

Thermotropic polyesters: Synthesis, structure and thermal transitions of poly(*p*-oxybenzoate-co-*p*-phenylene isophthalate)

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A range of wholly aromatic polyesters has been prepared from *p*-acetoxybenzoic acid, hydroquinone diacetate, and isophthalic acid, by a modified melt acidolysis. X-ray diffraction indicated the presence of four different types of ordered structure dependent upon composition and thermal history. The 100/0 homopolymer poly(*p*-oxybenzoate) has a structure described as type A, and the 0/100 homopolymer poly(*p*-phenylene isophthalate) a structure described as type B. The 75/25 copolymer has pseudo-hexagonal order termed modified type A, which persists in the 67/33 and 50/50 copolymers. These latter two copolymers also contain a modified type B structure. Copolymers within the composition range 67/33 to 50/50 exhibit a nematogenic temperature range of at least 50°C; consequently, these materials may be regarded as potentially useful thermotropic copolymers based on readily available monomers.

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

INTRODUCTION

Polymers which can form a thermally stable nematic mesophase, the thermotropic nematics, have recently received considerable attention because of their potential applications as high performance fibres and plastics^{1,2}. Our specific interest in poly(*p*-oxybenzoate-co-*p*-phenylene isophthalate)s originated from the finding by Milburn that, within a certain composition range, they belong to this class of polymers. The features of chemical structure which are necessary to obtain thermotropic nematics are now reasonably well understood^{1,2}. In particular, the polymer chain must contain rigid rod-like sequences of sufficient length to diameter ratio. Such rigid nematogenic sequences usually consist of bifunctional arylene groups with outgoing bonds that are either collinear, or parallel and oppositely directed. The arylene groups are joined by linking groups that, at least in their preferred conformation, also have outgoing bonds that are essentially parallel and oppositely directed.

Aromatic polyesters undoubtedly represent the most important class of thermotropic nematics¹⁻⁵. Fully aromatic rod-like homopolymers such as poly(*p*-oxybenzoate) or poly(*p*-phenylene terephthalate) melt at temperatures which are too high to form a stable nematic mesophase⁴. However, if the regular chemical structure of a homopolymer is disrupted, the melting temperature is reduced and it is possible to obtain thermotropic nematics¹⁻⁵. The methods employed for reducing the melting temperature can be classified as follows:

- 1 randomization of the ester group direction;

- 2 use of rod-like arylene moieties of different lengths and/or shapes (e.g. *p*-phenylene in conjunction with *p,p'*-biphenylene or with 2,6-naphthylene);
- 3 use of rod-like arylene moieties unsymmetrically substituted with groups such as chloro-, bromo- or methyl;
- 4 use of angular units such as *m*-phenylene;
- 5 incorporation of flexible spacers.

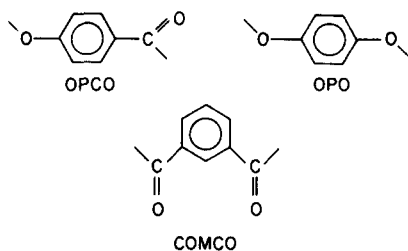
While the modifications 1-3 do not interfere with the rod-like character of the molecule, the modifications 4 and 5 lead to reduced chain rigidity. The nematogenic character of the polymer is maintained only if the mean length of the rod-like sequences exceeds certain limiting values^{1,2}. It should be noted that ordered alternation of rod-like sequences and flexible spacers of a sufficient length leads to thermotropic smectics^{1,2}.

The poly(*p*-oxybenzoate-co-*p*-phenylene isophthalate) specimens were prepared from *p*-acetoxybenzoic acid mixed with isophthalic acid and with a quantity of hydroquinone diacetate equimolar to the isophthalic acid. Thus, the materials are derived from poly(*p*-oxybenzoate) by employing modifications 1 and 4 above. The main objective of the work presented here was to establish the nematogenic composition range. We were also interested in the effect of the composition on the physical structure of the ordered regions in the solid copolymers.

Conventionally, the composition of copolymers is expressed in mole% of the repeating units of the homopolymers, i.e. *p*-oxybenzoate units (A), and *p*-phenylene isophthalate units (B), (B = 100 - A). However, the integrity of B-units is not necessarily maintained in copolymers. It is therefore more appropriate to regard a copolymer chain as a sequence of *p*-oxybenzoate units

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(OPCO), *p*-phenylenedioxy units (OPO) and isophthaloyl units (COMCO).



The abbreviated notation is that introduced by McIntyre and Milburn⁶.

The molar fractions of these units are related to the mole% of A-units as follows:

$$[\text{OPCO}] = A/(200 - A)$$

$$[\text{OPO}] = [\text{COMCO}] = (100 - A)/(200 - A)$$

The molar fraction of *p*-linked rod-like units is therefore

$$x_p = 100/(200 - A)$$

These rod-like units form rod-like sequences terminated by angular COMCO units; the mean number of joined rod-like units is

$$n_p = x_p/(1 - x_p) = 100/(100 - A)$$

This parameter is related to the mean aspect ratio of the rod-like sequences and consequently it determines the nematogenic propensity of the polymer.

In this investigation, a number of copolymers have been prepared with different A/B ratios and hence different lengths of rod-like sequences (Table 1). Quenching and annealing after-treatments were also carried out and the thermal and structural characteristics of the materials determined.

EXPERIMENTAL

Materials

p-Acetoxybenzoic acid (m.p. 187°C) was prepared by reacting *p*-hydroxybenzoic acid (laboratory reagent from BDH) with acetic anhydride at 60°C in the presence of sulphuric acid catalyst; the product was recrystallized from ethanol-water mixture and dried under vacuum at 60°C for 24 h.

Hydroquinone diacetate (m.p. 124°C) was prepared in a similar manner from hydroquinone (laboratory reagent from BDH); the product was recrystallized twice from ethanol and dried under vacuum as above. Isophthalic acid (laboratory reagent from Aldrich Chemical Co.), glacial acetic acid (analytical reagent from BDH), trifluoroacetic acid, and dichloromethane (both laboratory reagents from BDH), were used as received without any further purification.

Polymer preparation

Polymers 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. Initially, the small-scale melt polymerization was carried out at 282°C, as described by McIntyre and Milburn⁶. However, this procedure

Table 1 Material composition, intrinsic viscosity $[\eta]$ and time interval t_s between dissolution of isophthalic acid and onset of shear opalescence

Composition A/B	x_p	$[\eta]$ (dl/g)	t_s (min)
0/100	0.50	<i>a</i>	—
33/67	0.60	0.69	70
40/40	0.63	0.75	65
43/57	0.64	0.52	55
50/50	0.67	0.69	40
55/45	0.69	0.75	23
60/40	0.71	1.31	6
67/33	0.75	1.54	4
75/25	0.80	<i>a</i>	3
80/20	0.83	<i>a</i>	3
85/15	0.87	<i>a</i>	2
100/0	1.00	<i>a</i>	2

^a Insoluble in trifluoroacetic acid/dichloromethane (30/70) mixture

resulted in an uncontrollable loss of hydroquinone diacetate. Limited solubility of isophthalic acid in the reaction mixture was also a cause for concern. After the exploration of different polymerization procedures⁷, the following method was selected for the preparation of the polymers listed in Table 1.

Monomers (0.4 mole in total) and acetic acid (76 ml) were charged into a glass polymerization tube (diameter 43 mm) fitted with a stainless steel helical stirrer, nitrogen inlet, vacuum outlet, and a tube connected via a condenser to a condensate collector. The reactor was placed in a silicone oil bath and purged with nitrogen while stirring the slurry at 50 rpm. After the fifth purge, the oil-bath temperature was increased to 305°C in 20 min. At the end of the heating stage the isophthalic acid dissolved; this was accompanied by a vigorous foaming. The homogeneous reaction mixture was then maintained at 305°C under nitrogen flow for 45 min. At this point, most of the acetic acid (both the excess incorporated into the reaction mixture and the reaction byproduct) had been collected. The next stage was carried out under vacuum for a further 65 min. During this period, the pressure decreased from around 1.5 mm Hg to less than 0.05 mm Hg. The shear opalescence observed at 305°C for the polymers with the molar fraction $x_p \geq 0.6$ (composition range from 33/67 to 100/0) revealed their thermotropic character. The time of onset of this shear opalescence was strongly influenced by the composition of the polymer (Table 1). Ultimately, all materials turned into opaque solids at 305°C. The polymers were ground and dried under vacuum (0.5 mm Hg) at 100°C for 16 h.

In the course of the optimization experiments carried out with the 67/33 composition, it was established that a relatively rapid heating of the reaction mixture from ambient temperature up to 305°C was essential. Slow heating (approximately 3°C min⁻¹) resulted in the precipitation of a prepolymer consisting mainly of *p*-linked moieties, prior to dissolution of the isophthalic acid. It was suspected that the copolymers obtained under these conditions may not be random. The standard polymer preparation procedure ensured that this precipitation did not occur.

Polymer characterization

Solution viscosities of polymers were measured in a 30/70 (v/v) mixture of trifluoroacetic acid and dichloromethane at 25°C. The sum of the Huggins and Kreamer constants for the 67/33 copolymer was approximately 0.5. The intrinsic viscosities were therefore

calculated from single point measurements⁸ obtained at 0.25 g/dl concentration. X-ray diffraction patterns were recorded in a flat-plate camera using nickel-filtered CuK_α radiation.

Thermal stabilities were assessed by thermogravimetric analysis (DuPont 990/951 TGA) carried out under nitrogen (50 ml min^{-1}) at a heating rate of $20^\circ\text{C min}^{-1}$. The temperature at which 5% weight loss had occurred was taken as the thermal stability limit.

Transition temperatures were determined using a DuPont 990/910 Differential Scanning Calorimeter at a heating rate of $50^\circ\text{C min}^{-1}$ (sample weight 1.5 mg). The assignment of the transitions was confirmed using a Reichert Thermovar hot-stage polarizing microscope, and by observing the behaviour of polymers protected by glass cover slips on a preheated hot plate.

Quenching and annealing after-treatments

The quenched specimens were prepared as follows: the 'as-made' polymers were wrapped in aluminium foil and the trapped air was replaced by nitrogen by means of repeated evacuation. The sandwich was then placed on a preheated hot plate, then, after 30 s, it was transferred rapidly to a cold aluminium plate. The annealing of powdered polymers was carried out under nitrogen in glass tubes.

RESULTS AND DISCUSSION

Structure of the 'as-made' polymers

All the polymers listed in Table 1 solidified at 305°C in the course of their preparation; wide-angle X-ray diffraction (WAXD) patterns revealed the presence of ordered crystal structures in each case, although the highest degree of order was found in the homopolymers. A selection of the powder patterns is given as Figure 1.

The X-ray diffraction pattern of poly(*p*-oxybenzoate), Figure 1a, was similar to that obtained by Economy *et al.*⁹. In a recent investigation, Lieser¹⁰ examined poly(*p*-oxybenzoate) and its oligomers by both X-ray and electron diffraction; evidence of polymorphism was found and it was assumed that this was a result of different conditions of crystal formation. The most common crystal form is orthorhombic ($a=0.752 \text{ nm}$, $b=0.570 \text{ nm}$, $c=1.249 \text{ nm}$) with two chains in a 2_1 helical conformation; the interplanar spacings found in this investigation are in good agreement with those calculated for this crystal form (Table 2). We shall refer to this orthorhombic structure as 'type A'.

Copolymerization results in a disruption of the type A structure (see Figure 1b and Table 3). Although the *p*-linked OPO units can be accommodated relatively easily in the type A unit cell, this cannot apply to the angular COMCO units. The X-ray powder pattern of the 75/25 copolymer (where the molar fraction of the COMCO units is 0.2) (see Figure 1c) showed only one ring with a *d*-spacing of 0.455 nm. This indicates the presence of the same lateral chain packing as in the high-temperature modification of poly(*p*-oxybenzoate)^{9,10}, which has been described as either pseudohexagonal ($a=b=0.53 \text{ nm}$) or orthorhombic ($a=0.92 \text{ nm}$, $b=0.53 \text{ nm}$, $c=1.24 \text{ nm}$). Blackwell *et al.*¹¹ found a similar disruption of the poly(*p*-oxybenzoate) structure in poly(*p*-oxybenzoate-co-ethylene terephthalate)s. The absence of reflections due to order in the chain direction indicates that the structure existing in an unoriented 75/25 copolymer is best described as

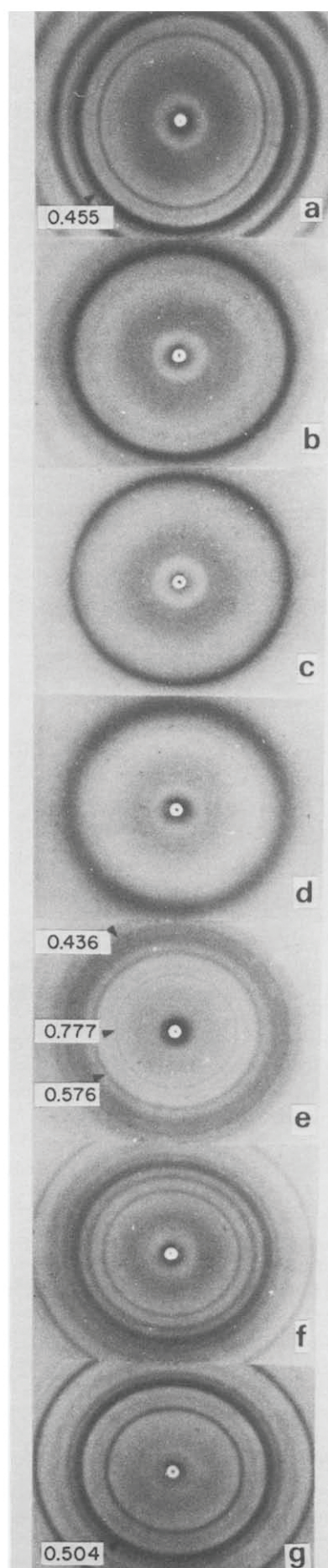


Figure 1 X-ray diffraction patterns of 'as-made' polymers: (a) 100/0; (b) 85/15; (c) 75/25; (d) 67/33; (e) 50/50; (f) 33/67; (g) 0/100

Table 2 X-ray reflections in poly(*p*-oxybenzoate)^a

<i>hkl</i>	002	010	011	110	111	200	013	004/210	211
d_{calc} (nm)	0.625	0.570	0.519	0.454	0.427	0.376	0.336	0.312/0.314	0.305
d_{obs} (nm)	0.620	0.569	0.521	0.455	0.424	0.382	—	0.312	—
Relative intensity	vw	m	vw	vs	w	s	—	m	—
Width	S	S	S	S	S	B	—	B	—

Key: vs, very strong; s, strong; m, medium; w, weak; vw, very weak; S, sharp; B, broad

^a Assignment and calculated d -spacings for the orthorhombic structure according to Lieser¹⁰

Table 3 Interplanar spacings, relative intensities, and widths, of X-ray reflections for 'as made' materials

Composition A/B	100/0	85/15	75/25	67/33	50/50	33/67	0/100
Molar fraction x_p	1.00	0.83	0.80	0.75	0.67	0.60	0.50
Structure type	A	A	Mod. A	Mod. A Mod. B	Mod. A Mod. B	B	B
Spacing (nm)							
0.777					mS		
0.688					wS	mS	sS
0.620	vwS						
0.607						vwS	vwS
0.576				vwS	vsS ^a	mS	vwS
0.569	mS	wB					
0.521	vwS						
0.504					mB	sS	vsS
0.482					mB	mS	sS
0.455	vsS	vsS	sS	sB	mH	wH	
0.453						wS	mS
0.436					sS		
0.424	wS						
0.402					mB ^a	mB	vwB
0.382	sB	wB					
0.352					vwS	mS	sS
0.331				vwS	vwS ^a	vwS	vwS
0.314				vwS	vwS	vwB	vwB
0.312	mB	wB					
0.293					vwS	vwB	vwB
0.274					vwS		

Key: vs, very strong; s, strong; m, medium; w, weak; vw, very weak; S, sharp; B, broad; H, halo

^a Found in quenched material

pseudohexagonal. We will refer to this pseudohexagonal structure as 'modified type A'.

With a further increase in the concentration of disrupting COMCO units, the 0.455 nm reflection broadens further and decreases in intensity (see *Figures 1d* and *1e*). In the powder diagram of the 33/67 copolymer (where the molar fraction of the disruptive COMCO units is 0.4) (see *Figure 1f*) this reflection is present only as a weak halo.

The X-ray diffraction pattern of poly(*p*-phenylene isophthalate) (see *Figure 1g*) showed that, as expected, it has a structure which differs substantially from that of poly(*p*-oxybenzoate); see *Table 3*. This structure will be referred to as 'type B'. As yet there has been no attempt to determine the unit cell parameters of the type B structure.

Careful inspection of the X-ray powder diagrams of the 33/67, 50/50 and 67/33 copolyesters (shown in *Figures 1f, e* and *d*) shows that the incorporation of OPO units in the poly(*p*-phenylene isophthalate) chain results in changes other than a mere decrease in the perfection of the type B structure. These changes seem to reach a maximum in the 50/50 copolymer which contains equimolar quantities of OPO, COMCO and OPO units. Although some reflections that are found in the powder diagram of the 0/100 homopolymer (shown in *Figure 1g*) are indeed less intense or missing in the powder diagram of the 50/50

copolymer (shown in *Figure 1e*) there are also reflections which are either stronger or sharper or both stronger and sharper. In addition there are two new reflections at spacings of 0.777 nm and 0.436 nm which were not found in either of the homopolymer patterns. This indicates the existence of another type of structure, which is rather similar to the type B structure; this will be referred to as 'modified type B'. Although this modified type B structure is most easily detected in the 50/50 copolymer, it also appears to be present, together with the modified type A structure, in the 67/33 copolymer.

To summarize, four different types of structure were identified in the 'as made' polymers. Two structures, types A and B, arise from the crystallization of the two homopolymers. The other two structures, modified type A and modified type B, are found in copolymers where they may co-exist.

Transition temperatures in the 'as made' polymers

The objective of the next stage of the investigation was to establish the range of composition within which the materials are capable of forming a thermally stable nematic mesophase. T.g.a. measurements showed that the thermal stability limit was approximately 450°C irrespective of the polymer composition. The transition temperatures obtained from d.s.c. thermograms, and

confirmed by both hot-stage light microscopy and direct observation on a pre-heated hot plate, are given in Table 4. Polymers within the composition range 0/100 to 43/57 exhibit only the crystal–isotropic melt transition, while polymers with a higher content of *p*-linked rod-like units form a nematic mesophase. However, for the composition range from 80/20 to 100/0, the crystal–nematic mesophase transition takes place at temperatures exceeding the thermal stability limit.

Melting temperatures, i.e. crystal–nematic or crystal–isotropic melt transitions, of all the materials, were higher than the final temperature employed during the polymer preparation. As a consequence, all the copolymers were annealed to a certain extent during their preparation. However, the supercooling as well as the effective duration of the annealing varied with material composition. Owing to these incidental differences in thermal histories, a direct comparison of the transition temperatures of the ‘as made’ materials is not justified.

Examination of quenched polymers

In order to minimize the effect of any annealing that took place in the course of polymer preparation, the ‘as made’ polymers (composition range from 0/100 to 75/25) were heated to 460°C for 30 s and then cooled rapidly to ambient temperature.

In the case of poly(*p*-phenylene isophthalate) this treatment yields a transparent material with an X-ray powder diagram typical of a non-crystalline polymer. The thermogram showed a crystallization exotherm (peak temperature 170°C) followed by a melting endotherm (peak temperature 370°C). Hot-stage light microscopy confirmed that the resulting melt is isotropic; evidently, this material exhibits behaviour typical of crystallizable flexible chain polymers such as poly(ethylene terephthalate).

All the quenched copolymers were opaque solids; their thermograms showed a stepwise increase of heat capacity in the region 120–140°C, a feature which can be ascribed to the existence of a glass transition. It must be noted that the glass transition temperature is not affected significantly by the copolymer composition. None of the copolymers showed a distinct crystallization exotherm, but a broad melting exotherm was observed in all cases. The peak temperatures of these melting endotherms were generally lower compared with those found for the ‘as

made’ copolymers (Table 4). The most substantial decrease, approximately 40°C, was found for the 50/50 and 60/40 copolymers, while for the other copolymers the quenching had a much less significant effect. The isotropization temperature of the 50/50 copolymer was not affected by the remelting/quenching treatment.

As already stated, the ‘as made’ copolymers within the composition range from 33/67 to 43/57 exhibited only a crystal–isotropic melt transition. Although after the remelting/quenching treatment it was still impossible to detect a separate isotropization endotherm, hot-stage light microscopy indicated that there is in fact a narrow temperature range within which the nematic mesophase exists. This is in agreement with the observation of shear opalescence at 305°C in the course of preparation of these copolymers. Obviously, the isotropization temperature is lower than the melting temperature of annealed copolymers. However, when the melting temperature is reduced by the quenching treatment, the isotropization temperature becomes higher than the melting temperature. Although this behaviour is interesting, the narrowness of the nematogenic temperature range rules out utilization of these materials as thermotropic nematics.

The usefulness of the 75/25 composition is impeded by the closeness of the crystal–nematic mesophase transition temperature to the thermal stability limit. The quenching treatment did not result in a significant broadening of the temperature interval within which the nematic mesophase is thermally stable (see Table 4).

It is clear that copolymers within the composition range from 50/50 to 67/33 exhibit sufficiently broad nematogenic temperature regions. For this reason, the materials at the extremes of this composition range were chosen for further investigation.

50/50 copolymer

In the 50/50 copolymer the molar fraction of *p*-linked rod-like units was $x_p = 0.67$. Consequently, the mean number of linked rod-like units was $n_p = 2$. This conferred sufficient rigidity on the chains for the formation of a nematic mesophase with an isotropization temperature of 410°C. At the same time, the chemical structure of this copolymer was sufficiently regular to allow crystallization.

It has been shown that the modified type B crystal structure existing in the ‘as-made’ material differs from both the type A and type B structures found in the 100/0, 0/100 homopolymers. The X-ray investigation of remelted/quenched specimens revealed that this treatment did not prevent the development of crystalline order, i.e. it has not been possible to obtain a non-crystalline 50/50 copolymer consisting of a frozen nematic mesophase. This occurred irrespective of whether the remelting temperature was above the isotropization temperature (*viz.* 415 and 460°C) or below it (*viz.* 330, 350 and 400°C). In fact, the X-ray powder diagrams of all these quenched specimens were very similar. However, compared with the ‘as-made’ material, there were fewer reflections (see Table 3). It must be noted that those reflections which are common to the ‘as-made’ 0/100 and 50/50 materials, but are stronger and/or sharper in the latter, persist in the diffraction patterns of the quenched 50/50 specimens. This indicates that these quenched specimens contain ordered regions with an imperfect

Table 4 Transition temperatures^a

Composition A/B	As made		Quenched ^b	
	T (°C)	Assignment	T (°C)	Assignment
0/100	385	c–i	375	c–i
33/67	330	c–i	324	see text
40/60	342	c–i	327	see text
43/57	340	c–i	335	see text
50/50	345	c–n	307	c–n
	410	n–i	410	n–i
55/45	350	c–n	–	–
60/40	362	c–n	320	c–n
67/33	375	c–n	375	c–n
75/25	440	c–n	435	c–n
80/20	(465)	c–n	–	–

^aD.s.c., heating rate 50°C/min; peak temperatures for melting endotherms (i.e. crystal–nematic mesophase, or crystal–isotropic transition), end temperature for isotropization endotherm

^bQuenched after remelting at 460°C

modified type B structure. Accordingly, the melting temperature of the quenched specimens was substantially lower than that of the 'as made' material (see Table 4).

Subsequent annealing of the re-melted/quenched specimens resulted in an enhancement of the order and in an increase of the melting temperature. Thus, a specimen re-melted at 350°C which was quenched and subsequently annealed for 30 min at 290°C gave an X-ray powder diagram which was essentially the same as that of the 'as-made' material; it had a melting temperature of 335°C.

The investigations reported above showed that the process of structure formation in the 50/50 copolymer is reversible. Both the degree of order and the melting temperature are influenced considerably by the thermal history.

67/33 copolymer

When compared with the 50/50 copolymer, the 67/33 copolymer contained an increased fraction of *p*-linked rod-like units ($x_p = 0.75$). The mean number of linked rod-like units was $n_p = 3$. The increase in chain rigidity resulted in an increase in the isotropization temperature above the thermal stability limit.

As already indicated, the 'as made' 67/33 copolymer contained ordered regions of both modified type B and modified type A structure. The X-ray powder diagram shows only those reflections found in the quenched 50/50 material, and the broad reflection with *d*-spacing 0.455 nm assigned to the pseudo-hexagonal modified type A structure. This indicates that the ordered regions of both types are small and imperfect. Accordingly, the melting endotherm is very broad (temperature range from 330 to 405°C) with a shallow peak at around 375°C.

The results of different thermal treatments (Table 5) show that the 67/33 copolymer was substantially affected by thermal treatment in terms of both melting behaviour and structure. Heating to 400°C followed by quenching resulted in the disappearance of the reflections assigned to the modified type B structure, although the melting behaviour was not altered. Annealing of the 'as made' material at 250°C resulted in an enhancement of the modified type B reflections. The thermogram of this material showed a separate small but relatively sharp endotherm with a peak at about 295°C, while the endotherm occurring between 330 and 405°C remained

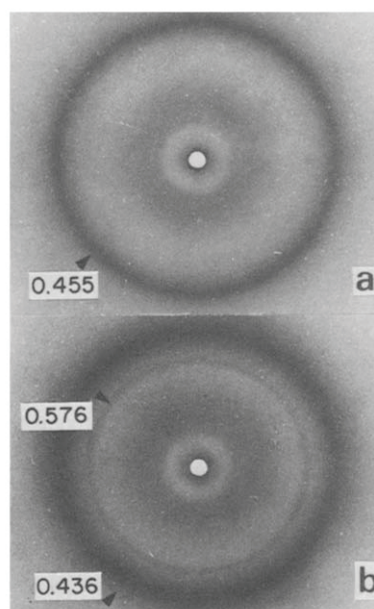


Figure 2 X-ray diffraction patterns of 67/33 copolymer, (a) annealed for 30 min at 335°C, (b) annealed for 30 min at 335°C, quenched and annealed 30 min at 250°C

essentially unchanged. It can be concluded that the small endotherm occurring between 280 and 310°C arises from the melting of the modified type B structure, whereas the upper endotherm is due to the melting of the pseudo-hexagonal modified type A structure.

Specimens annealed at 275 and 300°C also showed enhancement of reflections assigned to the modified type B structure. The thermograms of these materials no longer showed two separate endotherms since, in this case, the melting range of the modified type B structure overlaps with the melting range of the pseudo-hexagonal structure. It seems that the melting behaviour of the modified type B structure is strongly influenced by the annealing temperature. As expected, an increase in the annealing temperature results in an increase of the melting temperature.

The annealing carried out at 325°C did not have any appreciable effect on the X-ray diffraction pattern or on melting behaviour. It is apparent that this temperature is too high to result in an enhancement of the modified type B structure, but too low to affect the pseudo-hexagonal structure.

An increase in the annealing temperature to 335°C brings about a significant change in structure. The X-ray powder diagram (see Figure 2a) did not show any reflections arising from the modified type B structure, while the reflection with the *d*-spacing of 0.455 nm became both sharper and stronger. The melting endotherm also became slightly sharper and the melting range was shifted upwards. Thus, annealing at 335°C eliminated the modified type B structure and resulted in the enhancement of the modified type A structure.

A further increase in the annealing temperature to 345°C also resulted in the elimination of the modified type B structure, but in this case, there was no significant improvement in the order of the pseudo-hexagonal structure. Finally, a combined heat treatment carried out first at 335°C and then, after quenching, at 250°C, showed that in this way it is possible to produce a material with both structures enhanced (see Figure 2b).

Table 5 Heat treatment of the 67/33 copolymer

Treatment ^a	Melting endotherm		Structure type	
	Range (°C)	Peak (°C)	Mod. A	Mod. B
None	330–405	375	+	+
0.5 min at 400°	325–400	375	+	
30 min at 250°	280–310	295		++
	330–405	375	+	
30 min at 275°	300–410	310 ^b		++
		375	+	
30 min at 300°	310–410	330		++
		380 ^b	+	
30 min at 325°	335–410	380	+	+
30 min at 335°	360–425	400	++	
30 min at 345°	330–405	375	+	
30 min at 335°	270–315	295		++
30 min at 250°			330–425	400

Key: + present; ++ enhanced

^a In all cases the heat treatment is terminated by quenching

^b Shoulder

This investigation has shown that both modified type B and modified type A structures may co-exist in the 67/33 material. By means of suitable annealing conditions, it is possible to enhance either one or both types of structure. While the melting behaviour of the material is also affected by the annealing, the end point of the upper endotherm (which signifies the transition of a solid into a nematic mesophase) is much less variable than in the case of the 50/50 material.

CONCLUSIONS

Copolymers in which the molar fraction of *p*-linked OPCO and OPO units is between 0.67 and 0.75 (composition range from 50/50 to 67/33) exhibit a nematogenic temperature range of at least 50°C; consequently, they can be regarded as potentially useful thermotropic materials. Both a decrease below 0.67, and an increase above 0.75, in the content of rod-like units results in a narrowing of the nematogenic temperature range and an eventual loss of nematogenic properties.

Four different types of ordered structure have been identified; structures described as type A and type B arise from the crystallization of poly(*p*-oxybenzoate) and poly(*p*-phenylene isophthalate) respectively. A poorly ordered pseudo-hexagonal structure, similar to the high-temperature modification of poly(*p*-oxybenzoate), was found in the 75/25 copolymer (molar fraction of angular COMCO units 0.2) and referred to as modified type A. A crystalline structure similar to type B, prominent in the 50/50 copolymer (containing equimolar quantities of OPCO, OPO and COMCO units) is referred to as modified type B.

The potentially useful copolymers in the composition range 50/50 to 67/33 have modified type A and modified type B structures which may coexist. The perfection of each structure was strongly influenced by both composition and thermal history.

Quenching of all copolymers from 460°C causes a reduction in the melting transition temperature. This is most marked with the 50/50 copolymer. It is believed that this kind of behaviour may be found in other nematogenic copolymers.

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