

Preparation and characterization of thermotropic liquid crystal copolyesters containing *m*-hydroxybenzoic acid units

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Wholly aromatic, main-chain copolyesters derived from terephthalic acid and phenylhydroquinone modified with *m*-hydroxybenzoic acid were prepared and characterized by elemental analyses, ¹³C nuclear magnetic resonance, thermogravimetric analysis, optical observations, differential scanning calorimetry and wide-angle X-ray diffraction. The phases behaviours depended on copolymer composition. Poly-(*p*-phenylphenylene terephthalate-*co-m*-hydroxybenzoate)s with molar percentages of the *p*-phenylphenylene terephthalate units in excess 70 mol% displayed thermotropic mesophases at relatively low temperatures and exhibited good thermal stability up to about 400°C. Increasing content of *m*-hydroxybenzoic acid units, which increased the amount of structural irregularity, decreased the isotropization temperature and the temperature at which the melt started to flow, and also caused a loss of both crystallinity and of liquid crystallinity. Copyright © 1996 Elsevier Science Ltd.

(Keywords: liquid crystal polymers; hydroxybenzoic acid; characterization)

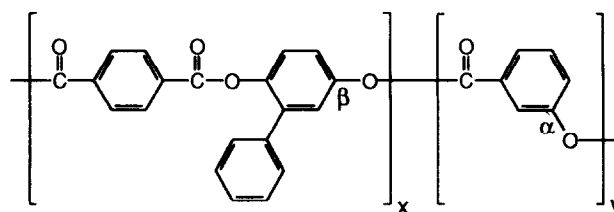
INTRODUCTION

In recent years considerable interest has developed in the properties of thermotropic liquid crystalline polymers. This is a consequence not only for their scientific interest but also from an industrial point of view. One of the most distinguishing properties of these polymers is the ease in producing a uniform molecular orientation under elongational flow. Such molecular orientation results in low melt viscosity along the flow direction and gives rise to high strength fibres by melt extrusion¹⁻⁵.

Most liquid crystalline, main-chain thermotropic polymers are aromatic copolyesters, many of which are composed entirely of rigid, linear, aromatic ester units and, as a result, they have high melting temperatures. These transition temperatures can be lowered to a melt-processable range through the introduction of flexible aliphatic units, but this possibility is not always desirable. Such segments will inherently weaken the structure, adversely affecting the strength and stiffness properties. Alternatively, either structural modifications with substituents on the aromatic rings, such as the use of phenylhydroquinone, or the inclusion of comonomers of different size, or the use of *meta*-substituted units, can also decrease the polyester melting point without adversely affecting the mechanical properties^{6,7}.

The above concepts concerning the molecular engineering of thermotropic liquid crystal polymers are fairly well established; however, as pointed out by Cai and Samulski⁸, correlations between structure and liquid crystalline mesophase formation are not extensive. In addition, a complete understanding of how structural changes affect the rheological properties of the thermotropic polymers is lacking⁹.

In order to study the monomer structural effects first on liquid crystallinity, and later on the melt rheology, we synthesized a series of poly(*p*-phenylphenylene terephthalate-*co-m*-hydroxybenzoate)s (PY) that are composed of different ratios of phenyl-*p*-phenylene-dioxyterephthaloyl (PhHQ/TA) and *m*-oxybenzoyl units (*m*-HBA). The composition of these copolymers was changed by gradually increasing the proportion of the non-linear *m*-hydroxybenzoyl units (*y*) in order to alter the backbone rigidity (persistence length). The



Structure 1 PY

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report¹⁰ that wholly aromatic liquid crystal copolyesters containing *m*-hydroxybenzoyl units showed higher mechanical properties than the corresponding copolyesters containing the same molar proportion of linear *p*-hydroxybenzoyl units made the kinked monomer attractive for inclusion in the polymer backbone. It is expected that copolymers containing this monomer will show optimal mechanical properties in addition to lower thermal transitions than those of the corresponding homopolymers. We report here on the compositional influence on thermal and mesomorphic properties of PY polymers.

EXPERIMENTAL

Monomers

Terephthalic acid (TA), *m*-hydroxybenzoic acid (*m*HBA) and phenylhydroquinone (PhHQ) were obtained commercially and used without further purification. *m*-Acetoxybenzoic acid (*m*ABA) was prepared by the acetylation of *m*HBA as follows. *m*HBA (100 g, 0.724 mol) was dissolved in an aqueous solution of sodium hydroxide, 900 ml of ice–water mixture were added, and acetic anhydride (93 ml, 0.905 mol) was added into the cold solution. The resulting mixture was stirred for 2–3 min and 95 ml of HCl (35%) were added. The white precipitate was filtered, washed with distilled water, and dried first in a current of dry air, then in a vacuum oven at 95°C for 24 h. The final product was subsequently purified by three recrystallizations from CHCl₃. Phenylhydroquinone diacetate (PhHQDA) was prepared by the acetylation of PhHQ. A mixture of PhHQ (0.422 mol), 50 ml of acetic anhydride and 10 ml of acetic acid was heated until complete dissolution. The mixture was then poured into an ice–water mixture. The precipitate was filtered and dried, and the product was recrystallized from toluene at 4°C.

Copolymers

All copolymers were synthesized by melt polycondensation reactions without an added catalyst. The synthesis of the copolymer P20 is described in detail. A mixture of PhHQDA (6.27 g), TA (4.12 g) and *m*ABA (1.12 g) was placed in a flask equipped with inlet and outlet tubes for nitrogen flow, and a magnetic stirrer. The reaction vessel was evacuated and purged with nitrogen three times to remove all traces of air, and then immersed into a salt bath at 180°C to dry the reactants. The bath was subsequently heated to 265°C to initiate the reaction while the reaction mixture was continuously stirred under nitrogen. After 210 min at 265°C, the bath temperature was increased to 275°C and maintained at this temperature for 270 min. When this step of the reaction was completed the mixture looked homogeneous, with some material sublimed on the top of the vessel. The bath temperature was then increased to 285°C, and at this stage the reaction mixture was viscous enough to stop the stirrer. After 12 h at 285°C, the temperature was increased to 295°C and maintained at this temperature for 6 h under vacuum (0.1–0.01 mmHg). Analysis: calcd for (PhHQ/TA)_{0.8}-(*m*HBA)_{0.2}: C 75.42, H 3.78. Found: C 75.23, H 3.75.

The reaction mixture for the preparation of the copolymer P30 was a beige melt at 265°C. It was maintained for 24 h at this temperature, after which the

bath temperature was increased to 275°C and, after 1 h, vacuum was applied for 24 h. Analysis: calcd for (PhHQ/TA)_{0.7}-(*m*HBA)_{0.3}: C 75.11, H 3.76. Found: C 74.37, H 3.28.

For the preparation of P40, the reaction mixture was maintained at 265°C for 210 min, then heated to 275°C for 4 h, and finally to 285°C for 14 h, then vacuum was applied at this temperature for 10 h. All copolymers were dissolved in a CHCl₂CHCl₂:ClC₆H₄OH (2 : 1) solvent mixture, filtered and precipitated in ethanol, washed twice with ethanol, purified by Soxhlet extraction for 24 h with methanol, and dried at reduced pressure at 90°C for 24 h. Analysis: calcd for (PhHQ/TA)_{0.6}-(*m*HBA)_{0.4}: C 74.74, H 3.72. Found: C 73.90, H 3.81.

Polymer characterization

Elemental analysis was performed by the Microanalytical Laboratory of the University of Massachusetts. ¹³C nuclear magnetic resonance (n.m.r.) spectra of the polymers were recorded on a Varian XL300 spectrometer at room temperature for solutions in deuteriochloroform (CDCl₃)/trifluoroacetic acid (TFA) (1 : 1 (v/v)) mixtures. The signal at 149–149.6 ppm corresponding to C_α atoms (see *Structure 1*) and the doublet at 150–151.3 corresponding to the C_β were used to measure the copolymer compositions. The experimental conditions reported by Komber *et al.* were used for the measurements of quantitative ¹³C n.m.r. spectra¹¹. Inherent viscosities of the copolymers were determined with an Ubbelohde viscometer at 22°C in CDCl₃/TFA (1 : 1 (v/v)). Thermogravimetric analysis (t.g.a.) measurements were performed on a Perkin Elmer TGS 2 under an atmosphere of nitrogen. Optical microscopy observations were carried out in a Carl Zeiss Ultraphoto II Polarizing Microscope equipped with a Mettler FP2 hot-stage. The temperature at which the melt started to flow (*T_f*) was taken as the temperature at which the material started to move between the glass covers. The differential scanning calorimetry (d.s.c.) measurements were performed on a Perkin Elmer DSC 2. The temperature and power ordinates of the d.s.c. equipment were calibrated with tin and zinc standards. The thermal transitions are reported as the maximum or minimum of the endothermic or exothermic peaks, respectively. Glass transitions (*T_g*) were taken at the middle of the change in the heat capacity. Wide-angle X-ray diffraction (WAXD) patterns were recorded with a Philips APD1700 Automated Power Diffractometer System 1.

RESULTS AND DISCUSSION

The compositions of the different copolymers determined by ¹³C n.m.r. spectroscopy, inherent viscosities and polymer yields are listed in *Table 1*. The analyses of the ¹³C n.m.r. spectra indicated that the actual compositions of the copolyesters were very close to those desired for the polymerization reactions in accordance with the initial monomer compositions. The results of elemental analyses are also in good agreement with these values.

The solid phases of P20 and P30 were birefringent and their mesophases exhibited thread-like textures which were characteristic of nematic liquid crystals at 330°C and 270°C, respectively. Photomicrographs obtained with the optical microscope under crossed polarizers are shown in *Figures 1a* and *2a*.

Table 1 Copolymers PY prepared by melt polycondensation reactions

Polymer	Monomer composition (mole ratio PhHQDA-TA/ <i>m</i> ABA)	Observed copolymer composition ^a (<i>x</i> / <i>y</i>)	Copolymer yield (%)	[η] ^b (dl g ⁻¹)
P20	80 : 20	81 : 19	86	0.70
P30	70 : 30	69 : 31	91	0.70
P40	60 : 40	57 : 43	90	0.44

^a Mole ratio of monomer units in isolated copolyesters as determined by ¹³C n.m.r. spectroscopy

^b Measured in CHCl₃/TFA (1 : 1, v/v) solution at 22°C

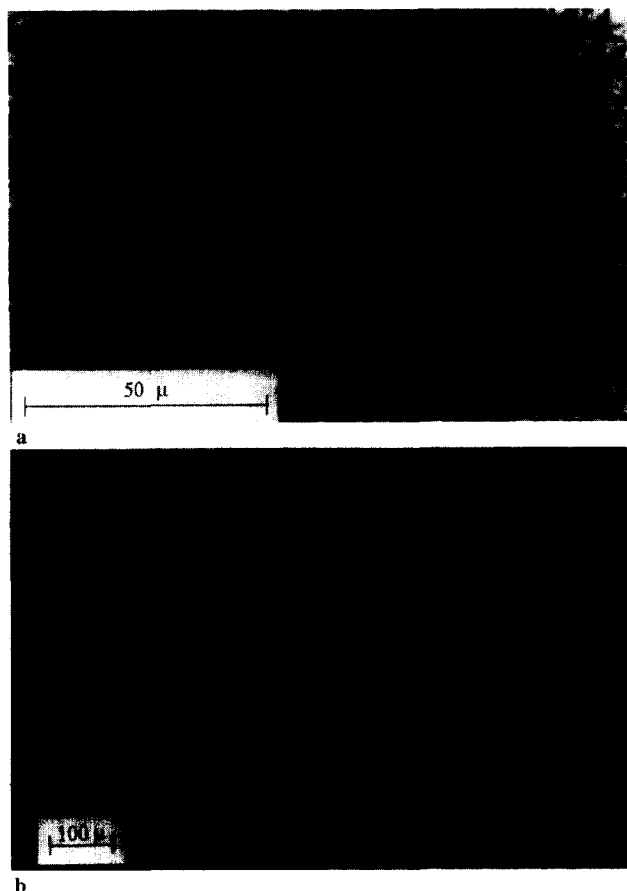


Figure 1 Optical microscopy photomicrographs obtained with crossed polarizers of the P20 copolymer: (a) at 330°C, anisotropic melt; (b) at 373°C, biphasic melt

As the temperature was increased from 330°C at 10°C min⁻¹, phase separation of isotropic domains occurred for P20 at 360°C. The domains grew with increasing temperature and time until a phase inversion occurred (*Figure 1b*). That is, the continuous phase changed from anisotropic to isotropic at 380°C. On cooling from the isotropic melt at 10°C min⁻¹, the transition to the mesophase was observed at 347°C. Thread-like texture developed very rapidly with decreasing temperature, and this organization was retained while the copolymer was cooled to room temperature. In the case of the P30 copolymer, the mesophase–isotropic transition began at 310°C (*Figure 2b*). Isotropization occurred at 350°C. On cooling at 10°C min⁻¹ from the isotropic, the thread-like texture started to develop slowly at 275°C. To observe a more sharp thread-like texture, it was necessary to cool this copolymer from the isotropic to 275°C and maintain it at this temperature for

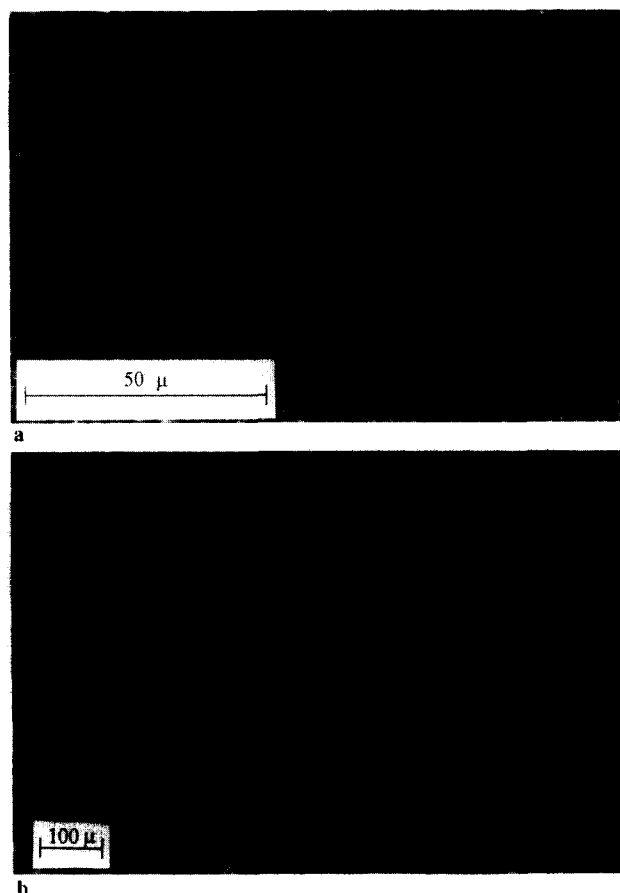


Figure 2 Optical microscopy photomicrographs taken with crossed polarizers of P30 copolymer: (a) at 270°C, anisotropic phase; (b) at 335°C, biphasic melt

some hours. No birefringence was observed for the P40 copolymer under any thermal conditions.

The nematic mesophases of the P20 and P30 copolymers exhibited stirred opalescence, while the isotropic phases of the three copolyesters were transparent. The P20 copolymer started to flow at 310°C, the P30 copolymer at 270°C and the P40 copolymer at 200°C.

D.s.c. thermograms for the as-prepared P20 copolymer are shown in *Figure 3*. During the first heating cycle, at a heating rate of 20°C min⁻¹, two endothermic peaks appeared with maxima at 334°C and 352°C, corresponding respectively to the melting (T_m) and to the clearing (T_i) transitions (*Figure 3a*). This behaviour agreed with that observed on the optical microscope. On cooling at 10°C min⁻¹, two exothermic peaks appeared at 344 and 192°C (*Figure 3b*). The transition at 344°C is attributed to the isotropic–nematic transition as observed in the optical microscope. The peak at 192°C can be assigned to a crystal–crystal transition because fluidity was not observed on the sample at this temperature. The nematic–crystal transition was not observed during the cooling. On the second and subsequent heatings at 10°C min⁻¹ the glass transition (T_g) was observed at 140°C (*Figure 3c*). One exothermic peak, typical of ‘cold crystallization’, appeared at 254°C. The melting point was detected at 290°C, but the isotropic transition was not observed.

To further investigate the reasons for the thermal behaviour, the P20 copolymer was subjected to thermal treatments at three different annealing temperatures (T_a). The copolymer was first heated to the isotropic

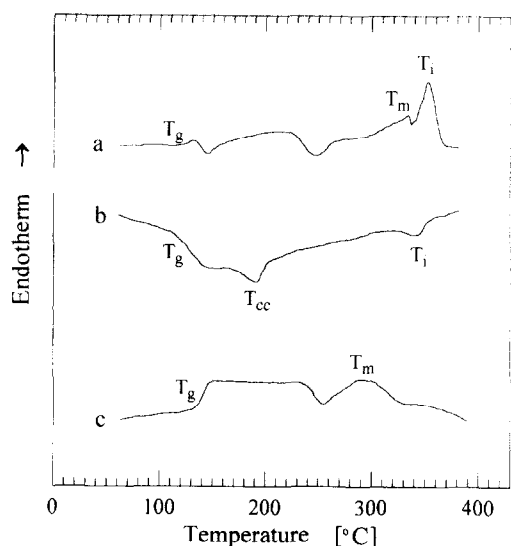


Figure 3 D.s.c. thermograms of P20 copolymer: (a) first heating cycle recorded at $20^{\circ}\text{C min}^{-1}$; (b) first cooling cycle at $10^{\circ}\text{C min}^{-1}$; (c) second heating cycle at $10^{\circ}\text{C min}^{-1}$

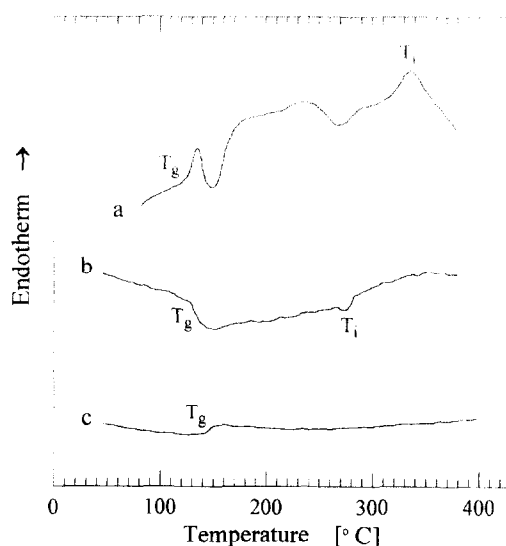


Figure 5 D.s.c. thermograms of P30 copolymer: (a) first heating cycle recorded at $40^{\circ}\text{C min}^{-1}$; (b) first cooling cycle at $10^{\circ}\text{C min}^{-1}$; (c) second heating cycle at $10^{\circ}\text{C min}^{-1}$

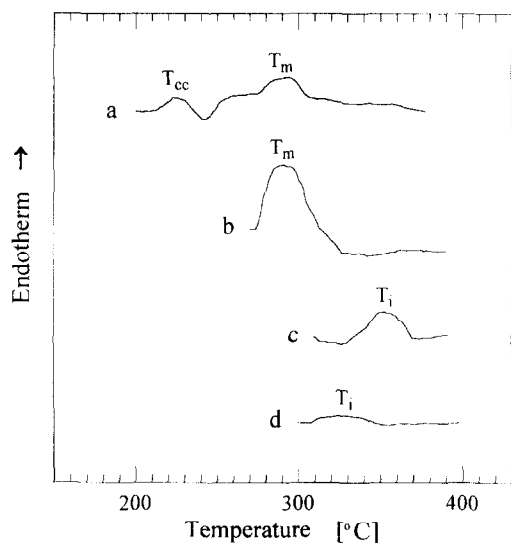


Figure 4 D.s.c. thermograms of P20 copolymer after annealing for 5 h at (a) 200°C , (b) 270°C , and (c) 310°C , and of P30 copolymers after annealing for 5 h at (d) 300°C

phase (390°C) at $40^{\circ}\text{C min}^{-1}$ and then cooled to the annealing temperature at the same rate and maintained at this temperature for 5 h. When the polymer was maintained at $T_a = 200^{\circ}\text{C}$ for 5 h and then heated from T_a at a heating rate of $5^{\circ}\text{C min}^{-1}$, two endothermic peaks with maxima occurring at 225°C and 290°C were observed (Figure 4a). The peaks corresponded to a crystal-crystal transition and to the melting point, respectively. If the copolymer was maintained at $T_a = 270^{\circ}\text{C}$ for 5 h, then heated at $5^{\circ}\text{C min}^{-1}$ from the T_a , only one endothermic peak with a maximum at 290°C was observed (Figure 4b). This peak corresponded to the melting transition because, under the optical microscope, the copolymer started to flow at this temperature. Annealing at 310°C for 5 h and heating from T_a at the same rate as in the previous experiments resulted in one endothermic peak with a maximum occurring at 352°C (Figure 4c) that corresponded to the isotropization transition of the polymer melt.

We have also observed on the optical microscope the behaviour of polymer samples submitted to thermal treatments under similar conditions to the annealing processes carried out with d.s.c. When the temperature of the hot-stage is lowered from the isotropic state and kept at 347°C for several hours, polymer P20 shows an increase in the perfection of the thread-like structure and in the quality of the birefringence. Polymer P30 exhibits similar behaviour when annealed at 275°C , but requires longer times than polymer P20 to reach an equivalent degree of perfection in the quality of the thread-like structures.

It is well known that main-chain liquid crystalline polymers exhibit ill-defined d.s.c. traces where the melting and isotropization transitions are hardly discernible in many instances. In this case one may speculate about the absence of the isotropization peaks on the second and subsequent d.s.c. runs. The optical observations suggest that both polymers may require some time to achieve good alignment into liquid crystalline domains. Thus, heating at $10^{\circ}\text{C min}^{-1}$ as was done in the d.s.c. studies may not give the polymers enough time to reach a considerable degree of order. The amount of heat involved in this transition is probably too low to be detected by d.s.c. When annealing of the sample is performed at temperatures where the polymers are in the liquid crystalline state close to the isotropization temperature, better alignment of the liquid crystals is obtained. This results in detectable isotropization endotherms in the d.s.c. scans. Annealing at lower temperatures just below the T_{CN} , where the mobility of the polymer chain is substantially reduced may result in local reorganization within a small concentration of defective three-dimensional crystallites with no major rearrangements of the rest of the polymer¹². Heating of these samples beyond the annealing temperature will improve the quality of the fusion endotherm but not that of the isotropization transition.

Figure 5 shows the d.s.c. thermogram of the as-prepared P30 copolymer. In the first heating cycle at $40^{\circ}\text{C min}^{-1}$ the endothermic peak at 336°C corresponded to the isotropic transition (Figure 5a). On

Table 2 Thermal properties of copolyesters PY as determined by d.s.c.

Copolymer	D.s.c. cycle	Transition temperatures (°C)				Heats of transition (J g ⁻¹)		
		<i>T_g</i>	<i>T_{kk}</i>	<i>T_m</i>	<i>T_i</i>	ΔH_{kk}	ΔH_m	ΔH_i
P20	1st heat	128	210	334	352			
	1st cool	130	192		344	1		3
	2nd heat	140		290			5	
	<i>T_a</i> = 200°C ^a		225	290		3	5	
	<i>T_a</i> = 270°C ^a			290			11	
	<i>T_a</i> = 310°C ^a				352			3
P30	1st heat	128			336			
	1st cool	135			275			1
	2nd heat	148						
	<i>T_a</i> = 200°C ^a							
	<i>T_a</i> = 250°C ^a							
	<i>T_a</i> = 300°C ^a				330			1
P40	1st heat	145						
	1st cool	142						

^a D.s.c. heating cycle starting from this annealing temperature

cooling at 10°C min⁻¹, there was only one exothermic peak at 275°C and this peak was associated with the isotropic–anisotropic transition (Figure 5b); these assignments were confirmed by optical microscopy, as discussed previously. No melting transitions were observed. On the second and subsequent heatings at 10°C min⁻¹, the d.s.c. scans did not show either melting or isotropization transition (Figure 5c), and only the glass transition was observed at 148°C.

The P30 copolymer did not exhibit melting point transitions even after annealing, so this copolymer may have been either intrinsically amorphous or extremely slow to crystallize. The structural irregularity caused by the random sequence of the two types of repeating units, together with the existence of a bent structure in the *m*-oxybenzoyl units, probably hindered crystallization. When the copolymer was maintained at 300°C for 5 h, then from this *T_a* only one weak endothermic peak with a maximum at 330°C was observed, and this peak corresponded to the isotropic transition (Figure 4d).

Copolymer P40 did not exhibit any endothermic or exothermic peaks in any heating or cooling cycle. Instead, a prominent glass transition was observed at 145°C on heating.

The phase transition temperatures and the heats of transition of these copolyesters are summarized in Table 2. Low heats of the isotropic–nematic transition were observed on cooling of the P20 and P30 copolymers. To detect the same phenomena on heating, long annealing times were required. The low heat of melting observed on heating the P20 copolymer, and the absence of a crystallization exotherm in the cooling cycle, might be taken as an indication that only a small part of the sample experienced that thermal transition. Thus, it is possible that the morphological formation process observed in the d.s.c. corresponded to a lateral crystallization, as one might expect from parallel-aligned polymer chains in the nematic state, which favours the two-dimensional arrangement of neighbouring molecules¹³.

It is worth mentioning that the parent homopolymer

of PhHQ and TA has melting and isotropization transitions of 345°C and 475°C (ref. 14). Lower melting transitions and narrower temperature mesophase ranges of approximately 60°C, according to the optical observations and the d.s.c. data, were observed for P20 and P30. These results are in agreement with previous work which indicates that the introduction of non-linear units into polyesters lowers melting temperatures and, at the same time, decreases the mesophase temperature range⁸. Jackson disclosed that copolymers of HQ, TA and *m*HBA with more than 50% of non-linear units melted to an isotropic state⁷. In our case, only 40% of non-linear units on the polymer backbone were needed to lose liquid crystallinity. However, the PY polymers with lower contents of *m*HBA units melted to a liquid crystalline state. This indicates that both cooperative effects of introducing the bulky substituted monomer PhHQ and the non-linear *m*HBA are needed to decrease the melting transitions of this system to temperature ranges suitable for rheological studies. In addition, the broad melting transitions by PY copolymers offer the possibility of studying the mechanical properties of two-phase melts.

As mentioned earlier, the samples of the P30 and P40 copolymers did not show melting endotherms in their d.s.c. thermogram, implying that they were totally amorphous; their amorphous nature was supported by X-ray diffraction studies. Figures 6a and 6c show the WAXD powder patterns of the P30 and P20 copolymers. They exhibited only broad peaks centred around $2\theta = 20$, corresponding to interchain spacing characteristic of amorphous polymers. In order to induce crystallization, the P30 and P20 copolymers were subjected to the same thermal treatments as used to obtain the d.s.c. thermograms. The X-ray diffractograms shown in Figures 6b and 6d for the annealed polymers provided similar information to the d.s.c. thermograms. After annealing the P20 copolymer at 270°C for 5 h, the WAXD pattern showed a sharp peak at $2\theta = 22$ and two small peaks at $2\theta = 14$ and $2\theta = 29$. This result is clear evidence that the copolymer with the lowest content

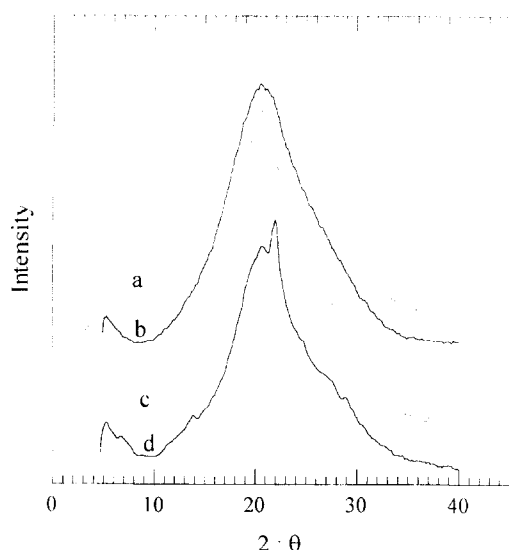


Figure 6 WAXD patterns of the P30 copolymer: (a) original powder sample; (c) after annealing at 270°C for 5 h; and the P20 copolymer; (b) original powder sample; (d) after annealing at 250°C for 5 h

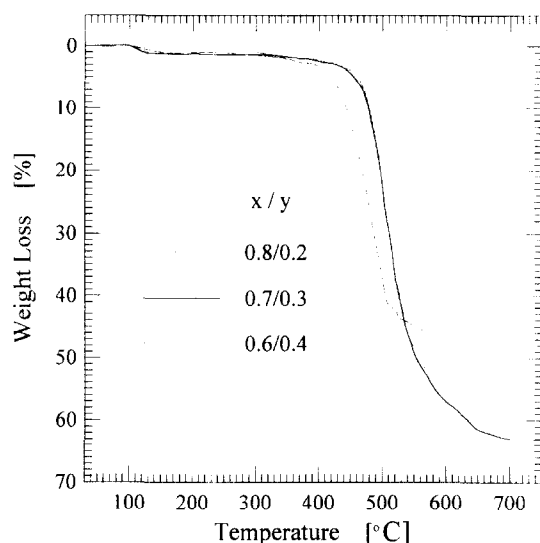


Figure 7 Thermogravimetric analysis of the P20, P30 and P40 copolyesters

of *m*HBA was semicrystalline. The P30 and P40 copolymers showed no crystallinity after being subjected to annealing at $T_a = 250^\circ\text{C}$ for 5 h.

Thermal stabilities of the copolymers were measured by t.g.a. The weight loss of the samples was measured continuously under a nitrogen atmosphere while the temperature was increased at a heating rate of $10^\circ\text{C min}^{-1}$. The observed weight losses for each of the three copolymers are plotted as a function of the temperature in *Figure 7*. The polymers exhibited approximately 1% weight loss near 100°C , which could be associated with the desorption of water. The temperature range at which the P70 and P60 copolymers showed a 10% weight loss extended from 430°C to 480°C . The equivalent range for the P80 copolymer extended from 390°C to 440°C . These results correspond to the decomposition peaks which began at 390°C in the d.s.c. thermograms of the P80 copolymer.

Weight loss of the copolymers was also measured as a

function of time at constant temperatures near the melting and isotropization points. The P30 polymer exhibited only a slight, slow decomposition at 290°C and 350°C and lost only 4% of the initial weight after 5 h at these temperatures. A similar behaviour was exhibited by the P40 copolymer. In this case the weight loss was 4% of the initial weight after 5 h at 320°C . The P20 copolymer lost 4% of the initial weight after 5 h at 330°C , but at 370°C the decomposition was rapid. After 30 min at 370°C this copolymer had lost 8% of the initial weight, and after 5 h at this temperature, the weight loss was 30% of the initial weight.

CONCLUSIONS

Three wholly aromatic, main-chain copolyesters derived from terephthalic acid, phenylhydroquinone and *m*-hydroxybenzoic acid were synthesized to investigate their liquid crystalline properties. Two of them exhibited liquid crystallinity and had good thermal stabilities up to about 400°C . The copolymers with the lower ratio $(\text{PhHQ/TA})_x(\text{mHBA})_y$ were amorphous. Thus, as expected, the type and extent of melt-state anisotropy and the degree of crystallinity of the $(\text{PhHQ/TA})_x(\text{mHBA})_y$ copolyesters, under comparable thermal conditions, were direct functions of the x/y unit ratio. Lower ratios of $(\text{PhHQ/TA})_x/(\text{mHBA})_y$ resulted in lower temperatures at which the melt started to flow and in the isotropization temperatures until a composition was reached where further inclusion of *m*HBA units destroyed the anisotropy altogether. The increase in *m*HBA unit content also caused loss of crystallinity of the copolyesters. Rheological studies are now in progress and preliminary results indicate typical liquid crystalline behaviour, such as onset of negative normal stresses followed by several positive oscillatory maxima on start-up shear experiments, oscillatory damped maxima on the transient shear viscosity and the three regions of steady shear viscosity as described by Onogi and Asada¹⁵.

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