Thermotropic polyesters: modelling of the meridional diffraction patterns of poly(p-oxybenzoate-co-p-phenylene isophthalate) fibres

D. J. Johnson, I. Karacan and J. G. Tomka*

Textile Physics Laboratory, Department of Textile Industries, University of Leeds, Leeds LS2 9JT, UK

Previous work has shown that poly(p-oxybenzoate-co-p-phenylene isophthalate) (50/50 and 67/33) fibres spun from nematic mesophase are highly oriented but lack crystalline order. Heat treatment of these 'as-made' fibres results in structure regarded as a mosaic of thin crystalline regions consisting of p-phenylene isophthalate sequences in a paracrystalline matrix. This work is concerned with atomic modelling of the copolymer chains. One-dimensional Fourier transforms generated from the models are compared with the observed meridional diffraction traces of the 'as-made' fibres. A good match is obtained for the extended chain models containing 'trans' conformations of p-oxybenzoate and p-phenylene dioxy units.

INTRODUCTION

Semi-rigid poly(p-oxybenzoate-co-p-phenylene isophthalate)s (POPI), which can be produced from readily available monomers (p-acetoxybenzoate, hydroquinone diacetate and isophthalic acid) are nematogenic within the composition range extending from 33/67 to 75/25. Compositions between 50/50 and 67/33 exhibit a nematic temperature interval of at least 50°C and are therefore particularly suitable for melt processing, including fibre spinning[1]. Initial investigations of the structure of fibres produced from the 50/50 and 67/33 copolymers showed that the 'as-made' fibres were highly oriented but lacked crystalline order[2]. Annealing at temperatures ranging from 240 to 300°C induced crystallization. Interpretation of wide-angle X-ray diffraction patterns (in particular, analysis of the equatorial scatter) led to the conclusion that annealed fibres can be regarded as a mosaic of thin crystalline regions containing p-phenylene isophthalate sequences. The chains emerging from the crystallites form a paracrystalline array similar to that present in the 'as-made' fibres. However, neither the crystallite thickness nor the correlation length of the paracrystalline material were evaluated.

The aim of this paper is to improve our understanding of the structure of POPI fibres, by analysing their meridional diffraction patterns and comparing them with Fourier transforms generated from atomic models of the copolymer chains. A similar approach was utilized by Blackwell and coworkers[3-6]. Initially[3], a simple 'point model' was used to predict the positions of the aperiodic meridional maxima, which are a result of the difference in the lengths of the constituent units in the copolyester fibres containing p-phenylene and 2,6-naphthylene moieties. An analytical method based on a 'point model' described by Davies and Jakeways[7] gave a similar result. Further work based on atomic models was aimed at

predicting the relative intensities of the meridional peaks[4] and has been extended to three-dimensional arrays of copolymer chains[5].

It should be emphasized that the aromatic moieties in the copolymers studied by Blackwell and coworkers have outgoing bonds that are either colinear (p-phenylene) or parallel (2,6-naphthylene). In contrast, the POPI copolymers studied here contain angular m-phenylene moieties, which substantially complicates the chain modelling. The only copolymer containing angular units investigated so far by the modelling approach is an aromatic copolyamide that is the basis of Technora aramid fibres[6]. However, in this case the angular entities (ether oxygen and m-phenylene) are directly linked and this alleviates the modelling difficulties.

EXPERIMENTAL

The 'as-made' and heat-treated fibres prepared from the 50/50 and 67/33 copolymers were the same as those used previously[2].

Wide-angle X-ray diffraction patterns of fibres were taken with a flat-plate camera. The optical density of the wide-angle X-ray diffraction patterns was recorded with a double-beam scanning microdensitometer interfaced with a local microprocessor for digital data acquisition. The optical density from a selected area of the pattern is scanned at raster intervals of 0.05 mm. The intensity data are normally collected in block format before transfer to the University of Leeds Amdahl mainframe computer. Once the data are transfered, the blocks of data are then converted to an array within a program called RASTER. Typical dimensions for an entire pattern are 200 × 200 data points with a maximum storage capacity of 4 Mbyte. Within the RASTER program, there are various graphical output options available, such as grey level (at least 10), contour map, three-dimensional isometric projection, or intensity traces in a specified direction.

In this work, the centre of the film and the camera length were determined by using a silver calibration ring (usually the 1 1 1 reflection). Hexamethylenetetramine was used for the instrumental broadening correction. Lorentz and polarization corrections were only applied to single scans (equatorial or meridional). No corrections were applied to raster scans of an entire diffraction pattern.

Additional data on very weak meridional reflections were obtained using an X-ray diffractometer[2].

COMPUTER MODELLING

The copolymer chains consist of rod-like *p*-oxybenzoate (OPCO) and *p*-phenylene dioxy (OPO) units, and angular isophthaloyl (COMCO) units[1]. In the 50/50 copolymer the molar fractions of these units are [OPCO] = [OPO] = [COMCO] = 0.333, and in the 67/33 copolymer [OPCO] = 0.50 and [OPO] = [COMCO] = 0.25. Sequences of the constituent units were generated by a computer program, which excludes any inappropriate chemical combinations. An example of such a sequence representing a 50/50 copolymer chain has been shown previously (see figure 7 in ref. 2).

Owing to the complications arising from the presence of the angular COMCO units, modelling was limited to planar chains containing not more than 36 units. The bond lengths and angles employed are listed in *Table 1*. The '*cis*' and '*trans*' planar conformations used for OPCO and OPO units are shown in *Figures 1a–d*. For COMCO

Table 1 Bond lengths and angles[8,9]

Bond[a]	Length (nm)
O—C(=O)	0.137
C(=O)—C(b)	0.149
C(b)—O	0.141
C(b)—C(b)	0.139
C=O	0.123

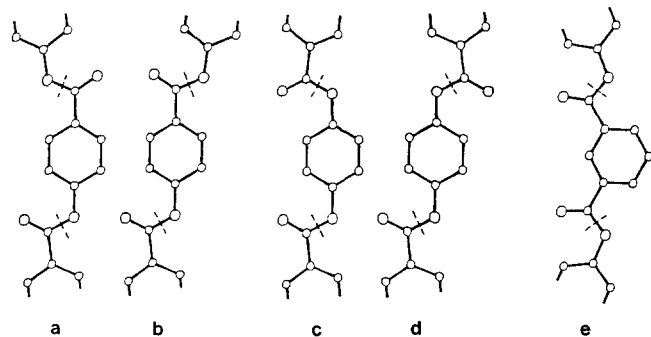| Bonds	Angle (deg)
O—C(=O)—C(b)	110.9
C(b)—C(b)—C(=O)	120.0
C(b)—C(b)—C(b)	120.0
C(b)—C(b)—O	120.0
C(b)—O—C(=O)	118.3
C(b)—C=O	123.0

[a] C(b) denotes aromatic carbon

Figure 1 Conformations of the constituent units: (a) *p*-oxybenzoate '*cis*'; (b) *p*-oxybenzoate '*trans*'; (c) *p*-phenylene dioxy '*cis*'; (d) *p*-phenylene dioxy '*trans*'; (e) isophthaloyl. The units are limited by broken lines
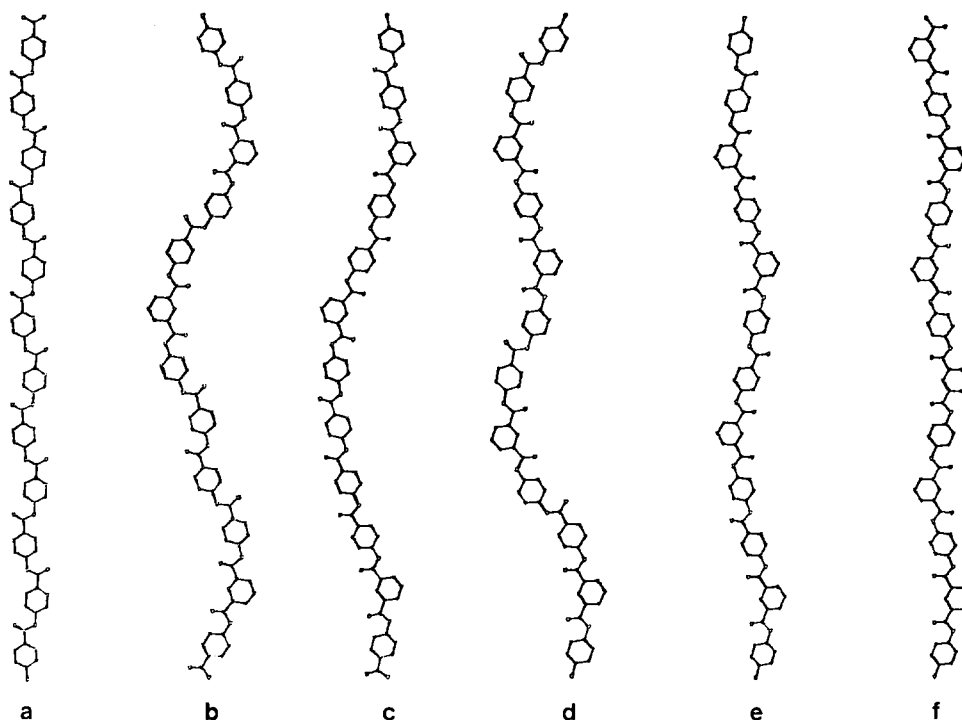
units only the conformation that maximizes the chain extension is used (*Figure 1e*). The mirror images of these conformations are also utilized in the modelling.

Before specifying the rules employed for generating the copolymer chain models, it is necessary to consider the appropriate planar models of the parent homopolymers. As far as poly (*p*-oxybenzoate) is concerned, an extended chain can only be obtained from the OPCO '*cis*' units (*Figure 1a*); such a chain is shown in *Figure 2a*. It should be noted that it differs from the non-planar conformation proposed for the poly(*p*-oxybenzoate) crystal lattice[10,11] only with respect to the out-of-plane rotation of the *p*-phenylene groups. Because the outgoing bonds of a planar ester group are not parallel, the chains generated from OPCO '*trans*' units (*Figure 1b*) are curved, and have been disregarded.

A fully extended poly(*p*-phenylene isophthalate) chain is shown in *Figure 2f*. It consists of COMCO units (*Figure 1e*) and OPO '*trans*' units (*Figure 1c*). Both units alternate in a 'left' and 'right' fashion. This chain conformation with a repeating length of 2.46 nm has been proposed[2] for the type C crystalline structure found in heat-treated 50/50 and 67/33 POPI fibres.

Consequently, the main rule for constructing the copolymer chain models from computer-generated unit sequences was that the angular COMCO units alternate between the 'left' and 'right' versions of the conformation shown in *Figure 1e*. Although our intention was to construct two types of chains according to the conformation of the OPCO and OPO units, i.e. either '*trans*' or '*cis*', it was found that this was possible only for the '*trans*' conformations. Attempts to construct chains entirely from '*cis*' conformations resulted in highly non-linear models. In order to 'straighten' these chains, it was necessary to replace some of the '*cis*' conformations adjacent to COMCO units by '*trans*' conformations (e.g. OPO in a COMCO–OPO–COMCO sequence). The resulting models are referred to as '*cis*-based'.

For model construction, it was necessary to define the chain direction; this was taken as a straight line connecting the two aliphatic carbon atoms of the first COMCO unit. It was found that the completed chains tend to deviate considerably from the initial direction. The completed chains were therefore repositioned so that the first and last skeletal oxygen atoms were located on the *z* axis to be used for the Fourier transforms.

Examples of 50/50 and 67/33 models are shown in *Figure 2*. It is obvious that the '*trans*' chains are more extended than the '*cis*-based' chains.

For the calculations of theoretical meridional intensity, it was only necessary to use the *z* coordinates of the carbon and oxygen atoms. One-dimensional Fourier transforms are given by:

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

where the summation is over all *N* atoms of the chain containing *n* units; f_j is the atomic scattering factor, *Z* is the reciprocal-space vector and z_j is the atomic coordinate of the *j*th atom. $|F_c(Z)|^2$ is then averaged over 100 chains to obtain the averaged squared Fourier transform $\langle |F_c(Z)|^2 \rangle$. This has been corrected for the Lorentz and polarization factors, and smoothed by a process that takes the arithmetic average of 10 neighbouring points for each value of *Z*. The transforms have been evaluated for

Figure 2 Planar chain models: (a) 100/0 '*cis*'; (b) 67/33 '*cis*-based'; (c) 67/33 '*trans*'; (d) 50/50 '*cis*-based'; (e) 50/50 '*trans*'; (f) 0/100 '*trans*'

2θ between 0 and 50° at 20 steps per degree and were resolved by a minimization procedure[12] in order to determine the positions and widths of the individual peaks.

RESULTS AND DISCUSSION

Observed features

The main feature of the WAXS patterns of the 50/50 and 67/33 'as-made' fibres is a broad intense equatorial reflection with a d-spacing of 0.44 nm; quantitative analysis of the equatorial scatter has been carried out previously[2] and led to the conclusion that these fibres consist of a paracrystalline array of highly oriented chain molecules. We have now found that WAXS photographs of these 'as-made' fibres reveal an extremely weak meridional reflection with a d-spacing of around 0.6 nm. After tilting the fibres, the WAXS patterns show two other meridional reflections with d-spacings around 0.3 and 0.2 nm. These three reflections at 0.6, 0.3 and 0.2 nm are hereafter referred to as PM1, PM2 and PM3, respectively.

Figure 3a shows the WAXS pattern of a tilted 50/50 'as-made' fibre; the corresponding contour map (*Figure 4a*) gives clear indication of the azimuthal spread of the reflections PM2 and PM3. The reflection PM1 showed a similar azimuthal spread. The meridional intensity trace (*Figure 5a*) shows that the PM3 reflection is asymmetrical and can therefore be resolved into two peaks; the positions and widths of these resolved peaks are given in *Table 2*. Results for the 67/33 'as-made' fibres are similar (see *Table 2*).

Heat treatment of 50/50 fibres (30 min at 280°C) brought about additional features in the WAXS pattern, in particular the three strong and sharp equatorial reflections with d-spacings of 0.559, 0.392 and 0.322 nm together with several layer-line reflections (see table 3 in ref. 2). These features were assigned to the crystalline
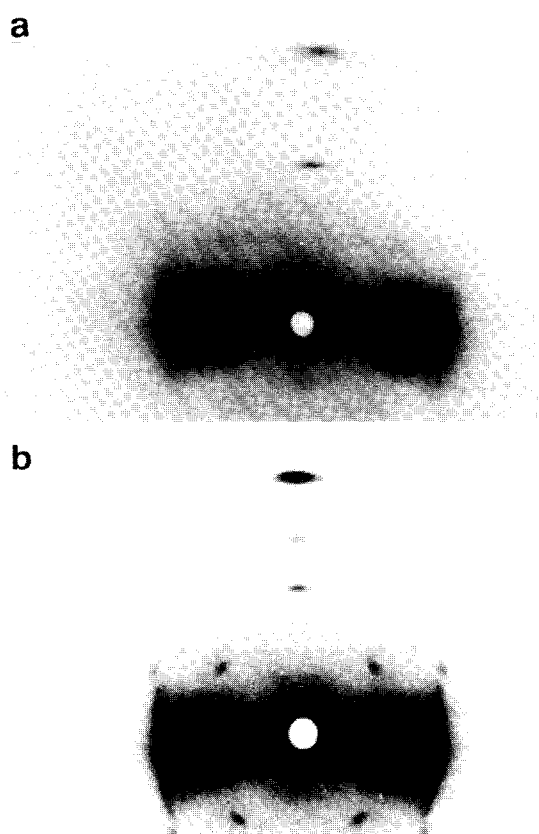

Figure 3 WAXS patterns of (a) 'as-made' and (b) heat-treated (30 min at 280°C) 50/50 fibres. The fibre axes are vertical. The fibres are tilted by 20° from the position perpendicular to the X-ray beam

regions containing p-phenylene isophthalate sequences (type C structure)[2]. The most prominent additional meridional reflection (*Figures 3b* and *4b*), designated as CM3, has a d-spacing of 0.242 nm. The azimuthal spread
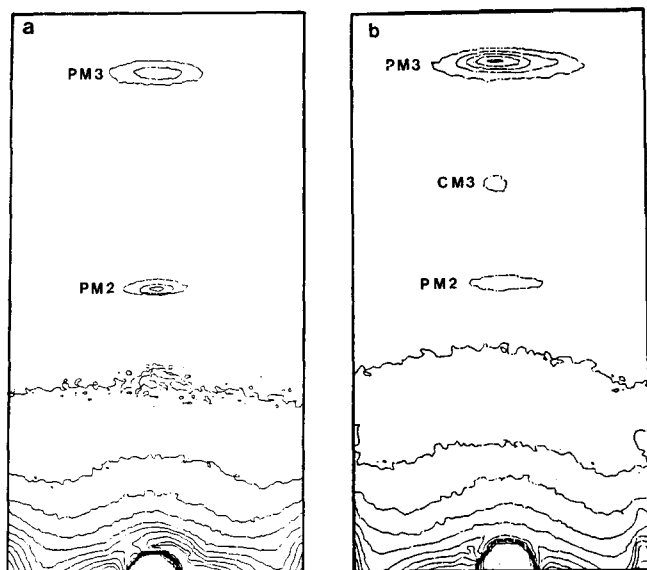
Figure 4 Contour maps of (a) 'as-made' and (b) heat-treated (30 min at 280°C) 50/50 fibres. The fibre axes are vertical
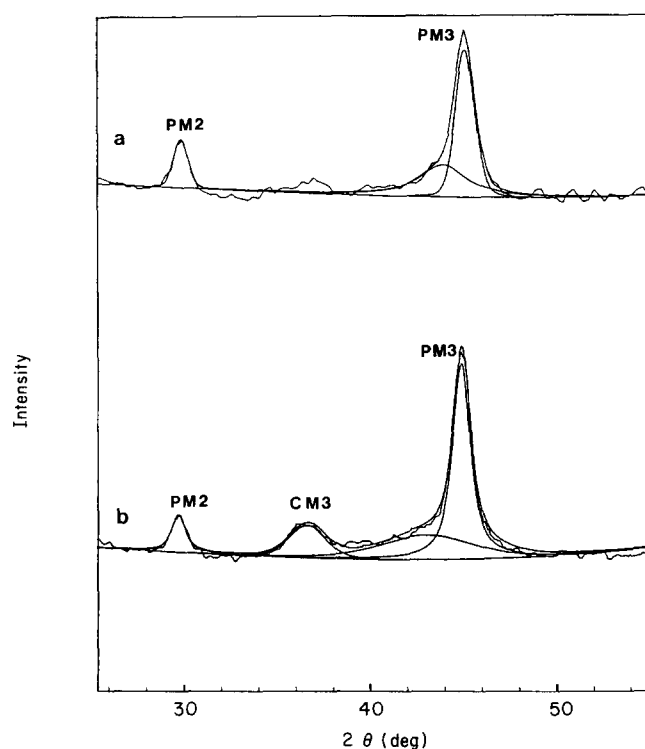

Figure 5 Resolved meridional X-ray diffraction traces of (a) 'as-made' and (b) heat-treated (30 min at 280°C) 50/50 fibres. The traces were obtained by scanning microdensitometer; for *d*-spacings see *Table 2*

of this reflection is much smaller than that of the PM2 and PM3 reflections (*Figure 4b*) but its width along the meridian is larger (*Figure 5b*); indeed, its character is similar to that of the equatorial type C reflections, which are also vertical streaks rather than azimuthal arcs[2]. Another prominent streaked meridional reflection, CM1, has a *d*-spacing of 1.215 nm and there is also a very weak reflection of the same character, CM2, with a *d*-spacing of 0.408 nm. These streaked meridional reflections are ascribed to the type C crystalline structure.

The WAXS pattern of heat-treated 67/33 fibre shows, in addition to the features found in the 'as-made' fibre, reflections assigned to the crystalline type C structure.

However, these crystalline reflections are weaker than in the case of heat-treated 50/50 fibre; indeed, some of them are absent[2], a condition that also applies to the meridional reflections (*Table 2*).

Features obtained from modelling

The meridional intensity profiles for the extended-chain conformations of the homopolymers (i.e. '*cis*' model of poly(*p*-oxybenzoate) shown in *Figure 2a*, and '*trans*' model for poly(*p*-phenylene isophthalate) shown in *Figure 2f*) are presented in *Figure 6*. Although the ratio of the repeating lengths of poly(*p*-phenylene isophthalate) (composition 0/100) and poly(*p*-oxybenzoate) (composition 100/0) is almost exactly 2, the computed diffraction profiles differ considerably regarding the number of peaks

Table 2 Meridional reflections of 'as-made' and heat-treated (30 min at 280°C) fibres (HT): peak positions (*d*) and peak widths at half-weight (*w*)

| | 50/50 | | | | 67/33 | | | |
| | 'As-made' | | HT | | 'As-made' | | HT | |
Reflection	*d* (nm)	*w* (deg)	*d* (nm)	*w* (deg)	*d* (nm)	*w* (deg)	*d* (nm)	*w* (deg)
PM1	0.608	–[a]	0.609	–[a]	0.611	–[a]	0.612	–[a]
PM2	0.301	0.86	0.302	0.88	0.307	0.75	0.305	0.71
PM3[b]	0.207	2.66	0.209	4.01	0.205	2.34	0.205	2.11
	0.201	1.22	0.202	1.14	0.204	1.02	0.204	0.84
CM1	–	–	1.215	–	–	–	1.216	–
CM2	–	–	0.408	1.80[c]	–	–	–	–
CM3	–	–	0.242	2.38	–	–	0.245	5.04[c]

[a] Too weak for a reliable evaluation
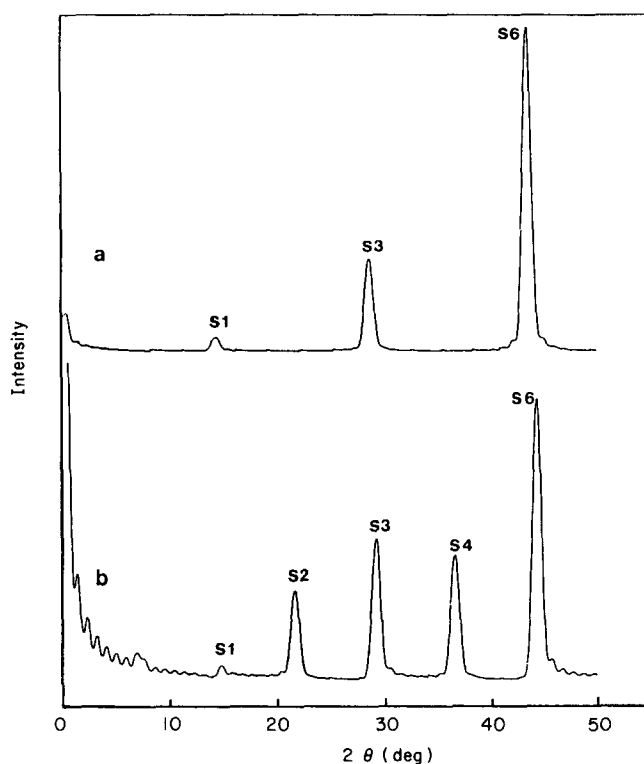[b] Resolved into two peaks
[c] Diffractometer data

Figure 6 Calculated meridional intensity profiles for models of the homopolymers: (a) poly(*p*-oxybenzoate) (100/0); (b) poly(*p*-phenylene isophthalate) (0/100)
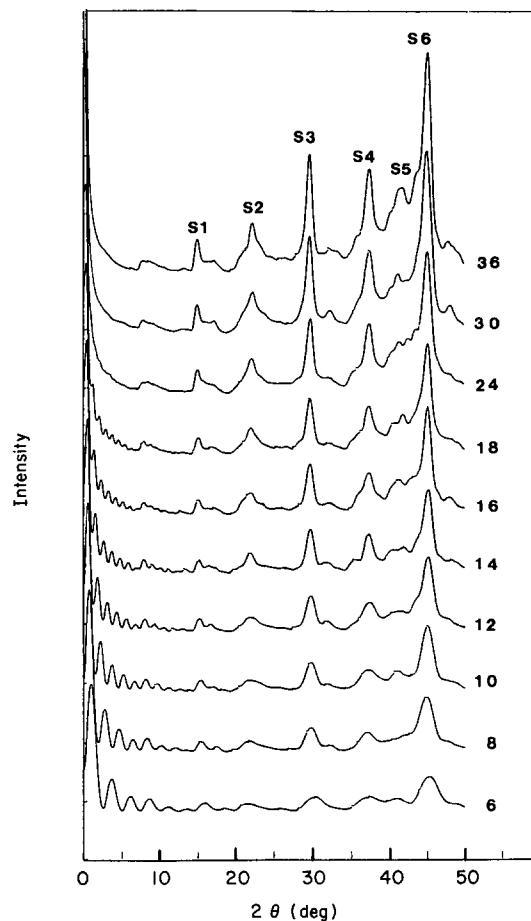
Table 3 Features of meridional intensity traces obtained from modelling: peak positions (*d*) and relative heights (*h*) with respect to the S3 peak. The chains contain 16 units

| | 100/0 | | 67/33 | | | | 50/50 | | | | 0/100 | |
| | cis | | cis-based | | trans | | cis-based | | trans | | trans | |
Peak	d (nm)	h	d (nm)	h	d (nm)	h	d (nm)	h	d (nm)	h	d (nm)	h
S1	0.624	0.2	0.576	0.7	0.614	0.1	0.585	0.4	0.613	0.1	0.614	0.1
S2	–	–	0.387	0.6	–	–	0.400	0.4	–	–	0.410	0.6
S3	0.312	1.0	0.299	1.0	0.309	1.0	0.300	1.0	0.307	1.0	0.307	1.0
S4	–	–	0.241	1.2	–	–	0.244	0.9	–	–	0.246	0.9
S5	–	–	0.213	1.4	0.216	1.1	0.216	1.1	0.218	1.1	–	–
S6	0.208	4.1	0.200	2.7	0.206	2.7	0.200	2.2	0.205	2.3	0.205	2.2
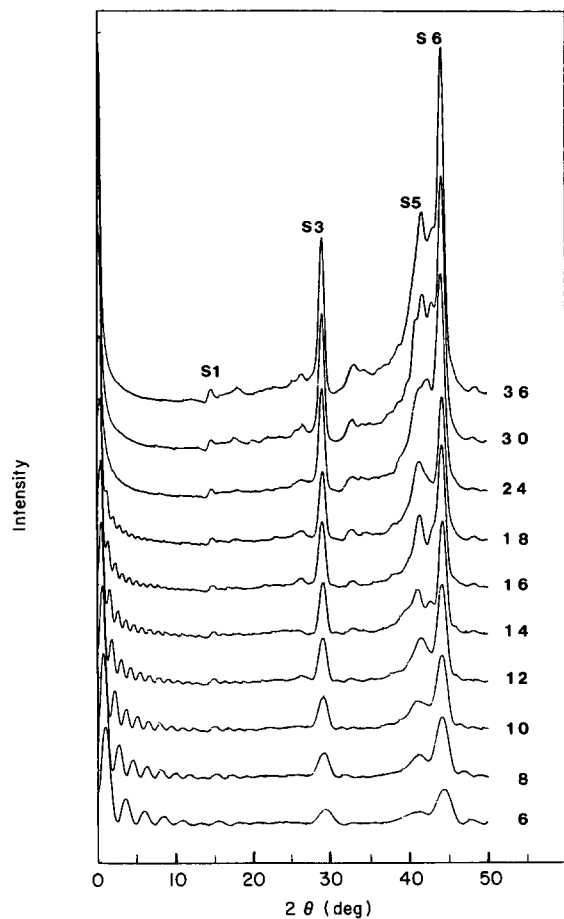
Figure 7 Calculated meridional intensity profiles for 'trans' models of the 50/50 composition. Number of units per chain is indicated on each curve

Figure 8 Calculated meridional intensity profiles for 'cis-based' models of the 50/50 composition. Number of units per chain is indicated on each curve

and their relative intensities expressed as relative heights with respect to the S3 peak with a *d*-spacing around 0.3 nm (*Table 3*).

The intensity profiles obtained for 'cis-based' and 'trans' models of the 50/50 chains containing between six and 36 units are shown in *Figures 7* and *8*, respectively. The profiles for the 'cis-based' model can be resolved into at least six peaks, while those for the 'trans' model can be resolved into at least four peaks (*Figure 9*); data obtained for models with the number of constituent units $n = 16$ are listed in *Table 3*. The effect of n on the peak position is very small, but the peak widths decrease with increasing n. This is analogous to the effect of crystal size (L) on the width of reflections arising from crystals. According to the Scherrer equation, the peak width is inversely propor-

tional to L. Similarly, we find that the widths (w) of the peaks increase linearly with $1/n$. However, the peak width for an infinite chain obtained by extrapolation ($1/n \rightarrow \infty$) is finite. This is shown in *Figure 10* for the peak S3 of the 'trans' model. In this case:

$$w = w_\infty + b/n \tag{2}$$

where $w_\infty = 0.20°$ and $b = 10.59°$.

The intensity profiles obtained for the models of the 67/33 chains (*Figure 11*) are similar to those for the 50/50 chains. The change in the copolymer composition has only a small effect on the peak positions and on their relative intensities (*Table 3*). The effect of chain length on the peak widths is similar to that found for the 50/50 copolymer (*Figure 10*).
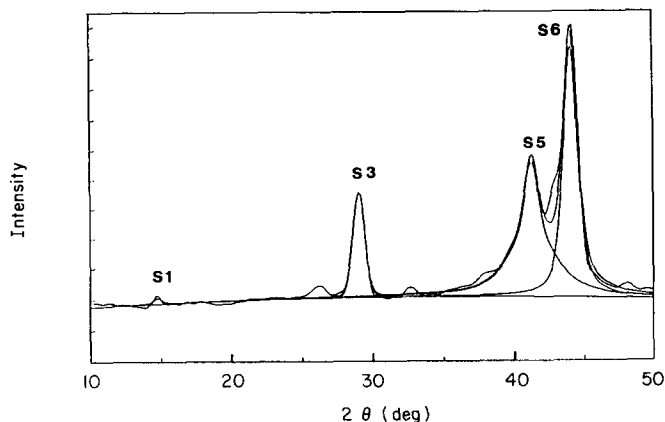
Figure 9 Resolution of calculated meridional intensity profile for *'trans'* model of the 50/50 composition with $n = 16$. Resolved peak parameters are listed in *Table 3*
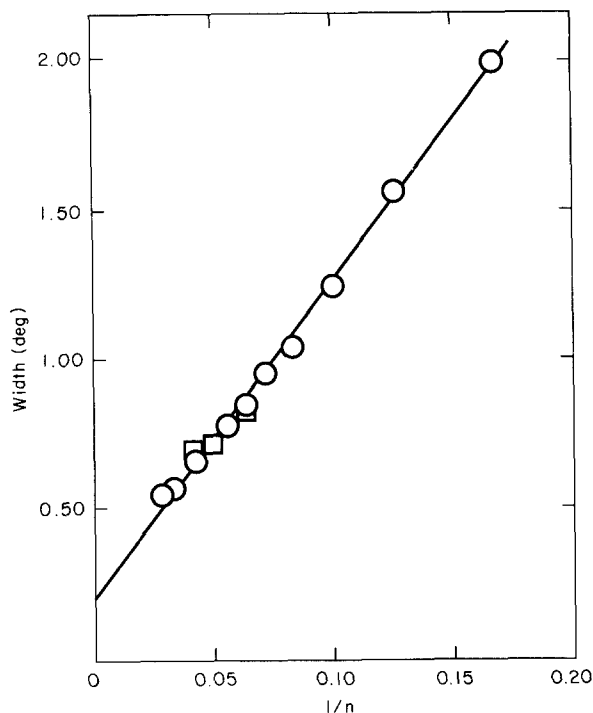

Figure 10 Effect of number of units per chain (n) on the width of the S3 peak obtained for *'trans'* model: (O) 50/50; (□) 67/33

Comparison of the observed features with modelling data

It should be emphasized that the sets of individual chains used in our modelling are only suitable for representation of a structure containing an array of parallel chains which do not form a three-dimensional crystal lattice. This condition is fulfilled for the 'as-made' 50/50 and 67/33 fibres. For the heat-treated fibres, which contain a paracrystalline matrix as well as crystalline regions, the modelling relates only to the matrix.

Comparison of the meridional intensity trace of the 50/50 'as-made' fibre (*Figure 5a*) with the modelling results shows that the *'cis*-based' models do not yield realistic intensity profiles (*Figure 8*). In contrast, the profiles generated using the *'trans'* models (*Figures 7* and *9*) reproduce very well the main observed features (see *Tables 2* and *3*):

(i) low-intensity peak S1 matches the weak reflection PM1;

(ii) peak S3 corresponds to the prominent reflection PM2;

(iii) peaks S5 and S6 correspond to the asymmetrical reflection PM3, which was resolved into two peaks.

The same conclusion is also reached for the 67/33 'as-made' fibres (see *Tables 2* and *3*).

The agreement between the observed features and those obtained using the *'trans'* models suggests that the more extended conformations (see *Figure 2*), facilitating better chain packing, are preferred in reality. However, deviations from planarity and the presence of a few *'cis'* conformations should not be ruled out. These additional refinements could not be considered in the modelling at this stage without making it excessively complex.

In spite of this reservation, we are confident that a realistic estimate of the chain correlation length can be obtained by comparing the observed peak widths with those resulting from the planar *'trans'* models with different numbers of constituent units. To this end, the meridional reflection PM2 and the peak S3 obtained by modelling are the obvious choice since the reflection PM1 is too weak and the reflection PM3 is asymmetrical. The width of the PM2 reflection for the 50/50 'as-made' fibre matches the S3 peak width for $n = 16$, which corresponds to the correlation length of approximately 10 nm. For the 67/33 'as-made' fibre we obtain $n = 19$, i.e. a correlation length around 12 nm.

As already stated, the meridional intensity traces of the heat-treated fibres show reflections due to the paracrystalline matrix together with additional reflections arising from the presence of type C crystallites. The parameters of
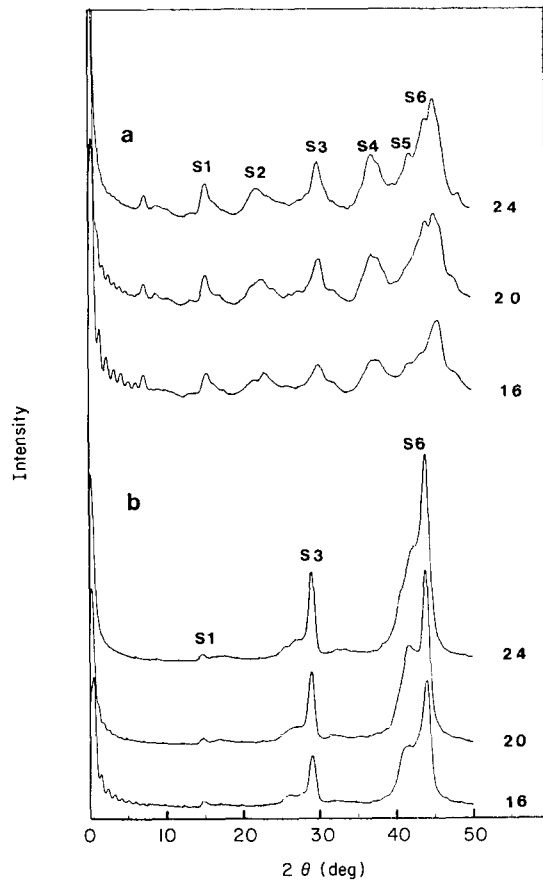

Figure 11 Calculated meridional intensity profiles for (a) *'cis*-based' and (b) *'trans'* models of the 67/33 composition

the resolved peaks assigned to the paracrystalline matrix are similar to those obtained for the corresponding 'as-made' fibres (*Table 2*). This is not surprising since the crystallinity of the heat-treated fibres is rather low, approximately 17% for the 50/50 fibre and even less, about 11%, for the 67/33 fibre[2]. Thus, the formation of the crystallites containing the p-phenylene isophthalate sequences results only in small changes of the average composition of the matrix. For the 50/50 copolymer ([OPCO] = [OPO] = [COMCO] = 0.333), the average concentrations of the constituent units will be [OPCO] = 0.40 and [OPO] = [COMCO] = 0.30, which corresponds to a 57/43 composition. Similarly, for the 67/33 copolymer the composition of the matrix after crystallization changes to 72/28. From the modelling results it is obvious that the effect of these changes in composition on the meridional traces will be very small.

With the correct identification of the meridional reflections arising from the type C crystallites, it is possible to estimate the mean apparent size of these crystallites in the chain direction (i.e. thickness). Using the integral breadths of the resolved peaks CM2 and CM3 of the 50/50 heat-treated fibres, we obtain values of 4.3 and 3.9 nm, respectively. This corresponds to only 6–7 constituent units, i.e. less than two repeating units of the extended-chain conformation of poly(p-phenylene isophthalate) shown in *Figure 2f*. For the 67/33 heat-treated fibre the CM2 peak is absent; the breadth of the CM3 peak indicates that the mean crystallite thickness is about 2 nm, i.e. less than the length of the poly(p-phenylene isophthalate) repeating unit.

In contrast, the analysis of the equatorial reflections indicated that the crystallites contain more than 200 laterally packed chains[2]. Such unusual crystallites can only be formed if their end surface free energy is very small, not only due to the obvious absence of the chain folding but due to the minimal steric interference, resulting from the similarity of the lateral chain packing densities in the crystal and in the paracrystalline matrix[2].

CONCLUSIONS

'As-made' poly(p-oxybenzoate-co-p-phenylene isophthalate) (50/50 and 67/33) fibres, which lack three-dimensional crystalline order, show meridional reflections due to a paracrystalline array of oriented chain molecules. One-dimensional Fourier transforms, generated from copolymer models consisting of 'trans' conformations of p-oxybenzoate and p-phenylene dioxy units and of extended conformations of isophthaloyl units, reproduce the main observed meridional diffraction features of these 'as-made' fibres. The chain correlation lengths, obtained by comparison of the peak widths of the prominent meridional reflection (d-spacing around 0.3 nm) with the modelling results, are 10 nm (i.e. 16 units) for the 50/50 fibres and 12 nm (i.e. 19 units) for the 67/33 fibres.

Heat-treated fibres (30 min at 280°C) consist of crystalline regions containing p-phenylene isophthalate sequences (type C structure) and of a paracrystalline matrix. Crystallization does not affect significantly the meridional scatter arising from the paracrystalline matrix. The additional meridional reflections are due to the type C crystallites. The thickness of these crystallites, which comprise 17% of the heat-treated 50/50 fibre, is around 4 nm. In the case of the 67/33 fibre, which has only 11% crystallinity, it is about 2 nm, i.e. smaller than the type C crystal repeating length. The width-to-thickness ratio of the crystallites is around 2:1 for the 50/50 fibre and 3:1 for the 67/33 fibre.

REFERENCES

1   Erdemir, A. B., Johnson, D. J. and Tomka, J. G. *Polymer* 1986, **27**, 441
2   Erdemir, A. B., Johnson, D. J., Karacan, I. and Tomka, J. G. *Polymer* 1988, **29**, 597
3   Blackwell, J. and Gutierrez, G. *Polymer* 1982, **23**, 671
4   Gutierrez, G. A., Blackwell, J. and Chivers, R. A. *Polymer* 1985, **26**, 348
5   Blackwell, J. and Biswas, A. Paper presented at 'Speciality Polymers '88 Conference', September 1988, Cambridge, UK
6   Blackwell, J., Cageo, R. A. and Biswas, A. *Macromolecules* 1987, **20**, 667
7   Davies, G. R. and Jakeways, R. *Polym. Commun.* 1985, **26**, 9
8   Hummel, J. P. and Flory, P. J. *Macromolecules* 1980, **13**, 479
9   Erman, B., Flory, P. J. and Hummel, J. P. *Macromolecues* 1980, **13**, 484
10 Blackwell, J., Leiser, G. and Gutierrez, G. A. *Macromolecules* 1983, **16**, 1418
11 Geiss, R., Volksen, W., Tsay, J. and Economy, J. *J. Polym. Sci., Polym. Lett. Edn.* 1984, **22**, 433
12 Hindeleh, A. M. and Johnson, D. J. *J. Phys. (D), Appl. Phys.* 1971, **4**, 259