

Thermotropic polyesters: synthesis and properties of poly(chloro-1,4-phenylene terephthalate-co-4,4'-hexamethylenedioxy-bisbenzoate)s

J. E. McIntyre, P. E. P. Maj* and J. G. Tomka†

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

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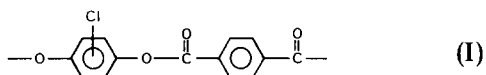
Poly(chloro-1,4-phenylene terephthalate-co-4,4'-hexamethylenedioxy-bisbenzoate)s are synthesized and the effect of composition on thermal transitions is evaluated. The materials are nematogenic throughout the whole composition range. The transition of the solid copolymers into nematic liquids is a complex process, ultimately involving melting of crystalline regions consisting of ester-linked 1,4-phenylene moieties. Comparison of a 50/50 copolymer with a corresponding poly(chloro-1,4-phenylene terephthalate-co-4,4'-oxybisbenzoate), which contains an ether oxygen disruptor in place of a hexamethylenedioxy flexible spacer, shows that the latter is, in all aspects, a more promising material for producing high performance load-bearing mouldings and fibres.

(Keywords: aromatic polyesters; thermotropic; nematic; liquid crystalline; transition temperatures; mouldings)

INTRODUCTION

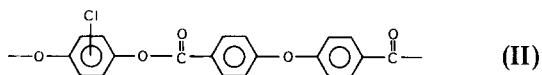
The current interest in main chain thermotropic nematogenic polymers stems mainly from their practical importance as new engineering materials for production of mouldings with unique properties¹⁻⁴. Several nematogenic copolyesters have already been commercialized. These materials are also potentially useful for manufacture of high-strength high-modulus fibres. Moreover, a systematic investigation of the phase transitions and the physical structure of these materials is of importance in order to expand our knowledge of self-assembling polymers.

The materials described in this paper are based on a rigid-chain nematogenic polymer, poly(chloro-1,4-phenylene terephthalate) (I).



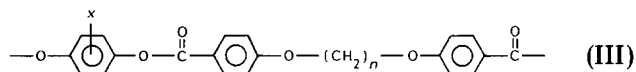
Although its melting temperature (340–372°C (refs 5, 6)) is reduced substantially compared with unsubstituted poly(1,4-phenylene terephthalate) (melting temperature *c.* 600°C (ref. 7)), it is still considered to be rather high for successful melt processing.

Our previous work⁶ showed that by partly replacing the terephthalic acid by 4,4'-oxybisbenzoic acid, i.e. by introducing angular ether oxygen units into the rigid chain of poly(chloro-1,4-phenylene terephthalate), it was possible to obtain nematogenic copolymers (I-co-II)



with melting temperatures less than 300°C. Compositions with molar fraction of units (II) ranging from 0.25 to 0.75 gave a nematic temperature interval in excess of 100°C which is sufficient for melt processing. Fibres and mouldings from selected compositions were prepared and characterized⁸.

The work reported here involves modification of the poly(chloro-1,4-phenylene terephthalate) by means of a hexamethylenedioxy flexible spacer. The copolymers investigated consist of repeating units A (I) and B (III, X = Cl, n = 6). The homopolymer consisting of B units was also included in our investigation.



Mesogenic homopolymers containing flexible spacers have been the subjects of numerous studies but the corresponding copolymers have so far received much less attention⁹. It seems to be accepted that copolymerization resulting in differences in the length either of the flexible spacer or of the rigid mesogen, or of both, suppresses the tendency to form a smectic mesophase^{9,10}.

In the materials described in this paper the rigid mesogenic sequences are terminated by hexamethylenedioxy units. In poly(chloro-1,4-phenylene 4,4'-hexamethylenedioxybisbenzoate) each mesogenic sequence contains three 1,4-phenylene moieties. As the molar fraction of B units ([B]) decreases, there is an increase in the number, n_p , of 1,4-phenylene moieties linked to each other only through ester groups and therefore forming the mesogenic sequences. The mean value, \bar{n}_p , is related to [B] as follows

$$\bar{n}_p = (2 + [B])/[B] \quad (1)$$

(see Table 1). However, individual mesogenic sequences in

* Present address: ATOCHEM, 27470 Serquigny, France

† To whom correspondence should be addressed

Table 1 Effect of composition expressed as molar fraction of B units ([B]) on the mean number of 1,4-phenylene moieties in the mesogen (\bar{n}_p) and on polymer properties determined by the hot-stage optical microscopy: T_f , flow temperature (heating rate 6°C min^{-1}); T_i , isotropization temperature (heating rate $30^\circ\text{C min}^{-1}$); T_d , onset of decomposition (heating rate $30^\circ\text{C min}^{-1}$)

[B]	\bar{n}_p	$[\eta]$ (dl g^{-1})	T_f ($^\circ\text{C}$)	T_i ($^\circ\text{C}$)	T_d ($^\circ\text{C}$)
0	^a	Insoluble	350	–	450
0.25	9.00	0.34	278	–	400
0.30	7.67	0.32	275	–	390
0.40	6.00	0.33	258	–	420
0.50	5.00	0.35	260	–	420
0.60	4.33	0.36	260	410	390
0.75	3.67	0.32	250	395	380
1.00	3.00	0.28	265	372	390

^a Whole chain length

a copolymer always contain an odd number of 1,4-phenylene moieties (e.g. 7 for –BAAB–).

The main objectives are to establish the effect of copolymer composition on the nematic temperature range and to compare the effect of the flexible hexamethylenedioxy spacer with that of the ether oxygen disruptor.

EXPERIMENTAL

Monomers

The purification and purity assessment of chlorohydroquinone diacetate have been described previously⁶.

Terephthalic acid of fibre-grade purity (supplied by ICI Plc) was used without further purification.

The dimethylester of 4,4'-hexamethylenedioxy-bisbenzoic acid was prepared from the sodium salt of methyl-4-hydroxybenzoate and 1,6-dibromohexane in absolute ethanol¹¹. The ester (m.p. 118°C) was dissolved in 2-methoxyethanol and hydrolysed using a solution of potassium hydroxide in methanol. The product was dissolved in hot water and acidified with diluted sulphuric acid. The precipitate was filtered off, washed, and dried. The product recrystallized from dimethylacetamide/water had a m.p. of 305°C (in ref. 11 290 – 292°C).

Polymer preparation

Polymers were prepared at 282°C , without added catalyst, from a mixture of diacids (0.01 mole total) and an equimolar quantity of chlorohydroquinone diacetate⁶. The reaction mixture was maintained for 1 h under atmospheric pressure and then for 1 h at reduced pressure (0.2 mmHg).

Larger quantities of the copolymer [B]=0.50 were prepared on a 0.4 mole scale using a 2% excess of chlorohydroquinone diacetate. The reaction was carried out at 285°C as previously described⁶.

Polymer characterization

Solution viscosities of polymers were measured in *p*-chlorophenol at 45°C . Microscopic observations were carried out using a polarizing microscope equipped with a Stanton–Redcroft hot-stage (Type TH 600) fitted with nitrogen purge. Transition temperatures and enthalpies were determined using a DuPont 990/910 Differential Scanning Calorimeter at a heating rate of $20^\circ\text{C min}^{-1}$ (sample weight 6–8 mg). The glass transition temperature

of the copolymer [B]=0.50 was determined using a Perkin-Elmer DSC 2 at a heating rate of $10^\circ\text{C min}^{-1}$. The apparent melt viscosities were measured with an Instron capillary rheometer (capillary diameter 0.765 mm, length 25.5 mm).

Melt spinning was carried out using a hydraulically operated rod-spinning machine⁸. Procedures for the production and characterization of mouldings have been described previously⁸.

RESULTS AND DISCUSSION

Effect of composition on polymer properties: preliminary observations

With the exception of the homopolymer poly(chloro-1,4-phenylene terephthalate) ([B]=0) all the polymers investigated (Table 1) remained liquid after the completion of the polymerization at 282°C and exhibited stir opalescence indicative of a nematic mesophase. The intrinsic viscosities of these polymers were around 0.3 dl g^{-1} , similar to the values usually achieved for other polymers containing flexible spacers⁹.

The wide angle X-ray (WAXR) patterns¹² indicated the presence of some ordered structures in all the 'as made' materials. As expected, the highest degree of order was found in the two homopolymers. The diffractometer traces of copolymers with [B] \geq 0.50 were similar to those of the homopolymer [B]=1.00. The trace of the copolymer [B]=0.25 indicated only a poor degree of order with few sharp peaks. However, a reflection with a *d*-spacing of 0.63 nm, present in the rigid chain homopolymer ([B]=0) but absent in the homopolymer containing the flexible spacer ([B]=1.00), was found in the traces of all the copolymers investigated. The *d*-spacing of this reflection corresponds to the distance between the centres of 1,4-phenylene groups linked by an ester group, i.e. to half the length of the repeating unit of the homopolymer [B]=0.

The temperature of the onset of decomposition observed by hot-stage optical microscopy at a heating rate of $30^\circ\text{C min}^{-1}$ decreased from 450°C for the homopolymer [B]=0 to $400 \pm 15^\circ\text{C}$ for the materials containing the flexible spacer (Table 1). This compares unfavourably with the stability limit of $425 \pm 10^\circ\text{C}$ found for copolymers (I-co-II) containing an ether oxygen atom⁶. Thus, the presence of the aliphatic spacer has a noticeable effect on the thermal stability.

The temperatures of the onset of flow T_f are listed in Table 1. Thread-like textures typical of a nematic mesophase were observed in all the materials approximately 5 – 10°C above T_f . Incorporation of B units into the rigid chain of poly(chloro-1,4-phenylene terephthalate) resulted initially in a substantial reduction of T_f but a further increase of [B] caused only a much smaller change. As expected, the isotropization temperature increased with increasing chain rigidity (Figure 1).

These observations indicate that the materials investigated are nematogenic. Incorporation of the flexible spacer into the rigid chain of poly(chloro-1,4-phenylene terephthalate) results in a substantial decrease of the flow temperature, but also reduces the thermal stability.

Phase transitions of the homopolymers

The phase transitions of poly(chloro-1,4-phenylene terephthalate) ([B]=0) have been discussed previously⁶.

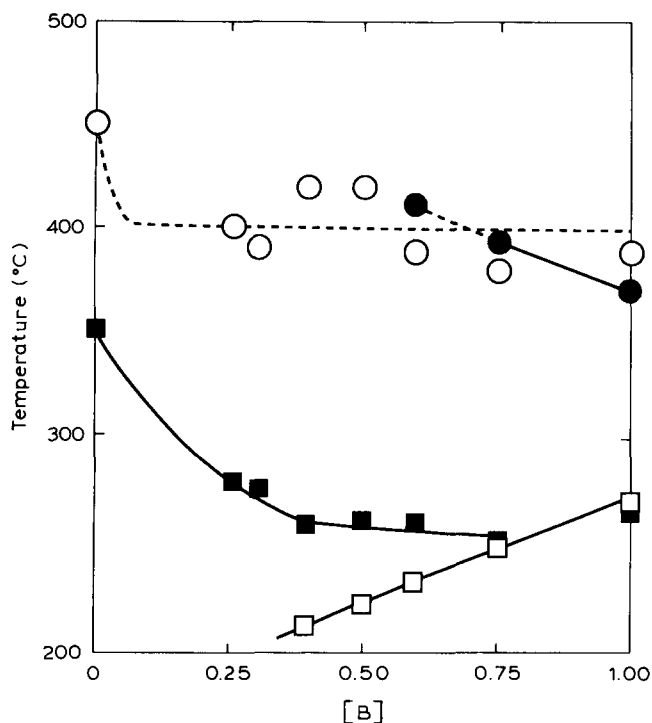


Figure 1 Effect of composition on decomposition temperature T_d (○), isotropization temperature T_i (●), flow temperature T_f (■), end temperature of the endotherm assigned to melting of B-type crystallites T_c^B (□)

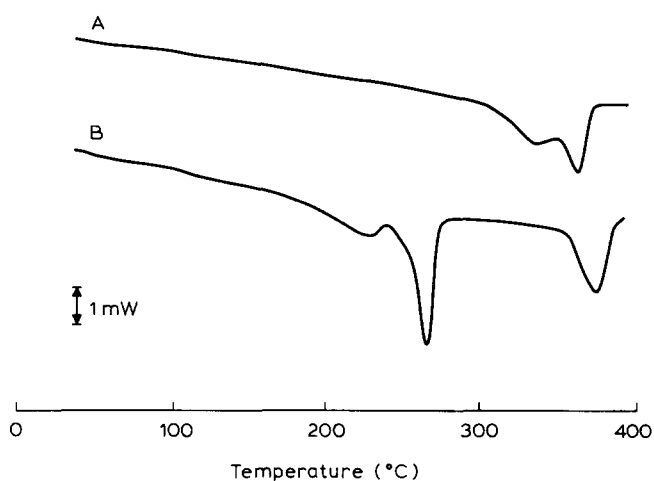


Figure 2 D.s.c. curve of poly(chloro-1,4-phenylene terephthalate) (A), after quenching from 390°C, and (B) of poly(chloro-1,4-phenylene 4,4'-hexamethylenedioxy-bisbenzoate) after quenching from 350°C

The absence of a crystallization exotherm in the d.s.c. curve of a quenched specimen (Figure 2) shows that crystallization from the nematic mesophase proceeds very rapidly.

The d.s.c. curve of the 'as made' homopolymer $[B] = 1.00$ showed a double endotherm with the main peak at 264°C. This is in good agreement with the onset of flow and formation of the nematic mesophase observed by hot-stage optical microscopy. An endotherm occurring between 350 and 375°C (peak temperature 368°C) is due to isotropization. The d.s.c. curves obtained after quenching from temperatures within the nematic range were similar. The temperature of the main endothermic peak remained at $264 \pm 2^\circ\text{C}$ irrespective of the choice of the remelting temperature, whilst the peak temperature of the

smaller endotherm varied between 220 and 230°C. The total enthalpy change associated with these two endotherms is approximately 35 J g^{-1} . The absence of a crystallization exotherm in any of the quenched specimens again indicates that quenching from the nematic mesophase does not prevent crystallization. A typical d.s.c. curve is shown in Figure 2.

Hot-stage optical microscopy did not reveal any changes in the texture associated with the endotherm occurring around 225°C. This suggests that no smectic mesophase is formed in the homopolymer $[B] = 1.00$. The low temperature endotherm is therefore ascribed to the complex melting behaviour frequently observed with nematogenic polymers^{6,8,13}, including poly(chloro-1,4-phenylene terephthalate) (Figure 2).

It is concluded that the homopolymer B ($[\eta] = 0.28 \text{ dl g}^{-1}$) is a nematogenic material with a crystal-nematic transition temperature of 264°C. Its isotropization takes place between 350 and 375°C.

Correlation of the transition temperatures with the chemical structure is complicated by the effects of molecular weight, thermal history, and the differences in experimental method used for the evaluation of these transitions¹⁰. Nevertheless, the results obtained for the homopolymer $[B] = 1.00$ fit into the pattern of results for related polymers containing flexible spacers. For polymers containing a decamethylenedioxy spacer¹⁴⁻¹⁶ (III, $n = 10$), replacement of hydrogen in the phenylenedioxy unit by chlorine ($X = \text{Cl}$) reduced the crystal-nematic transition by 70–80°C. The resulting decrease of the isotropization temperature was less than 20°C. The effect of replacing hydrogen by methyl group was similar (Table 2).

The unsubstituted polymer containing the hexamethylenedioxy spacer (III, $X = \text{H}$, $n = 6$) has been described by Strzelecki and van Luyen¹⁴ as smectogenic with the crystal-smectic mesophase transition at 220°C and smectic-nematic transition at 280°C. However, because the $n = 10$ polymer is certainly not smectogenic¹⁵, the formation of a smectic mesophase for $n = 6$ is highly unlikely. According to a patent¹⁷, the flow temperature of the polymer III, $X = \text{H}$, $n = 6$ is 325°C, i.e. about 60°C higher than that found here for the homopolymer B. This difference is similar to that resulting from the introduction of a methyl substituent¹⁷ (Table 2).

Comparing the transitions of the homopolymer $[B] = 1.00$ with those of poly(chloro-1,4-phenylene 4,4'-oxybisbenzoate)⁶ of the same intrinsic viscosity, we find that the crystal-nematic transition of the polymer containing the

Table 2 Transition temperatures of polyesters containing a flexible spacer (repeating unit III)

X	n	T_{CN}^a (°C)	T_{NI}^b (°C)	Reference
H	10	225 ^a	270	14
		236	294	15
Cl	10	157	274	15
		169	282	16
CH ₃	10	162	279	15
		280 ^a	380	14
H	6	325 ^b	–	17
		264	372	This work
Cl	6	264	372	This work
		260 ^b	–	17

^a Assigned to smectic-nematic transition (see text)

^b Reported as 'flow temperature'

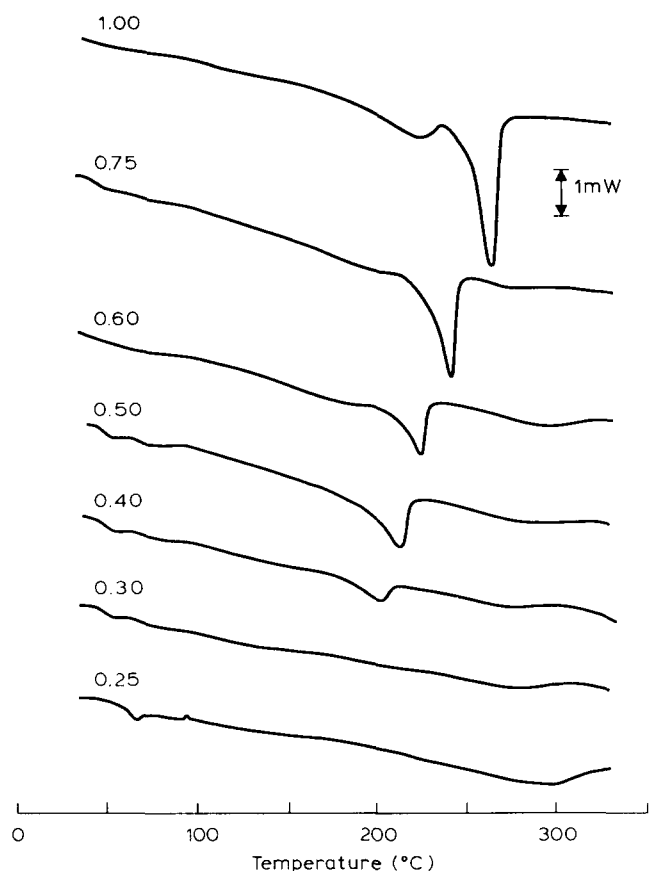


Figure 3 Effect of composition (expressed as molar fraction of B units) on melting behaviour: d.s.c. curves of quenched materials

Table 3 Features of the endotherm (d.s.c., heating rate $20^{\circ}\text{C min}^{-1}$) assigned to the melting of B-type crystallites: T_p^B , peak temperature; T_e^B , end temperature; ΔH^B , enthalpy of fusion

[B]	T_p^B ($^{\circ}\text{C}$)	T_e^B ($^{\circ}\text{C}$)	ΔH^B (J g^{-1})
1.00	264 ^a	270	35
0.75	238	248	14
0.60	220	232	10
0.50	212	220	6
0.40	202	210	4

^a Also a smaller peak at 225°C

flexible spacer is approximately 30°C lower than that of the polymer containing the angular disruptor. In contrast, its isotropization temperature is about 50°C higher. This suggests that the rigid segment in the homopolymer $[\text{B}] = 1.00$ is extended due to induced conformational ordering of the hexamethylenedioxy sequence^{9,18}.

Melting behaviour of the copolymers

The d.s.c. curves of the materials obtained after quenching from 300°C (Figure 3) and for the 'as made' materials were similar. As the concentration of the B units decreases, the prominent endotherm becomes smaller and occurs at a lower temperature (Table 3). At $[\text{B}] = 0.30$ the endotherm is no longer noticeable. Obviously, this endotherm is due to melting of crystalline regions consisting of B units, hereafter referred to as B-type crystallites. Their presence in the 'as made' materials was revealed by WAXR.

Dependence of the melting temperatures of the B-type crystallites on $[\text{B}]$ is described surprisingly well by the relationship derived for the equilibrium melting of copolymers¹⁹.

$$1/T_m^B = (1/T_m^0) - (R/\Delta H_u) \ln(1 - [\text{B}]) \quad (2)$$

where T_m^B and T_m^0 are taken as the end temperatures of the melting endotherm of the copolymer and homopolymer, respectively. The linearity of the plot (Figure 4) over a wide range of $[\text{B}]$ is most likely due to a combination of two factors: the length of the B units (over 2.5 nm) and the absence of chain folding, resulting in a small value of the end surface energy of the crystallites²⁰. The value of the heat of fusion per mole of repeating units B, ΔH_u , is 30.8 kJ mol^{-1} (i.e. 83 J g^{-1}). Whilst it is still probably underestimated¹⁹, it is much higher than the values reported in the literature²¹ which are based on direct measurements and do not take into consideration the crystallinity of the materials investigated.

All the copolymers show also a very small endotherm spread over a broad temperature range, although in the copolymer $[\text{B}] = 0.75$ it is hardly noticeable. Its onset is between 240 and 250°C and its end temperature is between 300 and 330°C . The shape of the endotherm makes an accurate evaluation of the enthalpy change difficult. The values obtained were between 2 and 6 J g^{-1} .

Since the WAXR diffraction of the copolymers showed a reflection with a d -spacing of 0.63 nm arising from sequences of 1,4-phenylene moieties linked by an ester group (i.e. essentially A-type structures), it is proposed that the broad endotherm is due to the melting of ordered regions consisting of an array of such sequences of variable lengths.

It is concluded that in materials where $[\text{B}] \leq 0.30$ the B-type crystallites are absent and the melting involves only the A-type structures. In the copolymers where $[\text{B}]$ is between 0.40 and 0.75 both types of structure are present. The B-type structures melt first (Figure 1) and the melting of the A-type structures takes place at higher temperatures, up to 300 – 330°C .

A polymer should become fluid only after the completion of melting of the crystalline regions with the highest melting temperature. However, the flow temperatures of copolymers listed in Table 1 are consistently lower than the end temperatures of the endotherm assigned to the melting of the A-type structures. The low molecular weight of the materials prepared on the 0.01 mole scale

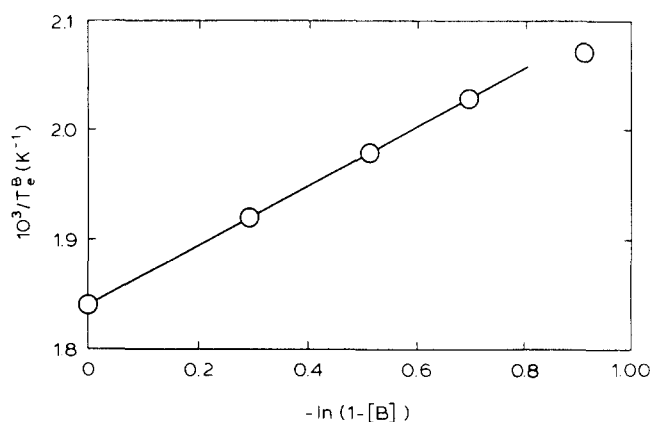


Figure 4 Effect of composition ($[\text{B}]$) on the end temperature (T_e^B) of the endotherm assigned to melting of B-type crystallites

Table 4 Effect of molecular weight on flow temperature (T_f) and melting behaviour of copolymer [B]=0.50. The values of \bar{M}_n were calculated using (a) data for the copolymer containing an ether oxygen disruptor⁶, and (b) the relationship obtained by Blumstein *et al.*²² (for details see text)

Sample	1	2	3
$[\eta]$, dl g ⁻¹	0.18	0.29	0.70
\bar{M}_n (a)	3980	6420	15490
\bar{M}_n (b)	2540	4760	15170
\bar{P}_n	9 ± 2	15 ± 2	41
T_f , °C	255	267	290
T_e^B , °C	209	208	202
T_e^A , °C	215	213	211
ΔH^B , J g ⁻¹	8	7	8
T_p^A , °C	293	307	326
T_e^A , °C	330	327	333
ΔH^A , J g ⁻¹	6	7	6

might be responsible for the flow prior to the completion of melting. We therefore investigated the effect of molecular weight on the melting and flow behaviour using copolymers [B]=0.5 prepared on a 0.4 mole scale (Table 4). Their molecular weights were estimated using the result obtained previously⁶ for (I-co-II) (50/50) (viz., $[\eta]/\bar{M}_n = 4.52 \times 10^{-3}$). The application of a relationship derived for a different, albeit related, material needs some justification. Since similar values of molecular weight were also obtained using the Mark-Houwink coefficients obtained by Blumstein *et al.*²² for other mesogenic polymers containing aliphatic spacers (viz., $K = 4.65 \times 10^{-4}$, $a = 0.76$), we are satisfied that the estimates of \bar{P}_n are realistic.

Hot-stage optical microscopy showed that the flow temperatures of the copolymers increased significantly with increasing molecular weight (Table 4). However, since the assessment of the flow temperature by this method is somewhat subjective, the flow behaviour of sample 2 ($[\eta] = 0.29$ dl g⁻¹, $T_f = 267^\circ\text{C}$) was evaluated using a capillary rheometer at 240 and 290°C, i.e. below and above T_f (Figure 5). Although it was possible to extrude the material at both temperatures, the apparent viscosity at 240°C at an apparent shear rate of 10 s⁻¹ was in excess of 10³ Pa s. Because the apparent viscosity increases strongly with decreasing shear rate, it is not surprising that no flow was observed on the hot-stage at this temperature. An increase of temperature to 290°C resulted in a ten-fold decrease of the apparent viscosity at the same shear rate. Thus, the flow temperature determined by the hot-stage microscopy can be roughly bracketed by apparent viscosity values of 10² and 10³ Pa s at 10 s⁻¹.

The plots of apparent viscosity *versus* shear rate also indicated a discontinuity as observed for other thermotropic polymers, where it was ascribed to a change in the flow mechanism from polydomain to monodomain^{23,24}.

D.s.c. curves of quenched [B]=0.50 materials showed both the lower endotherm assigned to the melting of B-type crystalline regions and the broad upper endotherm assigned to the melting of the A-type structures (Table 4). The molecular weight did not affect the crystallinity evaluated from the enthalpy changes. The upper limit of the B-type crystallinity was approximately 10%. The same value was estimated for the A-type crystallinity using $\Delta H_u = 19$ kJ mol⁻¹ (i.e. 70 J g⁻¹) evaluated for poly(chloro-1,4-phenylene terephthalate) from the depres-

sion of melting temperatures of (I-co-II)⁶. The molecular weight caused some changes of the peak temperatures of both endotherms, and of the end temperatures of the lower endotherm, T_e^B . The differences between the end temperatures of the upper endotherm, T_e^A , were within the limit of experimental error. In all cases $T_e^B < T_f < T_e^A$ (Table 4).

This unusual melting/flow behaviour is interpreted as follows. After the melting of the B-type crystallites, flow is prevented by A-type crystallites which act as multifunctional junctions ensuring the connectivity of the material. As melting of the A-type crystallites takes place, the number of junctions is reduced until the remaining crystallites can no longer 'crosslink' the whole material. The longer the chains, the lower the crystallinity required to maintain the connectivity. This is analogous to the effect of molecular weight of a linear precursor polymer on the level of chemical crosslinking required for the formation of a three-dimensional network. Further information about the size/shape distribution of the crystallites is needed to formulate a quantitative relationship between the crystallinity and the chain length required for maintaining connectivity.

This proposed explanation applies not only to other copolymers in the series, but also to several other nematogenic copolymers synthesized in our laboratory. Furthermore, the unusual rheological behaviour reported for some nematogenic copolymers may be ascribed to the presence of a small number of crystalline regions resulting in a 'physical crosslinking' similar to gel formation^{25,26}.

Fibres and mouldings

Investigation of fibres and moulding was limited to copolymers [B]=0.50. This composition permits direct comparison with the properties of articles produced from the corresponding copolymer containing an ether oxygen disruptor (I-co-II) (50/50)⁸.

Attempts to produce fibres from a low molecular weight copolymer ($[\eta] = 0.18$ dl g⁻¹) were unsuccessful. A

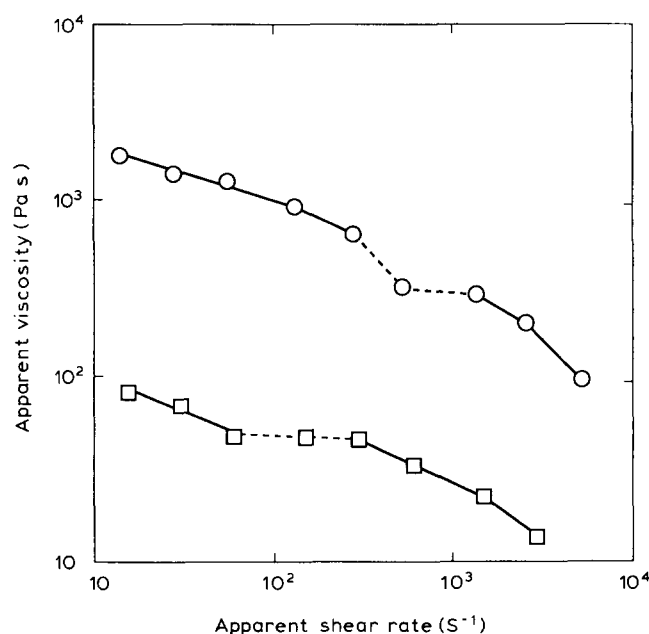


Figure 5 Shear rate dependence of the apparent viscosity of copolymer [B]=0.50 ($[\eta] = 0.29$ dl g⁻¹) at 240°C (○) and 290°C (□)

Table 5 Mechanical properties of 'as made' fibres and mouldings from copolymer [B]=0.50 (columns 1a and 1b) and from the corresponding copolymer containing an ether oxygen disruptor (column 2)

Column	1a	1b	2
Spacer/disruptor [η] (dl g ⁻¹)	0.40	0.70	1.25
Spacer/disruptor structure			
	$-\text{O}-(\text{CH}_2)_6-\text{O}-$	$-\text{O}-$	$-\text{O}-$
'As made' fibres: tensile properties			
Number of tests	15	—	15
Strength (GPa)	0.12 ± 0.02	—	0.66 ± 0.04
Extension at break (%)	1.0 ± 0.2	—	1.9 ± 0.1
Modulus (GPa)	15 ± 3	—	38 ± 3
Mouldings: tensile properties			
Number of tests	8	5	10
Strength (GPa)	0.04 ± 0.02	0.04 ± 0.01	0.13 ± 0.01
Extension at break (%)	0.5 ± 0.03	0.6 ± 0.2	1.6 ± 0.3
Modulus (GPa)	10.2 ± 1.5	8.1 ± 0.7	13.4 ± 1.8
Mouldings: flexural properties			
Number of tests	5	—	6
Strength (GPa)	0.09 ± 0.02	—	0.18 ± 0.02
Extension at break (%)	1.9 ± 0.4	—	4.0 ± 0.8
Modulus (GPa)	6.1 ± 1.7	—	8.7 ± 1.1

copolymer of a higher molecular weight ($[\eta] = 0.40 \text{ dl g}^{-1}$) gave a sufficiently stable spinline at a spinning temperature of 280°C. The resulting fibres were too brittle to be wound onto a package, but could be hauled off by hand. The fibres obtained in this way (diameter approximately 80 μm) were rather irregular and affected the variability of the data in Table 5. The tensile properties, particularly the Young's modulus, are better than those reported by Krigbaum *et al.*²⁷ for other semiflexible thermotropic polyesters, but are distinctly inferior to those obtained for fibres from (I-co-II) (50/50) (Table 5). Although an improvement should be achievable by increasing the polymer molecular weight and by optimization of the spinning conditions, it seems unlikely that the properties would reach a level typical of a high performance fibre.

Tensile and flexural properties of mouldings produced without optimization of the processing conditions are listed in Table 5. The results, particularly for tensile strength and for extension at break, were highly variable. An increase of intrinsic viscosity from 0.4 to 0.7 dl g⁻¹ did not result in a significant improvement of the properties. A plot of tensile strength against extension at break for 13 samples resulted in a linear relationship with a correlation coefficient of 0.95. This indicates that the failure is predominantly due to flaws and explains why the effect of increased molecular weight was insignificant. A comparison with the data for (I-co-II) (50/50) mouldings (Table 5) shows the inferiority of the copolymer containing the flexible spacer.

Thermal expansion of the mouldings was assessed by thermomechanical analysis⁸ (t.m.a.) at a probe pressure of 13 MPa and a heating rate of 5°C min⁻¹. The total expansion up to 190°C in the flow direction was less than 0.4%, whilst the corresponding expansion in the lateral direction was much larger (2–4%). This shows that the mouldings have a high degree of anisotropy. The variability of the results in a given direction is due to a complex distribution of orientation in the mouldings, as discussed previously⁸. Scanning electron microscopy showed a distinct skin-core effect.

The t.m.a. probe penetrated the sample, irrespective of the direction, at around the melting temperature of the

B-type crystallites. This melting process results in a distinct 'softening' of the material, thus considerably restricting its useful temperature range.

Dynamic mechanical analysis⁸ (heating rate 2°C min⁻¹) showed a substantial decrease of the storage modulus with increasing temperature (Figure 6) due to mechanical loss processes. The prominent α loss peak occurs at around 100°C, about 20°C lower than in the (I-co-II) (50/50). This loss process is associated with the glass transition. Although the glass transition is not distinct in the d.s.c. curve shown in Figure 3, it was identified at a higher sensitivity as a small endothermic step ($\Delta c_p \approx 0.04 \text{ J g}^{-1} \text{ K}^{-1}$) occurring between 55 and 65°C, i.e. more than 40°C lower than in (I-co-II) (50/50).

The β loss peak is around ambient temperature, which is also lower than in (I-co-II) (50/50). There is also a loss process starting at around 140°C which is assigned to the melting of the B-type crystallites. The combined effect of these three loss processes causes a reduction of the storage modulus of the copolymer [B]=0.50 to only 1 GPa at 180°C.

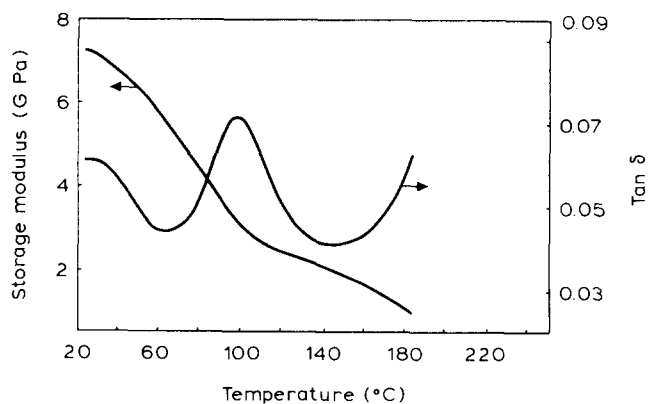
The copolymer containing the flexible spacer is inferior in its mechanical properties at ambient temperature and in its modulus retention at elevated temperatures to the corresponding material containing the ether oxygen disruptor. Optimization of the polymer and moulding production conditions should result in improvement of both the level and the uniformity of the mechanical properties at ambient temperature. The loss process temperatures are unlikely to be changed substantially by such optimization and the performance at elevated temperatures will remain unsatisfactory.

CONCLUSIONS

Poly(chloro-1,4-phenylene terephthalate-co-4,4'-hexamethylenedioxy-bisbenzoate)s (A-co-B) are nematogenic throughout the composition range. Transition temperatures of the homopolymer [B]=1.00 fit into the pattern of results for related homopolymers containing flexible spacers.

Materials with [B] ≥ 0.40 contain crystalline regions consisting of B units (B-type crystallites), but all the copolymers investigated also contain crystalline regions consisting of sequences of ester-linked 1,4-phenylene moieties (A-type crystallites).

In materials containing both types of crystallites the melting of B-type crystallites takes place first and results

**Figure 6** Dynamic mechanical analysis of a [B]=0.50 moulding

in a distinct softening. Melting of A-type crystallites follows at higher temperatures, over a broad temperature interval (240–330°C), and results in formation of a nematic melt. Flow occurs before completion of melting, when the number of remaining A-type crystallites is no longer sufficient to maintain connectivity throughout the material. This explanation may also apply to anomalies observed with other nematogenic copolymers.

Comparison with copolymers containing an ether oxygen disruptor shows that, when the effect of molecular weight is taken into consideration, the use of a hexamethylenedioxy spacer does not result in lower flow temperatures. This flexible spacer also causes a decrease in decomposition temperature, which reduces the temperature range available for processing, and a shift of both α and β loss processes to lower temperatures which results in very poor retention of mechanical properties at elevated temperatures.

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