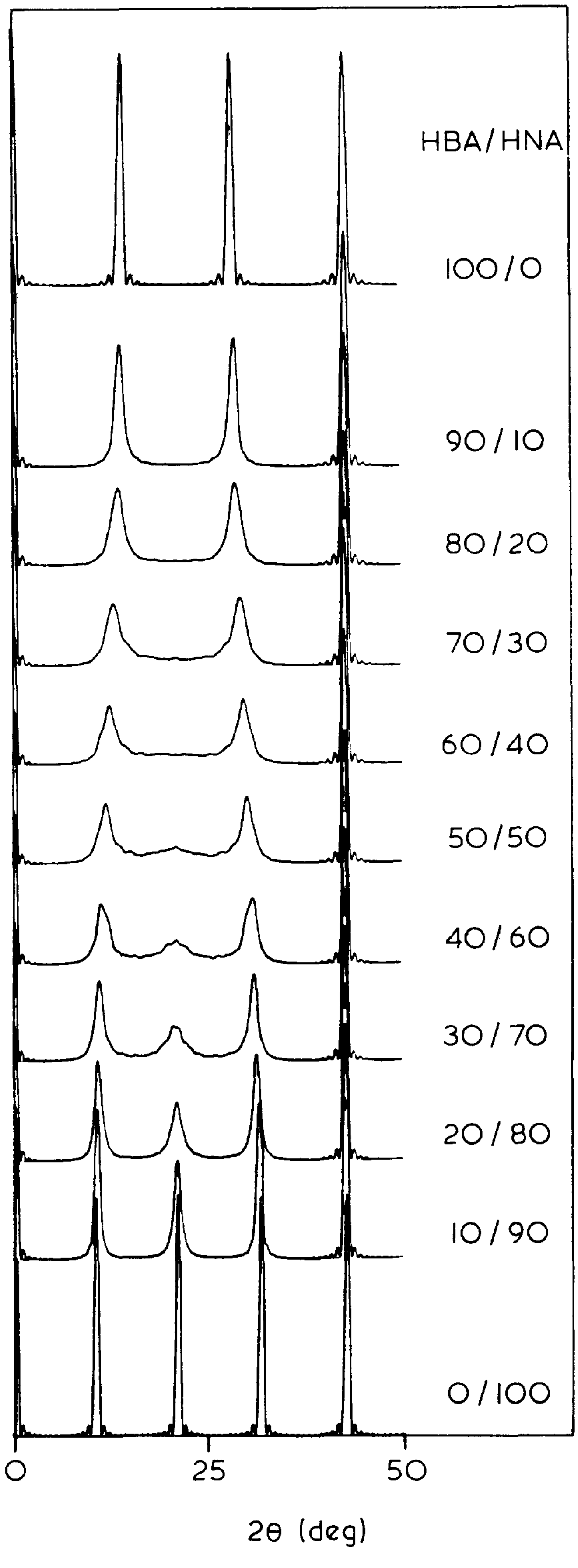


Figure 4 Squared averaged Fourier transforms of point models for random HBA/HNA sequences for different monomer ratios. The monomer ratios are indicated on the curves. $|F(Z)|^2$ is on the same linear scale as in *Figure 3*

intensities we need to consider the effects of intra-residue interferences by using atomic coordinates and scattering factors rather than a point model for the chains. We also must allow for the interchain (packing) effects, especially any regular staggering of adjacent chains. For a periodic (homopolymer) chain, interferences will affect the intensities but will not change the positions of the maxima. This is not necessarily true for an aperiodic chain, but should be approximately so in this case in view of the similarity of the monomer structures. The validity of this approximation is demonstrated by the success in predicting the positions of the maxima for HBA/DHN/TPA copolymers and the present HBA/HNA copolymers (see below), and by preliminary calculations for an atomic model for the former system.

In the transforms in *Figure 4*, four maxima are predicted for the 25/75, 30/70 and 50/50 ratios, and three for the 58/42 and 75/25 ratios. The *d*-spacings of the calculated maxima are compared to the observed data in *Table 1* and are seen to be in very good agreement: within ~0.1 Å in each case, which is less than the experimental error and statistical fluctuation. The predicted maximum at $d = 4.26$ Å for the 50/50 ratio is extremely weak and is not detected experimentally. It should be noted also that a maximum is predicted at $d \simeq 1.6$ Å for all five ratios (outside the range shown in *Figure 4*). This is not detected experimentally, and it seems reasonable that its absence is due to intra- or intermolecular interferences, or the effect of distortions. The numerical agreement for the observed reflections is remarkable, and could in fact be improved further by making small stereochemically acceptable changes in the residue lengths. Thus the prediction method developed in our previous paper has successfully reproduced the positions of the meridional maxima for a second set of stiff chain copolymers, and these data are fully compatible with a model consisting of oriented chains of completely random monomer sequence.

These calculations have been done for a chain length of 15, which corresponds to a persistence length rather than the degree of polymerization. The calculated maxima have widths that appear to be roughly comparable to the observed maxima. Use of longer chains results in a noisier transform that requires averaging over more chains, more frequent sampling and smoothing, but leads to predicted peaks at the same positions. Further analysis of the intensities and line profiles requires consideration of an atomic model for the chain, which will be the subject of a future paper. This will also discuss the sensitivity of the X-ray data to possible block copolymer character. The chain sequences have been calculated assuming equal reactivities for the monomer groups, although we have the ability to vary the reactivities, and so generate blocky sequences. Currently there is no chemical evidence with regard to the monomer distribution during synthesis. However, it is significant that our previous calculations for the analogous HBA/DHN/TPA copolymers are against extensive blockiness[3]. This problem requires further attention because it could have a major effect on the lateral ordering of the molecules. The possible development of blocks as a result of transesterification in HBA/ethylene terephthalate copolymers has been discussed by Lenz and Feichtinger[12].

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