Thermotropic polyesters: structure of oriented poly(*p*-oxybenzoate-*co*-*p*-phenylene isophthalate)s

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Previous work has shown that poly(*p*-oxybenzoate-*co*-*p*-phenylene isophthalate)s are nematogenic within the composition range 33/67 to 75/25. X-ray investigations of oriented fibres showed that, with respect to the physical structure, they differ from the corresponding unoriented materials. The main emphasis has been placed on structural characterization of fibres from 50/50 and 67/33 copolymers, which have a broad nematic temperature range. The fibres spun from the nematic mesophase were highly oriented but crystalline order was absent. Annealing at temperatures ranging from 240 to 300°C causes crystallization. The structure of annealed fibres can be regarded as a mosaic of thin crystalline regions containing *p*-phenylene isophthalate sequences, together with paracrystalline regions.

(Keywords: aromatic polyesters; thermotropic; nematic; liquid crystalline; crystal structure; high-performance fibres)

INTRODUCTION

There is now a considerable scientific and technological interest in nematogenic polymers[1]. Our previous work[2] showed that the semi-rigid poly(*p*-oxybenzoate-*co*-*p*-phenylene isophthalate)s, which consist of rod-like *p*-oxybenzoate (OPCO) and *p*-phenylene dioxy (OPO) units and of angular isophthaloyl (COMCO) units, are nematogenic provided that the molar fraction of OPCO and OPO rod-like units is in the range 0.60 to 0.80. Expressed in the conventional manner, i.e. in terms of the mole per cent ratios of *p*-oxybenzoate units (A) and *p*-phenylene isophthalate units (B), the nematogenic composition range extends from 33/67 to 75/25 (*Table 1*). However, only the fibres within a composition range from 50/50 to 67/33, which have a nematic temperature interval of at least 50°C, are considered suitable for successful melt processing.

The earlier X-ray diffraction investigations[2] of the whole range of homopolymers and copolymers indicated the presence of four different types of ordered structures depending upon the polymer composition and the thermal history; these are summarized in *Table 2*. The 100/0 homopolymer, poly(*p*-oxybenzoate), had an orthorhombic crystal structure designated as type A. The 0/100 homopolymer, poly(*p*-phenylene isophthalate), had a different crystal structure designated as type B. The 75/25 copolymer had a pseudohexagonal structure similar to the high-temperature modification of poly(*p*-oxybenzoate), which has been termed modified type A (Mod A). This type of structure was also found in the 67/33 and 50/50 copolymers, where it occurred in conjunction with another crystal structure designated as modified type B because of its similarity with the type B structure. The structure of the 67/33 copolymer was strongly influenced by the annealing conditions.

This paper is concerned with structural characterization of both 'as-made' and heat-treated fibres obtained from the nematogenic copolymers. The main emphasis is placed on fibres from 50/50 and 67/33 copolymers, which exhibit a nematic temperature interval sufficient for melt processing. Investigation of fibres obtained from copolymers at the extremes of the nematogenic composition range (i.e. 33/67 and 75/25) was carried out only to an extent required to enhance understanding of the 50/50 and 67/33 fibres. The physical properties of these fibres will be reported later.

EXPERIMENTAL

Polymer preparation and characterization

The polymers listed in *Table 1* were prepared, in the absence of catalyst, from equimolar amounts of isophthalic acid and hydroquinone diacetate mixed with the required amount of *p*-acetoxybenzoic acid, except for the 50/50 (E4) polymer, which had 4 mol% excess of hydroquinone diacetate in the initial reaction mixture in order to compensate for the loss of this monomer during the early stages of the reaction[2,3]. Their solution viscosities were measured in 30/70 (v/v) mixtures of trifluoroacetic acid and dichloromethane at 25°C (see ref. 2).

Fibre preparation

In order to establish the optimum melt spinning temperature, dried polymer granules were melted under nitrogen and the melt temperature was then gradually raised until fine, flexible, even and long (at least 0.5 m) fibres could be withdrawn from the melt using a fine stainless-steel hook. The 33/67 composition fibres were obtained by this procedure at 332°C. Fibres from 50/50 and 67/33 copolymers were melt spun at temperatures established by the procedure described above (*Table 1*)

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Table 1 Polymer composition and fibre formation conditions

Polymer composition			Spinning conditions			[η] (dl g^{-1})	
	Molar fraction						
A/B	[OPCO]	[OPO] [COMCO]	Procedure^a	Temp. (°C)	Drawdown	Polymer	Fibre
33/67	0.200	0.400	A	332	–	0.69	–
50/50	0.333	0.333	B	362	~80	0.90	0.80
50/50 (E4)	0.333	0.333	B	362	~80	0.85	0.78
67/33	0.500	0.250	B	405	~25	1.60	1.40
75/25	0.600	0.200	C	450	–	^{b}	–

^{a} Procedures: A, manual; B, rod-spinner; C, micro-spinner
^{b} Insoluble in trifluoroacetic acid/dichloromethane (30/70) mixture

Table 2 Principal structures present in unoriented 'as-made' polymers and in fibres

Composition A/B	Unoriented material	'As-made' fibre	Annealed fibre
0/100	B	–	–
33/67	B	C	C
50/50	Mod A+Mod B	Paracrystalline	C
67/33	Mod A+Mod B^a	Paracrystalline	C^b
75/25	Mod A	Imperfect A	Imperfect A
100/0	A	–	–

^{a} Annealing at 335°C yields Mod A structure only
^{b} Annealing at 335°C yields imperfect A structure

using a hydraulically operated rod-spinning machine with a maximum polymer capacity of approximately 0.07 kg. A spinneret with 10 holes, each of diameter 0.23 mm, has been employed; the length of the spinline was approximately 1.5 m and the winding speed was 250 m min^{-1}. The drawdown ratios given in *Table 1* were estimated from the polymer throughput per spinneret hole and from the winding speed.

Attempts to produce fibres from the 75/25 copolymer by the same method were unsuccessful due to the narrow temperature interval between the melting temperature and the onset of decomposition[2]. Fibres from this material were obtained by using a microspinner with a polymer capacity of approximately 0.5×10^{-3} kg. Polymer was extruded at 450°C through a single spinneret hole (diameter 0.230 mm). No winding device was used in this case; the extrudate was allowed to solidify under gravity.

Fibre heat treatment was carried out under nitrogen at atmospheric pressure in an electrically heated glass tube (diameter 30 mm, length 450 mm). Initially, both fibre ends were fixed to a wire frame to prevent shrinkage. It has been established that the heat treatment actually resulted in a small spontaneous elongation (approximately 1–2 %) and consequently further heat treatments were carried out with slack fibres. Further details of the fibre preparation procedures can be found elsewhere[3].

Fibre characterization

D.s.c. characterization of the fibres was carried out in the same manner as for the polymers[2].

Wide-angle X-ray diffraction patterns were taken with a flat-plate camera. For the diffraction patterns of tilted fibres, the fibres were tilted 20° from the position perpendicular to the X-ray beam.

Quantitative work was carried out on a Hilger and Watts Y115 diffractometer mounted on a Hilger and Watts Y90 constant-output generator utilizing Cu K_α radiation. The diffractometer has been modified for step motor drive and microprocessor control, with intensity data recorded on disc through a scintillation counter/pulse-height analyser system. Additional data are taken from a database. Each data set is transmitted to the University of Leeds Computing Service's Amdahl 5860 mainframe computer for analysis following methods detailed earlier[4]. The whole process has been written as one interactive program and is very simple and convenient to use. Correction and normalization are followed by peak resolution and evaluation of crystallite size. Interplanar spacings are calibrated by a silver foil reference in each specimen.

RESULTS AND DISCUSSION

Qualitative characterization of fibre structure

Wide-angle X-ray diffraction patterns of the 'as-made' fibres are shown in *Figure 1*; fibres melt spun from nematic mesophases of 50/50 and 67/33 copolymers using relatively high drawdown ratios (see *Table 1*) are shown to be well oriented (*Figures 1c* and *1e*), but with no detectable three-dimensional order. The diffuse equatorial scatter is the only feature in the X-ray diffraction patterns of the 'as-made' 50/50 and 67/33 fibres; their traces, presented in *Figures 2* and *3*, reveal a broad asymmetrical peak with an interplanar spacing (*d*-spacing) of approximately 0.44 nm. Despite the lack of meridional and off-equatorial reflections, the d.s.c. traces of the fibres showed broad endotherms between 240 and 320°C and 300 and 380°C, respectively. Hot-stage microscopy showed that these endotherms arise from transitions resulting in formation of nematic mesophases. Thus, there is an obvious discrepancy between the X-ray and d.s.c. evidence similar to that noted by Blundell[5] for other quenched nematogenic copolyesters. He suggested that this is due to the presence of microcrystals, which are too small to give a sharp X-ray diffraction pattern. An alternative explanation for the materials investigated here is to assign the broad endotherms to the melting of paracrystalline structures. This interpretation is supported by the analysis of resolved equatorial diffractometer traces and by chain packing considerations, which will be discussed later.

Annealing of the 50/50 and 50/50 (E4) fibres carried out for 30–120 min at temperatures ranging from 240 to

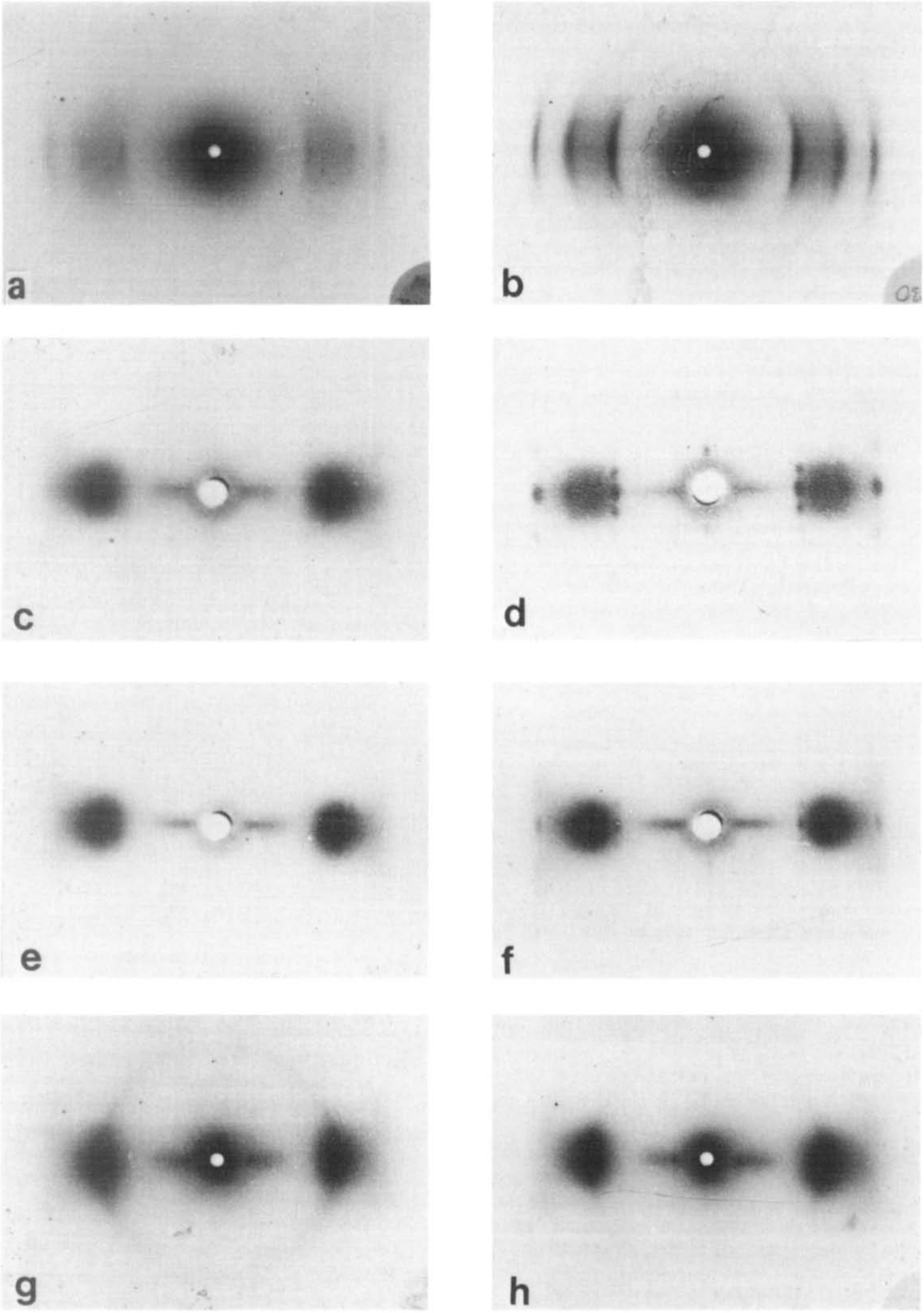

Figure 1 WAXS patterns of 'as-made' and heat-treated poly(*p*-oxybenzoate-*co*-*p*-phenylene isophthalate) fibres: (a) 33/67 'as-made'; (b) 33/67 260°/30 min; (c) 50/50 'as-made'; (d) 50/50 280°C/30 min; (e) 67/33 'as-made'; (f) 67/33 280°C/30 min; (g) 75/25 'as-made'; (h) 75/25 280°C/30 min. The fibre axis is vertical in each case

300°C caused crystallization. The X-ray diffraction pattern of the 50/50 fibre annealed for 30 min at 280°C is shown in *Figure 1d*. Increases in annealing temperature and annealing time resulted in enhancement of intensity of the crystalline reflections as well as in the appearance of some additional reflections. Nevertheless, the X-ray diffraction pattern obtained for the 50/50 (E4) fibre after 120 min annealing at 300°C still showed the diffuse equatorial scatter at 0.44 nm found in the 'as-made' fibre. Comparison of the *d*-spacings of the crystalline structure present in the heat-treated 50/50 fibres (see *Table 3*) with those assigned to structures present in the unoriented materials (see *Table 2*; for details see Table 3 in ref. 2) showed that the highly oriented heat-treated fibres

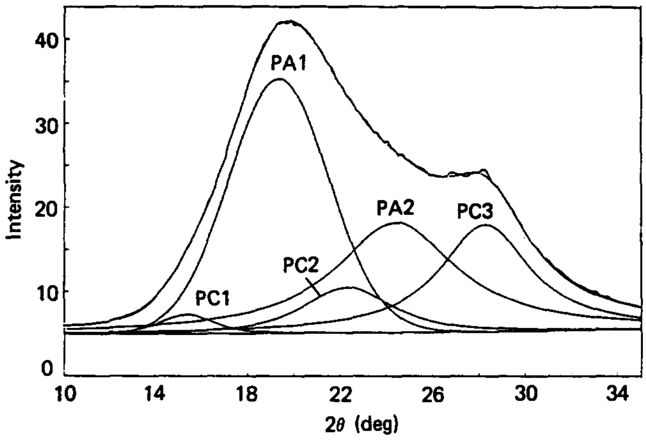

Figure 2 Resolved equatorial X-ray diffraction trace of the 50/50 'as-made' fibre: PA1, 0.458 nm; PA2, 0.364 nm; PC1, 0.577 nm; PC2, 0.398 nm; PC3, 0.316 nm

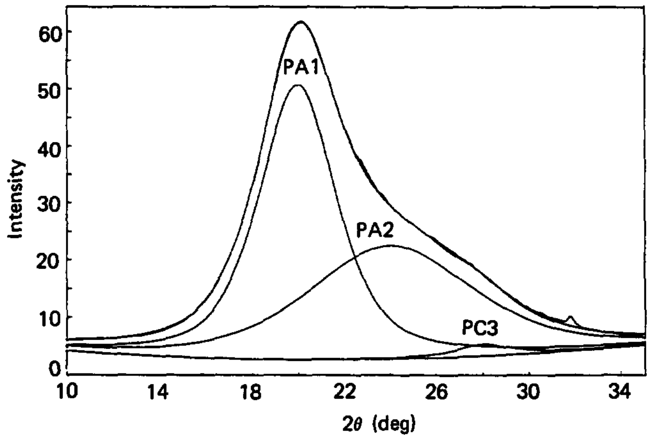

Figure 3 Resolved equatorial X-ray diffraction trace of the 67/33 'as-made' fibre: PA1, 0.444 nm; PA2, 0.371 nm; PC3, 0.322 nm

evidently contain a new type of structure, which will be referred to as type C.

Annealing of the 67/33 fibre carried out for 30 min at 280°C also resulted in the appearance of reflections assigned to the type C structure (*Figure 1f*). However, they are much weaker than those of the 50/50 annealed fibre and, indeed, some of the reflections were either absent or perhaps too weak to be detected under the conditions employed.

Inspection of the X-ray diffraction patterns of the 33/67 fibres (*Figures 1a* and *1b*) showed that the reflections assigned to the type C structure are already present in the 'as-made' fibre and that they are enhanced after annealing. The diffuse equatorial reflection at 0.44 nm is observed in both 'as-made' and annealed fibres.

However, at the other end of the nematogenic composition range, the structure of 75/25 fibres cannot be interpreted in terms of the type C structure. The fibres obtained by extrusion of a nematic mesophase and solidification of the extrudate without application of an external force are less well oriented than the 50/50 and 67/33 fibres (*Figure 1g*). The most prominent features of the X-ray pattern are an asymmetrical diffuse equatorial peak at 0.44 nm, two sharp meridional arcs ($d = 0.618$ and 0.308 nm) and a diffuse off-equatorial reflection ($d = 0.31$ nm) on the 1.2 nm layer line. Annealing for 30 min at 280°C did not result in the appearance of any additional reflections. However, a somewhat improved orientation is apparent from the azimuthal spread of the meridional reflections and of the broad equatorial reflection. Similar reflections were observed by Blackwell *et al.*[6] in 80/20 composition fibres from poly(*p*-oxybenzoate-*co*-ethylene terephthalate).

Our previous work showed that the unoriented 75/25 material has a structure with a pseudohexagonal packing of chains ($d \simeq 0.455$ nm) which are randomly displaced along the chain axis. We have designated this structure as modified type A. The off-equatorial reflection on the 1.2 nm layer line ($d \simeq 0.31$ nm) found in the fibres can be indexed as the (2 1 1) reflection of the orthorhombic structure[7] of poly(*p*-oxybenzoate) designated in the previous paper[2] as type A. Although the reflection is very broad, it offers sufficient evidence for a preferred axial register of adjacent chains[6]. Thus, the structure of both 'as-made' and annealed 75/25 fibres is best described as a highly imperfect type A. We suggest that the deformation associated with the fibre formation causes an axial displacement of the adjacent chains, which facilitates the formation of a more ordered structure with an axial chain register.

Having established the differences in the structural features of the 75/25 and 67/33 fibres annealed at 280°C, we wish to comment on the effect of annealing temperature on the structure of the 67/33 fibres. Our investigation of the unoriented 67/33 copolymer showed that the resulting structure was strongly influenced by the annealing temperature[2]. Whilst annealing at low temperatures (particularly at 250°C) enhanced the modified type B structure, annealing at high temperatures (particularly at 335°C) eliminated the type B structure but enhanced the pseudohexagonal modified type A structure (*Table 2*). In order to establish whether a corresponding effect of annealing temperature can be detected in the oriented 67/33 fibres, annealing treatments (60 min) have been carried out at both 250 and 335°C. Annealing at 250°C resulted in an increased number of reflections

Table 3 Type C structure: *d*-spacings (nm) observed in 50/50 (E4) fibre annealed for 120 min at 300°C, and calculated from an orthorhombic unit cell with $a = 1.116$ nm, $b = 0.784$ nm and $c = 2.432$ nm

				d-spacings (nm)	
Location	*h*	*k*	*l*	Obs.	Calc.
Equator	2	0	0	0.558	0.558
	0	2	0	0.392	0.392
	2	2	0	0.322	0.321
Meridian	0	0	2	1.215	1.216
	0	0	4	0.609	0.608
	0	0	6	0.408	0.405
	0	0	8	0.302	0.304
	0	0	10	0.242	0.243
	0	0	12	0.202	0.203
First layer line	2	0	1	0.543	0.544
	0	2	1	0.386	0.387
Second layer line	2	0	2	0.506	0.507
	2	2	2	0.310	0.312
Third layer line	2	2	3	0.299	0.298
Fourth layer line	2	0	4	0.409	0.411
	2	2	4	0.283	0.283
Fifth layer line	2	0	5	0.365	0.366
	0	2	5	0.303	0.305
	2	2	5	0.267	0.267

assigned to the type C structure compared with the annealing carried out for 30 min at 280°C. On the other hand annealing for 60 min at 335°C resulted in the appearance of the diffuse off-equatorial reflection as well as two meridional reflections with *d*-spacings of 0.617 and 0.306 nm; both these features are similar to those found in the annealed 75/25 fibre. It is clear that whilst the structures found in oriented 67/33 fibres differ from those in the unoriented material, the effect of annealing temperature is still significant. It is also worth noting that the high-temperature annealing of the 67/33 fibre caused a decrease in orientation.

The results of the investigation of 'as-made' and annealed fibres are summarized in *Table 2*. The X-ray patterns of the 50/50 and 67/33 'as-made' fibres do not reveal any evidence for the presence of three-dimensional order, whilst all the other fibres obviously contain some material with three-dimensional order. Structurally, the ordered regions in fibres differ from those found in the corresponding unoriented materials. The type C structure, already present in the 'as-made' 33/67 fibres, has been found in the annealed 33/67 and 50/50 fibres, as well as in 67/33 fibres annealed at lower temperatures (250 and 280°C). The 75/25 fibres did not show reflections assigned to the type C structure; the structure of the ordered regions in these fibres can be described as an imperfect type A structure of poly(*p*-oxybenzoate). High-temperature (335°C) annealing of the 67/33 fibre also resulted in the formation of this highly imperfect type A structure.

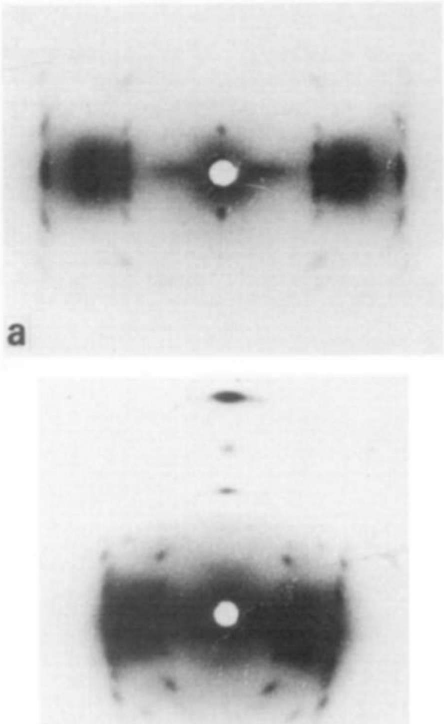

Figure 4 WAXS patterns of the 50/50 (E4) 'as-made' fibre heat-treated at 300°C for 120 min: (a) untilted; (b) tilted by 20° from the position perpendicular to the X-ray beam. The fibre axis is vertical

Type C structure

The qualitative discussion presented above showed that the type C structure is more prominent in the copolymers with a higher content of the angular isophthaloyl units. It is reasonable to suggest, therefore, that these units are incorporated in the type C structure.

Inspection of the X-ray diffraction pattern of the type C structure in the 50/50 (E4) fibre annealed at 300°C for 120 min (see *Figure 4*), together with the ratio of the main equatorial spacings (see *Table 3*), suggests an orthorhombic lattice with $a/b = 0.558/0.392$ and an area per chain of 0.219 nm^2. The spacings of the meridional and layer line reflections suggest a crystallographic repeat in the chain direction of $c = 2.43$ nm. This is slightly less than the value of 2.456 nm, which is the length calculated for the planar chain segment consisting of two *p*-phenylene isophthalate units as shown in *Figure 5*. In reality, such a planar conformation is ruled out due to steric interference. Whilst rotation of the *p*-phenylene ring eliminates the steric interference, it does not affect the length of the crystallographic repeat. On the other hand, rotation around the *m*-phenylene–CO bond, which is also required to avoid steric hindrance, results in a shortening of the crystallographic repeat. It has been estimated that a rotation angle of 25° would be consistent with the *c*-value obtained from the X-ray diffraction pattern.

Preliminary consideration of the *d*-spacings and of the chain packing suggest an orthorhombic unit cell with four molecular chains and parameters $a = 1.111$ nm, $b = 0.784$ nm and $c = 2.432$ nm, giving a density of 1.49 g cm^{-3}. The indexing and the calculated *d*-spacings based on this unit cell are given in *Table 3*. It has been noted that the annealing conditions affect the *d*-spacings of the type C structure slightly; such behaviour is by no means unusual (see e.g. refs. 7 and 8). Similarly, the copolymer composition also affects the *d*-spacings. Although more detailed investigations of the type C structure are proceeding, it is quite clear that this structure is unexpectedly similar to the structure of poly(*p*-oxybenzoate) referred to as type A. For example, the cross-sectional area per chain in the type C structure (0.219 nm^2) is very close to that for the type A structure (0.214–0.223 nm^2, see ref. 7), and the length of the crystallographic repeat in the chain direction for the type C structure (2.432 nm) is only slightly less than double the repeat for the type A structure (1.240–1.269 nm, see ref. 7).

Structure of the 50/50 and 67/33 fibres

As already stated, the X-ray diffraction patterns of the 50/50 and 67/33 'as-made' fibres do not indicate the

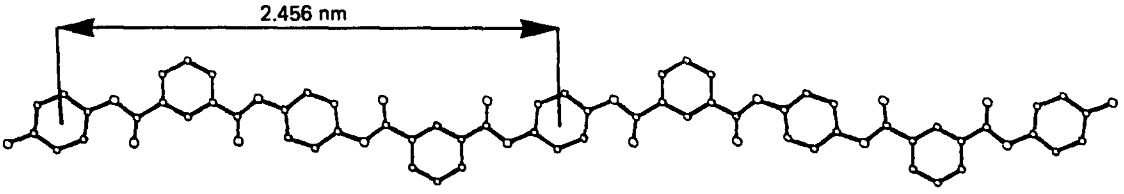

Figure 5 Fully extended planar chain conformation of poly(*p*-phenylene isophthalate)

presence of three-dimensional order. The observation that these fibres remain solid above the glass transition region (120–140°C) together with the d.s.c. evidence clearly rules out the possibility that the fibres at room temperature consist solely of a vitrified nematic mesophase.

In order to establish whether the diffuse equatorial scatter of the 50/50 and 67/33 'as-made' fibres is consistent with the presence of small crystallites of both type A and type C structures, attempts were made to resolve the envelopes (*Figures 2* and *3*) into the appropriate number of peaks based on the positions of the type A and type C dominant reflections (see *Table 4*). The envelope of *Figure 2* indicates that it should be resolvable into at least two peaks; indeed, a reasonable fit is obtained with a resolution based on the type A peak at 0.452 nm together with a smaller peak at 0.330 nm. A much improved fit was obtained by increasing the number of profiles to five so that this final resolution (*Figure 2*) gives two type A and three type C peaks with spacings listed in *Table 4*. A similar strategy was attempted with the envelope for the 67/33 'as-made' fibre (*Figure 3*); however, the best fit was found with a three-peak resolution consisting of two type A peaks and one small type C peak (see *Table 4*). A five-peak resolution gave unacceptable parameters.

It must be emphasized at this point that the results of profile resolution shown in *Figures 2* and *3* are not unique; it is always possible to put two peaks where one existed previously. Nevertheless, this work illustrates that the traces obtained can indeed be interpreted in terms of broad profiles positioned around the spacings expected for the type A and type C structures. The presence of these broad equatorial peaks and the absence of meridional or off-equatorial reflections rule out a description of the structures of 50/50 and 67/33 'as-made' fibres in terms of discrete type A and type C crystallites. It is our view that the best interpretation of the fibre is that of a paracrystalline array of chains aligned parallel to the fibre axis so that interchain distances approach locally those found in the type A and type C arrangements. This is feasible because of the similarity of the chain-packing densities in the two crystalline structures.

The paracrystalline structure of the 50/50 copolymer is illustrated by the line printer patterns of *Figure 6*. To produce the patterns, a set of 50 copolymer chains each consisting of 30 of the constituent units (OPCO, OPO or COMCO) in the appropriate ratios were generated by a computer program which excludes sequences ruled out by inappropriate chemical combination (see ref. 9). Part of such a sequence is shown in *Figure 7*. The character sequences were then transformed so that each unit was replaced by a set of three characters; this gives a realistic

Table 4 Positions of the peaks obtained by resolution of the equatorial traces of the 'as-made' fibres

	Corresponding reflection			*d*-spacing (nm)	
Peak	Type	*hkl*	*d* (nm)	50/50	67/33
PA1	A	110	0.454	0.458	0.444
PA2	A	200	0.376	0.364	0.371
PC1	C	200	0.558	0.577	–
PC2	C	020	0.392	0.398	–
PC3	C	220	0.321	0.316	0.322

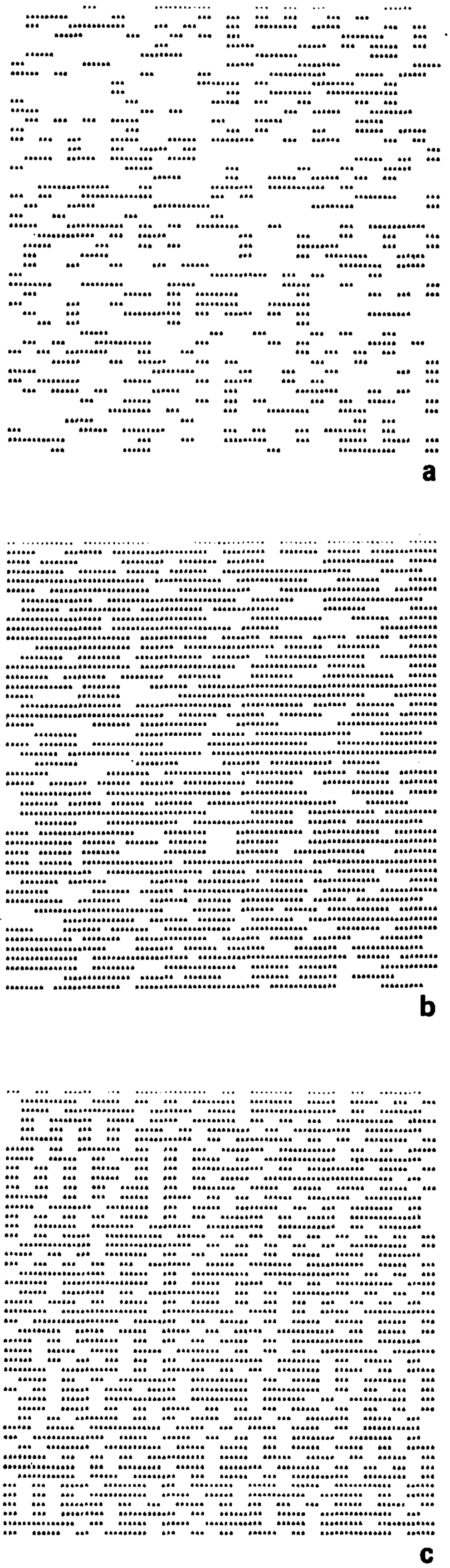

Figure 6 Transformed sequences of OPCO, OPO and COMCO units in 50/50 copolymer to show the probability of various structures. (a) Type A crystalline structure simulated by replacing OPCO with *** and OPO, COMCO with blanks. (b) Type C crystalline structure simulated by replacing COMCO and adjacent OPCO or OPO with ******; consecutive *p*-phenylene moieties are ** **. (c) Paracrystalline structure simulated by replacing both OPCO and OPO units by ***

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Figure 7 Section of computer simulated sequences of OPCO, OPO and COMCO units in 50/50 copolymer

relationship between each unit length and interchain distance on the printer. To simulate the feasibility of the formation of type A crystallites, OPCO units were replaced by three asterisks (***) and OPO and COMCO by blanks; *Figure 6a* is the result. No attempt was made to displace the chains in order to improve the lateral correlation of the OPCO units, but this is justified for the 'as-made' fibre formed by rapid cooling of oriented nematic mesophase. Although the pattern is an oversimplification of the real structure, it clearly illustrates that representation of the 50/50 copolymer in terms of type A crystallites is unrealistic. The pattern shown in *Figure 6b* simulates the feasibility of the formation of the type C structure; in this case COMCO and adjacent OPCO or OPO units were marked with three asterisks (***). The consecutive *p*-phenylene moieties were then replaced by two asterisks, two blanks and two more asterisks (** **) to indicate that a sequence of two units containing *p*-phenylene moieties interrupts the array of units required for the formation of the type C structure. The simulation indicates that, without displacing the domains, it is difficult to envisage the description of this structure in terms of discrete type C crystallites. Finally, *Figure 6c* shows a simulation where all the units containing *p*-phenylene moieties are marked by three asterisks (***).

Simulations show that there is no evidence of extensive areas of perfect order, and it is plausible to describe the 'as-made' 50/50 fibre as based on a paracrystalline array derived from the type A structure as simulated in *Figure 6c*. Accordingly, the two broad peaks PA1 and PA2 account for the majority of the equatorial scatter of this material. Similar simulations have been carried out for the 67/33 material, and, as expected, the patterns favour even more thoroughly the paracrystalline array based on the type A structure. Whilst the modelling illustrated here is relatively crude, it provides strong supporting evidence for the feasibility of the paracrystalline character of the 'as-made' fibres. It is hoped that it will help to overcome the scepticism encountered when such descriptions are proposed. More detailed modelling, which takes into account chain conformation, is now in progress.

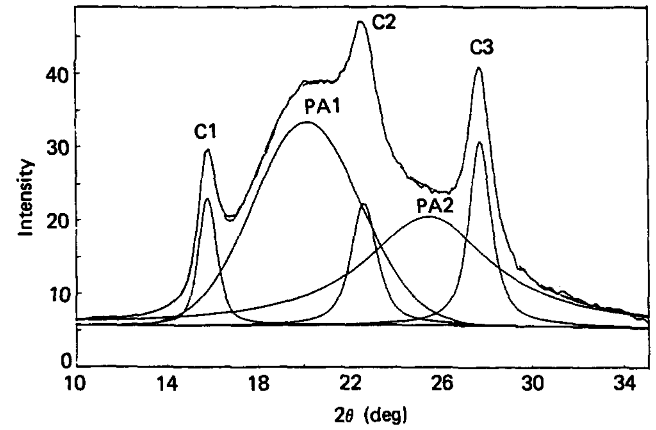

Figure 8 Resolved equatorial X-ray diffraction trace of the 50/50 fibre heat-treated at 280°C for 30 min: C1 (2 0 0), 0.559 nm; C2 (0 2 0), 0.392 nm; C3 (2 2 0), 0.322 nm; PA1, 0.448 nm; PA2, 0.355 nm

We now turn to the fibres that were subjected to a 30 min heat treatment at 280°C. As already stated, these fibres contain crystalline regions with the type C structure arising from the orthorhombic packing of *p*-phenylene isophthalate sequences. Following the strategy adopted for the 'as-made' fibres, the equatorial diffraction traces (*Figures 8* and *9*) were resolved into three sharp and two broad peaks. The sharp peaks were assigned to the crystalline type C structure and the broad peaks to the paracrystalline type A structure. The spacings for all these peaks are given in *Table 5*; there are slight differences in the *d*-spacings for the 50/50 and 67/33 fibres. The resolved sharp peaks C1, C2 and C3, arising from the type C structure, account for 17% of the equatorial scatter for the 50/50 fibre but only 11% for the 67/33 fibre (*Table 5*).

The apparent lateral dimensions of the type C crystallites, calculated from the widths of the resolved equatorial peaks, are also listed. The data indicate that the lateral dimensions of type C crystallites are surprisingly large; the crystallites appear to contain more than 200 laterally packed chains.

Inspection of the X-ray diffraction patterns shows that the equatorial reflections of the type C structure are short

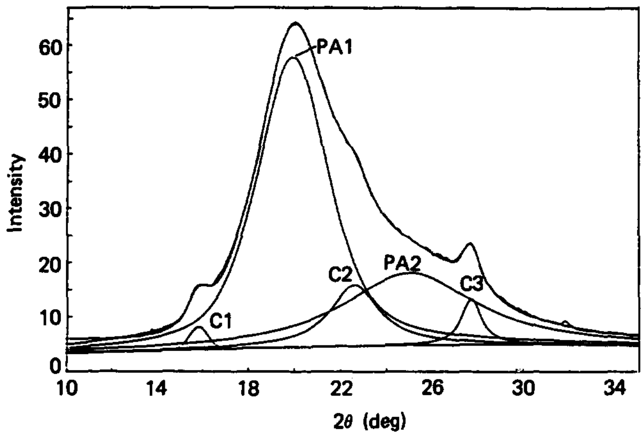

Figure 9 Resolved equatorial X-ray diffraction trace of the 67/33 fibre heat-treated at 280°C for 30 min: C1 (2 0 0), 0.560 nm; C2 (0 2 0), 0.393 nm; C3 (2 2 0), 0.322 nm; PA1, 0.445 nm; PA2, 0.356 nm

vertical streaks rather than the arcs normally found in the fibre diagrams. Consequently, no attempt has been made to obtain the orientational parameters. The equatorial diffraction patterns suggest that the crystallites are highly oriented along the fibre axis, and also that the correlation length in the chain direction is very short.

In order to obtain additional information about crystallite thickness, we have begun an investigation of the meridional diffraction patterns; this is a complex subject and will be the subject of a future paper.

In spite of the lack of exact data about the thickness of the type C crystallites, it is clear that these crystallites are formed by the molecules packed in register with very high orientation, and that they are surrounded by regions where the same molecules pack in a paracrystalline manner. The formation of such a structure is most unusual; it is only possible because of a similarity between the chain cross-sectional areas in the type C structure (0.219 nm^2) and in the type A structure (0.223 nm^2).

CONCLUSIONS

The results of this investigation, in conjunction with those published earlier[2], showed that the physical structure of poly(*p*-oxybenzoate-*co*-*p*-phenylene isophthalate)s is strongly influenced by the conditions of its formation as well as by the composition of the copolymer.

As expected, fibres from nematogenic copolymers are well oriented, but their structure differs from that found in the corresponding unoriented 'as-made' materials (see *Table 2*). A new type of structure, designated as type C, has been found in both 'as-made' and annealed 33/67 fibres, and in annealed 50/50 and 67/33 fibres. There is good evidence that the type C structure arises from regular packing of the *p*-phenylene isophthalate sequences.

Table 5 Resolved peak parameters for fibres heat-treated at 280°C for 30 min

Peak	Fibre	*d*-spacing (nm)	Half peak width, 2θ (deg)	Apparent size (nm)	Area (%)
C1	50/50	0.559	0.95	8.0	3.7
	67/33	0.560	0.96	9.0	0.6
C2	50/50	0.392	1.32	5.8	6.1
	67/33	0.393	2.53	3.6	8.0
C3	50/50	0.322	1.17	6.5	7.5
	67/33	0.322	1.05	6.8	2.3
PA1	50/50	0.448	5.50	–	31.7
	67/33	0.445	3.68	–	47.2
PA2	50/50	0.355	6.67	–	24.5
	67/33	0.356	6.82	–	21.6

Annealing temperature affects the type of structure found in the 67/33 copolymer in both unoriented and oriented states. The lower annealing temperatures (250–280°C) favour the formation of structures found in corresponding 50/50 materials, whilst annealing at 335°C favours the formation of structures found in 75/25 materials.

A more detailed investigation has been carried out on fibres produced from 50/50 and 67/33 copolymers, which have been identified as potentially useful materials with a sufficiently broad nematogenic temperature range. The 'as-made' fibres were highly oriented with paracrystalline packing of chains. Annealing for 30 min at 280°C resulted in formation of thin highly oriented type C crystallites. The chains emerging from the crystallites are packed in a paracrystalline array similar to that present in the 'as-made' fibres.

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