Thermotropic polyesters: Synthesis and properties of poly(chloro-1,4-phenylene terephthalate-co-4,4′-oxybisbenzoate)s

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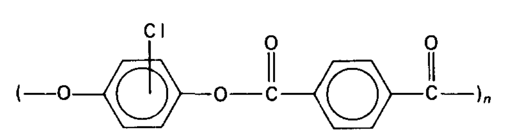
Poly(chloro-1,4-phenylene terephthalate), poly(chloro-1,4-phenylene 4,4′-oxybisbenzoate), and their copolymers are synthesized and the effect of composition on thermal transitions is evaluated. All the materials are nematogenic; copolymer compositions from 75/25 to 25/75 display a nematic temperature range in excess of 100°C which is sufficient for melt processing. The crystal–nematic transition temperature of the 50/50 copolymer is strongly affected by the molecular weight, but the glass transition, although low, is molecular weight independent. Brief annealing at temperatures below the crystal–nematic transition does not reduce the nematic temperature range of this copolymer.

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

INTRODUCTION

Several reviewers have discussed the reasons for the growing interest in thermotropic nematogenic polymers (see e.g. ref. 1). The principles underlying the chemical design of such polymers are now reasonably well understood[1–3]. The unsubstituted fully aromatic rod-like polyester, poly(1,4-phenylene terephthalate), has a sufficiently rigid chain for the formation of a nematic mesophase, but its melting temperature (600°C) exceeds the thermal stability limit of the polymer[3]. Unsymmetrical substitution on one or both of the aromatic rings of the repeating unit results in reduction of the melting temperature[4] without reducing the chain rigidity. Consequently, the first parent homopolymer of the copolymer series investigated here, poly(chloro-1,4-phenylene terephthalate) (**I**), is a thermotropic nematogenic polymer[5–7]. However, the recorded melting temperature of I (340°C[5]; 350°C[6]; 372°C[7]) is still rather high for successful melt processing. Indeed, according to a du Pont patent[8], this homopolymer melts with decomposition above 400°C and they therefore considered it unsuitable for melt spinning.



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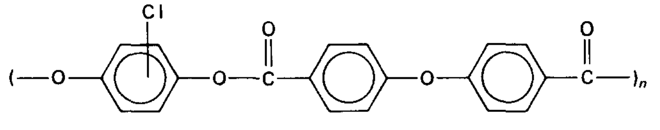

(II)

The second parent homopolymer of the copolymer series investigated, poly(chloro-1,4-phenylene 4,4′-oxybisbenzoate) (**II**), has also been reported to be nematogenic[8,9], although in this case the length of the rod-like sequences, which are terminated at each end by the ether oxygen atoms, is only about 1.8 nm. The 'flow temperature' of this homopolymer with inherent viscosity $\eta_{inh} = 0.51$ dl/g has been given as 321°C; a higher 'flow temperature' (339°C) has been given[9] for a polymer with $\eta_{inh} = 0.56$ dl/g.

Since both parent homopolymers are nematogenic it is not surprising that the copolymers are also found to be nematogenic[8–10]. The 'flow temperature' of a 70/30 copolymer ($\eta_{inh} = 1.0$ dl/g) has been reported[8] as 289°C, and that of a 20/80 copolymer ($\eta_{inh} = 0.78$ dl/g) as 306°C. The results of Griffin and Cox[10] show that the melting temperature of a 50/50 copolymer is around 250°C.

Although there is prior evidence that poly(chloro-1,4-phenylene terephthalate-co-4,4′-oxybisbenzoate)s are nematogenic throughout the whole composition range, no systematic investigation of the transition temperatures and thermal stability limits of these materials has been carried out. The effect of thermal history on the transition temperatures, which has proved to be important for other thermotropic copolyesters[2], has not previously been investigated. The objective of the work presented in this paper was to establish the effect of copolymer composition on the nematic temperature range available for processing. For a selected composition (50/50) the effects of molecular weight and thermal history were also investigated.

EXPERIMENTAL

Monomers

Chlorohydroquinone diacetate was purified by a double recrystallization from ethanol (at about 900 g/l) to give a product with melting point (m.pt.) 71.5°C (literature[11] 72°C). Purity was assessed by ultra-violet

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spectroscopy. A scan between 280 and 310 nm of a solution of concentration 5 g/l in ethanol showed that the absorption peak, centred at 270 nm, developed a shoulder above 290–300 nm if impurities were present.

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

4,4′-Oxybisbenzoic acid was synthesized in two stages. Firstly, 4,4′-diacetyl diphenyl ether was prepared by the acetylation of diphenyl ether with acetyl chloride in dichloromethane (Friedel–Crafts reaction). The method used was based on that described by Sorenson and Campbell[12]. By using dichloromethane as solvent and doubling the reactant concentrations compared with the published method, an increased yield was obtained (85% compared with 63%). The product was recrystallized twice from ethanol (m.pt. 103°C; literature[12] 98°C–99°C). The purified 4,4′-diacetyl diphenyl ether was then oxidized to 4,4′-oxybisbenzoic acid. Oxidation by bubbling oxygen through a refluxing solution of the ether in propionic acid, in the presence of manganese acetate as a catalyst, gave a discoloured product which could not be purified. A purer product was obtained by oxidation using potassium permanganate (stoichiometric ratio permanganate/acetyl 3:1) giving a 73% yield, m.pt. 331.5°C. The most satisfactory method of purification was simple refluxing with a large amount of water to give a product of m.pt. 333°C. The purity was monitored by measuring the absorbance of a 1% w/w solution in 1M aqueous NaOH at 340 nm (path length 1 cm). Ultimately it became possible to obtain a product with an absorbance as low as 0.13.

Polymer preparation

Polymers were prepared, without added catalyst, from a mixture of diacids and, unless otherwise stated, an equimolar quantity of chlorohydroquinone diacetate. Polymerization procedure (a) was similar to that described elsewhere[13]; it was carried out on a scale using 0.01 mole of chlorohydroquinone diacetate at 282°C for 1 h under atmospheric pressure and then for 1 h at reduced pressure (0.2 mmHg). Polymerization procedure (b) was carried out, unless otherwise stated, at 285°C on a 0.4 mole scale using a glass reactor[6] fitted with a glass helical stirrer. The reaction mixture was kept under nitrogen (200 ml/min) for 60 min. The pressure was then reduced within 15 min to 1.5 mmHg. During the final stage lasting 45 min the pressure was 0.1 mmHg.

Polymer characterization

Solution viscosities of polymers were measured in *p*-chlorophenol at 45°C. Since the sum of the Huggins and Kraemer constants for a 50/50 copolymer was 0.5 the intrinsic viscosities were calculated from single point measurements[14] obtained at 0.2 g/dl concentration.

A published method for determining carboxyl end groups in aliphatic polyesters[15] dissolved in 2,6-dimethylphenol was unsatisfactory, since the polymers were insoluble in this solvent. However, 0.5 g of polymer did dissolve under reflux in a mixture of phenol (5 g) and of 2,6-dimethylphenol (9 g) and remained in solution when chloroform (75 ml) was added, and thereafter during titration with 0.2M potassium hydroxide in methanol. Bromophenol blue dissolved in ethanol diluted with chloroform was used as an indicator. The method gave reproducible results up to a carboxyl end group concentration of 100 μeq/g with a precision better than 1 μeq/g and a blank less than 0.3 μeq/g. To simplify the comparison of polymers of different compositions the carboxyl end group concentrations (*CEG*) are expressed in milliequivalents per mole of repeating units.

Attempts to measure acetoxy groups by the method of Merienne *et al.*[16], using proton n.m.r. of a solution of the polymer degraded in trifluoroacetic acid, were not successful. After two months at 60°C in a sealed tube with trifluoroacetic acid, the polymer had only degraded slightly. Modification of the method, using mixtures of methylene chloride and trifluoroacetic acid, in which the polymers were soluble, was also unsuccessful.

Thermal stabilities were assessed by thermogravimetric analysis at a heating rate of 20°C/min and also by observing the behaviour of polymers under the microscope for signs of discolouration and gas evolution. A Stanton Redcroft hot-stage (type TH 600) fitted with nitrogen purge was used for this purpose; the heating rate was 30°C/min.

Transition temperatures were determined using a Du Pont 990/910 Differential Scanning Calorimeter at a heating rate of 20°C/min (sample weight 6–8 mg). The assignment of the transitions was confirmed using a polarizing microscope with the Stanton Redcroft hot-stage.

The apparent melt viscosity was measured using an Instron capillary rheometer (capillary diameter 0.765 mm, length 25.5 mm).

RESULTS AND DISCUSSION

Effect of composition on mematogenic temperature range

In order to establish whether poly(chloro-1,4-phenylene terephthalate-co-4,4′-oxybisbenzoate)s could be melt-processed from a nematic mesophase, it was necessary to determine and identify their transition temperatures and their thermal stability limits.

From the values of intrinsic viscosities and carboxyl end group concentrations (*Table 1*) it was concluded that the copolymers within the composition range from 25/75 to 75/25 prepared by procedure (a) at 282°C were of sufficiently high molecular weights to be used for evaluation of the effect of composition on the processing temperature range. It was noted that the copolymers remained liquid at 282°C and exhibited signs of stir opalescence typical of a nematic mesophase. On cooling to ambient temperature all the copolymers became opaque solids.

As expected from the literature[5–9] both homopolymers solidified during their preparation at 282°C. This accounts for the relatively low intrinsic viscosity and high carboxyl end group concentration (hence low molecular weight) of poly(chloro-1,4-phenylene 4,4′-oxybisbenzoate) prepared by procedure (a). By using procedure (b) with a higher polymerization temperature of 320°C it was possible to increase the molecular weight of this homopolymer to an acceptable level.

Poly(chloro-1,4-phenylene terephthalate) was insoluble in the solvents employed for intrinsic viscosity and for carboxyl end group determination; attempts to find other solvents proved unsuccessful (cf. refs. 6, 7). However, from its brittleness it was judged likely to be of relatively low molecular weight. Consequently, its properties should be interpreted with caution.

Table 1 Effect of composition on properties of polymers prepared by procedure (a): melting endotherm was measured by d.s.c. (heating rate 20°C/min) after quenching pretreatment. The onset of the decomposition (T_d) was assessed by hot-stage microscopy (heating rate 30°C/min)

			Melting endotherm			
Composition	$[\eta]$ (dl/g)	(*CEG*) (meq mol^{-1})	1st peak (°C)	2nd peak (°C)	End (°C)	T_d (°C)
100/0	insol.	insol.	325	355	360	450
75/25	0.54	insol.	–	287	315	440
70/30	0.70	29	–	279	302	430
60/40	0.91	21	252	276	281	420
50/50	0.88	23	255	275	279	410
25/75	0.84	–	253	286	292	425
0/100	0.28	79	–	295	[b]	420
0/100[a]	1.04	17	–	334	340[c]	430

[a] Prepared by procedure (b) at 320°C
[b] Overlapping with the isotropization endotherm
[c] Isotropization endotherm between 385°C and 420°C, peak at 405°C

Wide-angle X-ray investigation[17] revealed the presence of ordered crystalline structures in all 'as made' materials. The highest degree of order was found in the homopolymers; as expected their crystal structures differed from each other. The copolymers showed only a few sharp reflections and it was not possible to decide whether the ordered regions were structurally similar to those present in either of the homopolymers.

The thermal stability limit, assessed from t.g.a. as the temperature at which a 5% weight loss occurred, varied from 430°C to 490°C; there was no systematic effect of composition. Observation of the behaviour of the polymers using a hot-stage microscope (heating rate 30°C/min) indicated an onset of rapid gas evolution and discolouration between 410°C and 450°C (see *Table 1*). These temperatures clearly represent more realistic upper limits for processing than the t.g.a. values.

Hot-stage light microscopy showed that between approximately 340°C and 360°C the 'as made' poly(chloro-1,4-phenylene terephthalate) (i.e. the 100/0 composition) formed a nematic mesophase which persisted up to the thermal stability limit. The melt observed on a hot plate exhibited typical shear opalescence. The d.s.c. curve of this 'as made' material displayed an endotherm corresponding to the crystal–nematic phase transition that consisted of two overlapping peaks with the main peak at 360°C. This is somewhat lower than the value of 375°C reported by Krigbaum *et al.*[7] for a polymer prepared at 340°C which was presumably of a higher molecular weight.

As already noted, the 100/0 homopolymer solidified in the course of its preparation and this resulted in annealing. The transitions of a sample quenched from the nematic mesophase at 390°C to ambient temperature were determined in order to eliminate the effect of this annealing (see e.g. ref. 2). The d.s.c. curve of the quenched material showed a melting endotherm with a main peak temperature of 355°C; hence the effect of annealing on this transition was relatively small. The absence of a crystallization exotherm proved that quenching from a nematic mesophase did not prevent crystallization. Neither the 'as made' nor the quenched material showed a stepwise increase of heat capacity arising from a glass transition.

The phase transitions of poly(chloro-1,4-phenylene-4,4′-oxybisbenzoate) (i.e. the 0/100 composition) were strongly influenced by the molecular weight. The d.s.c. curve of the 'as made' low molecular weight polymer revealed a glass transition between 95°C and 120°C and a small endotherm (peak at 304°C) which had a distinct shoulder at approximately 318°C. By hot-stage microscopy it was possible to assign the main endotherm to the crystal–nematic mesophase transition, whilst the shoulder was due to the nematic–isotropic transition. In order to eliminate the effect of annealing which had taken place during the polymer preparation at 282°C, a sample quenched from an isotropic melt at 330°C to ambient temperature was also examined. The d.s.c. curve of the polymer displayed a glass transition between 95°C and 115°C followed by a distinct crystallization exotherm (peak at 128°C, $\Delta H = 9 \pm 1$ J/g); the melting exotherm (peak at 295°C) overlapped the isotropization endotherm (peak at 318°C). The total enthalpy change due to melting and isotropization was approximately 30 ± 3 J/g. Thus, crystallization did not take place during the quenching from the isotropic state. Although the melting temperature of the crystallites formed during the heating of quenched polymer was lower than that observed for the 'as made' material, there was still an overlap of melting and isotropization endotherms. Due to this overlap there is an insufficient nematic temperature range available for processing.

D.s.c. curves for the 'as made' 0/100 homopolymer of higher molecular weight showed that both the melting endotherm (peak at 337°C) and the isotropization endotherm (385°C–420°C, peak at 405°C) were shifted to higher temperatures in comparison with those found for the low molecular weight material. The d.s.c. curve of a sample quenched from the nematic mesophase at 370°C did not exhibit the crystallization exotherm. The melting endotherm was only slightly affected by this quenching (peak at 334°C) and, as expected, there was no change in the isotropization endotherm. The melting enthalpy was 17 ± 2 J/g, and the isotropization enthalpy was 11 ± 1 J/g; hence, within the limits of experimental error, the total enthalpy was the same as the value of 30 ± 3 J/g found for the low molecular weight material.

The increase in molecular weight affected the isotropization temperature more than the melting temperature. Consequently, the higher molecular weight material exhibited a distinct nematic temperature range. The interval between the end of the melting endotherm and the onset of the isotropization endotherm is approximately 45°C, which is still rather narrow for successful processing.

Hot-stage light microscopy confirmed that the 'as made' copolymers (composition range from 75/25 to 25/75) formed nematic mesophases which, as in the case of the 100/0 homopolymer, persisted up to the thermal stability limits. In all cases melting occurred over a broad temperature range. D.s.c. curves featured broad and often complex endotherms at temperatures corresponding to the crystal–nematic phase transitions observed by microscopy. Although the copolymers did not solidify during their preparation at 282°C, the subsequent cooling to ambient temperature was uncontrolled and non-uniform. In order to eliminate effects arising from this uncontrolled cooling, samples were heated in a d.s.c. cell to temperatures approximately 20°C higher than the end of the melting endotherm and then quenched to ambient temperature. As in the case of the homopolymers the copolymers crystallized during the quenching from the nematic mesophase. D.s.c. curves for all copolymers showed glass transitions with an onset at 97 ± 3°C; the transition took place over a temperature interval of approximately 20°C. The melting endotherms of some copolymers consisted of two overlapping peaks (see *Table 1*); the peak occurring at the higher temperature was always more prominent. *Table 1* shows that within the composition range investigated the main peak temperatures were within a narrow temperature interval of 12°C with a minimum of 275°C for the 50/50 material. The end temperatures of the melting endotherms represent realistic lower limits of nematic temperature ranges and are also given in *Table 1*. Comparison of the results obtained for the 'as made' materials showed that quenching reduced the end temperatures of the melting endotherms only by about 5°C. For all the copolymers investigated the end temperatures of their melting endotherms were more than 100°C below their thermal stability limits.

Neither of the homopolymers appears to be promising nematogenic material. Although poly(chloro-1,4-phenylene terephthalate) exhibits a sufficiently broad nematic temperature range for processing, its melting temperature is rather high. The nematic temperature range of poly(chloro-1,4-phenylene 4,4′-oxybisbenzoate) is considered to be too narrow even in the case of the higher molecular weight material. On the other hand, the copolymers within the composition range from 75/25 to 25/75 exhibit nematic temperature intervals which are more than sufficient for melt processing. The change of the melting temperature with composition within this range is relatively small, but there is an indistinct minimum around the 50/50 ratio. Consequently, the 50/50 copolymer was selected for a more detailed investigation.

Molecular weight of 50/50 copolymer

For purposes of polymer processing it was desirable to increase the polymer molecular weight. Two important factors affecting the molecular weight of a polymer prepared by either procedure were identified: (1) purity of 4,4′-oxybisbenzoic acid, and (2) stoichiometric balance.

In the course of optimization of the synthesis and purification of 4,4′-oxybisbenzoic acid it was established that its purity is related to the absorbance of its aqueous alkaline solution measured at 340 nm. As expected, improved monomer purity resulted in an increase of intrinsic viscosity. This is illustrated by the data presented in *Table 2*, which also show that, for a monomer of high purity, procedure (b) results in a higher intrinsic viscosity than procedure (a). It was also noted that the melting temperatures of the 50/50 copolymers increased with increasing molecular weight, like those of the 0/100 homopolymer.

Table 2 Effect of purity of 4,4′-oxybisbenzoic acid on properties of 50/50 copolymers prepared by procedure (a): peak temperature of the main melting endotherm (T_m) was measured by d.s.c. (heating rate 20°C/min) after quenching pre-treatment

Absorbance at 340 nm	$[\eta]$ (dl/g)	T_m (°C)
0.60	0.59	259
0.30	0.68	266
0.17	0.82	273
0.13	0.90	274
0.13	1.13[a]	277[a]

[a] Polymer prepared by procedure (b)

Table 3 Effect of excess (E) of chlorohydroquinone diacetate on properties of 50/50 copolymers

E (%)	$[\eta]$ (dl/g)	(CEG) (meq/mol)	Thermal stability limit (°C)	
			T.g.a.	Hot-stage
16.30	0.38	<0.5	–	–
4.00	1.21	4.2	485	445
2.5	1.36	9.0	500	450
1.25	1.30	12.5	–	–
0	1.13	24.1	–	–
−1.25	1.00	28.0	480	455

During the early stages of polymer preparation chlorohydroquinone diacetate evaporates from the reaction mixture and this upsets the stoichiometric balance. It was possible to compensate for this loss by charging an excess of this monomer. A series of polymers with different levels of excess diacetate was synthesized by procedure (b) using the 4,4′-oxybisbenzoic acid with the minimum content of impurities. From the results, summarized in *Table 3*, it was concluded that the optimum excess is around 2% and that this should give a polymer with an intrinsic viscosity of approximately 1.4 dl/g. It must be emphasized that the optimum excess will be strongly dependent on polymerization conditions and equipment including the geometry of the reaction vessel.

The optimum excess should yield a stoichiometrically balanced polymer with a concentration of acetoxy end groups equal to that of the carboxyl end groups. The value of the latter, obtained by interpolation, for the balanced polymer ($[\eta]\simeq1.4$ dl/g) is approximately 10.4 meq/mole. Assuming further that there are no inert end groups the number average molecular weight of this polymer is estimated as 31000. This molecular weight represents the upper limit for 50/50 copolymers prepared by procedure (b).

Properties of 50/50 copolymers

Further investigations into some properties relevant to processing were carried out on the 50/50 copolymers. It is known that extended heat treatment strongly affects the melting behaviour of some menatogenic copolyesters[2]. At this stage the interest lay in the effect of short annealing which might take place inadvertently in the course of polymer processing prior to melting. Samples quenched from the nematic mesophase (*ca.* 20°C above the end of the melting endotherm) were annealed in the DSC cell at temperatures ranging from 210°C to 260°C for 10 min and then quenched again. D.s.c. curves of the annealed samples are shown in *Figure 1*. As can be seen, this short annealing did not affect the main endothermic peak exhibited by the original quenched sample. However, it did result in the appearance of an additional peak at a temperature approximately 20°C above the annealing temperature; this peak became stronger and sharper as the annealing temperature increased. Similar results were obtained for samples annealed for 30 min and, as expected, the additional peaks were stronger than those obtained after 10 min. It is concluded that the upper limit of the melting endotherm obtained for the quenched material can be safely taken as the lower limit of the processing temperature range.

As already mentioned the melting behaviour of both 0/100 homopolymer and 50/50 copolymer was found to be affected by their molecular weight (see *Tables 1* and *2*). For polymers which are identical with respect to composition and physical structure the effect of molecular weight $\bar{M}_n$ on melting temperature T_m (K) can be expressed by the following relationship

$$1/T_m = 1/T_m(\infty) + 2(R/\Delta H_u)(M_u/\bar{M}_n) \qquad (1)$$

where ΔH_u is the melting enthalpy per mole of repeating units of a molecular weight M_u. Assuming further that the polymers investigated have identical molecular weight distributions, equation (1) can be recast in the following form

$$1/T_m = 1/T_m(\infty) + S[\eta]^{-b} \qquad (2)$$

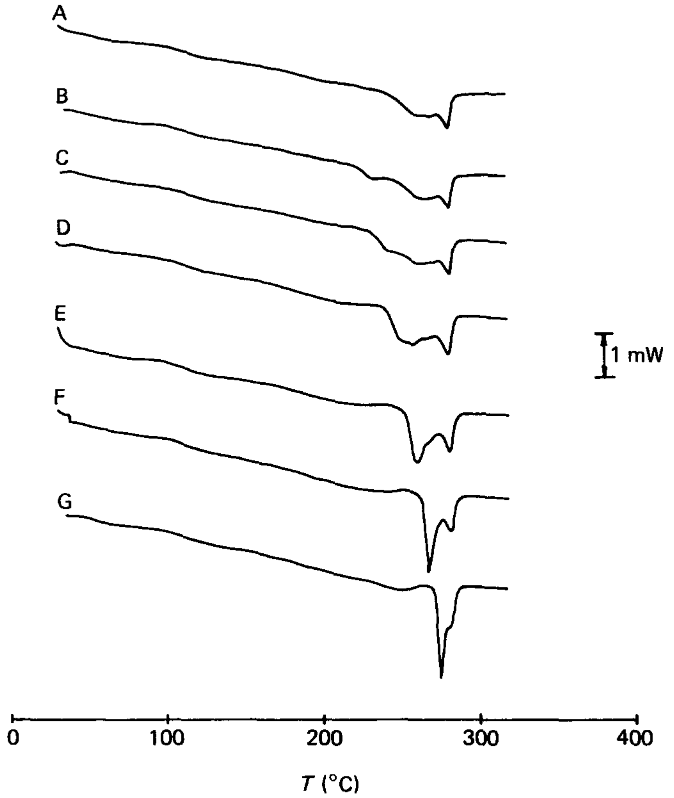

Figure 1 D.s.c. curves of a 50/50 copolymer after quenching pretreatment (curve A) followed by 10 min annealing at 210°C (B); 220°C (C); 230°C (D); 240°C (E); 250°C (F); 260°C (G)

where S is a constant and b is the reciprocal value of the exponent a in the Mark–Houwink equation. The value of the exponent a is not known for the 50/50 copolymer but it is expected to be less than the value of 1.25 found by Ying *et al.*[18] for a rigid chain polymer, poly(1,3-phenylene terephthalamide); it is also expected to be higher than the value of 0.66 found by Berkowitz[14] for a flexible chain polyester, poly(ethylene terephthalate), in *o*-chlorophenol. Thus, reasonable limits for the value of b are between 0.8 and 1.5.

Altogether 28 copolymers with intrinsic viscosities ranging from 0.38 to 1.36 dl/g were investigated. The peak temperatures of the main melting endotherms of quenched samples were taken as the melting temperatures T_m in relationship (2). Statistical analysis of the data was carried out for b values within the above limits at intervals of 0.1. The values of the correlation coefficients ranged from 0.906 to 0.925, the maximum being obtained for $b = 1$. Thus, the data analysis indicates that the most probable value of the Mark–Houwink exponent is $a = 1$, which is in agreement with the value suggested by Jackson[3] for poly(phenyl-1,4-phenylene terephthalate).

For $b = a = 1$ the coefficients in equation (2) were: $1/T(\infty) = 1.762 \times 10^{-3}\,\mathrm{K}^{-1}$, and $S = 5.7 \times 10^{-5}\,\mathrm{dl\,g}^{-1}\,\mathrm{K}^{-1}$. Hence, the melting temperature of a quenched 50/50 copolymer with $[\eta] \rightarrow \infty$ was estimated as 294°C with 95% confidence limits of 291–298°C.

Accurate determination of the melting enthalpies was hindered by difficulties in establishing the baseline position. The values obtained for five quenched samples were between 9.5 ± 1 and 11 ± 1 J/g, i.e. significantly lower than the value of 17 ± 2 J/g obtained for the 0/100 homopolymer. No significant effect of the molecular weight was detected.

Unlike the melting temperature, the glass transition temperature (onset at 96 ± 1°C) was not affected by the molecular weight.

The thermal stability of the higher molecular weight 50/50 copolymers prepared by procedure (b) (see *Table 3*) was distinctly better than that of the lower molecular weight copolymer (*Table 1*). It is not clear whether this is entirely due to the molecular weight or whether it has been caused by the improved purity of 4,4′-oxybisbenzoic acid. Nevertheless, the processing temperature range of the 50/50 copolymers of higher molecular weight remains more than adequate.

Finally, it was of interest to establish whether the melt viscosity of the polymers is suitable for melt processing. The apparent melt viscosity η_{app} of a polymer of $[\eta] = 1.25$ dl/g was measured at 290°C (i.e. close to the lower limit of the processing temperature range) at apparent shear rates $\dot{\gamma}_{app}$ ranging from 30 to 3000 s^{-1}. Throughout this range the polymer exhibited non-Newtonian behaviour which can be expressed in power-law form

$$\eta_{app} = K\dot{\gamma}_{app}^{(n-1)}$$

with $n = 0.66$ and $K = 385$ Pa s^n. The apparent viscosity at 100 s^{-1} was 80 Pa.s which is acceptable for melt processing.

CONCLUSIONS

For poly(chloro-1,4-phenylene terephthalate-co-4,4′-oxybisbenzoate) copolymer compositions from 75/25 to

25/75 the nematic temperature range is greater than 100°C, which is more than adequate for convenient melt processing.

The molecular weight of the 50/50 copolymer is adversely influenced by evaporation of the volatile monomer, chlorohydroquinone diacetate, during the early stages of the polymer preparation, so excess of this reactant is required for attainment of the highest molecular weight. This will also apply to other compositions.

The crystal–nematic transition temperature of 50/50 copolymers is strongly influenced by their molecular weight. There is evidence that this also applies to the 0/100 homopolymer. It is suggested that this is a common feature of nematogenic copolymers arising from a low value of their heat of fusion.

The isotropization temperature of the 0/100 homopolymer is affected by the molecular weight even more strongly than the crystal–nematic transition. Thus, the effects of molecular weight should always be taken fully into consideration when drawing conclusions about the effect of chemical structure on the transition temperatures.

In common with other thermotropic polymers the glass transition temperature of the materials investigated was found to be unexpectedly low. This is one of the features of thermotropic materials which is of crucial importance for their practical utilization. It therefore requires further work aimed towards understanding of the glass transition in thermotropic polymers and towards synthesis of materials which do not suffer from this shortcoming.

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