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Thermotropic polyesters: synthesis and properties of modified poly(4-oxybenzoate-*co*-1,4-phenylene isophthalate)s

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The constitution of poly(4-oxybenzoate-*co*-1,4-phenylene isophthalate)s, consisting of rod-like 4-oxybenzoyl and 1,4-phenylenedioxy units and angular isophthaloyl units, is modified by gradually replacing (i) the 1,4-phenylenedioxy units with chloro-1,4-phenylenedioxy units, and (ii) the angular isophthaloyl units with rod-like terephthaloyl units. The former modification results in a gradual decrease of the melting temperature, while the latter one has the opposite effect. When both modifications are employed simultaneously, their effects essentially compensate each other. Thus, a fully aromatic nematogenic copolyester consisting of equimolar quantities of rod-like 4-oxybenzoyl, chloro-1,4-phenylenedioxy and terephthaloyl units melts at 313°C, more than 100°C below its thermal stability limit. Although the melting behaviour of the materials investigated is strongly affected by annealing, the changes can be reversed by remelting.

(Keywords: aromatic polyesters; thermotropic; nematic)

INTRODUCTION

Rigid polyesters and copolyesters consisting of unsubstituted 1,4-phenylene groups linked by ester groups are not melt-processable because they do not melt below the onset of thermal decomposition[1]. One of the methods employed successfully for achieving melt-processability is based on partial replacement of the rod-like 4-oxybenzoyl (OPCO), 1,4-phenylenedioxy (OPO) or terephthaloyl (COPCO) units by the corresponding rigid angular units containing 1,3-phenylene groups in place of the 1,4-phenylene groups. Provided that the length of rod-like sequences, consisting of rod-like units and terminated by the angular disruptor units, is sufficient, the resulting copolymers are nematogenic. The mean number of rod-like units in the rod-like sequences $\bar{n}_p$, is[2]:

$$\bar{n}_p = x_p/(1 - x_p) \qquad (1)$$

where x_p is the molar fraction of all the rod-like units, i.e. [OPCO] + [OPO] + [COPCO].

As shown previously[3], the use of angular isophthaloyl units[2,4–11] (COMCO) is advantageous compared with 1,3-phenylenedioxy units[3,12–14] (OMO) or 3-oxybenzoyl units[15,16] (OMCO). It has been established[2,4,7] that poly(4-oxybenzoate-*co*-1,4-phenylene isophthalate)s (POPI), consisting of rod-like OPCO and OPO units and angular COMCO units, are melt-processable nematogenic materials with a sufficiently broad 'processing window' when [COMCO] is between about 0.25 and 0.33 (i.e. $0.67 \leq x_p \leq 0.75$ and $2 \leq \bar{n}_p \leq 4$).

This paper is concerned primarily with the effect of modifications of the constitution of POPIs on the transition temperatures. The modifications employed consisted of:

(i) replacement of angular units (COMCO) with rod-like terephthaloyl units (COPCO); and
(ii) replacement of unsubstituted rod-like OPO units with the corresponding substituted chloro-1,4-phenylenedioxy units (OP(Cl)O).

The combined effect of both of these modifications was also studied. Thus, the materials investigated contained up to four out of the five units shown in *Figure 1*.

Since the transition temperatures and structure of nematogenic copolymers are known to be strongly influenced by thermal history[3,4,17,18], the effects of quenching and annealing were studied for selected materials. The transition temperatures and structures were compared with those of the appropriate parent POPIs and also with those of the relevant parent homopolymers. Five parent homopolymers should be considered (*Table 1*). It should be noted that although the two materials containing OP(Cl)O units are referred to as homopolymers, the locations of chlorine atoms in successive repeating units may differ; it is likely that the chains of these polymers consist of random sequences of units substituted in the 2 and 3 positions. The structure and properties of four of the polymers listed in *Table 1* are described in the

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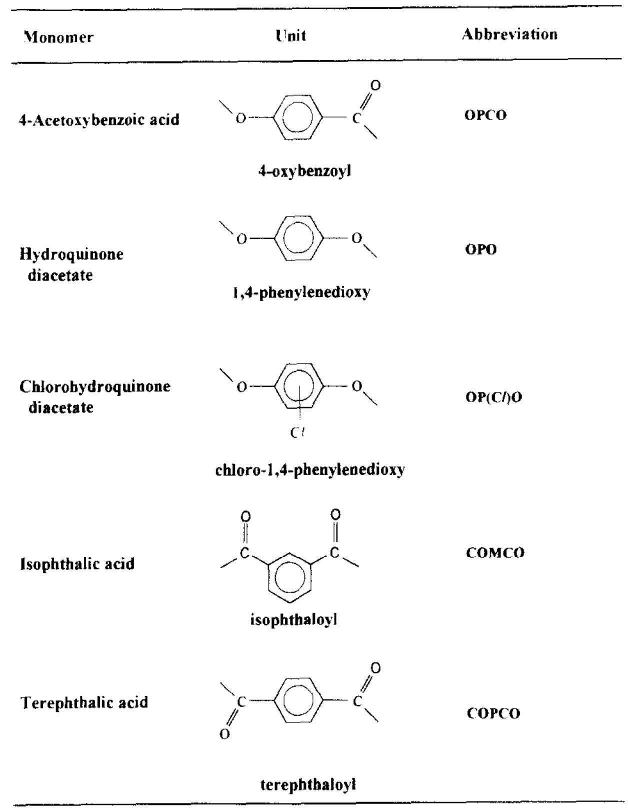

Figure 1 Constituent units of the materials investigated

literature[19–24], but poly(chloro-1,4-phenylene isophthalate) has not been studied previously and its characterization is included in this work.

EXPERIMENTAL

The polymers (*Table 2*) were prepared on a 0.4 mol scale from monomers used previously (4-acetoxybenzoic acid[4], hydroquinone diacetate[4], chlorohydroquinone diacetate[23], isophthalic acid[4] and terephthalic acid[23]) using a procedure described previously[4]. Their solution viscosities were measured at 25°C in a 30/70 (v/v) mixture of trifluoroacetic acid and dichloromethane[4].

Microscopic observations of flow (T_f) and decomposition (T_d) temperatures were carried out using an Olympus polarizing microscope equipped with a Stanton–Redcroft hot stage (type TH600) fitted with nitrogen purge[25]; the heating rate was 20°C min^{-1}. Thermal stability was also assessed by means of a Du Pont 951 Thermogravimetric Analyser controlled by a Thermal Analyst 2000 system. The samples (8–10 mg) were heated (20°C min^{-1}) under nitrogen (50 ml min^{-1}). Temperatures T(5%) correspond to 5% weight loss.

Transition temperatures and enthalpies were determined by differential scanning calorimetry (d.s.c.) using a Du Pont 910 Differential Scanning Calorimeter controlled by a Thermal Analyst 2000 system. The sample weight was approximately 8 mg and the heating rate was 20°C min^{-1}. Quenched samples were obtained by re-melting the encapsulated polymers in the d.s.c. cell (30 s at temperatures 20–40°C above the end of the melting range) and placing them on a steel bar at room temperature. All the annealing treatments were also carried out in the d.s.c. cell.

Wide-angle X-ray scattering (WAXS) patterns were recorded on film in a flat-plate camera using nickel-filtered CuK$_\alpha$ radiation. The intensity traces were obtained from X-ray films using a Quantimet 570 Image Analyzer.

RESULTS AND DISCUSSION

Poly(chloro-1,4-phenylene isophthalate)

As expected, this polymer (*I*) with alternating rod-like OP(Cl)O and angular COMCO units, does not form a nematic mesophase. The flow temperature of the as-made material (T_f = 325°C) is more than 100°C below the thermal stability limit (*Table 3*).

The WAXS pattern of the as-made material shows only a broad halo. The d.s.c. curve (see *Figure 2*) shows a glass transition followed by a crystallization exotherm. The melting endotherm (292–336°C) is preceded by a pre-melting exotherm, indicating that recrystallization takes place during heating. The thermal transitions of samples quenched after remelting at 360°C are similar to those observed for the as-made material, except for the crystallization exotherm which occurs at a slightly higher temperature (see *Figure 2b*). This indicates a reduction in the number of crystallization nuclei resulting from the remelting at 360°C. Details concerning the transition temperatures and enthalpies are given in *Table 3*.

From the evidence obtained, it is concluded that this material forms a conventional non-crystalline glassy solid at temperatures below the glass transition temperature (T_g). However, it crystallizes above T_g.

Annealing experiments were carried out using samples which were first quenched from 360°C to room temperature; after annealing, the samples were again quenched. The d.s.c. curves of samples annealed at temperatures between 280 and 300°C show a single melting endotherm (*Figures 2c–2e*). As expected, the melting peak temperatures (T_m) increase with increasing annealing temperature (T_a) and time (t_a), reaching T_m = 329°C for T_a = 300°C and t_a = 240 min (*Table 4*). Samples annealed at 310°C show melting endotherms with two peaks (*Figure 2f*); the upper peak is obviously

Table 1 Parent homopolymers (for abbreviations see *Figure 1*)

Polymer	Repeating unit	Melting behaviour[a]	Ref.
Poly(4-oxybenzoate)	–OPCO–	Decomposition	1,19,20,21
Poly(1,4-phenylene terephthalate)	–OPO–COPCO–	Decomposition	1,21
Poly(1,4-phenylene isophthalate)	–OPO–COMCO–	T_{CI} = 388–410°C	18
Poly(chloro-1,4-phenylene terephthalate)	–OP(Cl)O–COPCO–	T_{CN} = 355–372°C	22,23,24
Poly(chloro-1,4-phenylene isophthalate)	–OP(Cl)O–COMCO–	T_{CI} = 315–329°C	This work

[a] T_{CI} = crystal–isotropic melt transition temperature; T_{CN} = crystal–nematic mesophase transition temperature

Table 2 Composition of polymers expressed in terms of molar fractions of constituent units (for abbreviations see *Figure 1*) and their melting behaviour; T_m is the melting peak temperature, ΔH is the heat of fusion

				Composition				
Polymer	$[\eta]$ (dl g^{-1})	T_m (°C)	ΔH (J g^{-1})	[OPCO]	[OPO]	[OP(Cl)O]	[COMCO]	[COPCO]
I	0.65	315	40	0	0	0.500	0.500	0
II	1.54	374	10	0.500	0.250	0	0.250	0
III	1.94	404	–	0.500	0.250	0	0.234	0.016
IV	2.46	463[b]	–	0.500	0.250	0	0.219	0.031
V	[a]	477[b]	–	0.500	0.250	0	0.187	0.063
VI	[a]	500[b]	–	0.500	0.250	0	0.125	0.125
VII	0.69	338[c]	21	0.333	0.333	0	0.333	0
VIII	0.75	287	13	0.333	0.232	0.102	0.333	0
IX	0.54	268	12	0.333	0.167	0.167	0.333	0
X	0.56	255	11	0.333	0.102	0.232	0.333	0
XI	0.52	236	10	0.333	0	0.333	0.333	0
XII	0.63	240	7	0.333	0	0.333	0.282	0.052
XIII	[a]	246	5	0.333	0	0.333	0.232	0.102
XIV	[a]	313	18	0.333	0	0.333	0	0.333

[a] Insoluble in trifluoroacetic acid/dichloromethane (30/70) mixture
[b] Above the thermal stability limit
[c] Quenched polymer showed a double melting endotherm, peak temperatures 302 and 332°C, $\Delta H = 16 \pm 2$ J g^{-1}

Table 3 Thermal transitions and stability of poly(chloro-1,4-phenylene isophthalate); d.s.c. data are mean values obtained from 20 runs

Transition	As-made	Quenched[a]
Flow temperature (°C)	325	325
Glass transition		
Range (°C)	138–157	143–157
T_g (°C)	147 ± 2	149 ± 2
ΔC_p (J g^{-1} K^{-1})	0.20 ± 0.08	0.25 ± 0.06
Crystallization exotherm		
Range (°C)	170–235	193–240
Peak (°C)	205 ± 2	216 ± 2
ΔH (J g^{-1})	25 ± 3	29 ± 3
Premelting exotherm		
Range (°C)	266–292	273–294
Peak (°C)	281 ± 1	284 ± 1
ΔH (J g^{-1})	4 ± 1	4 ± 1
Melting endotherm		
Range (°C)	292–336	294–330
Peak (°C)	315 ± 1	314 ± 1
ΔH (J g^{-1})	40 ± 2	38 ± 2
Thermal stability		
T_d (°C)	445	–
T (5%)	446	–

[a] After remelting at 360°C for 30 s

due to the melting of the crystallites formed during annealing. It should be noted that annealing at temperatures between 280 and 310°C eliminated the endothermic step arising from the glass transition. The d.s.c. curve of a sample annealed at 320°C, i.e. above the T_m of the crystallites formed during the heating of the quenched material, is similar to that of the quenched material; it shows a glass transition followed by a crystallization exotherm (*Figure 2g*). This annealing temperature is evidently too high for the formation of crystallites. *Figure 3* shows plots of (T_m–T_a) *versus* T_a for t_a = 10, 30 and 100 min. This is a modified version of a Hoffman

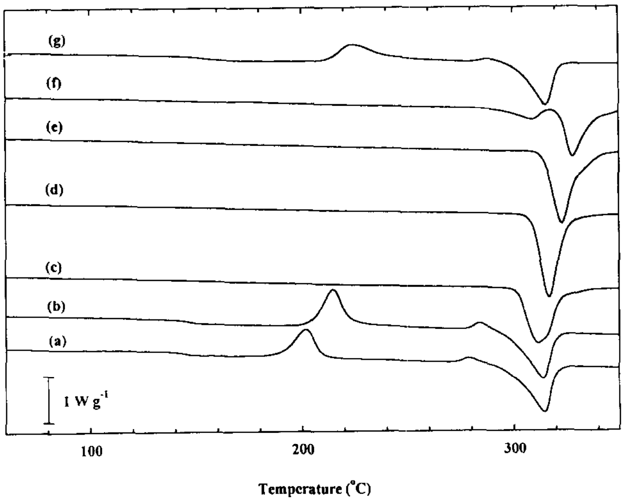

Figure 2 D.s.c. curves of poly(chloro-1,4-phenylene isophthalate) (*I*): (a) as-made; (b) quenched; (c) annealed at 280°C for 30 min; (d) annealed at 290°C for 30 min; (e) annealed at 300°C for 30 min; (f) annealed at 310°C for 30 min; (g) annealed at 320°C for 30 min

Table 4 Effect of annealing temperature (T_a) and time (t_a) on the melting endotherm features of poly(chloro-1,4-phenylene isophthalate)

		Endotherm		
T_a (°C)	t_a (min)	Range (°C)	Peak (°C)	ΔH (J g^{-1})
280	30	295–345	311	50
290	30	294–344	316	56
300	1	286–329	315	41
300	10	301–334	317	44
300	30	298–352	323	55
300	30	275–355	323	56
300	100	304–356	326	47
300	240	306–371	329	63
310	10	275–346	311, 324	44
310	30	269–360	309, 328	51
310	100	267–372	302, 331	39
320	30	288–331	315	35

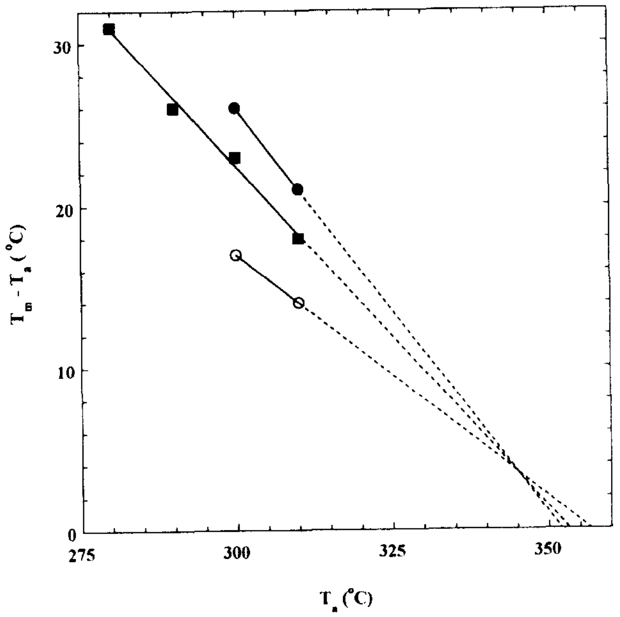

Figure 3 Effect of annealing temperature, T_a, and annealing time, t_a, on melting behaviour of poly(chloro-1,4-phenylene isophthalate) (*I*): ○, t_a = 10 min; ■, t_a = 30 min; ●, t_a = 100 min

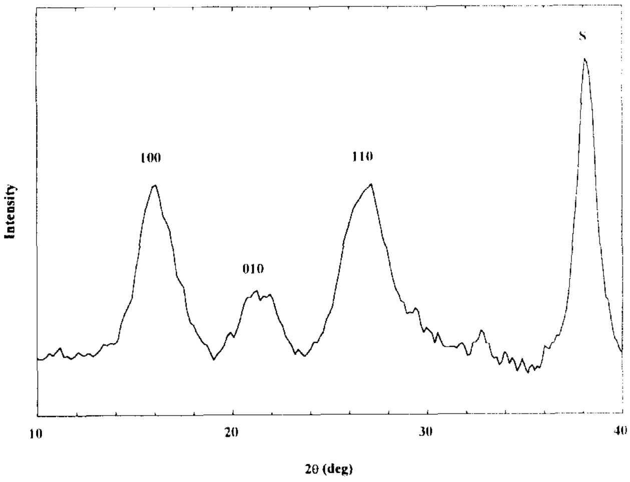

Figure 4 WAXS trace of poly(chloro-1,4-phenylene isophthalate) (*I*) annealed at 300°C for 240 min; s, silver reflection used for calibration

Table 5 Prominent wide-angle X-ray reflections of poly(chloro-1,4-phenylene isophthalate) (*I*) and modified POPIs containing OP(Cl)O units (*IX*, *XI*) in comparison with those of structure C (ref. 14) of poly(1,4-phenylene isophthalate); annealing conditions: temperature T_a, time t_a

Polymer	T_a (°C)	t_a (min)	*d*-spacing (nm) 1 0 0	0 1 0	1 1 0
Structure C	–		0.558	0.392	0.321
I	300	240	0.561	0.413	0.333
IX	280	1000	0.561	0.393	0.322
XI	240	1080	0.561	0.418	0.335

plot[26] used for estimating the equilibrium melting temperature (T_m^0); the intercept with the horizontal axis (corresponding to (T_m−T_a)= 0) should yield T_m^0. The data for all three annealing times give similar intercept values, 357, 354 and 352°C. Thus, the estimated equilibrium melting temperature is 354 ± 3°C, which is about 25°C above the highest observed T_m.

Comparison with the results for the corresponding unsubstituted polymer, poly(1,4-phenylene isophthalate), shows that the introduction of the chlorine substituent reduced the melting temperature by 70–80°C (*Table 1*). Similar decreases in melting temperatures due to chlorine substituents have been found for other semirigid polyesters[24,27]. In contrast, in a rigid polyester the effect of chlorine is much more pronounced; the melting temperature of poly(chloro-1,4-phenylene terephthalate) is 355–372°C, whilst that of poly(1,4-phenylene terephthalate) is more than 600°C.

A scan of the wide-angle X-ray film of a sample annealed at 300°C for 240 min is shown in *Figure 4* and the *d*-spacings of the prominent reflections are listed in *Table 5*; additional weak reflections visible on the film have *d*-spacings of about 1.2, 0.30 and 0.27 nm. The WAXS pattern is similar to that of one of the poly(1,4-phenylene isophthalate) polymorphs[18], structure C, found initially in POPI fibres[2,14]; the prominent reflections of poly(chloro-1,4-phenylene isophthalate) were therefore indexed accordingly.

The *d*-spacings of the 1 0 0 reflections are practically identical in the substituted and unsubstituted polymer, but those of the 0 1 0 and 1 1 0 reflections increased in the substituted polymer (*Table 5*). This corresponds to a relatively small increase of chain cross-sectional area, from 0.220 to 0.232 nm^2. The similarity of chain packing in poly(chloro-1,4-phenylene isophthalate) and poly(1,4-phenylene isophthalate) is in agreement with that established previously[24] for poly(chloro-1,4-phenylene terephthalate) and poly(1,4-phenylene terephthalate).

*Modified poly(4-oxybenzoate-*co*-1,4-phenylene isophthalate)s*

All the polymers (*Table 2*) showed good thermal stability, as expected for fully aromatic polyesters. The decomposition temperatures T_d, determined by hot-stage optical microscopy, were between 435 and 480°C, with a mean value of 454 ± 14°C. The temperatures of 5% weight loss, *T* (5%), determined by thermogravimetric analysis (t.g.a.), were between 445 and 474°C, with a mean value of 459 ± 10°C.

The first series of modified polymers (*III–VI*) is derived from POPI with [COMCO] = 0.25 (polymer *II*) by a partial replacement of angular COMCO units with rod-like COPCO units. The number of constituent units increased from three to four. This modification caused substantial increases of melting temperatures (*Table 2*). The melting endotherms were very broad and small; their end temperatures overlapped with the onset of decomposition. None of these polymers is therefore suitable for melt-processing. The observed melting temperatures are about the same as those obtained for unmodified POPIs with a corresponding concentration of the rod-like units[4,7]. The effect of increased chain rigidity is obviously very much stronger than that of the randomization due to an increase in the number of constituent units.

The second series (polymers *VIII–XI*) is derived from POPI with [COMCO] = 0.33 (polymer *VII*); the rod-like OPO units are gradually replaced by substituted OP(Cl)O units. The melting peak temperatures, T_m, and the heats of fusion determined by d.s.c. decreased gradually with increasing [OP(Cl)O] (*Table 2*). The end temperatures of the melting endotherms were about 25°C above T_m. The flow temperatures, T_f, were close to T_m and in all cases a nematic mesophase was formed above T_f. Complete replacement of OPO units with OP(Cl)O units (polymer *XI*) caused a decrease of melting temperature by about 100°C; the heat of fusion decreased from 21 to $10\,J\,g^{-1}$.

Except for the unmodified POPI (polymer *VII*, *Table 2*), quenching from temperatures about 60°C above T_m did not significantly affect the melting behaviour of these materials. All the quenched samples displayed a glass transition, decreasing from 136 ± 2°C for unsubstituted polymer *VIII* to 127 ± 2°C for polymer *XI*; the ΔC_p values were about $0.17 \pm 0.04\,J\,g^{-1}\,K^{-1}$.

Polymer *XI*, poly(4-oxybenzoate-*co*-chloro-1,4-phenylene isophthalate) with [OPCO] = [OP(Cl)O] = [COMCO] = 0.333, melts at a sufficiently low temperature ($T_m = 236$°C, $T_f = 240$°C) to be considered as a processing aid for conventional linear flexible chain polymers[25]. It was therefore selected for more detailed investigation.

The third series is derived from polymer *XI*. As in the first series, the rigid angular COMCO units are gradually replaced by rod-like COPCO units (polymers *XII–XIV*). As expected from the results of the first series, this caused a gradual increase of melting temperatures. However, in this case the polymers with four constituent units (*XII* and *XIII*) showed the lowest heats of fusion (*Table 2*). All the polymers were nematogenic and the flow temperatures were again close to the endotherm peak temperatures, T_m.

The last member of this third series (*XIV*) consists entirely of rod-like units ([OPCO] = [OP(Cl)O] = [COPCO] = 0.333), and yet its melting temperature ($T_m = 313$°C, $T_f = 320$°C) is lower than that of unmodified POPI (*VIII*) with [COMCO] = 0.333. This polymer, poly(4-oxybenzoate-*co*-chloro-1,4-phenylene terephthalate), therefore warrants further investigation.

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

The effect of annealing temperatures, T_a, between 170 and 270°C on the melting behaviour of polymer *XI*, with [COMCO] = [OP(Cl)O] = [COMCO] = 0.333, was first evaluated using a constant annealing time of 30 min. All the samples were first remelted at 295°C and quenched to room temperature. D.s.c. curves obtained for T_a between 170 and 200°C show two melting endotherms (*Table 6*). The upper endotherm corresponds to that found in the quenched sample; its peak temperature is around 238°C. The peak temperature of the second endotherm is about 23°C above the annealing temperature. Samples annealed at 220–240°C display a single endotherm, which is again about 23°C above T_a. Samples annealed at 250 and 270°C show only the endotherm found in the quenched material. All the annealed samples show a glass transition at around 127°C; those annealed at $T_a \geq 220$°C also show a small and broad crystallization exotherm between 140 and 190°C ($\Delta H = 2 \pm 1\,J\,g^{-1}$) which is also found for the quenched polymer.

For $t_a = 30$ min, the maximum melting peak temperature of 264°C is reached at $T_a = 240$°C (*Table 6*). It should be noted that this most effective annealing temperature is above the melting peak temperature of the quenched material, but below the end temperature of its melting endotherm. Thus, at 240°C most of the polymer is present as a nematic melt.

Table 6 Effect of annealing temperature (T_a) and time (t_a) on the melting endotherm features of polymer *XI*

		Endotherm		
T_a (°C)	t_a (min)	Range (°C)	Peak (°C)	ΔH ($J\,g^{-1}$)
Quenched[a]		207–255	236	7
170	30	182–257	193–236	11
190	30	201–257	214–238	11
200	30	206–257	223–240	11
210	30	219–259	234	10
220[a]	1	219–258	234	7
220[a]	30	224–259	242	11
220	1080	248–297	269	20
230[a]	30	232–267	253	8
240[a]	1	213–260	234–252	7
240[a]	10	211–270	230–258	6
240[a]	100	203–295	245–273	10
240	1080	257–323	293	19
250[a]	30	210–252	233	7
270[a]	30	202–253	234	6

[a] D.s.c. curves show a small and broad crystallization exotherm between 140 and 190°C ($\Delta H = 2 \pm 1\,J\,g^{-1}$)

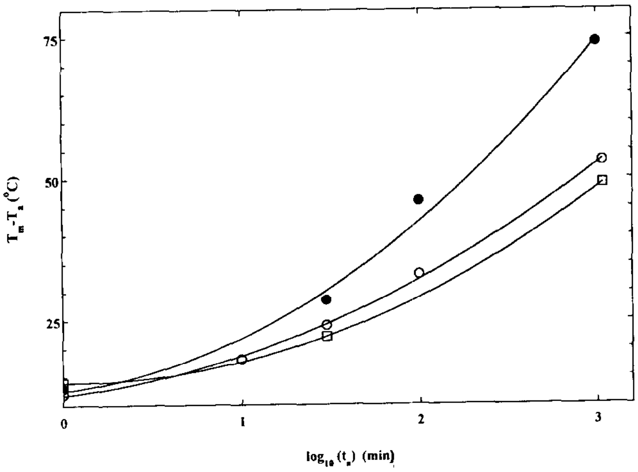

Figure 5 Effect of annealing time, t_a, on melting behaviour: ●, polymer *IX* at 280°C; ○, polymer *XI* at 240°C; □, polymer *XI* at 220°C

An increase in annealing time at 240°C results in further increases of the peak temperatures of the 'variable' melting endotherm (*Table 6* and *Figure 5*). After 1080 min the melting endotherm found in the quenched material is no longer present and the melting peak temperature increases to $T_m = 293$°C (i.e. $(T_m - T_a) = 53$°C); the heat of fusion increases from 7 to $19\,J\,g^{-1}$. Similar increases in melting temperature are also obtained at $T_a = 220$°C (*Table 6* and *Figure 5*); after 1080 min the melting temperature increases to 269°C (i.e. $(T_m - T_a) = 49$°C) and $\Delta H = 20\,J\,g^{-1}$, which is about one-third of the value obtained for annealed poly(chloro-1,4-phenylene isophthalate) (*Table 4*). It should be noted that all the annealed samples still show the glass transition, although extensive annealing caused a decrease of ΔC_p.

Although both the as-made and quenched polymer are semicrystalline, as evidenced by d.s.c., their WAXS patterns did not show any discrete reflections. This is obviously due to the small size and imperfection of the crystallites present in these materials. However, WAXS of an annealed sample revealed reflections with *d*-spacings similar to those found for the parent homopolymer, poly(chloro-1,4-phenylene isophthalate) (*Table 5*). This is analogous to the previously established[18] behaviour of the corresponding unsubstituted polymer *VII* with [OPCO] = [OPO] = [COMCO] = 0.333.

The results obtained show that by an extensive heat treatment of polymer *XI* at a suitable temperature, it is possible to increase its melting temperature by about 55°C. The crystallites formed are due to a regular packing of –(OP(Cl)O–COMCO)– unit sequences corresponding to the parent homopolymer (*I*).

Lenz *et al.*[28] noted that in some copolyesters, extensive heat treatment in the liquid state causes a crystallization-induced derandomization. In order to check this possibility, a sample of polymer *XI* annealed for 100 min at 240°C (T_m = 273°C) was remelted at 295°C and quenched. The melting behaviour reverted to that found for the as-made or quenched material. Thus, the observed changes in the melting behaviour of this polymer, prepared in the absence of catalyst, cannot be ascribed to a reorganization of unit sequences. The same conclusion has been reached[18] for poly(4-oxybenzoate-*co*-1,4-phenylene isophthalate).

Although several similarities between the behaviour of substituted polymer *XI* and the corresponding unsubstituted POPI (polymer *VII*) have been noted, there is one significant difference. In the case of the unsubstituted polymer *VII*, the difference ($T_m - T_a$) for a given annealing time decreased with increasing annealing temperature[18]. This behaviour, also observed here for poly(chloro-1,4-phenylene isophthalate) (*Figure 3*), is typical and can be used for estimating the equilibrium melting temperature. In contrast, in the case of the substituted polymer *XI*, the difference between the peak temperature of the variable melting endotherm and the annealing temperature remained essentially constant for a given annealing time. *Figure 5* indicates that, within the limits of experimental error (±3°C), this seems to apply to a range of annealing times up to 1000 min. Although this behaviour is unusual, it is not unique; it has been noted previously[3] for poly(4-oxybenzoate-*co*-1,3-phenylene terephthalate)s.

Since polymer *IX*, with [OPCO] = [COMCO] = 0.333 and [OPO] = [OP(Cl)O] = 0.167, is effectively an equimolar combination of polymers *VII* and *XI*, it was of interest to evaluate the effect of annealing on its melting behaviour. For t_a = 30 min and T_a between 230 and 280°C, the difference between the 'variable' melting endotherm peak temperatures and annealing temperatures remained essentially constant, $(T_m - T_a) = 29 \pm 2$°C. A sample annealed at 290°C showed only the endotherm found in the quenched material ($T_m = 269 \pm 1$°C). Increases in annealing time at 280°C (i.e. above T_m of the quenched sample) resulted in increases in melting temperature (*Figure 5*), and after 1080 min the melting temperature reached a value of 354 ± 2°C (*Table 7*), which is 85°C above T_m of the quenched sample. It should be noted that this melting temperature exceeds that observed for annealed poly(chloro-1,4-phenylene isophthalate) (*Table 4*) and it is close to its estimated equilibrium melting temperature, T_m^0. Evidently, the crystallites formed in polymer *IX* must consist of unsubsituted –(OPO–COMCO)– sequences. In confirmation, the WAXS pattern of an annealed sample revealed reflections assigned to structure C of poly(1,4-phenylene isophthalate) (*Table 5*). Nevertheless, the response of polymer *XI* to annealing is of the same type as observed for the substituted polymer *XI*.

Table 7 Thermal transitions of annealed polymers

	VII[a]	*IX*	*XI*	*XIV*
Annealing conditions				
T_a (°C)	315	280	240	310
t_a (min)	1080	1000	1080	1000
Glass transition				
T_g (°C)	[b]	136	140	[b]
ΔC_p (J g^{-1} K^{-1})	[b]	0.17	0.10	[b]
Melting endotherm				
Peak (°C)	379	354	293	337
End (°C)	403	365	323	348
ΔH (J g^{-1})	52	16	19	25

[a] Data from ref. 18

[b] Not detected

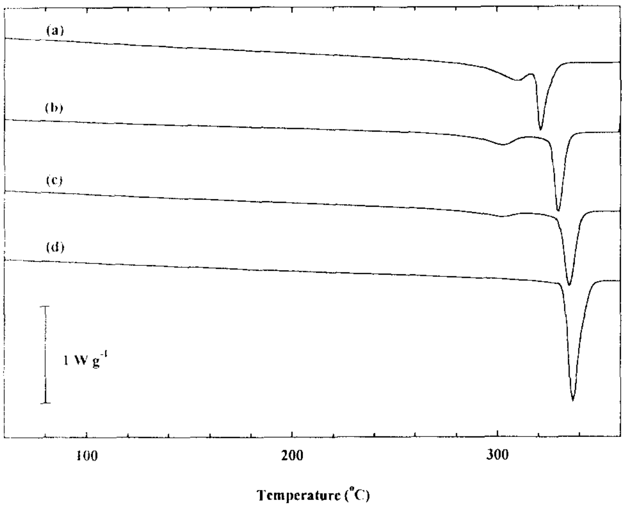

Figure 6 D.s.c. curves of poly(4-oxybenzoate-*co*-chloro-1,4-phenylene terephthalate) (*XIV*) annealed at 310°C: (a) 1 min; (b) 30 min; (c) 100 min; (d) 1000 min

*Poly(4-oxybenzoate-*co*-chloro-1,4-phenylene terephthalate)*

As already noted, this polymer (*XIV*) consists entirely of rod-like units. Since the melting temperature of the as-made polymer is more than 100°C below the thermal stability limit, it may be a useful melt-processable material.

The WAXS pattern of the as-made material shows that it is semicrystalline. The prominent reflection with a *d*-spacing of 0.434 nm corresponds to the 1 1 0 reflection of poly(chloro-1,4-phenylene terephthalate)[24]; two weaker reflections (0.32 and 0.26 nm) can also be assigned to this homopolymer. There is also a strong reflection with a *d*-spacing of 0.46 nm, corresponding to 1 1 0 reflections in high-temperature modifications[21] of both poly(4-oxybenzoate) and poly(1,4-phenylene terephthalate). In polymer *XIV* it probably arises from pseudohexagonal packing of sequences of unsubstituted OPCO and COPCO units.

It has been found that quenching from 360°C did not significantly affect the melting behaviour or the crystalline structure of this polymer. On the basis of preliminary experiments, a temperature of 310°C was selected for the investigation of annealing. *Figure 6* shows that, as expected, the peak temperature of the 'variable' endotherm increases with increasing annealing time, while the endotherm present in the quenched material is gradually eliminated. Note that none of the samples shows a glass transition. After 1000 min the melting temperature increased from 313 to 337°C (*Table 7*). The structure of this annealed sample was similar to that of the as-made material.

Although the increase in T_m (24°C) is much lower than those obtained for polymers *IX* and *XI* (85 and 55°C, respectively), it should be noted that the melting temperature of the sample annealed for 1000 min at 310°C is only 20–30°C lower than that of poly(chloro-1,4-phenylene terephthalate).

CONCLUSIONS

In poly(4-oxybenzoate-*co*-1,4-phenylene isophthalate), replacement of 1,4-phenylenedioxy (OPO) units with substituted chloro-1,4-phenylenedioxy (OP(Cl)O) units causes a gradual decrease in melting temperature. No minimum in the melting temperature resulting from partial replacement has been detected. This is ascribed to similar chain packing of sequences containing the substituted OP(Cl)O and unsubstituted OPO units, as shown by the similar crystalline structures of poly(chloro-1,4-phenylene isophthalate) and poly(1,4-phenylene isophthalate).

Polymer *XI*, consisting of equimolar quantities of 4-oxybenzoyl (OPCO), chloro-1,4-phenylenedioxy (OP(Cl)O) and isophthaloyl (COMCO) units, melts at a sufficiently low temperature (236°C) to be considered as a processing aid for conventional linear flexible chain polymers.

Partial replacement of angular COMCO units with rod-like terephthaloyl (COPCO) units causes an increase in melting temperature, in spite of an increase in the number of constituent units from three to four. Evidently, the effect of increased chain rigidity is more important than that of randomization.

When both modifications are employed simultaneously, their effects essentially compensate each other. A fully aromatic nematogenic copolyester *XIV*, consisting of equimolar quantities of rod-like OPCO, OP(Cl)O and COPCO units, melts at 313°C, more than 100°C below the onset of thermal decomposition. It is therefore a melt-processable rod-like copolyester.

The melting behaviour of the materials investigated is strongly influenced by annealing. The most pronounced increases in melting temperature are achieved when the polymer is partially in a molten state (i.e. as a nematic mesophase). Thus, for polymer *IX* ([OPCO] = [COMCO] = 0.333, [OPO] = [OP(Cl)O] = 0.167) the melting temperature increased by as much as 85°C after prolonged annealing (1080 min) at the optimum annealing temperature.

The changes in melting behaviour resulting from annealing can be reversed by remelting. They are therefore due to increased size and/or perfection of the crystallites rather than due to crystallization-induced derandomization.

As in the case of unmodified poly(4-oxybenzoate-*co*-1,4-phenylene isophthalate)s, the crystalline structures formed in the modified polymers correspond to those of the parent homopolymers.

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