

Thermotropic polyesters: thermal transitions and polymorphism of poly(4-oxybenzoate-co-1,4-phenylene isophthalate)s

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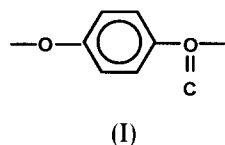
Differential scanning calorimetry and wide-angle X-ray diffraction techniques are employed to investigate the melting behaviour and crystalline structure of poly(1,4-phenylene isophthalate) and poly(4-oxybenzoate-co-1,4-phenylene isophthalate) containing equimolar quantities of the constituent 4-oxybenzoyl, 1,4-phenylenedioxy and isophthaloyl units. These materials can contain two different crystalline structures, both consisting of 1,4-phenylene isophthalate sequences. The formation of these polymorphs in both the homopolymer and copolymer is influenced by the crystallization and/or annealing conditions. The melting behaviour of the copolymer is strongly influenced by annealing, but these changes can be reversed by remelting. Consequently, they are not caused by changes in chain constitution arising from transesterification.

(Keywords: aromatic polyesters; polymorphism; transition temperatures)

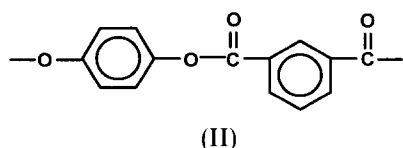
INTRODUCTION

Poly(4-oxybenzoate-co-1,4-phenylene isophthalate)s or poly(*p*-oxybenzoate-co-*m*-phenylene isophthalate)s (POPI)^{1–11} consist of rod-like 4-oxybenzoyl (OPCO) and 1,4-phenylenedioxy (OPO) units, and rigid angular isophthaloyl (COMCO) units (*Table 1*). They are produced from readily available monomers, namely 4-acetoxibenzoic acid, hydroquinone diacetate, and isophthalic acid. An acronym HIQ is also used for identification of these copolymers^{4–6}; it is based on the names of the notional monomers (4-Hydroxybenzoic acid, Isophthalic acid and hydroQuinone).

In the literature the composition is expressed either in terms of mol% of the repeating units of the parent homopolymers, i.e. poly(4-oxybenzoate) (I)



and poly(1,4-phenylene isophthalate) (II)



or in terms of molar fractions of the actual constituent units (i.e. [OPCO], [OPO] and [COMCO]), corresponding to the molar fractions of the monomers in the reaction mixture. Here, we use the latter approach which is also suitable for expressing the composition of multiconstituent copolymers. The molar fractions of the constituent units are related to the mol% of the homopolymer (I) units (A) as follows¹:

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

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

Thus, the composition of POPIs is fully specified by the molar fraction of any of the constituent units. Here, the materials will be identified by the molar fraction of the angular isophthaloyl units, [COMCO], irrespective of the convention used originally in the references.

Neither of the parent homopolymers is nematogenic. Poly(4-oxybenzoate) (I) is sufficiently rigid to form a nematic mesophase, but its melting temperature exceeds the decomposition temperature^{12,13}. In contrast, poly(1,4-phenylene isophthalate) (II), where the rod-like OPO units alternate with the angular COMCO units, does not have sufficient rigidity for the formation of a mesophase. Its melting (at ~385°C) results in an isotropic melt^{1,8}. The copolymers with [COMCO] < 0.40 were found to be nematogenic, but those with [COMCO] between 0.36 and 0.40 displayed only a narrow nematic temperature range even after quenching^{1,7,8}.

Kiss⁴ investigated the rheology of POPIs and noted a number of anomalies, including a 'shear-induced isotropic to anisotropic transition' in melts of copolymers with

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[COMCO]=0.365 and 0.375. Work by Hsiao *et al.*^{5,6} concerned with the behaviour of the copolymer with [COMCO]=0.40 showed that the nematic temperature interval increases with increasing pressure (called barotropic liquid crystallinity¹⁴). Although the behaviour of copolymers near the critical concentration of the angular units is interesting, it has been established^{1,2,7,8} that a sufficiently broad 'processing window' is obtained when [COMCO] is between ~0.33 and 0.25.

Melting behaviour and crystal structure of POPIs are affected by both composition and thermomechanical history^{1,2,5-9}. At least four different crystalline structures have been identified in these materials; two of them correspond to those found in poly(4-oxybenzoate) and the other two are due to regular (-OPO-COMCO-) sequences present in poly(1,4-phenylene isophthalate). In addition, a poorly ordered structure, described as 'paracrystalline', has been found^{2,3} in fibres made from copolymers with [COMCO]=0.25 and 0.33. In the literature, the designation of these structures varies and it is therefore important first to unify the nomenclature.

Detailed investigation of poly(4-oxybenzoate) structures has been carried out by Lieser¹⁵. The most common structure, identified by Lieser as 'Phase I', has an orthorhombic unit cell where $a=0.752$ nm, $b=0.570$ nm

and $c=1.249$ nm. The prominent reflections are listed in Table 2. In the literature concerned with POPIs this structure has been referred to as 'type A'^{1,2} and 'Form III'⁷. Here, this structure will be referred to as A(I).

Lieser¹⁵ also found another crystal modification in poly(4-oxybenzoate), which he identified as 'Phase II'. Its unit cell is also orthorhombic where $a=0.377$ nm, $b=1.106$ nm and $c=1.289$ nm. This structure is closely related to the A(I) structure, but there are some additional reflections as shown in Table 2. These reflections were also found by Windle and co-workers^{16,17} in the homopolymer in addition to the dominant A(I) reflections. Here, Lieser's 'Phase II' will be referred to as A(II).

Lieser¹⁵ established that the crystalline structure of poly(4-oxybenzoate) was transformed at elevated temperatures into 'Phase III', where the prominent (110) and (200) reflections of the A(I) structure merged. Although this corresponds to hexagonal packing, there are some additional reflections. Consequently, he suggested an orthorhombic unit cell where $a=0.92$ nm, $b=0.53$ nm and $c=1.24$ nm. Subsequently, Windle and co-workers^{16,17} carried out a very detailed investigation of the structural changes taking place in poly(4-oxybenzoate) at elevated temperatures and found, at 380°C, an orthorhombic unit cell where $a=0.913$ nm, $b=0.535$ nm and $c=1.249$ nm, which is similar to Lieser's result. This structure is frequently observed in copolymers containing OPCO units and it has been pointed out that there is a similarity between the disordering effect of heat and that of comonomer units¹⁷. In the literature^{1,2} concerned with POPIs, this structure has been described as 'modified type A'. Here, it will be referred to as A(III). The d -spacing of the most prominent (110/200) reflection is around 0.46 nm (Table 2).

It is likely that the 'paracrystalline structure' found in as-made POPI fibres with [COMCO]=0.33 and 0.25 is also due to packing of rod-like OPCO or OPCO/OPO sequences. The WAXS pattern of these fibres showed a broad asymmetrical equatorial scatter which was resolved into two very broad peaks² with d -spacings of 0.458 and 0.364 nm. Tilted fibres also showed three weak meridional reflections³ with d -spacings of 0.61, 0.30 and 0.20 nm. A similar WAXS pattern was also found by Blundell *et al.*⁷ in the copolymer with [COMCO]=0.25; these authors described this structure as 'amorphous'.

Table 1 Constituent units

| Unit | Abbreviation | Structure |
|--------------------|--------------|-----------|
| 4-Oxybenzoyl | OPCO | |
| 1,4-Phenylenedioxy | OPO | |
| Isophthaloyl | COMCO | |

Table 2 Prominent reflections of crystalline structures based on poly(4-oxybenzoate) (structures A(I), A(II), A(III)) and on poly(1,4-phenylene isophthalate) (structures B and C)

| Structure | | | | | | | |
|-------------|-----------|-------------|-----------|-------------|----------|----------|----------------|
| A(I) | | A(II) | | A(III) | | B | C |
| hkl | d (nm) | hkl | d (nm) | hkl | d (nm) | d (nm) | hkl d (nm) |
| | | 020 | 0.55–0.57 | | | 0.67 | |
| 110 | 0.45–0.46 | | | 110/ 200 | 0.46 | 0.48 | 100 0.56 |
| 111 | 0.42–0.43 | | | | | 0.45 | |
| 200 | 0.37–0.38 | 100 | 0.37–0.38 | | | | 010 0.39 |
| 004/ 210 | 0.31–0.32 | 112/ 120 | 0.31–0.32 | 211 | 0.31 | 0.35 | 110 0.32 |

Table 3 Effect of composition ([COMCO]) and processing on the structures found in POPIs: A, based on OPCO sequences; P, 'paracrystalline' or 'amorphous'; C and B, based on (-OPO-COMCO-) sequences

| Material | [COMCO] | | | |
|-----------------|---------|-----------|-----------|-----------|
| | A | P | C | B |
| As-made polymer | 0–0.20 | 0.25 | 0.30–0.35 | 0.47–0.50 |
| Melt-processed | | | 0.25–0.43 | |
| As-made fibre | 0.20 | 0.25–0.33 | 0.40 | |
| Annealed fibre | 0.20 | | 0.25–0.40 | |

We now turn to structures based on the second homopolymer, poly(1,4-phenylene isophthalate) (II). The crystalline structure found mainly in the homopolymer and in the copolymers with low concentrations of OPCO units has not so far been investigated in detail. The *d*-spacings of this structure reported by Blundell *et al.*⁷ are listed in Table 2. In the literature, this structure has been named 'type B'^{1,2}, 'Form I'⁷ and 'structure K1'^{5,6}. Here, it will be referred to as structure B.

Another structure resulting from regular packing of (-OPO-COMCO-) sequences has been found, initially by Erdemir *et al.*², in fibres produced from POPI copolymers with [COMCO] between 0.25 and 0.40; they called this structure 'type C' and proposed an orthorhombic unit cell. Later, Blundell *et al.*⁷ found the same structure in injection mouldings produced from similar copolymers; they called it 'Form II'. As shown by Hsiao *et al.*^{5,6}, this structure (designated by them as 'K2') is also formed in copolymer where [COMCO] = 0.40 by crystallization at high pressures. Following a detailed investigation of heat treated copolymer fibres, Johnson *et al.*¹⁸ proposed an orthorhombic unit cell where *a* = 0.558 nm, *b* = 0.392 nm and *c* = 2.432 nm. Here, this type is referred to as structure C; its prominent reflections are listed in Table 2.

After this clarification of the nomenclature of the structures found in POPIs and identification of their prominent reflections (Table 2), it is possible to summarize the results^{1,2,5–9} concerning the occurrence of these structures (Table 3). It should be noted that in some cases the assignment is based on inspection of the published WAXS patterns, although the authors did not comment on the structural differences. Compositions with [COMCO] ≤ 0.20 (i.e. [OPCO] ≥ 0.60) show only the poly(4-oxybenzoate) structures. Poly(4-oxybenzoate) ([COMCO] = 0) shows the A(I) structure, often together with some A(II) structure. As the concentration of the COMCO units increases the peaks become broader and weak peaks disappear. The WAXS patterns presented by Tsai *et al.*⁸ suggest that at [COMCO] = 0.167 the structure is A(III). When the concentration of [COMCO] increased to around 0.25, the as-made copolymer showed only a broad peak assigned to 'amorphous'⁷ or 'paracrystalline' structure². However, an injection moulding⁷ and annealed fibre² produced from copolymer with [COMCO] = 0.25 already showed the structure C arising from (-OPO-COMCO-) sequences.

Structure C is found in copolymers where [COMCO] is between 0.30 and 0.35. The copolymers where [COMCO] is between 0.375 and 0.444 show both C and B structures, depending on thermomechanical history. It should be recalled that these copolymers are borderline concerning the stability of nematic mesophase. Particularly interest-

ing are the results obtained for [COMCO] = 0.40 by Hsiao *et al.*^{5,6}. Their results suggest that crystallization at pressures higher than 300 bar* (i.e. from a nematic mesophase) yields structure C, whilst crystallization at atmospheric pressure (i.e. from an isotropic melt) results in formation of structure B; crystallization at pressures between 1 bar and 300 bar results in a mixture of structures B and C. Similarly, crystallization from an oriented melt of this copolymer (i.e. in the case of melt processing) appears to favour the formation of structure C. The results for poly(1,4-phenylene isophthalate) homopolymer ([COMCO] = 0.5) and for copolymer [COMCO] = 0.474, which are not nematogenic, indicate that in these materials crystallization results in structure B.

In summary, the survey of the literature suggests that ordered structures resulting from (-OPO-COMCO-) sequences are formed when [COMCO] ≥ 0.25. Structure C appears to be favoured when the nematic mesophase is transformed into a crystalline structure, whilst structure B seems to be favoured by crystallization from an isotropic melt.

The main purpose of this work is to investigate the polymorphism in the materials where the crystallization results from regular packing of (-OPO-COMCO-) sequences (i.e. structures B and C) and its effect on the melting behaviour.

EXPERIMENTAL

The polymers were the same as those used previously^{1,2}. Microscopic observations, aimed at evaluation of softening, flow and decomposition temperatures, were carried out using a polarizing microscope equipped with a Stanton-Redcroft hot-stage¹⁹; the heating rate was 20°C min⁻¹. Thermogravimetric analysis (t.g.a.) was carried out on a Du Pont 951 equipment controlled by Du Pont Thermal Analyst 2000 operating software at a heating rate of 20°C min⁻¹ under nitrogen.

Transition temperatures and enthalpies were measured with a Du Pont 910 differential scanning calorimeter controlled by Du Pont Thermal Analyst 2000 operating software at a heating rate of 20°C min⁻¹ under nitrogen. Quenched samples were obtained by heating the polymer in the differential scanning calorimeter to a specified remelting temperature, where it was held for 30 s. The sample was then removed from the d.s.c. cell and placed on a steel bar at room temperature. Annealing was also carried out in the differential scanning calorimeter using samples which were first remelted and quenched.

Preliminary information concerning the structure of as-made, quenched and annealed polymers was obtained from wide-angle X-ray photographs taken with a flat-plate camera. The wide-angle X-ray traces were obtained using a Spectrolab series 3000 diffractometer with Inel XRG-3000 generator and Inel CPS-120 curved position sensitive detector. A microprocessor running Inel software was used to store the data on the hard-disc drive of a Personal Computer. Additional quantitative work was carried out on a Hilger and Watts Y115 diffractometer mounted on a Hiltonbrook DG2 generator equipped with an Elliot 315/TX 1.2 kW sealed tube. The diffractometer has been modified for stepper motor drive and microprocessor control, with intensity data recorded

* 1 bar = 1 × 10⁵ Pa

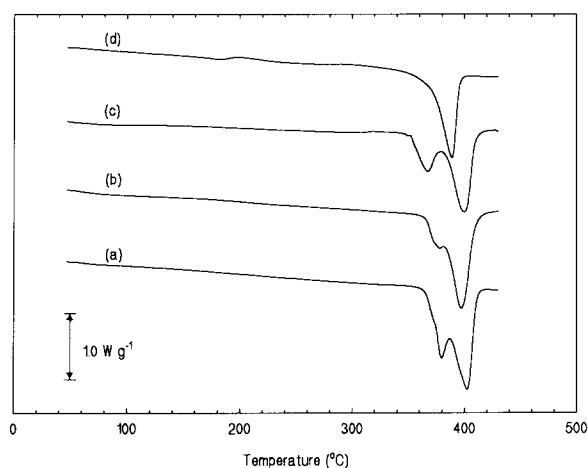


Figure 1 D.s.c. curves of poly(1,4-phenylene isophthalate): (a), (b), (c) as-made samples; (d) quenched sample (remelting conditions: 30 s at 430 °C)

on the hard-disc drive of a Personal Computer through a scintillation counter pulse-height analyser system. Both diffractometer systems utilized nickel-filtered $\text{CuK}\alpha$ radiation and voltage and current settings of 40 kV and 16 mA, respectively. Each data set was analysed according to the procedures detailed earlier²⁰. The mainframe versions of the analysis programs have been modified to run on a Personal Computer and applied to the analysis of the data collected from both diffractometers. Intensity correction and normalization were followed by peak resolution. Interplanar spacings were calibrated by a silver foil reference in each specimen.

RESULTS AND DISCUSSION

As-made poly(1,4-phenylene isophthalate)

The hot stage optical microscopy confirmed that the homopolymer does not form a nematic mesophase. The melting process, resulting in an isotropic melt, was completed between 417 and 425°C. However, under a load the samples showed softening at 385°C; decomposition was observed at ~445°C. T.g.a. measurements showed that the temperature corresponding to 2% weight loss was 381°C and that of 5% weight loss was 446°C.

Representative d.s.c. curves are shown in Figure 1. None of the curves showed a clear glass transition. The melting endotherm was between ~340°C and 425°C. The end temperature of this endotherm was in good agreement with the hot stage microscopy observation. The majority of samples showed two peaks. The upper peak was larger and the peak temperatures were between 397°C and 403°C; the mean value from 26 runs was 400°C. The lower peak varied in both position and size. The peak temperatures were between 365 and 381°C. In some samples the peak turned into a shoulder; an example of such a curve is shown in Figure 1. The values of the total heat of fusion were between 100 J g⁻¹ and 120 J g⁻¹; the mean value was 114 J g⁻¹. The results obtained are in reasonable agreement with the literature. Blundell *et al.*⁷ and Tsai *et al.*⁸ reported a melting temperature of 387°C, determined by d.s.c.; the reported⁸ total heat of fusion is 96 J g⁻¹.

It should be noted that the melting temperature exceeds the temperature corresponding to the 2% weight loss. The temperature interval between the end of the melting range (425°C) and severe decomposition (5% weight loss at 446°C) is rather narrow. Consequently, melt processing of this material would present considerable difficulties.

Contrary to the published results concerning the structure of this homopolymer, the X-ray photographs of a number of samples selected at random from the as-made material revealed the presence of both B and C structures. Examples of WAXS traces are shown in Figure 2; curve a corresponds to a sample where structure B prevails, whilst curve b indicates that structure C is dominant (note the prominent peak 4 corresponding to the 100 reflection of structure C). It was of interest to establish whether the two melting peaks in the d.s.c. curves of the as-made material (Figure 1) are related to the presence of structures B and C. However, first we shall consider the chain packing in structure B.

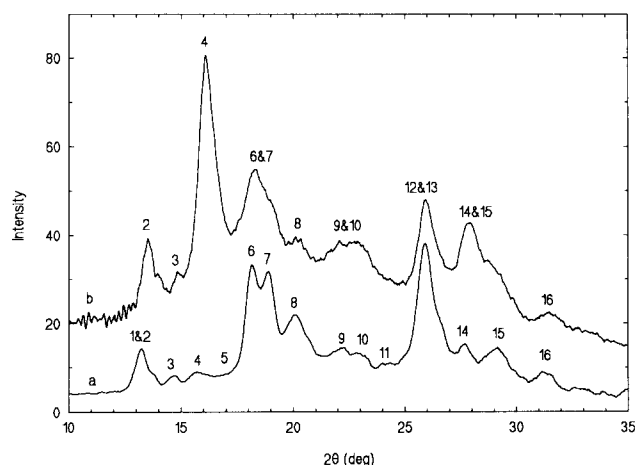


Figure 2 WAXS traces of as-made poly(1,4-phenylene isophthalate) homopolymer indicating polymorphism: (a) structure B dominant; (b) structure C dominant: the peak numbers correspond to those in Figure 3 and Table 4

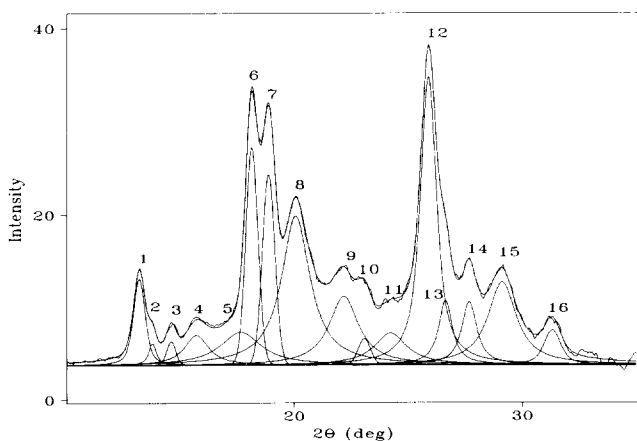


Figure 3 Resolved WAXS trace of as-made poly(1,4-phenylene isophthalate) sample with dominant structure B; *d*-spacings of all the resolved peaks are listed in Table 4

Table 4 Structure of poly(1,4-phenylene isophthalate): d -spacings (d), areas (A) and half-height widths (W) of resolved peaks (Figure 3). Structure B: calculated d -spacings for monoclinic unit cell with $a=0.697$ nm, $b=0.692$ nm, $c=2.432$ nm; $\alpha=95^\circ$, $\beta=\gamma=90^\circ$. Structure C: calculated d -spacing for orthorhombic unit cell with $a=0.558$ nm, $b=0.392$ nm, $c=2.432$ nm

| Peak | d (nm) | A (%) | W (deg) | Structure B | | Structure C | |
|------|-------------|------------|--------------|-------------|----------|-------------|----------|
| | | | | hkl | d (nm) | hkl | d (nm) |
| 1 | 0.675 | 3.76 | 0.70 | 101 | 0.670 | | |
| 2 | 0.646 | 0.74 | 0.40 | 011 | 0.648 | | |
| 3 | 0.607 | 0.70 | 0.55 | 004 | 0.606 | | |
| 4 | 0.559 | 2.59 | 1.28 | | | 100 | 0.558 |
| 5 | 0.503 | 5.69 | 2.18 | | | 102 | 0.502 |
| 6 | 0.491 | 8.00 | 0.75 | 110 | 0.490 | | |
| 7 | 0.472 | 7.08 | 0.78 | 111 | 0.475 | | |
| 8 | 0.444 | 18.39 | 1.52 | 112 | 0.445 | | |
| 9 | 0.404 | 8.66 | 1.55 | 006 | 0.404 | 104 | 0.406 |
| 10 | 0.385 | 0.99 | 0.77 | | | 010 | 0.391 |
| 11 | 0.367 | 4.42 | 1.72 | 114 | 0.370 | 105 | 0.366 |
| 12 | 0.346 | 18.97 | 0.89 | 020 | 0.345 | | |
| 13 | 0.336 | 3.83 | 0.71 | 021 | 0.337 | | |
| 14 | 0.323 | 4.07 | 0.81 | 022 | 0.324 | 110 | 0.321 |
| 15 | 0.307 | 9.98 | 1.51 | 023 | 0.307 | 112 | 0.310 |
| 16 | 0.286 | 2.20 | 0.96 | 024 | 0.289 | 114 | 0.284 |

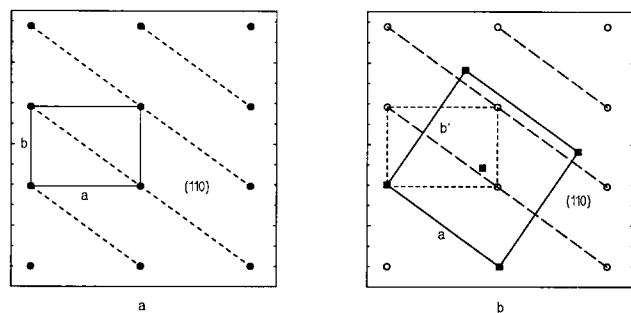


Figure 4 Chain packing in the plane perpendicular to the chain direction: (a) structure C; (b) structure B superimposed on structure C (open symbols)

Structure B

A sample of poly(1,4-phenylene isophthalate) where the structure B was dominant was examined using the Hilger and Watts diffractometer. The WAXS trace (Figure 3) was resolved into 16 peaks; their d -spacings, areas and half-height widths are listed in Table 4. The positions of the prominent peaks are in good agreement with those reported by Blundell *et al.*⁷ for structure B (see Table 2). However, in place of a single peak ($d \approx 0.48$ nm) there are two overlapping peaks, 6 and 7, with d -spacings of 0.491 and 0.472 nm, respectively. Some of the peaks (4, 5, 9–11 and 14–16) may be assigned to structure C (see Table 4).

In the absence of a well oriented sample, the determination of the unit cell dimensions usually presents considerable difficulties. We have considered a possibility that structure B arises from structure C by a displacement of (110) planes (Figure 4). When the prominent peak 6 of structure B ($d \approx 0.491$ nm) was indexed as its 110 reflection, an orthorhombic unit cell with $a=0.682$ nm, $b=0.642$ nm and $c=2.432$ nm was obtained. After adjusting the unit cell dimensions and introducing a small 'monoclinic shear' (cf. ref. 17) a good agreement between the observed and calculated d -spacings (Table 4) was

obtained for the following tentative unit cell: $a=0.697$ nm, $b=0.692$ nm, $c=2.432$ nm, $\alpha=95^\circ$, $\beta=\gamma=90^\circ$. It should be noted that some of the observed peaks (4, 5 and 10) can only be assigned to structure C.

The suggested relationship between the B and C structures is illustrated in Figure 4. However, the near-tetragonal chain packing in the structure B is significantly poorer than that in structure C; in structure B the chain cross-sectional area is 0.240 nm², compared with 0.218 nm² for structure C. This implies that structure C should be more stable.

Heat-treated poly(1,4-phenylene isophthalate)

Quenched samples were obtained using a remelting temperature of 430°C ; this rather low remelting temperature (only 5°C above the end of the melting endotherm) was selected in order to avoid severe thermal decomposition.

The WAXS pattern of the quenched material did not show any sharp reflections (Figure 5). There were only two very broad peaks at 2θ positions around 18.5° and 25.5° , respectively, corresponding roughly to the most prominent reflections of the B structure (peaks 6&7 and 12&13). There were no broad peaks corresponding to the prominent reflections of structure C. It is therefore likely that the quenched homopolymer contains a highly imperfect structure B.

The d.s.c. curves of quenched homopolymer indicate a glass transition range between 150°C and 180°C . The mean value of the glass transition temperature (T_g) obtained from 12 runs is $170 \pm 2^\circ\text{C}$; ΔC_p is around $0.1 \text{ J g}^{-1} \text{ K}^{-1}$. The glass transition is followed by a very small and broad exotherm (peak temperature around 185°C , $\Delta H \sim 5 \text{ J g}^{-1}$). The melting endotherm (between 320°C and 405°C) showed a single peak at 388°C ; the heat of fusion was 67 J g^{-1} (Table 5). These results show that quenching from 430°C to room temperature did not suppress the crystallization although the crystallinity is reduced compared with the as-made material. Similar results were obtained by Tsai *et al.*⁸ for a sample cooled at $20^\circ\text{C min}^{-1}$ from 400 to 60°C . They observed a peak at 374°C with a shoulder at 384°C and a total heat of fusion of 67 J g^{-1} .

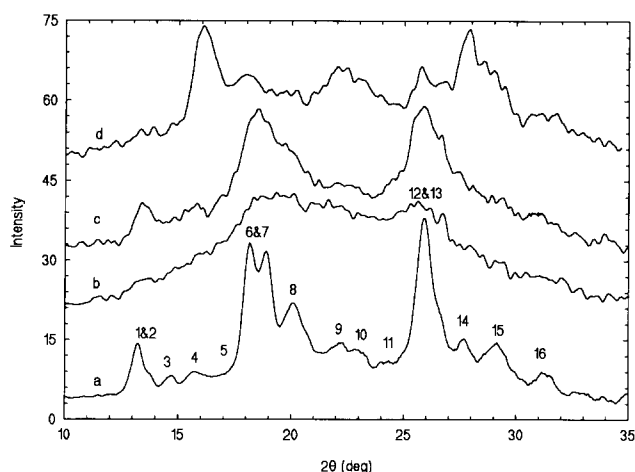


Figure 5 WAXS traces of poly(1,4-phenylene isophthalate) homopolymer: (a) as-made; (b) quenched; (c) annealed at 270°C for 18 h; (d) annealed at 370°C for 2 h

Table 5 Effect of annealing temperature (T_a) and annealing time (t_a) on melting behaviour of poly(1,4-phenylene isophthalate) homopolymer

| T_a (°C) | t_a (min) | Endotherm | | ΔH (J g ⁻¹) |
|-----------------------|----------------|---------------|----------------------|------------------------------------|
| | | Range (°C) | Peaks (°C) | |
| As-made | | 340–425 | 375 400 | 114 |
| Quenched ^a | | 320–405 | 388 | 67 |
| 270 | 1080 | 314–412 | 352 ^c 391 | 72 |
| 365 | 30 | 348–418 | 393 | 84 |
| 370 | 1 | 346–412 | 388 | 68 |
| 370 | 30 | 342–426 | 406 | 91 |
| 370 | 120 | 363–440 | 411 | 98 |
| 370 | 240 | 350–426 | 406 | 89 |
| 380 | 30 | 333–430 | 409 | 80 |
| 385 ^b | 30 | 311–425 | 369 409 | 74 |
| 390 ^c | 30 | 313–395 | 366 411 ^e | 37 |
| 400 ^d | 30 | 316–385 | 357 | 19 |

^aCrystallization exotherm with a peak at 185°C, $\Delta H \approx 5 \text{ J g}^{-1}$ ^bCrystallization exotherm with a peak at 211°C, $\Delta H \approx 3 \text{ J g}^{-1}$ ^cCrystallization exotherm with a peak at 224°C, $\Delta H \approx 8 \text{ J g}^{-1}$ ^dCrystallization exotherm with a peak at 225°C, $\Delta H \approx 4 \text{ J g}^{-1}$ ^eShoulder

The quenched polymer was subjected to an extended annealing (18 h) at 270°C, which is the same temperature as that used by Tsai *et al.*⁸. The WAXS trace (Figure 5) showed three rather broad peaks corresponding to the prominent reflections of structure B, in agreement with the pattern obtained by Tsai *et al.*⁸. Although the structure is better developed than in the quenched sample, it is clearly less perfect than that found in the as-made material. The d.s.c. curve of this annealed sample did not show the glass transition or the crystallization exotherm, but its melting behaviour was similar to that of the quenched material (Table 5). Thus, the effect of extended annealing at 270°C on both structure and melting behaviour is only marginal.

Clearly, more pronounced changes in the structure and melting behaviour require an annealing temperature closer to the melting temperature. In order to select such a temperature, a series of samples was obtained at T_a ranging from 365 to 400°C; the annealing time was kept constant (30 min). The d.s.c. curves of these annealed samples are shown in Figure 6 and the results are summarized in Table 5. When the T_a was between 365°C and 380°C, the d.s.c. curves showed only a single melting peak and its temperature increased with increasing T_a , reaching 409°C for $T_a = 380^\circ\text{C}$. At $T_a = 385^\circ\text{C}$ the d.s.c. curve showed a double melting endotherm with peak temperatures of 369 and 409°C, respectively. However, the heat of fusion was lower than that obtained at $T_a = 380^\circ\text{C}$. An increase in T_a to 390 and 400°C resulted in a substantial decrease in both melting temperature and ΔH . At these temperatures, most of the material is molten and it is suspected that thermal degradation is already taking place. Thus, temperatures between 370 and 380°C appeared to be suitable for increasing the degree of order of this material. However, a sample subjected to a long annealing (18 h) at 380°C was black and showed only a very small endotherm ($\Delta H \sim 4 \text{ J g}^{-1}$) albeit at a high temperature (peak at 425°C). Its WAXS pattern did not show any sharp reflections. All this evidence indicates pronounced degradation.

The effect of annealing time at $T_a = 370^\circ\text{C}$ is shown in Table 5. The maximum melting peak temperature (411°C)

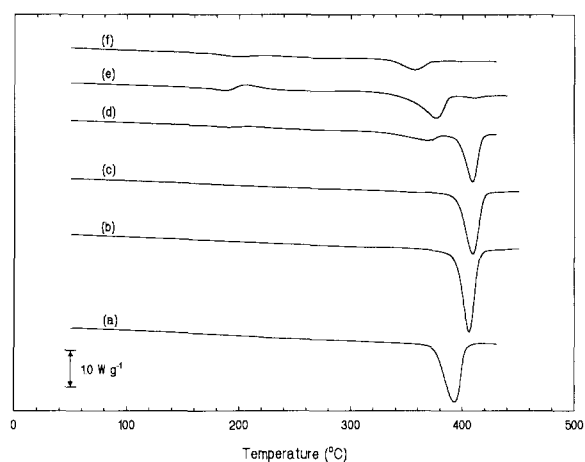
and heat of fusion (98 J g^{-1}) were obtained after 2 h. The WAXS pattern of the sample annealed under these conditions is shown in Figure 5. There were five rather broad peaks. The most prominent peak (4), at $2\theta = 16.2^\circ$, corresponds to the 100 reflection of structure C. The second prominent peak (14), at $2\theta = 27.8^\circ$, corresponds to the 110 reflection of structure C; it could also be indexed as the 022 reflection of structure B. There is also a peak (12&13) at $2\theta = 25.7^\circ$; it is most likely due to reflections 020 and 021 of structure B. Thus, it is likely that this annealed sample contains both B and C structures, with C probably prevailing, yet the d.s.c. curve showed only a single melting peak. This suggests that any possible differences in melting behaviour of structures B and C are obscured by the effects of crystallite size and/or perfection.

It is concluded that both B and C structures are found in the homopolymer, in some cases together. It has been established that coexistence of structures B and C is not always manifested in separate melting endotherms. Rapid cooling results in formation of a highly imperfect structure B, which therefore appears to be kinetically favoured. Annealing of the quenched homopolymer at a low temperature (270°C) results in some improvement of the structure. Structure C with higher chain packing density can be formed at 370°C, but detailed investigation of high temperature annealing presents difficulties due to thermal degradation. The maximum melting temperature of 411°C was obtained after annealing at 370°C for 2 h.

Poly(4-oxybenzoate-co-1,4-phenylene isophthalate)

Since the copolymer with $[\text{COMCO}] = 0.33$ displays a broad nematic temperature interval, it was selected for the investigation of the effect of heat treatments on the melting behaviour and polymorphism. Results obtained for the as-made material essentially confirmed those in the literature^{1,7,8}. T.g.a. measurements showed that the temperature corresponding to 2% weight loss was 388°C and that of 5% weight loss was 445°C. Using hot stage microscopy, the decomposition temperature was observed at $\sim 450^\circ\text{C}$.

The WAXS pattern of the as-made material did not reveal any sharp reflections (Figure 7). Nevertheless, the

**Figure 6** Effect of annealing temperature on the thermal transitions of poly(1,4-phenylene isophthalate) homopolymer: (a) 365°C; (b) 370°C; (c) 380°C; (d) 385°C; (e) 390°C; (f) 400°C. The annealing time was 30 min

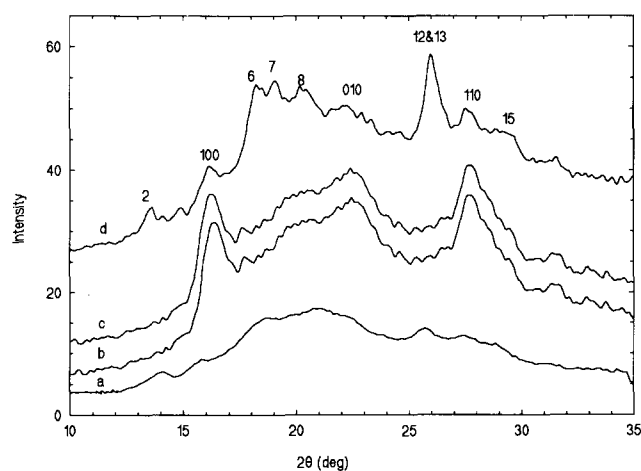


Figure 7 WAXS traces of annealed POPI copolymer with [COMCO]=0.33: (a) as-made; (b) annealed at 270°C for 18 h; (c) annealed at 290°C for 18 h; (d) annealed at 315°C for 18 h

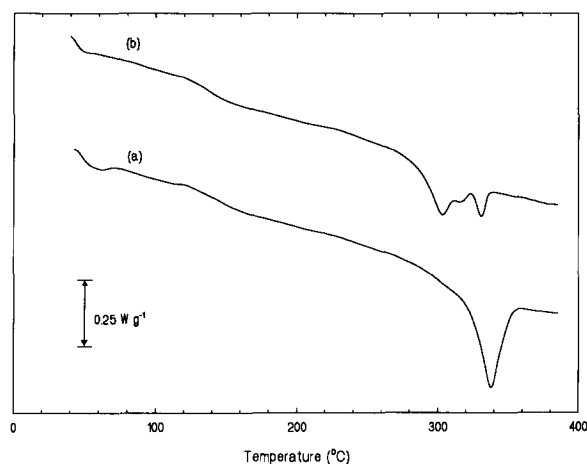


Figure 8 DSC curves of POPI copolymer, [COMCO]=0.33: (a) as-made copolymer; (b) quenched copolymer

material must be semicrystalline since its d.s.c. curve (Figure 8) shows a well-defined endotherm with a peak temperature of $338 \pm 2^\circ\text{C}$ ($\Delta H = 21 \pm 3 \text{ J g}^{-1}$) (Table 6). Hot stage optical microscopy confirmed that this endotherm corresponds to the crystal–nematic transition; the flow temperature is around 345°C . The d.s.c. curves also indicate a glass transition region between 125°C and 150°C ; the mean value of T_g obtained from 31 runs is $140 \pm 6^\circ\text{C}$ and ΔC_p is around $0.2 \text{ J g}^{-1} \text{ K}^{-1}$.

The d.s.c. curves of the material quenched from 390°C showed, apart from the glass transition, only a very broad melting endotherm (Figure 8), between 270°C and 340°C . It usually showed two peaks (332 and 302°C) together with a shoulder (around 316°C); the total heat of fusion was $16 \pm 2 \text{ J g}^{-1}$ (Table 6). Hot stage optical microscopy revealed that the quenched copolymer forms a nematic melt at around 320°C . It is clear that the quenching procedure used in this work did not suppress the crystallization. However, the transition of the solid material into a nematic mesophase takes place at a somewhat lower temperature compared with the as-made material and the total heat of fusion is also slightly lower. Similar effects were noted in the literature^{1,8}.

In order to select a suitable T_a , a series of samples was obtained at T_a ranging from 240 to 370°C ; the t_a was kept constant (30 min). The d.s.c. curves of these annealed samples (Figure 9) still showed the glass transition. When the T_a s were between 240°C and 275°C , the d.s.c. curves showed two melting peaks. One of the peaks is at around 333°C , which is identical with the peak temperature observed for the quenched samples. The other melting peak temperature increased with increasing T_a . When the T_a s were between 295°C and 320°C , there was only a single melting peak and its temperature increased with increasing T_a , reaching $352 \pm 2^\circ\text{C}$ for $T_a = 320^\circ\text{C}$. Within this range of T_a , the ΔH values were between 23 J g^{-1} and 28 J g^{-1} . At $T_a = 325^\circ\text{C}$ the d.s.c. curve showed a main peak at 352°C together with a small broad peak at around 310°C ; ΔH decreased to 24 J g^{-1} . A further increase in T_a (between 330°C and 370°C) resulted in a substantial decrease in both melting temperature and ΔH . It should be noted that at these temperatures most of the material is molten and therefore, these treatments are

Table 6 Melting behaviour of POPI, [COMCO]=0.33

| Sample | Conditions | Endotherm | | |
|--------|--|----------------------------|----------------------------|----------------------------------|
| | | Range ($^\circ\text{C}$) | Peaks ($^\circ\text{C}$) | ΔH (J g^{-1}) |
| AM | As made | 295–363 | 338 | 21 |
| Q | Quenched | 275–340 | 302 316 ^a 332 | 16 |
| A1 | Annealed for 18 h at 270°C | 306–377 | 352 | 41 |
| R1 | As A1 after remelting (30 s at 400°C) and quenching | 277–335 | 308 322 | 13 |
| A2 | Annealed for 18 h at 290°C | 318–384 | 359 | 44 |
| R2 | As A2 after remelting (30 s at 400°C) and quenching | 273–337 | 305 322 | 13 |
| A3 | Annealed for 18 h at 315°C | 337–403 | 379 | 52 |
| R3 | As A3 after remelting (30 s at 405°C) and quenching | 281–330 | 311 | 10 |

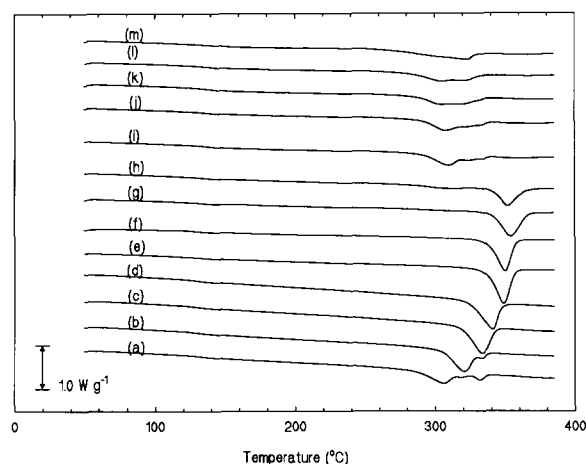


Figure 9 Effect of annealing temperature on the melting behaviour of POPI copolymer, [COMCO]=0.33: (a) 240°C ; (b) 275°C ; (c) 295°C ; (d) 305°C ; (e) 310°C ; (f) 315°C ; (g) 320°C ; (h) 325°C ; (i) 330°C ; (j) 340°C ; (k) 350°C ; (l) 360°C ; (m) 370°C . The annealing time was 30 min

Table 7 Effect of annealing time, t_a , at $T_a = 315^\circ\text{C}$ on melting behaviour of POPI, [COMCO]=0.33

| t_a (min) | Endotherm | | |
|----------------|-------------------------------|------------------------------|-------------------------------------|
| | Range ($^\circ\text{C}$) | Peak ($^\circ\text{C}$) | ΔH (J g^{-1}) |
| 1 | 306–350 | 336 ^a | 13 |
| 10 | 317–362 | 345 | 19 |
| 30 | 317–365 | 350 | 28 |
| 100 | 321–384 | 362 | 38 |
| 1080 | 337–403 | 379 | 52 |

^a Also a shoulder at 322°C

not actually annealing. It is also possible that, in the molten state, thermal degradation is already taking place. Thus, for the evaluation of the effect of annealing on the melting behaviour only the results for T_a between 240°C and 325°C are to be considered. Within this temperature range, there is a linear relationship between the 'variable' melting peak temperature, T_p , and T_a , namely:

$$T_p = 159.4 + 0.596T_a \quad (1)$$

The correlation coefficient is 0.984 and the standard error of the estimate is 3°C . The intercept with the $T_p = T_a$ straight line gives a value of $T_p = 395^\circ\text{C}$. This extrapolated peak temperature is close to the melting temperature of the as-made poly(1,4-phenylene isophthalate) (Table 5).

As expected, increased t_a resulted in a further increase in the melting peak temperatures and ΔH values. Results for $T_a = 315^\circ\text{C}$ are shown in Table 7; both T_p and ΔH increased linearly with $\log t_a$. Data for $t_a = 18\text{ h}$ ($T_a = 270, 290$ and 315°C) are listed in Table 6. In the samples subjected to this extended annealing the glass transition was no longer detectable. For $t_a = 18\text{ h}$, there is again a linear relationship between T_p and T_a :

$$T_p = 198.7 + 0.563T_a \quad (2)$$

The correlation coefficient is 0.985 and the standard error of the estimate is 2°C . It should be noted that the slopes of T_p versus T_a plots for $t_a = 30\text{ min}$ and 18 h , respectively, are rather similar. However, within the investigated interval of the T_a s, the melting peak temperatures obtained after 18 h are $\sim 30^\circ\text{C}$ higher than those obtained after 30 min . The intercept of the T_p versus T_a plot for $t_a = 18\text{ h}$ with the $T_p = T_a$ straight line gives a value of $T_p = 455^\circ\text{C}$ which is even higher than the observed melting temperature of annealed poly(1,4-phenylene isophthalate) homopolymer (Table 5). Even the directly measured melting temperature of the copolymer annealed for 18 h at 315°C (379°C) is close to that of the quenched poly(1,4-phenylene isophthalate) and only $\sim 30^\circ\text{C}$ lower than the maximum melting temperature observed for annealed poly(1,4-phenylene isophthalate).

Such a small difference between the melting behaviour of the copolymer ([COMCO] + [OPO] = 0.67; [OPCO] = 0.33) and homopolymer is unusual and could have possibly arisen, at least partly, from changes in chemical structure of the copolymer taking place during the annealing. In order to investigate this possibility, it was necessary to check the melting behaviour of annealed samples after remelting. The annealed copolymer samples were remelted in the differential scanning calorimeter ~ 10 – 15°C above the end of the melting temperature

range of annealed samples (Table 7) and quenched. Although the melting behaviour of annealed/remelted/quenched samples shows some minor differences (for details see Table 6), it is similar to that of the as-made copolymer after quenching. Thus, the substantial changes in melting behaviour caused by annealing are essentially reversible. The increases in melting temperature and ΔH resulting from annealing are therefore primarily due to changes in physical structure rather than due to any changes in chemical structure, such as transesterification, causing 'de-randomization'.

The WAXS patterns of the samples annealed at 270°C and 290°C for 18 h show three broad peaks (Figure 7). Comparison with data in Table 4 shows that the most prominent peak (4), at $2\theta = 16.2^\circ$, corresponds to the 100 reflection of structure C. The second prominent peak (14), at $2\theta = 27.6^\circ$, corresponds to the 110 reflection of structure C and/or to the 022 reflection of structure B. The third peak (10), at $2\theta = 22.5^\circ$, corresponds to the 010 reflection of structure C (Table 4). Thus, in samples annealed at 270°C and 290°C , the structure C is clearly dominant. This is in agreement with the literature⁸.

The WAXS pattern of the sample annealed at 315°C for 18 h is also shown in Figure 7. In contrast with the patterns discussed above, there are six broad peaks. The most prominent peak (12), at $2\theta = 26^\circ$, corresponds to the 020 reflection of structure B. The second prominent peak (14), at $2\theta = 27.6^\circ$, corresponds to the 110 reflection of structure C and/or to the 022 reflection of structure B. The third prominent peak (2), at $2\theta = 13.6^\circ$ corresponds to the 011 reflection of structure B. There is also a peak (4) at $2\theta = 16.2^\circ$ corresponding to the 100 reflection of structure C. Thus, it is likely that this annealed sample contains both B and C structures, with B probably prevailing, yet the d.s.c. curve showed only a single melting peak. This kind of behaviour has been already noted for poly(1,4-phenylene isophthalate) homopolymer.

SUMMARY AND CONCLUSIONS

In the literature concerned with poly(4-oxybenzoate-co-1,4-phenylene isophthalate)s, there are considerable differences in the ways of expressing the composition and in the nomenclature concerning the structures found in these materials. It was therefore necessary to introduce a unified notation. Only then did it become possible to compare the results in the literature. Careful scrutiny of published WAXS patterns showed that in copolymers with [COMCO] ≥ 0.25 , there are only two different crystalline structures, named here as B and C, arising from regular packing of (-OPO-COMCO-) sequences.

In contrast with the literature, it has been possible to establish that both B and C structures can be found in poly(1,4-phenylene isophthalate). Although the WAXS patterns of these structures are very different, it appears that the transformation $B \rightleftharpoons C$ can be achieved by a simple displacement of planes containing a parallel array of (-OPO-COMCO-) sequences.

Detailed investigation of the annealing effects on the structure and melting behaviour of the homopolymer is hindered by the narrow temperature interval between the melting temperature and the onset of severe decomposition. It has been established that coexistence of structures

B and C is not always manifested in separate melting endotherms. It is suggested that any possible differences in melting behaviour of structures B and C are obscured by stronger effects of crystallite size and/or perfection.

In common with other thermotropic copolymers, the melting behaviour of nematogenic poly(4-oxybenzoate-co-1,4-phenylene isophthalate) with [COMCO]=0.33 is strongly influenced by thermal history. Extended annealing of quenched polymer at high temperatures resulted in a substantial increase in melting temperature. Thus, after 18 h at 315°C the melting temperature rose from 332 to 379°C. The resulting melting temperature is only ~30°C lower than that of poly(1,4-phenylene isophthalate) (411°C); the heat of fusion (52 J g⁻¹) is about half of the value obtained for the homopolymer. In contrast with the literature, both B and C structures were found in this annealed unoriented copolymer. It has been established that the changes in melting behaviour caused by annealing can be reversed by remelting. They are therefore primarily due to changes in physical structure rather than due to any changes in chain constitution arising from transesterification.

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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 Johnson, D. J., Karacan, I. and Tomka, J. G. *Polymer* 1990, **31**, 8
- 4 Kiss, G. J. *Rheol.* 1986, **30**, 585
- 5 Hsiao, B. S., Shaw, M. T. and Samulski, E. T. *Macromolecules* 1988, **21**, 543
- 6 Hsiao, B. S., Shaw, M. T. and Samulski, E. T. *J. Polym. Sci., Polym. Phys. Edn* 1990, **28**, 189
- 7 Blundell, D. J., Chivers, R. A. and MacDonald, W. A. *High Perform. Polym.* 1989, **1**, 97
- 8 Tsai, H. B., Lee, C., Chang, N. A., Chen, M. S. and Chang, S. J. *J. Appl. Polym. Sci.* 1990, **40**, 1499
- 9 Tsai, H. B., Lee, C., Chang, N. S., Chang, S. J. and Chen, M. S. *Makromol. Chem.* 1990, **191**, 1301
- 10 Tsai, H. B., Lee, C., Chang, N. S., Lin, F. L., Hsu, H. H. and Hu, A. T. *J. Polym. Sci., Polym. Phys. Edn* 1991, **29**, 893
- 11 Spontak, R. J., Windle, A. H. and MacDonald, W. A. *J. Mater. Sci.* 1991, **26**, 4234
- 12 Economy, J., Storm, R. S., Matkovich, V. J., Cotis, S. G. and Nowak, B. E. *J. Polym. Sci., Polym. Chem. Edn* 1976, **14**, 2207
- 13 Jackson Jr, W. J. *Br. Polym. J.* 1980, **12**, 154
- 14 Brostow, W. *Polymer* 1990, **31**, 979
- 15 Lieser, G. J. *J. Polym. Sci., Polym. Phys. Edn* 1983, **21**, 1611
- 16 Hanna, S. and Windle, A. H. *Polym. Commun.* 1988, **29**, 236
- 17 Coulter, P. D., Hanna, S. and Windle, A. H. *Liq. Cryst.* 1989, **5**, 1603
- 18 Johnson, D. J., Karacan, I. and Tomka, J. G. *Polymer* 1993, **34**, 1749
- 19 Brown, P. J., Karacan, I., Liu, J., McIntyre, J. E., Milburn, A. H. and Tomka, J. G. *Polym. Int.* 1991, **4**, 23
- 20 Hindeleh, A. H., Johnson, D. J. and Montague, P. E. *Am. Chem. Soc. Symp. Ser.* 1983, **141**, 149