

Liquid Crystalline Aromatic Polyesters Formed with Terephthalic Acid, Phenyl Hydroquinone, and Naphthalene or Anthracene Diols

NAZIR KHAN,* ZAHIR BASHIR, and DUNCAN M. PRICE

Courtaulds, 72 Lockhurst Lane, Coventry CV6 5RS, United Kingdom

SYNOPSIS

The synthesis and characterization of aromatic copolyesters containing terephthalic acid and phenyl hydroquinone as the major constituents and either 1,4-naphthalene diol or 1,4-anthracene diol as the minority comonomer is described. Both polymers melted in the vicinity of 300°C, giving birefringent fluids. Optical microscopy showed Schlieren textures consisting predominantly of inversion walls characteristic of the nematic phase. The clearing temperature was in the vicinity of 460°C, but was accompanied by charring. DSC experiments showed a high glass transition temperature of 130–160°C for both polymers. Crystal–nematic and nematic–isotropic endotherms were observed on heating; however, degradation took place near the isotropization temperature. Thus, on cooling, the sequence was reversible only if the previous heating was beyond the crystal–nematic but below the isotropization temperature. The polymers were stable in terms of gross weight loss until about 450°C, though there were indications that crosslinking occurred above about 400°C over a short period of time. The polymers formed low-viscosity injection-molding compounds, but to use them effectively, it would require mold–gate designs that reduce the “jetting” tendency for liquid crystal polymer melts, which result in weld lines. © 1995 John Wiley & Sons, Inc.

INTRODUCTION

Certain aromatic polyesters show thermotropic liquid crystalline behavior and these are sought because of the ease with which they can be oriented and spun into high-modulus fibers or injection-molded into articles that combine rigidity with dimensional stability when compared with ordinary polyesters such as poly(ethylene terephthalate) or other conventional thermoplastics.

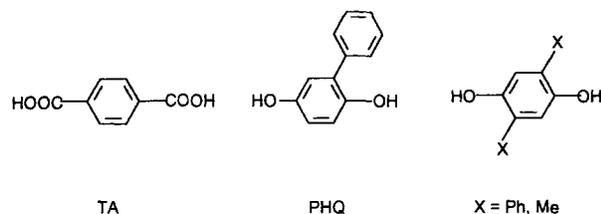
Liquid crystal polymers (LCPs) with very high glass transition and melting temperatures (400°C or over) are now commercially available.¹ Such high-melting temperatures can limit their use in conventional processing machinery. Thus, there is also a drive to make thermotropic LCPs with lower processing temperatures. There have been a number of investigations aimed at lowering the crystal melting

temperature to 300°C or below, while maintaining the liquid crystalline behavior.

Polyesters based on 100% *p*-hydroxybenzoic acid (*p*-HBA) or terephthalic acid (TA) and hydroquinone (HQ) are infusible and insoluble. From the several synthetic strategies available to reduce the melting temperatures and yet form liquid crystal phases from rigid rod polymers, we adopted the concept of “frustrated chain packing” proposed by Griffin and Cox.² This involves incorporating aromatic units with bulky, but rigid, substituents on the chain backbone which frustrates chain packing, thus lowering the crystallinity and depressing the melting point below the degradation temperature.

The literature contains several examples of this synthetic strategy: For instance, aromatic liquid crystal polyesters formed by the condensation of TA with methyl-, bromo-, chloro-, and methoxy-substituted HQ have been reported.³ Substitution of the HQ with a phenyl group to form phenyl-*p*-phenylene terephthalate was first disclosed by Payet.⁴ Jackson indicated the superior thermal stability of the phenyl

* To whom correspondence should be addressed.



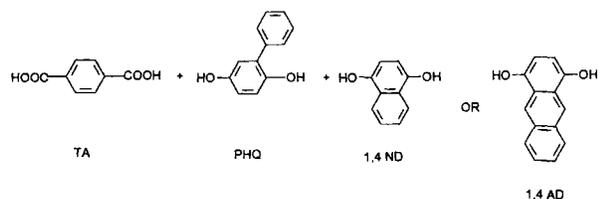
Scheme 1

substituent on the HQ compared with the chloro or methyl groups in such polyesters.⁵ It was reported that monosubstitution of the backbone aromatic ring with such large substituents depressed the crystal-to-liquid crystal melting temperatures without adversely affecting the mechanical properties.^{4,6} The analog of phenyl-*p*-phenylene terephthalate, namely, the polyester with the phenyl substituent on the TA instead of the HQ, has also been disclosed.⁷

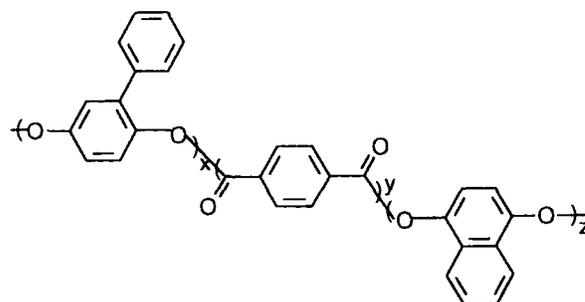
In our previous work, we explored the homopolymers made from TA and *symmetrically disubstituted* HQs.⁸ These polymers did not melt at all, even when the HQ was substituted with two instead of one bulky phenyl group. However, copolymers containing three monomers (TA, phenylhydroquinone [PHQ], and a small amount of a disubstituted HQ) were reported to form liquid crystalline melts at about 280–335°C with a clearing temperature around 440–480°C.⁸ The three constituents of our previous work are shown in Scheme 1. In contrast, in this work, we report on the preparation and characterization of liquid crystalline copolymers containing TA, PHQ, and a small amount of a naphthalene diol (ND) or an anthracene diol (AD), in place of the disubstituted hydroquinones that were previously used. This is shown in Scheme 2.

EXPERIMENTAL

The two polymers synthesized in this work are labeled A and B and are shown in Schemes 3 and 4. Table 1 shows the monomer compositions.



Scheme 2

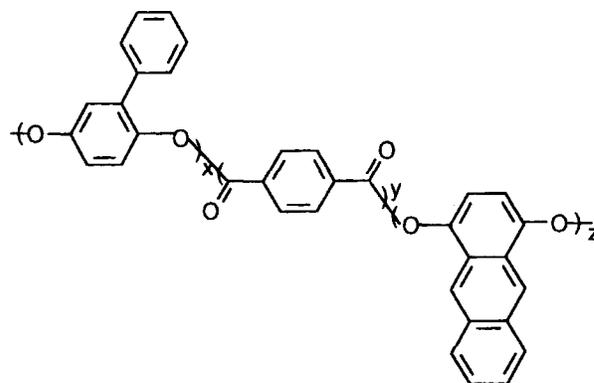


Scheme 3 Polymer A is the copolyester of TA, PHQ, and 1,4-ND.

Synthesis of Polymers

Terephthaloyl chloride, HQ (or 1,4-dihydroxybenzene), PHQ, 1,4-ND, and 1,4-AD were purchased from Aldrich. The monomer compositions used to make the copolymers are shown in Table I. Note that instead of using TA, terephthaloyl chloride was used owing to its higher reactivity. However, in the Discussion, these polyesters will be considered as being derived from the parent terephthalic acid.

The desired proportions of terephthaloyl chloride, PHQ, and the diol were placed into a polymerization flask equipped with a magnetic stirrer, a gas inlet/outlet, and a vacuum inlet. The polymerization flask was evacuated and then filled with nitrogen. This cycle was repeated four times. A slow stream of nitrogen was maintained in the flask to carry off the hydrogen chloride produced during the polymerization. The flask was heated in an oil bath to 190°C. To compensate for the melt becoming more viscous, the temperature was raised slowly to 240°C. When it was impossible to stir the melt further, vacuum (750 mbar) was applied and the melt was kept at this temperature for 5 h. The flask was cooled to room temperature, and the polymer was mechani-



Scheme 4 Polymer B is the copolyester of TA, PHQ, and 1,4-AD.

Table I The Monomer Ratios in Mol % for the Polyesters Used in This Work

Polyester	TPCL	PHQ	1,4-ND	1,4-AD
A	50	43.75	6.25	—
B	50	43.75	—	6.25

TPCL = terephthaloyl chloride; PHQ = phenylhydroquinone; 1,4-ND = 1,4-naphthalene diol; 1,4-AD = 1,4 anthracene diol.

cally crushed, extracted with acetone, and dried at 100°C.

Polarizing Optical Microscopy

All samples were examined with a Zeiss Axioplan polarizing microscope, equipped with hot-stage lenses. A Linkam hot-stage and allied temperature controller were used to heat and cool the sample at a controlled rate.

The normal technique of obtaining good textures by heating the sample up to the isotropization temperature and then cooling to the mesophase regime could not be adopted for these polymers because the clearing temperatures were in excess of 450°C and degradation occurred. The procedure adopted was as follows: The hot-stage was preheated to 380–400°C, with a glass coverslip resting on the heating block. A small fragment of polymer was dropped on the hot glass, whereupon it melted rapidly. A second coverslip was placed on top, and, initially, thinning the sample by pulling the top coverslip across the bottom one was attempted, but this led to an oriented melt without recognizable textures. The best method was to place the second coverslip on top of the molten sample and apply pressure to spread out the melt. This was necessary in order to thin the viscous melt and obtain recognizable textures.

Differential Scanning Calorimetry (DSC)

A Mettler DSC 30 was used in conjunction with a TC11 controller. Data analysis was performed on an IBM microcomputer. The DSC cell was calibrated for temperature and enthalpy response according to the melting points and heats of fusion of pure indium, tin, zinc, and lead. All measurements were made in a static air atmosphere.

In the first set of experiments, heating scans were recorded at 10°C/min for both polymers in the range 30–480°C, allowing both phase transitions to be recorded. The cooling scan from 480 to 30°C at –10°C/min was recorded immediately afterward; these showed that the transitions were not fully re-

versible, due to the occurrence of severe degradation after isotropization. However, it was possible to show that the first transition was reversible. For this, in a second set of experiments, the samples were heated at 10°C/min. from 30 to 400°C (i.e., beyond the *K*–*N* but below the *N*–*I* transition, *K* = crystal, *N* = nematic, *I* = isotropic) and then cooled at –10°C/min from 400 to 30°C.

Thermogravimetric Analysis (TGA)

The thermal stability of these polyesters was assessed by conducting TGA experiments. A DuPont Instruments Model 951 TGA and 9900 computer thermal analyzer were used. The thermobalance was calibrated for weight and temperature response according to the deflection caused by standard milligram masses and the melting of tin, respectively. Approximately 20 mg of each sample was placed in a platinum boat suspended from the arm of the instrument and heated from ambient to 750°C at 10°C/min under a stream of dry air (flow rate: 20 mL/min).

RESULTS AND DISCUSSION

Before introducing the results of specific experiments, it is worth making a few general comments on these polymers. Both polymers were dark brown, the anthracene-containing polymer being the darker of the two. As with most aromatic polyesters of this kind, molecular weight determinations could not be conducted because of the difficulty in obtaining nontoxic solvents. However, we are confident that both samples were polymeric in nature. The melt viscosities were, in fact, higher than those of our polymers with disubstituted hydroquinones, reported previously. Both the current polyesters formed oriented fibers even by slight elongation of the melt. Robust, free-standing films and compression-molded slabs were made from these polyesters. Figure 1 shows an injection-molded screwdriver handle made from the ND copolyester. The article shows the typical weld lines caused by “jetting” of the melt in the mold, which, in fact, confers an attractive appearance, though it has an adverse effect on mechanical properties. Jetting occurs when LCP melts are injection-molded using conventional gating to the mold; specially designed mold gates are necessary to avoid this.

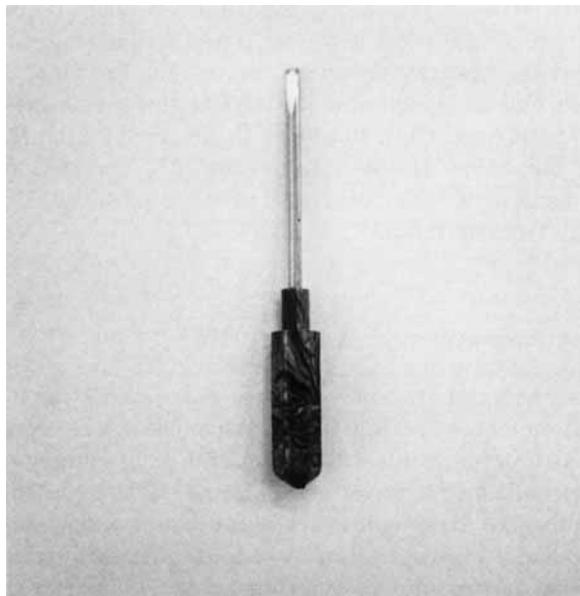


Figure 1 Injection-molded screw driver handle, formed from the ND polyester. Note the weld lines caused by jetting. This occurs typically with LCPs when using molds with gating designed for conventional thermoplastics.

Optical Microscopy and Phase Identification of Naphthalene and Anthracene Diol Polyesters

On heating, both polymers melted just above 300°C and formed a birefringent fluid, thus indicating the formation of a mesophase. As with the case of most

polymeric liquid crystals, it may be possible to observe a fluid phase that shows birefringence, but it is often difficult to obtain a recognizable optical texture.⁹⁻¹¹ This was the situation with these polymers and much perseverance was needed to thin the sample and obtain textures from which the mesophase could be identified.

Figure 2 shows a texture obtained from the ND polyester from which the mesophase can be identified. In Figure 2, the sample has planar orientation in large areas of the field of view, but it was populated with a few defects. An example of a defect with $s = \pm\frac{1}{2}$ (points with two brushes) is shown by the double arrows at the bottom of Figure 2. Defects with $s = \pm 1$ (four brushes emerging from a point) were rarer in these samples, but an example of this is shown by the single arrow in Figure 2. From the $\pm\frac{1}{2}$ singularities, it is possible to conclude that the mesophase was nematic.^{12,13} Note that Schlieren textures with $s = \pm 1$ can also be found in smectic C phases; however, in smectic C phases, singularities with $s = \pm\frac{1}{2}$ have not been found.^{12,13}

Figure 3 shows a texture obtained from the AD polyester at 385°C. This polymer was more difficult to obtain textures from owing to its higher viscosity and near-black color. The textures were also finer (i.e., smaller) than those in Figure 2. One textural feature is the inversion walls, starting and ending at $\pm\frac{1}{2}$ singularities (see black arrow in Fig. 3 for an example). From the presence of $\pm\frac{1}{2}$ singularities, one may conclude that the mesophase in the AD

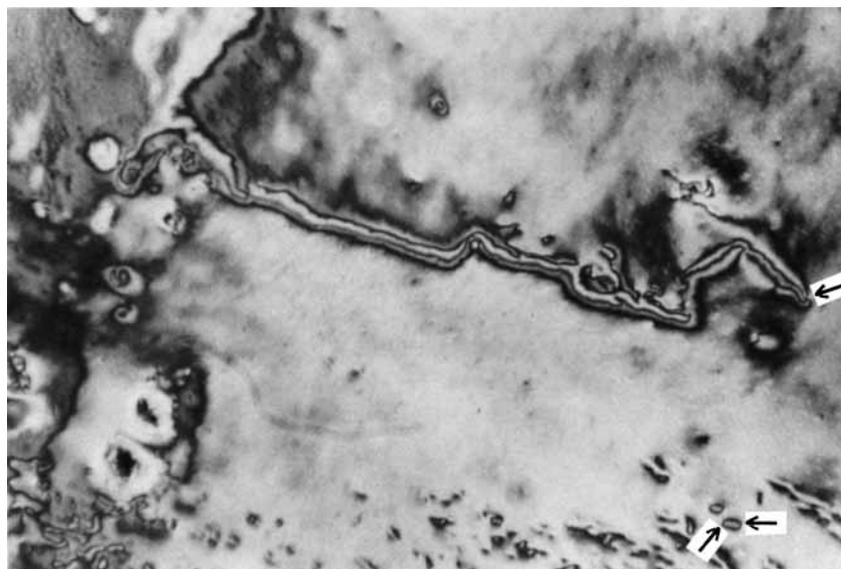


Figure 2 Nematic texture of the LCP of the ND copolyester. Crossed polars, 385°C. The orientation of the polars is north-south and east-west. The double arrows (bottom) show singularities with $s = \pm\frac{1}{2}$. Single arrow (right edge) shows singularity with $s = 1$.

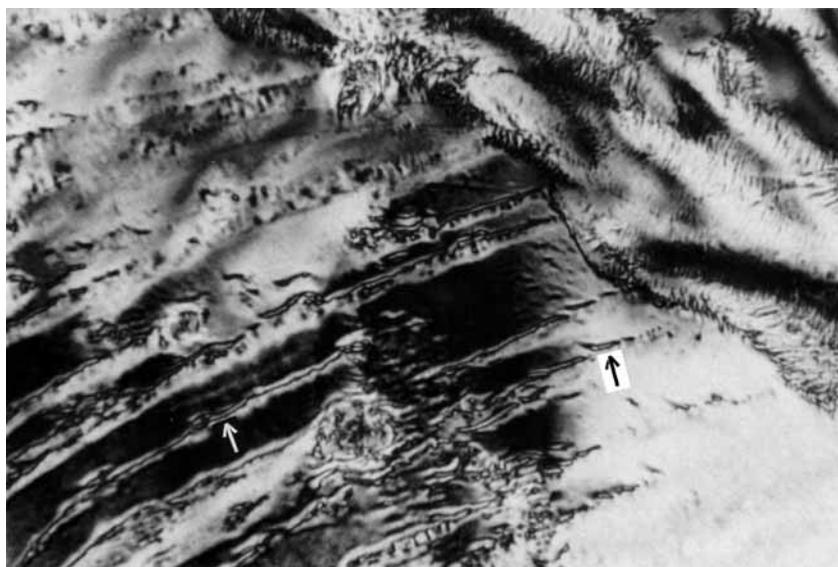


Figure 3 Nematic texture of the AD copolyester. Black arrow on the right side shows an inversion wall, starting and ending at singularities with $s = \pm\frac{1}{2}$. White arrow on the left side shows another inversion wall, whose center appears as a black line bordered by two bright stripes. Crossed polars, 385°C. The orientation of the polars is north–south and east–west.

polyester is also nematic. Another inversion wall whose beginning and end are either obscured or not in the field of view is shown by the white arrow in Figure 3. This wall runs diagonally from the bottom left corner of the picture. There is a $\pi/2$ turn of the molecular director at the center of the wall,¹² while the total change in orientation in crossing the wall is π . When the polarizers are parallel or perpendicular to the orientation outside the wall, as it is in the region over which the white arrow is placed in Figure 3, the region appears black, while the center of the wall can be seen as a black line which is bordered by two white stripes.

With both polymers, on isotropization, there was charring (detected by browning of the polymer), and, on cooling, some birefringence was regained but textures were not reobtained. However, in samples that had been heated up to only 400°C, on cooling the mesophase to room temperature, a mottling of the existing nematic texture occurred due to crystallization, but no distinctly different crystallization textures were formed.

DSC Thermograms

Figures 4(a) and 5(a) show the first heating scan of the ND and AD polymers. First, there is a glass transition that is observable in both polymers in the vicinity of 130–150°C. It can be seen that there is

an endothermic change about 300°C and this correlates with the crystal-to-nematic (*K-N*) transition observed by microscopy. This is followed by the endothermic *N-I* transition with a peak at about 410°C. The glass transition temperatures, peak

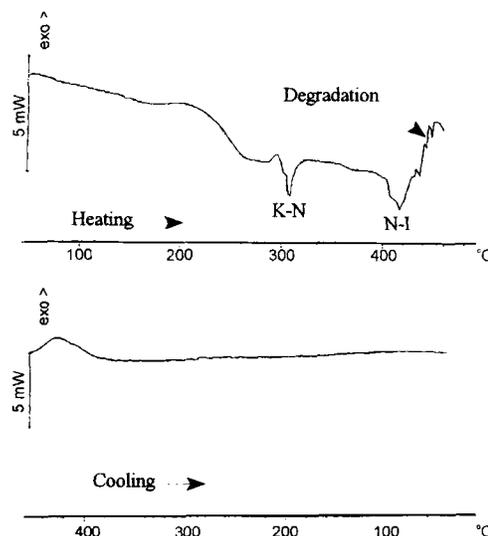


Figure 4 DSC heat-cool cycle of the ND copolyester: (a) the heating scan shows two major peaks, corresponding to the *K-N* and *N-I* transitions; (b) on the cooling scan after isotropization, the reverse transitions are affected by the degradation that had occurred on heating.

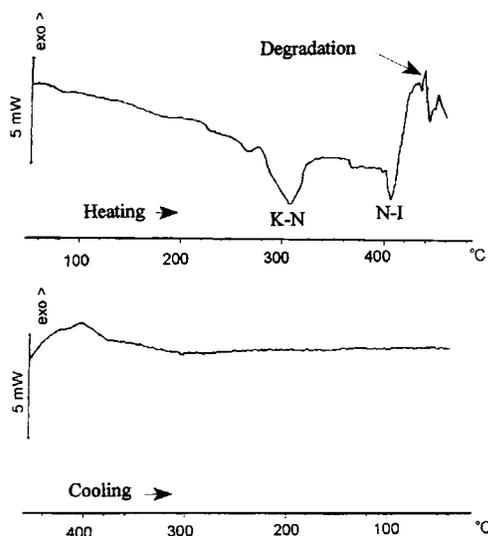


Figure 5 DSC heat-cool cycle of the AD copolyester: (a) the *K-N* and the *N-I* transitions are both observed in the first heating scan; (b) on the cooling scan after isotropization, the reverse transitions are affected by the degradation that had occurred on heating.

temperatures of the first-order phase transitions, and associated enthalpies are collected together in Table II. As observed by microscopy, the DSC heating scans also show that degradation occurs during or just after isotropization [Figs. 4(a) and 5(a)]. Thus, in the cooling scans after isotropization [Figs. 4(b) and 5(b)], there appears to be a broad exotherm starting above 400°C, possibly indicating that there is some reversibility in the *I-N* transition; however, there is no indication of a crystallization exotherm in either polymer. Evidently, these polymers are not sufficiently stable thermally to be cycled repeatedly up to the isotropization temperature.

Figures 6 and 7 show the scans recorded after the polymers were taken to an *intermediate* temperature of 400°C in the mesophase window and then cooled. On the heating scan, the melting peak due to the *K-N* transition is seen [Fig. 6(a) and 7(a)]. On cooling, the reverse *N-K* transition is now observ-

Table II T_g , T_{K-N} , T_{N-I} , ΔH_{K-N} , ΔH_{N-I} for the Polyesters, Obtained from the DSC Results^a

Polyester	T_g (°C)	T_{K-N} (°C)	T_{N-I} (°C)	ΔH_{K-N} (J/g)	ΔH_{N-I} (J/g)
A	131	308	416	3.7	9.8
B	157	306	405	16.9	2.4

^a T_{K-N} and T_{N-I} values are from the peak temperatures in Figures 4 and 5.

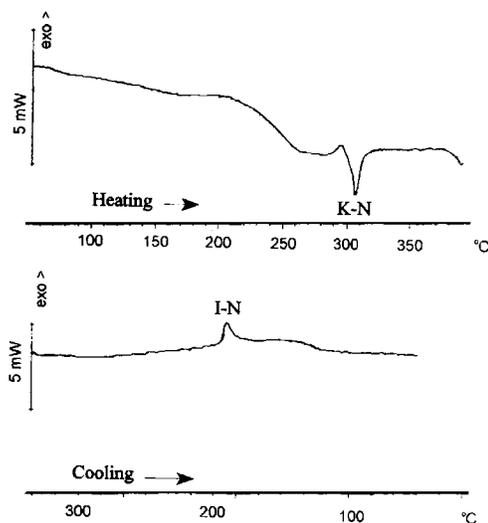


Figure 6 DSC scans of the ND copolyester: (a) on heating past the *K-N* transition to an intermediate temperature of 400°C; (b) on cooling, the *N-K* transition is now observed as severe degradation had not occurred in the heating scan.

able [see Figs. 6(b) and 7(b); compare with the cooling scans in Figs. 4(b) and 5(b)], though this crystallization occurs with supercooling. Again, the glass transition is also found, suggesting that the materials were partially amorphous.

The homopolymer of PHQ and TA has a *K-N* transition of 333–350°C.⁸ It is worth commenting on the efficacy of comonomers such as the ND and

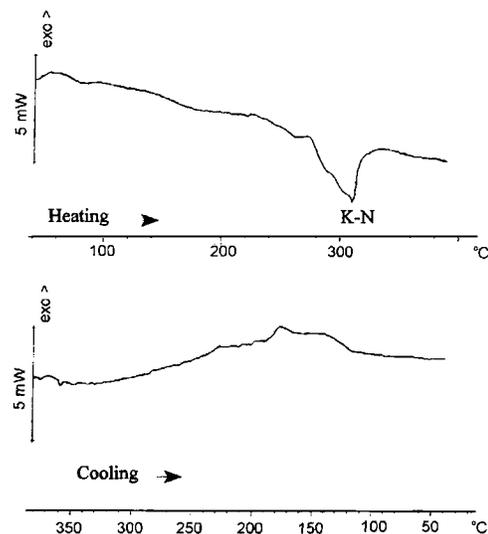


Figure 7 DSC cooling scan of the AD copolyester: (a) on heating past the *K-N* transition to an intermediate temperature of 400°C; (b) on cooling, the *N-K* transition is now observed as severe degradation had not occurred in the heating scan.

AD in lowering the $K-N$ melting temperature of polyesters containing PHQ and TA as principal constituents, this being one of the purposes of the present investigation. Inspection of Table II shows that these comonomers incorporated in small amounts lower the $K-N$ melting temperature by about 30°C. Their effect is comparable to that of using a *disubstituted* phenyl or methyl HQ as the comonomer.⁸ With the disubstituted comonomers of Scheme 1, this effect is achieved by the disruption in packing caused by the *two large substituents* and the consequent effect on crystallization. Here, a similar effect is achieved by using a single large, *meta*-linked comonomer such as the 1,4-ND and 1,4-AD. It appears that the $K-N$ temperature of the polyesters of PHQ and TA cannot be lowered much below 300°C if the comonomer is present in amounts such as 5–10 mol %. Increasing the comonomer content does reduce the melting temperature further but this affects mechanical properties. For obtaining melting transitions around 200°C or lower, one has to use polymers with rigid mesogens and flexible spacers, but this tends to compromise mechanical properties.¹⁴

Thermal Stability

A preliminary assessment of the thermal stability of these polyesters was conducted by thermogravimetric analysis (TGA). A TGA curve for the ND polymer is shown in Figure 8; the TGA curve of the AD polyester was very similar and, hence, is not shown separately. The TGA curves showed that at a heating rate of 10°C/min, the naphthalene and anthracene polymers started to lose weight significantly above about 450°C. The TGA curve is similar to that shown by Garay et al.¹⁵ for similar polyesters containing PHQ. The TGA curves only indicate the degradation that leads to weight loss. However, there was some indication that prolonged holding at 400°C or above leads to some form of degradation that involves crosslinking. This was observed during preparation of the samples for optical microscopy. When the polymers were melted between two glass plates and held for a fairly short time at 400°C, the plates lost the ability to be sheared, though when observed optically, they still showed the nematic texture without any sign of the charring observed after isotropization. Thus, the material transforms from a high-temperature thermoplastic to a thermoset. This may be a useful property as it could confer additional dimensional rigidity after processing. Such features cannot be easily deduced from a TGA curve. The change in flow properties with time in the mesophase

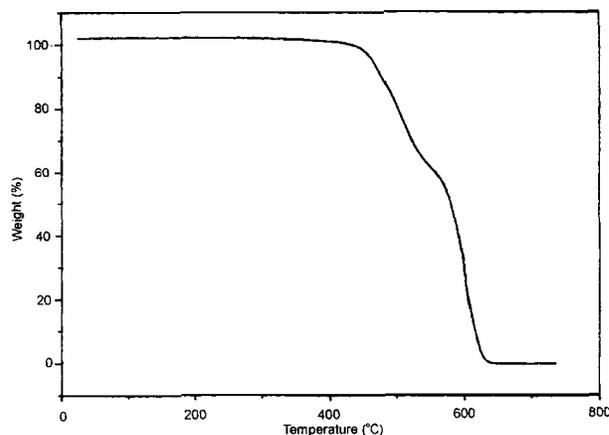


Figure 8 Thermogravimetric analysis curve of the ND copolyester.

is an important feature in assessing the possible use of these thermotropic polyesters.

In summary, the possible working range for these nematic polyesters is about 100°C (between 300 and 400°C). However, the optimum operating temperature would be lower, perhaps between 300 and 350°C, because of the rapid change in flow properties at higher temperatures. This, however, need not be a serious limitation because there is no reason to want to process at very high temperatures, given the relatively low viscosity of the nematic phase. Hence, these polymers could be satisfactorily injection-molded at 350°C, with no damage to the machine or mold.

CONCLUSIONS

The copolyesters of terephthalic acid, phenylhydroquinone, and naphthalene diol or anthracene diol melted and formed a birefringent liquid crystal phase. The predominant optical textural feature observed with these polymers in the mesophase was inversion walls, characteristic of nematics. The $K-N$ transition temperature was about 300°C, while the isotropization temperature was above 400°C and, in fact, was accompanied by severe degradation.

The DSC results also confirmed the presence of two first-order phase transitions which were in general accord with those observed by microscopy. Endothermic peaks corresponding to crystal–nematic and nematic–isotropic transitions were recorded on the first heating run. The reverse $N-K$ transition could be observed provided that the material had not been heated to isotropization temperatures. There was an amorphous component with a glass transition of about 140–160°C.

Preliminary thermal stability studies indicated that major weight loss starts above 450°C. However, above about 400°C, crosslinking reactions occurred fairly rapidly, converting the material from a thermoplastic to a thermoset.

REFERENCES

1. S. G. Cottis, J. Economy, and B. E. Nowak, U.S. Pat. 3,637,595 (1972) (to Carborundum).
2. B. P. Griffin and M. K. Cox, *Br. Polym. J.*, **12**, 147 (1980).
3. W. J. Jackson, Jr., *Contemp. Top. Polym. Sci.*, **5**, 177 (1984).
4. C. R. Payet, U.S. Pat. 4,159,365 (1979) (to Dupont).
5. W. Jackson Jr., *Br. Polym. J.*, **12**, 154 (1980).
6. R. R. Luise, U.S. Pat. 4,183,895 (1980).
7. J. F. Harris, Jr., U.S. Pat. 4,294,955 (1981).
8. N. Khan, D. M. Price, and Z. Bashir, *J. Polym. Sci. Phys.*, **32**, 2509 (1994).
9. P. K. Bhowmik, E. D. T. Atkins, and R. W. Lenz, *Macromolecules*, **26**, 447 (1993).
10. D. Dainelli and L. L. Chapoy, *Macromolecules*, **26**, 385 (1993).
11. P. J. Stenhouse, E. M. Valles, S. W. Kantor, and W. J. MacKnight, *Macromolecules*, **22**, 1467 (1989).
12. D. Demus and L. Richter, *Textures of Liquid Crystals*, Verlag Chemie, Weinham, New York, 1978.
13. J. Nehring and A. Saupe, *J. Chem. Soc. Faraday Trans. II*, **68**, 1 (1972).
14. D. Acierno, F. P. La Mantia, G. Polizzotti, A. Cifferri, W. R. Krigbaum, and R. Kotek, *J. Polym. Sci. Phys. Ed.*, **21**, 2027 (1983).
15. R. O. Garay, P. K. Bhowmik, and R. W. Lenz, *J. Polym. Sci. A Polym. Chem.*, **31**, 1001 (1993).

Received April 26, 1995

Accepted May 29, 1995