

X-ray analysis of the structure of wholly aromatic copolyesters with thiophenyl and oxyphenyl side groups

M. Ishaq, J. Blackwell* and S. N. Chvalun

Department of Macromolecular Science, Case Western Reserve University, Cleveland, OH 44106-7202, USA

and H. R. Kricheldorf

Institut für Technische und Makromolekulare Chemie, Bundesstraße 15, 20146 Hamburg, Germany

(Received 17 April 1995; revised 5 June 1995)

X-ray methods have been used to investigate the solid-state structures of wholly aromatic thermotropic copolyesters prepared from equimolar amounts of *p*-hydroxybenzoic acid, biphenol and thiophenyl- or oxyphenyl terephthalic acid. We have also compared these structures with that of the unsubstituted copolymer. The scattering data for melt-spun fibres show that the presence of the side chains results in considerably less lateral order. Non-periodic layer lines are observed, and their positions are reproduced in simulated scattering patterns for extended chains of completely random sequence. For the unsubstituted copolymer, the chains are not fully extended but are contracted by approximately 1%, probably due to the requirements to pack random sequences with three-dimensional order. A further contraction of 1.5% occurs for the backbones of the substituted copolymers, probably in an effort to minimize the free volume. Nevertheless, the presence of the side chains results in a reduction of the density by ~20%. The substituted copolymers adopt a distorted structure similar to that seen for poly(phenyl-*p*-phenylene terephthalate), in which the side groups on adjacent chains are interdigitated. This is possible even for random sequences because there is only one side chain for every four aromatic units along the backbone. Nevertheless, this interdigitation appears to preclude any registration of adjacent random sequences, and thus there is no evidence for the three-dimensional order observed for the unsubstituted copolymer.

(Keywords: X-ray analysis; aromatic copolyesters; side groups)

INTRODUCTION

This paper describes X-ray analysis of wholly aromatic copolyesters with *O*-phenyl and *S*-phenyl side chains. Specifically, we have studied the copolymers prepared from equimolar proportions of *p*-hydroxybenzoic acid (HBA), biphenol (BP) and thiophenyl or oxyphenyl terephthalic acid (STPA or OTPA, respectively). These copolyesters are analogous to the XYDAR[®] (Amoco) series of resins^{1–3}, in which the terephthalic acid (TPA) units are unsubstituted, and are part of a large group of wholly aromatic copolyesters that give rise to thermotropic nematic melts^{4,5}. The chemical structures of these monomers are shown in *Figure 1*. The analogous homopolymer prepared from HBA, and the alternating copolymer of BP and TPA, are crystalline, insoluble materials. Their melting points are above their decomposition temperatures, which precludes melt processing. Copolymerization results in a lowering of the melting point (solid state to nematic transition), since the presence of the comonomer breaks up the regular crystalline order of the homopolymer by introducing defects. Copoly(HBA/BP/TPA) (50/25/25) can be pro-

cessed by injection moulding in the region of 400°C. It has been shown previously^{6,7} that replacement of TPA by STPA or OTPA reduces the melting point to 280–300°C, depending on the monomer ratio, comparable to the processing range of the copolymers of HBA and 2-hydroxy-6-naphthoic acid (HNA), which are the basis of the VECTRA[®] (Hoechst Celanese) series of resins.

Previous work has shown that copoly(HBA/BP/TPA) adopts ordered structures in the solid state, with considerable three-dimensional order⁸. The X-ray fibre diagrams contain non-periodic layer lines, analogous to those reported for the more extensively studied HBA/HNA copolyesters^{9,10}. These data are characteristic of wholly random comonomer sequences: the observed intensities along the fibre axis direction arise from the structural correlations inherent in an array of parallel extended copolymer chains of random sequence. The three-dimensional order is believed to arise from limited axial register of short-chain segments¹¹. Simulated X-ray fibre diagrams for arrays of 10–12 monomer random sequences of copoly(HBA/HNA), with their centres registered on a plane perpendicular to the chain direction, contain all the observed sharp diffraction maxima (analogous to Bragg reflections)¹².

The present work has been undertaken to study the

* To whom correspondence should be addressed

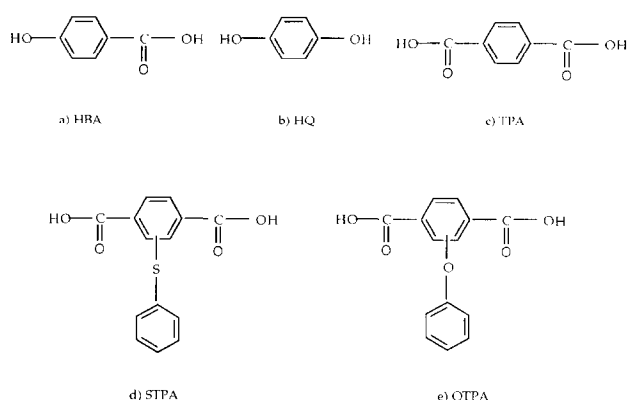


Figure 1 Chemical structures of the monomers: *p*-hydroxybenzoic acid (HBA), biphenol (BP), terephthalic acid (TPA), and S-phenyl and O-phenyl terephthalic acids (STPA and OTPA)

effects of random S-phenyl or O-phenyl substitution on the three-dimensional structure. It will be seen that the data are characteristic of a random comonomer sequence, and that the side chains are interdigitated to form a layer structure.

EXPERIMENTAL

Specimen preparation

Specimens of 33/33/33 (equimolar) copoly(HBA/BP/STPA) and 33/33/33 copoly(HBA/BP/OTPA) were prepared as described elsewhere⁶. Fibres of the three copolymers were drawn by hand from the melts using tweezers. Specimens for X-ray work were prepared as bundles of 20–30 parallel fibres. Densities were determined by flotation in aqueous potassium iodide solution, and are accurate to $\pm 0.01 \text{ g ml}^{-1}$.

X-ray diffraction

X-ray fibre diagrams were recorded on Kodak Direct Exposure X-ray film using a Searle toroidal focusing camera and Ni-filtered $\text{CuK}\alpha$ radiation. The *d*-spacings were calibrated with calcium fluoride powder (on the specimens). Intensity data along the fibre axis direction were also recorded as $\theta/2\theta$ scans using a Philips PN 3550/10 diffractometer operating in the transmission mode, with a slit width of 0.04 mm (0.03°).

Molecular models

Molecular models for the monomer units were constructed using the bond lengths and angles contained within the SYBYL[®] (Tripos Associates) software package. The ester groups were *trans*-planar; the phenyl-COO geometry in the HBA and unsubstituted TPA units was assumed to be planar (torsion angle 0° or 180°); the TPA units had the most extended *trans* conformation. The torsion angles were set at energy minima determined for the isolated chain using the Tripos force field. The mutual inclination of the two phenyl groups of the BP unit was 53° . For the STPA and OTPA units, the *cis* conformation (0°) for the phenyl-COO torsion is unfavourable because of the interaction with the substituent at the 2-position on the phenyl, and consequently the C=O bond points to the opposite side of the phenyl, close to 180° for the torsion angle. The actual energy minima for this torsion were at $\pm 164^\circ$. For these, the *z*-coordinates of the TPA unit are indistinguishable

from those for 180° , but this is not so for the coordinates of the side chain. For the latter, there are two energy minima for combinations of the TPA-S phenyl and TPAS-phenyl torsion angles for each backbone torsion. To simulate the probable variability in the side-chain conformation, we modelled the substituted TPA as a mixture of the four conformations: $164^\circ, 83^\circ, 49^\circ; 164^\circ, 101^\circ, 106^\circ; -164^\circ, 264^\circ, 74^\circ; \text{ and } -164^\circ, 284^\circ, 124^\circ$. These angles define the torsions at the phenyl-COO (adjacent to the side chain), TPA-S phenyl (or -O phenyl), and TPAS-phenyl (or TPAO-phenyl) bonds, respectively, and 0° corresponds to the *cis* conformation in each case. The phenyl-COO torsion not adjacent to the substituent was set at -16° or $+16^\circ$, so that the two ester groups were *trans*-coplanar. Since the substituents can be either at the 2- or 3-positions, the substituted TPAs were treated as a mixture of a total of eight structures in equal proportions. In reality, a wider range of side-chain conformations is likely to be present owing to the steric requirements for chain packing, but this averaging over eight structures is probably sufficient for predicting the scattering along the fibre axis direction.

Scattering by non-periodic copolymer chains

A model of a short segment of the unsubstituted copolymer with a random sequence is shown in Figure 2. The chain has an extended conformation, such that the axial advances per monomer are approximately constant for each monomer type, and are approximately equal to the distances between the terminal ester oxygens. The scattering intensity in the fibre axis direction, $I(Z)$, depends on the projection of the structure onto the chain axis (*z*). For a nematic structure, $I(Z)$ can be predicted from a consideration of a single chain averaged over all possible sequences. For a solid-state structure with three-dimensional chain register, the scattering predicted for the single chain will be modified by the effects of intermolecular interferences. However, it has been shown that while these effects change the relative intensities of the maxima in $I(Z)$, their positions are largely unaffected¹¹. Thus the sequence distribution and chain conformation in the three-dimensionally ordered structure can be investigated by comparison of the observed data with those predicted for a single extended infinite chain, or a finite chain averaged over all possible sequences. Since the phenyl-phenyl, phenyl-COO and COO-phenyl bonds in the backbone are approximately parallel to *z*, the axial advances for the different types of monomer, which determine the interference conditions, are largely independent of the backbone conformation. Significant variability is to be expected in the conformations of the O-phenyl and S-phenyl side chains, but this is likely to affect the intensities rather than the positions (*Z* coordinates) of the predicted scattering maxima.

The intensity scattered by a single copolymer chain along its axis direction, $I(Z)$, is derived as the Fourier

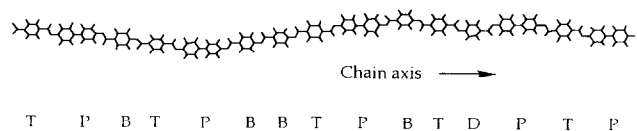


Figure 2 Model of a 15-monomer segment of 33/33/33 copoly(HBA/BP/TPA) chain of random monomer sequence. The monomers are further abbreviated to B, P and T, respectively

transform of its autocorrelation function, $Q(z)$. The latter function defines the monomer nearest-neighbour probability along the chain axis. The Fourier transform of $Q(z)$ is defined in terms of $H_1(Z)$, the Fourier transform of the first nearest-neighbour component which describes the probability that monomer A is followed by monomer B¹³. $I(Z)$ is given by:

$$I(Z) = 1 + 2 \operatorname{Re} \left[\frac{1 + H_1(Z)}{1 - H_1(Z)} \right]$$

where Re designates the real component. $H_1(Z)$ is defined as:

$$H_1(Z) = \sum_A \sum_B F_{AB}(Z) p_A M_{AB} \exp(2\pi i Z z_B)$$

where the subscripts designated monomers A and B and the summation is over all AB monomer pairs¹¹. $F_{AB}(Z)$ is the Fourier transform of the convolution of monomer A with monomer B:

$$F_{AB}(Z) = \sum_A \sum_B f_{j,A} f_{k,B} \exp[2\pi i Z(z_{j,A} - z_{k,B})]$$

where f is the scattering factor for the atom with axial coordinate z ; the subscripts designate the j th atom of monomer A and the k th atom of monomer B, respectively, and the summations are over all atoms in monomers A and B; p_A is the mole fraction of monomer A; z_B is the axial advance of monomer B; M_{AB} defines the probability that monomer A is followed by monomer B. In the present polymer there are three chemically distinct monomers. TPA and BP are symmetrical along the chain axis, but there is a sense to HBA, in that it can be oriented along the chain as either O-phenyl-CO or CO-phenyl-O, depending on the sequence. Consequently, from the physical point of view there are four monomers, with the total HBA content split equally between 'up' and 'down' options. However, of the 16 possible AB pairs, only eight are chemically possible. For example, TPA-TPA and BP-BP pairs cannot be formed, and HBA can follow TPA or BP in one 'up' or 'down' sense, but not the other. $M_{AB} = 0$ for the disallowed pairs; for the allowed pairs $M_{AB} = 2p_B r_{AB}$, where $r_{AB} = 1$ for the random copolymer. By setting $r_{AB} \neq 1$, we can simulate different microstructures, subject to the normalization $\sum_B M_{AB} = 1$, i.e. monomer A must be followed by one of the chemically allowed combinations if the chain is to continue. For the unsubstituted copolymer it has been shown⁸ that all but minimal non-randomness can be ruled out, based on the agreement between the observed and predicted $I(Z)$.

It can be seen in Figure 2 that although the unsubstituted copolymer chain is highly extended, there is some sinuous character that depends on the phenyl-ester torsional angles. Thus, the advance per monomer along the axis is only approximately constant for each monomer type, and there is a distribution of these lengths about mean values that are a little less than the ester oxygen-ester oxygen distances (since these vectors are not in general parallel to the overall chain axis). Distribution functions for each monomer type (in the unsubstituted polymer) were derived from surveys of models of a large number of different sequences constructed subject to different limits of sinuosity. We constructed 500 chains of 25 monomers of different

sequences, with random setting of the phenyl-OCO torsion angle at $\pm 60^\circ$ or $\pm 240^\circ$ and the phenyl-COO torsion at 0° or 180° . (Selection of the torsion angles also required a 60° mutual inclination of the backbone phenyl groups in successive phenyl-ester-phenyl units, as suggested by X-ray studies of the unsubstituted copolymers¹¹.) The chain axis was defined as the best least-squares line through all the atomic coordinates. Different degrees of sinuosity were simulated by requiring the centres of all the atoms (including hydrogens) to be within cylinders of diameters 8, 10, 11, 12, 13, 14, 15, 16, 17 or 18 Å. Chains not meeting the chosen requirement were discarded and new chains with different sequences and conformations were generated until the requisite 500 chains were obtained for each diameter. The monomer advances for the HBA, BP and TPA units were derived from the z coordinates of the ester oxygens, and their distributions were described as histograms. The expression for $H_1(Z)$ was modified as follows:

$$H_1(Z) = \sum_A \sum_B F_{AB}(Z) p_A M_{AB} \sum_m p_{m,B} \exp(2\pi i Z z_{m,B})$$

where $p_{m,B}$ is the probability that monomer B has the axial advance $z_{m,B}$ and $\sum_m p_{m,B} = 1$. The $F_{AB}(Z)$ functions are different for each $z_{m,B}$ component. The actual differences are very small across the range of $z_{m,B}$ and it is only a minor approximation to use the values for the fully extended monomers throughout. In the results presented below, $I(Z)$ has been corrected for the Lorentz and polarization effects, for comparison with the observed diffractometer data.

RESULTS AND DISCUSSION

X-ray data

The X-ray patterns recorded for the as-drawn fibres of the unsubstituted and S-phenyl- and O-phenyl-substituted 33/33/33 copolymers are shown in Figure 3.

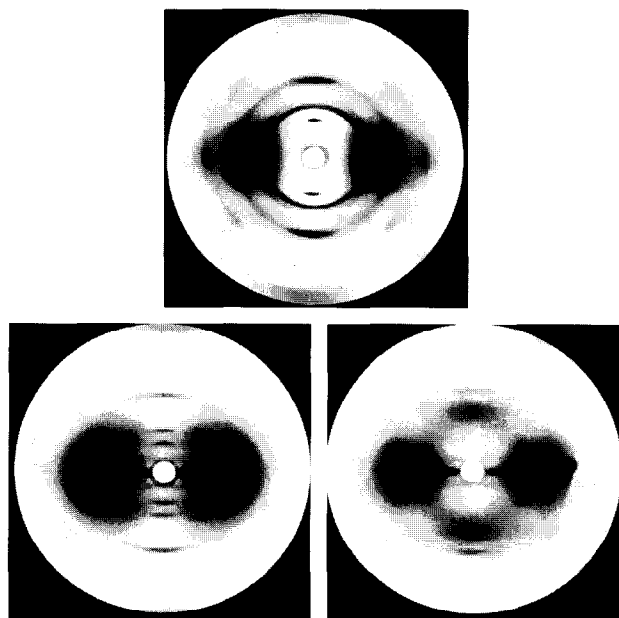


Figure 3 X-ray diffraction patterns for melt-spun fibres: (a) 33/33/33 copoly(HBA/BP/TPA); (b) 33/33/33 copoly(HBA/BP/STPA); and (c) 33/33/33 copoly(HBA/BP/OTPA). The fibre axis is vertical in each case

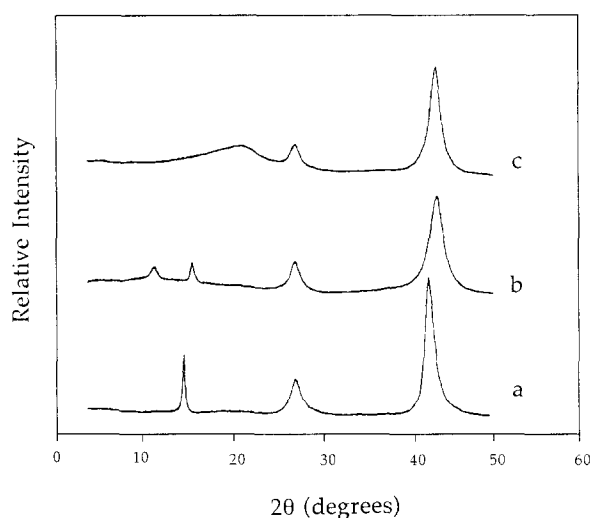


Figure 4 Diffractometer scans ($\theta/2\theta$) along the fibre axis direction: (a) copoly(HBA/BP/TPA); (b) copoly(HBA/BP/STPA); and (c) copoly(HBA/BP/OTPA)

The data were recorded with the fibre axes perpendicular to the X-ray beam. Figure 4 shows $\theta/2\theta$ diffractometer scans along the direction of draw for the fibres of the three copolymers.

It is apparent that the addition of side chains has led to a decrease in the three-dimensional order compared to that seen for the unsubstituted copolymer. In the fibre diagram of the unsubstituted copolymer (Figure 3a) we see sharp Bragg reflections on the equator at $d = 4.52$, 3.92 , 2.38 and 2.27 Å, plus a number of Bragg peaks on the non-periodic layer lines, indicating the presence of overall three-dimensional order. For both substituted copolymers (Figure 3b, c) we see a strong, sharp Bragg maximum on the equator at $d \approx 13.0$ Å. There is also a weaker, more diffuse equatorial at $d \approx 9.8$ Å, and two stronger diffuse equatorials in the range $d = 5-3$ Å. Above and below the equator, we see a series of layer-line streaks. There is no evidence of off-meridional Bragg maxima of the kind that are seen for the unsubstituted copolymer, which indicates that there is little three-dimensional registration when the substituents are present.

The d -spacings of the meridional maxima are listed in Table 1. Five maxima are seen for the unsubstituted copolymer. In contrast, we see four meridional maxima for the S-phenyl-substituted copolymer, but these have d -spacings that are close to four of those seen for the unsubstituted copolymer. For the O-phenyl-substituted copolymer, we observe only two sharp maxima which match the two outer maxima for the S-phenyl analogue, plus a broad, diffuse peak at $d \approx 4.3$ Å. The intensity of the latter peak is a striking difference between the data for the two substituted copolymers, and is perhaps

Table 1 Observed meridional d -spacings (Å) for the 33/33/33 copolyesters (experimental errors are given in parentheses)

TPA/BP/HBA	STPA/BP/HBA	OTPA/BP/HBA
7.7 (0.1)	7.84 (0.05)	—
5.77 (0.02)	5.58 (0.03)	—
3.28 (0.02)	3.24 (0.02)	3.24 (0.02)
2.90 (0.02)	—	—
2.09 (0.01)	2.06 (0.01)	2.06 (0.01)

surprising when one considers that the only chemical difference is the replacement of a sulfur by an oxygen on one-third of the monomers. There is no evidence for impurity in the bulk O-phenyl-substituted polymer, although it is possible that some degradation occurred during melt-spinning. However, degradation would be more likely to produce an isotropic, diffuse amorphous halo, whereas the diffuse maximum at $d \approx 4.3$ Å is disposed along the chain axis direction, and clearly arises from an oriented structure. Both polymers also show a layer-line streak at $d \approx 14$ Å, but with little or no intensity on the meridian. (No intensity is detected in this region of the diffractometer scans in Figure 4.) Intensity on a layer line half-way between the first meridional and the origin (beam stop) is also seen for the unsubstituted copolymer, and is explained⁸ by a physical repeat containing two monomers in which successive phenylenes are mutually inclined by $\sim 60^\circ$, as occurs for copoly(HBA/HNA)¹¹.

The equatorial maximum at $d \approx 13.0$ Å is reminiscent of that seen for the alternating copolymer of TPA and phenyl-hydroquinone at $d = 12.6$ Å¹⁴. The latter copolymer gives rise to a very detailed fibre diagram containing 16 Bragg reflections that can be indexed by a (metrically orthorhombic) monoclinic unit cell with dimensions $a = 12.77$ Å, $b = 10.08$ Å and $c = 12.58$ Å (chain axis). The high degree of crystallinity is striking in view of the probably random 2- and 3-substitution of the phenyl groups along the backbone. Refinement of the structure shows that the chains are packed with their side chains interdigitated, and sufficient space is available to accommodate the randomly substituted side chains. The same type of structure is also seen for the 50/25/25 copolymer of hydroquinone, phenyl-TPA and 1-phenylethyl-TPA¹⁵. However, this structure is more disordered, probably because two types of side chains are present, and the d -spacing of the first equatorial is increased to 13.0 Å to accommodate the larger 1-phenylethyl substituents.

Thus it appears that the O-phenyl- and S-phenyl-substituted copolyesters pack in an analogous fashion, with interdigitated side chains. Successive OTPA or STPA units must be separated by at least one other monomer unit, and are on average ~ 18 Å apart, since there is now only one side chain for every three monomers, i.e. every four phenyl moieties in the backbone. Consequently, interdigitation can probably still be achieved even for a random sequence, and this is probably the most efficient mode of packing. The observed densities for the S-phenyl- and O-phenyl-substituted copolymers are 1.09 and 1.08 g ml⁻¹, which are $\sim 20\%$ lower than the value of 1.37 g ml⁻¹ determined for the unsubstituted copolymer, and thus considerable free volume exists within both structures, even after accommodation of the random side chains. Nevertheless, the interdigitation probably requires axial shifts of the chains, such that even the minimal registration of the centres of short random sequences that is thought to occur in the unsubstituted copolymer is no longer possible when the substituents are present.

The d -spacings for the five meridional maxima seen for the unsubstituted copolymer match those reported previously, within experimental error, and have been shown to be characteristic of random comonomer sequence⁸. The four maxima seen for the S-phenyl-substituted

copolymer are close to the first, second, third and fifth maxima for the unsubstituted copolymer, although there are differences that are outside experimental error: the first is shifted to slightly higher d -spacing while the other three are shifted to lower d -spacing. The two sharp maxima for the O-phenyl-substituted copolymer match the third and fourth for the S-phenyl-substituted copolymer, and it appears likely that the two copolymers have similar structures. The approximate coincidence of the aperiodic layer lines for the unsubstituted and substituted copolymers suggests that the latter also have random monomer sequences. However, the source of the discrepancies needs to be examined by simulation of the scattering from model structures.

Simulation of X-ray scattering data

The X-ray scattering in the chain-axis direction, $I(Z)$, was predicted using the equations given above for an infinite chain. The models considered were the idealized straight chain, with all the ester oxygens colinear, and progressively more and more sinuous chains. For the latter, the axial advances were defined by histograms taken from surveys of models of 500 unsubstituted chains of 25 monomers that fit within cylinders of specified diameters ranging from 8 to 18 Å. Typical histograms for HBA, BP and TPA units in chains restricted to a cylinder of diameter 12 Å are shown in Figure 5, and yield average monomer advances of 6.22, 9.74 and 7.00 Å, respectively. These compare to 6.35, 9.84 and 7.22 Å, respectively, for the idealized linear chain conformation, which would have a diameter of ~ 5 Å.

The calculated $I(Z)$ data for these models of the unsubstituted copolymer are shown in Figure 6; the d -spacings of the predicted peaks are compared with those observed in Table 2. It can be seen that the predicted d -spacings for the idealized linear chain are similar to those observed, but all five predicted peaks are shifted to higher d -spacing by approximately 2%. It can be concluded that the linear model is too extended, i.e. the chain has a more sinuous character. Comparison of the peak positions for the chains with different degrees of sinuosity shows that we get the best agreement for a restricting cylinder diameter of 12 ± 1 Å. A diameter of 8 Å is about the minimum that can be achieved with the standard bond lengths and angles, and the random selection of sequences and torsion angles, i.e. an 8 Å diameter for a 25-monomer segment in reality corresponds to the fully extended chain. Consequently, the determination of a diameter of 12 ± 1 Å for the 25-monomer segment means that the chains of the

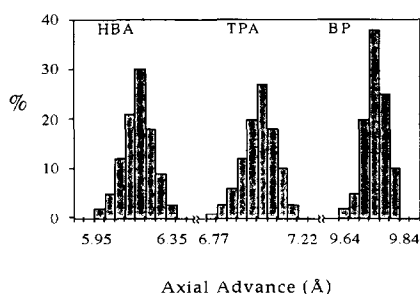


Figure 5 Monomer axial length distributions for 500 chains of 25 monomers of the unsubstituted copolymer restricted to a cylinder of diameter 12 Å

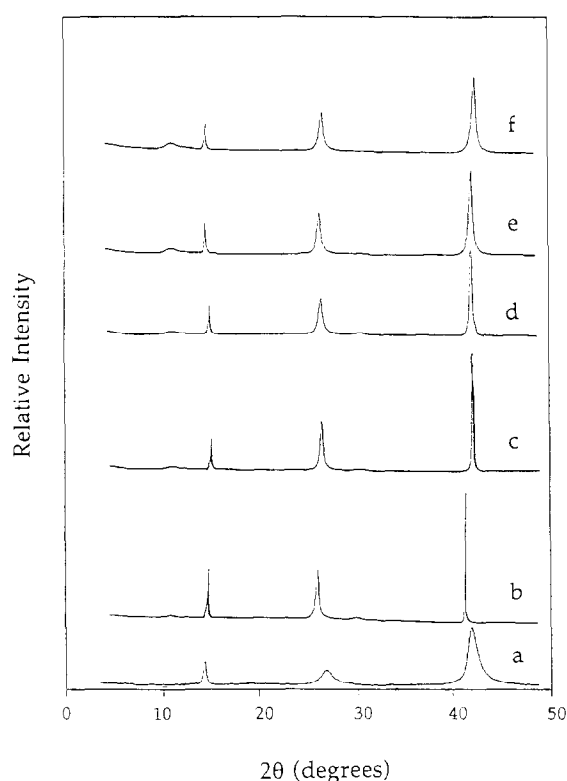


Figure 6 $I(Z)$ data for the unsubstituted copolymer plotted as a function of scattering angle 2θ (degrees). (a) Observed diffractometer scan; (b) predicted for an idealized, fully extended chain; (c)–(f) predicted for sinuous chains restricted to diameters of 10, 12, 14 and 16 Å, respectively

Table 2 Comparison of observed meridional d -spacings (Å) for copoly(TPA/BP/HBA) with those predicted for models of random copolymer chains with different sinuosities

Observed (\pm error)	Fully extended model	Restricting cylinder diameter (Å)						
		8	10	11	12	13	14	16
7.7 (0.1)	7.90	7.84	7.82	7.80	7.77	7.74	7.72	7.69
5.77 (0.02)	5.85	5.80	5.78	5.76	5.75	5.73	5.71	5.67
3.28 (0.02)	3.35	3.31	3.30	3.29	3.28	3.27	3.25	3.24
2.90 (0.02)	2.92	2.90	2.89	2.89	2.88	2.87	2.87	2.86
2.09 (0.01)	2.13	2.11	2.10	2.10	2.09	2.08	2.07	2.06

unsubstituted copolymer are $\sim 1\%$ less than fully extended, probably in order to optimize the three-dimensional packing. This is consistent with the work of Ward and co-workers¹⁶, who have concluded that some sinuosity of the chains is necessary to account for the tensile modulus of copoly(HBA/HNA).

Figures 7 and 8 and Table 3 show the equivalent data predicted for the S-phenyl- and O-phenyl-substituted copolymers. These data were derived for the same histograms of axial advances: the only differences in the calculation of $I(Z)$ were in the $F_{AB}(Z)$ terms, since the atomic coordinates for the TPA units included the side chains (averaged over eight possible positions). The predicted d -spacings are identical for the two copolymers, and the relative intensities are very similar. It is interesting that, in addition to the main peaks listed in Table 3, we predict a weak, broad peak at $d \approx 4.5$ Å for the O-phenyl-substituted copolymer, which may relate to the more intense broad peak observed at $d \approx 4.3$ Å. The

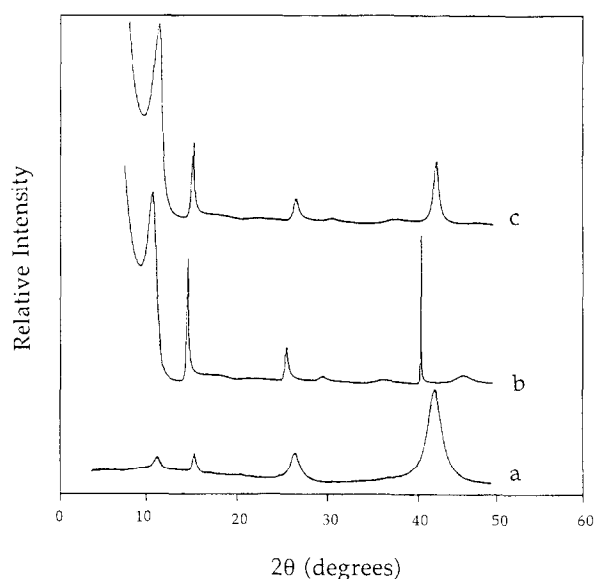


Figure 7 $I(Z)$ data for the S-phenyl-substituted copolymer plotted against scattering angle 2θ (degrees). (a) Observed diffractometer scan; (b) predicted $I(Z)$ for an idealized linear chain; (c) predicted $I(Z)$ for a sinuous chain restricted to a diameter of 16 Å

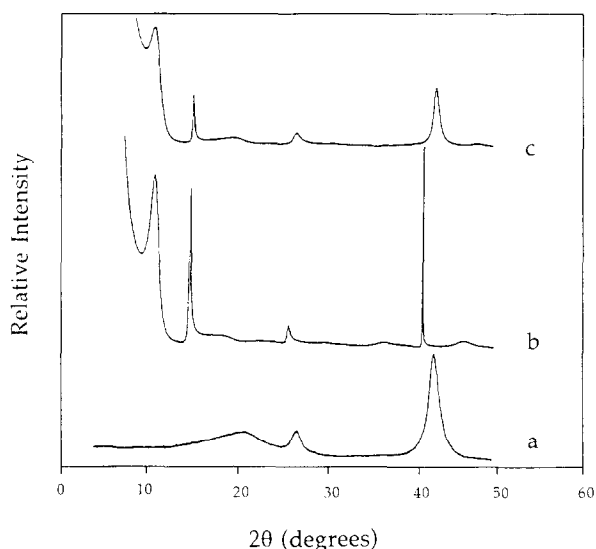


Figure 8 $I(Z)$ data for the O-phenyl-substituted copolymer plotted against scattering angle 2θ (degrees). (a) Observed diffractometer scan; (b) predicted $I(Z)$ for an idealized linear chain; (c) predicted $I(Z)$ for a sinuous chain restricted to a diameter of 16 Å

same feature is predicted for the S-phenyl-substituted copolymer, but is even weaker.

The predicted peaks for idealized fully extended models for the substituted copolymers match those for the unsubstituted copolymer except for the first maximum, which is shifted to higher d -spacing: $d = 8.10 \text{ \AA}$ versus 7.90 \AA , which correlates with the differences seen in the observed data: $d = 7.84 \text{ \AA}$ versus 7.7 \AA . The predicted intensity at smaller angles ($d < 5 \text{ \AA}$) is much higher for the substituted than for the unsubstituted copolymer. This arises because of the contribution to the scattering from the side chains, which are always separated by at least two monomers. The predicted maxima in $I(Z)$ result from the sum of the products of components of the interference function (due to the non-periodic axial advance) and the more slowly varying $F_{AB}(Z)$ terms. The former interference function is the primary determinant of the peak positions, but the slowly varying $F_{AB}(Z)$ terms can shift the position of the peaks, an effect that is usually more obvious at lower Z (higher d). The same effect has been reported for semicrystalline homopolymers, notably nylon 6¹⁷, where the 001 peaks are of finite width due to the limited crystallite size, and are shifted from the d -spacings predicted in the Laue function for the lattice as a result of the slow variation of the Fourier transform of the molecular repeat (unit cell contents). Likewise, the non-periodic layer lines observed for fibre of wholly aromatic copolyimides shift with increasing draw ratio, and this is explained by changes in the correlation lengths for the extended chain conformation¹⁸. This same effect is probably responsible for the difference in the predicted positions of the first peak for the substituted and unsubstituted copolyesters, since the same monomer advances are used in both structures.

Overall, the predicted d -spacings for the idealized, fully extended models of the substituted copolyesters are greater than those observed, again suggesting that the chains are more contracted, i.e. sinuous. The best agreement is obtained for chains of 25 monomers with diameters limited to $16 \pm 1 \text{ \AA}$ (see Table 3). The match for the second maximum is a little outside the limits of experimental error, but this is not a serious matter, because further small shifts in this position may also arise due to packing effects. As already noted, the predicted intensity for the isolated chain is much more intense in the $d > 5 \text{ \AA}$ region for the substituted chains, but this is not observed in the experimental data, probably due to interference effects that result when the side chains are interdigitated.

Thus we are able to generate the observed non-periodic layer lines for both the unsubstituted and substituted

Table 3 Comparison of the observed meridional d -spacings (\AA) for the substituted copolymers with those predicted for models of random copolymer chains with different sinuosities

HBA/BP/STA observed (error)	HBA/BP/OTA observed (error)	Fully extended model	Restricting cylinder diameter (\AA)				
			14	15	16	17	18
7.84 (0.05)	—	8.10	7.84	7.82	7.81	7.80	7.79
5.58 (0.03)	—	5.85	5.70	5.68	5.65	5.63	5.60
3.24 (0.02)	3.24 (0.02)	3.35	3.27	3.25	3.24	3.23	3.21
—	—	2.92	2.90	2.89	2.89	2.88	2.87
2.06 (0.01)	2.06 (0.01)	2.13	2.8	2.7	2.06	2.05	2.04

copolyesters in simulations based on models consisting of arrays of chains of completely random comonomer sequences. The differences in the observed *d*-spacings arise mainly from the fact that the substituted copolyesters have a less extended conformation. In all cases, the copolymer chains are less extended than the idealized straight-chain models, i.e. the chains are sinuous due to variation of the torsional angles at the phenyl-COO and OCO-phenyl bonds. The substituted copolymers are probably more contracted due to the need to minimize free volume when packing the side chains. This effect is relatively small, with a reduction of only $\sim 1.5\%$ in the chain length compared to the unsubstituted copolymer, and is probably as much as can be achieved with this backbone chemistry. The substituted copolymers appear to be packed such that the side chains are interdigitated and pairs of backbones are in contact with each other. This interdigitation is possible over relatively short distances despite the random sequences, but the structure is highly distorted and there is no evidence for the three-dimensional registration of adjacent chains seen for the unsubstituted copolymer.

ACKNOWLEDGEMENTS

This research was supported by NSF MRG DMR 8614093 on Liquid Crystalline Polymers and by a graduate fellowship to M. Ishaq from the State of Pakistan. We are indebted to Dr N. D. Field (Dartco) for the specimen of unsubstituted 33/33/33 copoly(HBA/BP/TPA).

REFERENCES

- 1 Economy, J. *Mol. Cryst. Liq. Cryst.* 1989, **169**, 1
- 2 Volksen, W., Lyerla, J. R., Economy, J. and Dawson, B. *J. Polym. Sci., Polym. Chem. Edn* 1983, **21**, 2249
- 3 Field, N. D., Baldwin, R., Layton, R., Frayer, P. and Scardiglia, F. *Macromolecules* 1988, **21**, 2155
- 4 Calundann, G. W. and Jaffe, M. 'Proceedings of Robert A. Welch Conferences in Chemistry, "Synthetic Polymers"', 1982, p. 247
- 5 Blackwell, J. and Biswas, A. 'Developments in Oriented Polymers 2', Elsevier, New York, 1987
- 6 Kricheldorf, H. R., Doering, V. and Eckhardt, V. *Makromol. Chem.* 1988, **189**, 1425, 1437
- 7 Kricheldorf, H. R., Schwartz, G. and Eckhardt, V. *Makromol. Chem., Rapid Commun.* 1989, **10**, 243
- 8 Blackwell, J., Cheng, H. M. and Biswas, A. *Macromolecules* 1988, **21**, 39
- 9 Gutierrez, G. A., Chivers, R. A., Blackwell, J., Stamatoff, J. B. and Yoon, H. *Polymer* 1983, **24**, 937
- 10 Biswas, A. and Blackwell, J. *Macromolecules* 1987, **20**, 2997
- 11 Biswas, A. and Blackwell, J. *Macromolecules* 1985, **21**, 3146, 3152, 3158
- 12 Hofmann, D., Schneider, A. I. and Blackwell, J. *Polymer* 1994, **35**, 5603
- 13 Blackwell, J., Gutierrez, G. A., Chivers, R. A. and Ruland, W. J. *J. Polym. Sci., Polym. Phys. Edn* 1984, **22**, 1343
- 14 Hong, S. K. and Blackwell, J. *Polymer* 1989, **30**, 225
- 15 Hong, S. K. and Blackwell, J. *Polymer* 1989, **30**, 781
- 16 Troughton, M. J., Unwin, A. P., Davies, G. R. and Ward, I. *Polymer* 1988, **29**, 1389
- 17 Waller, L. G. *Monatshifte für Chemie* 1948, 279
- 18 Wu, T. M., Chvalun, S. N., Blackwell, J., Cheng, S. Z. D., Wu, Z. and Harris, F. W. *Acta Polym.* in press