Synthesis and Mesophase Characterization of Liquid Crystalline Polyesters With Bulky, Rigid, Lateral Substituents

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SYNOPSIS

The synthesis and characterization of aromatic polyesters containing various symmetrically di-substituted hydroquinone monomers is described. The homopolyesters made from these monomers and terephthalic acid (TA) did not melt. Copolyesters of TA with mono- and di-substituted hydroquinone formed liquid crystalline melts. Optical microscopy showed schlieren, marbled, and droplet textures characteristic of the nematic phase. DSC experiments were also in accord with mesophase formation as multiple transitions characteristic of first-order phase changes were found. In general, the crystal–nematic transition was about 300°C, whereas the nematic–isotropic change was over 400°C. All the polyesters were prone to decomposition near or above the isotropization temperature. © 1994 John Wiley & Sons, Inc.

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INTRODUCTION

It is well known that certain aromatic polyesters can show thermotropic liquid crystalline behavior. The great interest in these materials stems from the facility with which they can be oriented and spun into high modulus fibers or injection molded into articles that have superior mechanical properties when compared with conventional thermoplastics.

One of the prerequisites of forming liquid crystalline phases is that the molecules be rod-like (or less commonly disk-like) in shape. Polyesters based on 100% p-hydroxy benzoic acid (p-HBA) or terephthalic acid (TA) and hydroquinone (HQ) (polymers I and II, Table I) are infusible and insoluble. This is because a very rigid chain leads to a low entropy of fusion, which raises the melting point above the degradation temperature.

Liquid crystal polymers (LCPs) with very high glass transition and melting temperatures are now commercially available and have applications that make them desirable. For instance Xydar (manufactured by Dartco) is a copolyester based on 4,4'-

biphenol, TA, and p-HBA; polymers such as this, however, have a crystal–nematic transition over 400°C¹ and this 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 point to temperatures of 300°C or below, while maintaining the liquid crystalline behavior.

There are several synthetic strategies to reduce the melting temperatures of rigid-rod polymers and yet form liquid crystal phases. One option is to introduce flexible alkyl spacers between the aromatic units.² Another method is to include kinks such as meta linkages, which disrupt the chain linearity of purely para-aromatic sequences.² Appending flexible side chains to create “hairy-rod” thermotropic polymers is another avenue explored by Ballauf and Schmidt.³ Griffin and Cox² have suggested that including aromatic units with bulky substituents on the chain backbone frustrates chain packing and this lowers the crystallinity and depresses the melting point below the degradation temperature. In this work, the concept of frustrated chain packing will be used to synthesize polyesters that exhibit liquid crystalline behavior at relatively moderate processing temperatures.

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Table I

The literature contains examples of aromatic polyesters with methyl-, bromo-, chloro-, and methoxy-substituted hydroquinone.⁴ Substitution of the hydroquinone with a phenyl group to form phenyl p-phenylene terephthalate (polyester III in Table I) was disclosed by Payet.⁵ Jackson has indicated the superior thermal stability of the phenyl-substituent compared with the chloro or methyl groups in such polyesters.⁶ It was reported that a liquid crystal melt was formed, and fibers based on this had excellent mechanical properties.^{5,7} According to Krigbaum and Tanaka, the phenyl-substituted polyester III has a T_g of 140°C, a crystal-nematic transition of 350°C, and a clearing temperature of 455–460°C;⁸ however, there is some variability in the transition temperatures cited by different authors for the same polymer. The analogue of this polymer, namely the polyester with the phenyl substituent on the terephthalic acid instead of the hydroquinone, has also been disclosed by Harris,⁹ and is reported by different authors to have a crystal-nematic transition of 300°C⁹ or 265°C.¹⁰

In this work, we have examined the synthesis and phase behavior of homopolyesters of terephthalic acid and some new *symmetrically di-substituted* hydroquinones (polymers VIII to X, Table I), as well

as copolyesters of terephthalic acid, phenyl hydroquinone, and the new di-substituted hydroquinones (polymers IV–VI, Table I).

EXPERIMENTAL

Synthesis of Monomers

Several of the monomers and intermediates were commercially available. Terephthaloyl chloride, hydroquinone (1,4 dihydroxy benzene), phenyl hydroquinone, 2,6-diphenylphenol, and 2,5-dimethylphenol were purchased from Aldrich. The 2,5-diphenylbenzoquinone was purchased from Lancaster Synthesis.

However, the di-substituted hydroquinones had to be synthesized. The reaction schemes are shown in Table II and the preparation details of the monomers and intermediates needed to make polyesters IV–VI and VIII–X are given below.

2,5-Diphenylhydroquinone (2,5-DPHQ)

Scheme A in Table II shows the reaction involved. The 2,5-diphenyl-1,4-benzoquinone (5 g, 0.019 mol) was dissolved in boiling ethanol (50 ml), and a five-

fold excess of sodium hydrosulphite (16.73 g, 0.096 mol, 10% aqueous solution) was added with vigorous stirring. The product precipitated immediately. The mixture was stirred for 0.5 h and then the product was filtered, washed with water several times, and dried in vacuum (22°C/750 mbar). The product was recrystallized from toluene/petroleum ether (bp 40: 60°C) to give 4.49 g (88%) of the purified compound with mp 212–214°C, ir $\nu_{\max}$ 1480, 1408, 1210, 1148, 1144, 816, 761, 698 cm^{-1} , NMR δCDCl_3 (80 MHz) 6.84 (2 H, s, Ar), 7.19–7.65 (10 H, m, Ar), and 8.35 (s, OH).

2,6-Diphenylbenzoquinone

Step 1 of scheme B in Table II shows the reaction involved in forming this intermediate. Jones reagent [prepared from sodium dichromate (80 g), concentrated sulphuric acid (50 ml), and water (120 ml)] was added dropwise at 0°C to a stirred solution of 2,6-diphenylphenol (15 g, 0.057 mol) in ether (200 ml), and then the reaction mixture was stirred at room temperature for 7 h. The reaction mixture was extracted with ether (4 × 100 ml) and the combined extracts were washed with 20% aqueous sodium hydrogen carbonate (2 × 50 ml), followed by water, and then dried over MgSO_4 . The solvent was evaporated to give an orange solid that was recrystallized from methanol to give 8.65 g (62%) of pure product, with mp 135–145°C, ir $\nu_{\max}$ 1660 (CO) and 1647 (CO) cm^{-1} , NMR δCDCl_3 (80 MHz) 6.91 (2 H, s), and 7.47 (2 H, m, Ar).

2,6-Diphenylhydroquinone (2,6 DPHQ)

Step 2 of scheme B in Table II shows the reaction involved. The 2,6-diphenyl-1,4-benzoquinone (5.0 g, 0.019 mol) produced in the previous reaction was

dissolved in boiling ethanol (50 ml), and a fivefold excess of sodium hydrosulphite (16.73 g, 0.09 mol, 10% aqueous solution) was added with vigorous stirring. The product precipitated immediately. The mixture was stirred for 0.5 h and then the product was filtered, washed with water several times, and dried in vacuum. The product was recrystallized from toluene to give 4.12 g (81%) of pure product, with mp 185–187°C, ir $\nu_{\max}$ 3482 (OH) cm^{-1} , NMR CDCl_3 (80 MHz) 5.57 (OH, s), 6.89 (2 H, s, Ar), 7.39–7.64 (10 H, m, Ar), and 8.4 (OH, s).

2,5-Dimethylbenzoquinone

Step 1 of scheme C in Table II shows the reaction involved in the formation of this intermediate. Jones reagent [prepared from sodium dichromate (165 g), concentrated sulphuric acid (110 ml), and water (235 ml)] was added dropwise at 0°C to a stirred solution of 2,5-dimethylphenol (30 g, 0.11 mol) in ether (500 ml), and then the reaction mixture was stirred at room temperature for 12 h. The reaction mixture was extracted with ether (4 × 100 ml) and the combined extracts were washed with 20% aqueous sodium hydrogen carbonate (2 × 50 ml), followed by water, and then dried over MgSO_4 . The solvent was evaporated to give an orange solid that was recrystallized from methanol to give 15.71 g (47%) of pure product mp 130–132°C, ir $\nu_{\max}$ 1660 (CO), and 1647 (CO) cm^{-1} , NMR δCDCl_3 (80 MHz) 2.0 (6 H, d, Me), and 6.55 (2 H, m, CH=).

2,5-Dimethylhydroquinone (2,5-DMHQ)

Step 2 of scheme C in Table II shows the reaction involved. The 2,5-dimethylbenzoquinone (7.5 g, 0.028 mol) from the previous reaction was dissolved in boiling ethanol (150 ml), and a fivefold excess of

Table II. Reaction Schemes for Monomer Preparation

sodium hydrosulphite (48 g, 10% aqueous solution) was added with vigorous stirring. The mixture was stirred at room temperature for 3–4 h. Ethanol was removed under reduced pressure and the resulting aqueous solution was extracted several times with ether. The combined extracts were dried over MgSO_4 and solvent was evaporated to give a white solid that was recrystallized from ether:petroleum ether (40:60) to give 5.79 g (76%) of purified product with mp 225–228°C, ν_{max} 3232 (OH) cm^{-1} , NMR δCDCl_3 (80 MHz), 2.1 (6 H, s, me), 6.5 (s, 2 H, Ar), and 7.5 (s, OH).

Synthesis of Polymers

The monomer compositions used to make the homo- and copolyesters are shown in Table III. Note that instead of using terephthalic acid, terephthaloyl chloride was used due 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 and derivatives of hydroquinone 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, the polymer was me-

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

In one case (polyester IV), two variants, a higher and a lower molecular weight material, were synthesized. Polyester IV A will denote the lower molecular weight and IV B will denote the higher molecular weight material. IV A was synthesized by reducing the standard polymerization time of 5 h to 2.5 h and conducting the entire reaction at 190°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 general procedure adopted to obtain the best textures was to heat the sample up to the clearing temperature with the fastest heating rate available (99°C/min) and then to cool the sample immediately. This minimized degradation and gave the best textures. In cases where the isotropization led to charring, the sample was heated close to the isotropization transition very rapidly, and then cooled to a lower temperature where the polymer was still fluid.

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.

Table III. The Monomer Compositions of the Polyesters Used in This Work

Polymer	Molar Percentage of					
	TPCL	PHQ	2,5-DPHQ	2,6-DPHQ	2,5-DMHQ	HQ
III	50	50	—	—	—	—
IV	50	43.75	6.25	—	—	—
V	50	43.75	—	6.25	—	—
VI	50	43.75	—	—	6.25	—
VII	50	37.50	—	—	—	12.5
VIII	50	—	50	—	—	—
IX	50	—	—	—	50	—
X	50	—	—	50	—	—

TPCL = terephthaloyl chloride; PHQ = phenyl hydroquinone; 2,5-DPHQ = 2,5-diphenyl hydroquinone; 2,6-DPHQ = 2,6-diphenyl hydroquinone; 2,5-DMHQ = 2,5-dimethyl hydroquinone; HQ = hydroquinone.

In the first series of experiments, the heating thermograms of all the polyesters were recorded at the fastest practical heating rate possible (40°C/min) to minimize degradation. From the optical microscopy, two transitions were expected, and hence the upper temperature limit was chosen accordingly for each polymer. After the second high temperature transition, the sample was cooled at 40°C/min and the cooling thermogram was recorded.

In the second set of experiments, the most thermally stable polyester IV A (Table I) was selected for studies on the effect of heating and cooling rates. Thermograms were recorded between 20 to 400°C and 400 to 20°C, at heating and cooling rates of $\pm 5^\circ\text{C}/\text{min}$, $\pm 10^\circ\text{C}/\text{min}$, and $\pm 40^\circ\text{C}/\text{min}$.

RESULTS AND DISCUSSION

Table I shows the polymers synthesized in this work (III–X). The homopolymers of terephthalic acid and the symmetrically di-substituted hydroquinones (VIII to X, Table I) did not melt and so no further work was carried out on these.

The remaining copolyesters III–VII melted and showed LC phases. The composition of the ingredients is shown in Table III. Due to the insolubility of the materials in common non-toxic solvents, molecular weight characterisation was not performed. However, all the materials had mechanical properties consistent with high molecular weight polymer. All were film and fiber forming. Dumbbells were made from polymers III–VII by compression molding. In addition, polyester IV A was injection molded to produce a screw-driver handle.

Polymer III is discussed fairly extensively in the literature^{4–8} and hence it will not be considered in detail here, but it will be used as a reference for comparison of the other polyesters. It is quoted by one set of authors as having a crystal–nematic transition at 350°C and a clearing temperature of 460°C.⁸ Our DSC and optical microscope results broadly tally with these findings (Table IV). The remainder of the work will concentrate on copolyesters IV–VII.

Optical microscopy and phase identification of polyesters IV–VII

Optical microscopy is a powerful tool in phase identification of liquid crystals. With molecular liquid crystals, often optical textures can be sufficient in identifying various liquid crystal phases and their transition temperatures. In the case of polymeric

Table IV. Glass Transition (T_g), the Crystal–Nematic (T_{K-N}), and Nematic–Isotropic (T_{N-I}) Temperatures of Polyesters III–VII

Polymer	T_g	T_{K-N}	T_{N-I}	Comments
I	—	~ 600	—	degrades
II	—	~ 600	—	degrades
III	140	350	455	ref. 8
III	—	335	450	ref. 5
III	132	333	450	this work
IV A	131	275	340	this work
IV B	136	295	470	this work
V	151	307	440	this work
VI	136	280	451	this work
VII	126	299	477	this work
VIII	—	—	—	infusible
IX	—	—	—	infusible
X	—	—	—	infusible

All temperatures are in centigrade and correspond to the onset (T_g) or peak temperatures in the DSC thermograms in Figure 5. T_{N-I} will be slightly lower than the clearing temperature observed by microscopy.

liquid crystals, it may be possible to observe a fluid phase that shows birefringence, but it is often difficult to obtain a recognizable texture. This is evident in some of the reported literature on thermotropic liquid crystal polymers, where the textures have a mottled appearance, lacking in clarity.^{11–17} In some of these works, it is the x-ray experiments rather than the optical textures that provide the decisive evidence for phase identification.^{12,18} Yet, in other works, textures from which phases can be unambiguously identified are shown.^{19–22}

As hot-stage x-ray facilities were not available, optical microscopy has been used for providing the primary information on phase identification of the mesophases in polyesters IV–VII. For this, we ensured that good textures were obtained in all cases to allow unambiguous identification of the phases. The polymer was fluid at the temperature and time the photographs of the textures were recorded; this could be detected by motion of the liquid or the movement of extraneous impurity particles. The DSC thermograms can be regarded as secondary evidence and will be presented after the microscopy results.

Polyester IV

Figures 1–3 shows the textures obtained from polyester IV A. Figure 1 is of a type referred to as a marbled texture by Demus and Richter²³ and is often found in nematics. This was obtained immediately after isotropization and cooling to 315°C. Marbled

Figure 1. Marbled texture of the nematic phase of polyester IV A showing areas of near homeotropic alignment (dark zones). Crossed polars, 315°C.

textures often appear with glass surfaces that have not been specially treated. The boundaries that separate different areas generally consist of threads, inversion walls of various types, or twist disclination lines.²³ There was considerable movement of the fluid and the closed loops in Figure 1 could be seen floating in the liquid. These were unstable and disappeared after some time.²³ The dark inclusions in the texture of Figure 1 are areas of near homeotropic alignment, while the colored zones arise from regions with a nearly defect-free planar alignment. When the hot stage was tapped gently, bright flashes in these dark areas were observed, due to the temporary collapse of the director from perpendicular to parallel alignment with respect to the glass slides. This is also a characteristic of the nematic phase and it often helps with phase identification.²³

Figure 2. Schlieren texture of the nematic phase of polyester IV A. White arrow shows point singularities with $s = \frac{1}{2}$; black arrow shows singularity with $s = 1$. Crossed polars, 330°C.

Figure 3. Droplet texture of the nematic phase of polyester IV A, emerging from the isotropic phase. Crossed polars, 365°C.

Figure 2 shows a second type of texture obtained with polyester IV A. This was recorded at 330°C after cooling from the isotropic state. It can be seen that point singularities with strengths $s = \pm\frac{1}{2}$ and $s = \pm 1$ are both present and this is sufficient to identify the phase unambiguously as nematic.²⁴ Note that schlieren textures are also characteristic of smectic C phases; however, in these, singularities with $s = \pm\frac{1}{2}$ do not occur and only those with $s = \pm 1$ are found.²⁴

Figure 3 displays another texture characteristic of nematics that was observed with polyester IV A at 365°C, while cooling from the clearing temperature. This is the droplet texture that is observed normally when the nematic phase emerges from the isotropic.^{21,23} The droplets typically showed extinction crosses, spiral structures, bipolar arrangements and other topologies. Theoretical studies confirm the stability of radial or bipolar orientations.²⁵ The droplets grew and coalesced into other textures. With polyester IV A, such a droplet texture was observed, not only when the sample was cooled from the isotropic state as in Figure 3, but also at the transition from the nematic to the isotropic.

The higher molecular weight polyester IV B also showed schlieren and marbled textures characteristic of the nematic phase. However, the homeotropic and the droplet textures found with the lower molecular weight version IV A were not observed with IV B. Homeotropic orientation of the homopolyester of phenyl hydroquinone and phenyl terephthalic acid has been reported by Garay et al.¹⁰ but the cause is not well understood. It has been suggested however that homeotropic orientation is more likely to occur with lower molecular weight polymers due to the increased number of chain ends.^{26,27} The observation

Figure 4. Texture of polyester V showing surface inversion walls, ending at point singularities with $s = \pm \frac{1}{2}$. Crossed polars, 412°C.

of the homeotropic orientation with polyester IV A, but not IV B, tends to support this view.

Two other observations are worth reporting. Firstly, cooling the mesophase even at 5°C/min or 10°C/min did not lead to any crystallization textures. When a molecular liquid crystal such as p-azoxyanisole is cooled from the nematic phase, crystallization eventually occurs, and this can be easily detected optically because the nematic texture is "overwritten." Instead, with both polyesters IV A and IV B, the schlieren or the threaded texture was simply frozen into a glassy state, presumably because the crystallization rate was very slow.

Secondly, it was observed that prolonged holding (over 60 min) at 330°C, or above the clearing temperature for a shorter period, led to degradation. The degradation product, however, was not the charred material that was found if the sample was held above the clearing temperature for long periods. Instead, it appeared to be crystalline, taking the form of birefringent rods and diamond-shaped crystals (not shown). We have observed this phenomenon with other high-temperature polyesters and it is most probably due to the formation of the diacid resulting from the hydrolysis of the ester. This can give a misleading impression of a liquid crystal texture growing from the isotropic phase.

Polyesters V–VII

Polyester V was liquid crystalline in the temperature regime 307–440°C (Table IV). Again, the best textures were obtained by rapidly heating above the clearing point (440°C), and cooling quickly. Figure 4 shows a texture from polyester V that was predominantly populated with surface inversion walls²³ (also called inversion walls of the first kind by

Nehring and Saupe²⁴), emerging and ending at $\pm \frac{1}{2}$ point singularities. There is a $\pi/2$ turn of the molecular director at the center of the wall.²⁴ From the $\pm \frac{1}{2}$ point singularities (arrowed in Fig. 4), it is possible to conclude unambiguously that the mesophase was nematic.

Polyester VI formed a mesophase in the interval 280–451°C (Table IV). Again, a schlieren texture similar to Figure 2 with ± 1 and $\pm \frac{1}{2}$ point singularities was formed (not shown) and once more it was possible to conclude unambiguously that the mesophase was nematic. Polyester VII showed both marbled and schlieren textures that again indicated a nematic mesophase between about 300°C and 475°C. None of the polyesters V–VII showed the droplet or the homeotropic textures.

DSC Thermograms

Figure 5 shows the heating behavior of the copolyesters IV–VII recorded at the fastest heating and cooling rates attainable (40°/min) to minimize degradation. It can be seen that all the polymers show two endotherms, one at about 300°C due to the crystal–nematic (K–N) transition, and another near or above 400°C that is due to the nematic–isotropization (N–I) transition. These transitions correlate with the melting behavior observed with the polarizing microscope. The glass transition temperatures, and the K–N and N–I transition temperatures obtained from DSC are listed in Table IV.

Double-melting endotherms, however, are not a sufficient criterion for the detection of LC phases in polymers, for such behavior can also be observed with non-liquid crystalline polymers.^{28,29} There are

Figure 5. DSC heating curves of polyesters III–VII. All samples show two endothermic peaks. The lower-temperature peak is due to the K–N transition and the second peak is the N–I transition. In some cases, degradation follows immediately after the N–I transition.

Figure 6. DSC thermogram of polyester IV A, showing the effect of heating and cooling rate. The bottom curves are the heating cycle and the associated cooling curves are shown on top.

examples in the literature citing the observation of more than one melting peak with polymers such as polyethylene³⁰ or polybutylene terephthalate during the heating scan.³¹ Multiple endotherms can occur during the heating of such flexible-chain polymers due to the phenomenon of annealing (crystal thickening) during the heating scan. The annealing effect is heating-rate dependent; thus, whereas single crystal-melting peaks are observed at very low and very high heating rates, multiple peaks are found at intermediate heating rates.²⁸

In the present case, crystal thickening is unlikely to occur in polymers with rigid chains, and hence the two principal endotherms in Figure 5 are likely to be due to two separate phase transitions. Note that with other types of LCPs that contain mesogens coupled with flexible spacers we have found the thermograms of the heating scan were difficult to analyze because peaks due to annealing effects also occur and are superimposed on mesophase transitions.

On cooling (after isotropization) at 40°C/min, no exothermic peaks were observed in the DSC with all the polyesters. There are two possible interpretations for this: there had been so much degradation at the isotropization temperature that no isotropic-

to-nematic exotherm was observed, or else quenching at 40°C/min led to an isotropic glass.

Heating and cooling rate effects will be illustrated by the behavior of one polymer, polyester IV A. Figure 6 (bottom) shows the DSC behavior of polyester IV A at heating rates of 40°C/min, 10°C/min, and 5°C/min. It can be seen that the two peaks that we have attributed to the K-N and the N-I transitions are present at low, intermediate, and high heating rates, suggesting that the two peaks are not merely due to annealing effects but are due to two consecutive phase transitions. Note, however, that the K-N peak shifts to slightly higher temperatures at slower heating rates.

On the cooling scan (after isotropization), Figure 6 (top) shows that at a cooling rate of 40°C/min, there were no phase transitions, implying that the material had quenched to an isotropic glass. However, Figure 6 (top) shows that at a cooling rate of 10°C/min, two small exothermic transitions were observed, indicating that the phase transitions observed on the heating scan were indeed reversible. From the cooling scan at 10°C/min in Figure 6 (top), the I-N transition is at 333°C (peak temperature) and this correlates with the microscope observations. Note that the I-N phase change does not show supercooling. The N-K transition in the cooling scan at 10°C/min occurred at 174°C; by comparing with the K-N transition, it can be seen that there is considerable supercooling during crystallization. A similar lack of supercooling in the transition from isotropic to mesophase and a strong supercooling effect during crystallization has been reported for other LCPs.¹⁶ Finally, in the sample heated and cooled at 5°C/min, no exothermic peaks were observed on cooling (Fig. 6, top), though two peaks had been found on heating (Fig. 6, bottom). This was because the material was not thermally stable at elevated temperatures and very slow heating led to degradation. Thus, at this rate, a second heating cycle (after the first heat-cool cycle) revealed no endothermic transitions as the material had undergone degradation.

Molecular Structure and Phase Transition Temperatures

All the glass and phase transition temperatures of the polyesters that are collected together in Table IV can now be related to the molecular structures of the constituents.

With polyester III, comparisons can be made with the data in the literature. It can be seen that our transition temperatures for this polymer are com-

parable to those of Krigbaum and Tanaka⁸ (333°C vs. 350°C) and Payet⁵ (333°C vs. 335°C). Differences may arise because in some works the peak temperatures in the DSC are cited whereas the clearing temperatures from microscopy are quoted in others. The latter would generally be somewhat higher because it is taken as the temperature at which birefringence vanishes completely. There may be other factors, such as molecular weight and heating rate, that lead to differences when comparing the transition temperatures in the literature for the same polymer.

The concept of frustrated chain packing mentioned by Griffin and Cox² is effective in lowering the transition temperatures of aromatic polyesters with all-para linkages. Thus, if polyester III is compared with I or II (Table I), it can be seen that the unsymmetrical structure with a single phenyl group on the hydroquinone suppresses the crystallinity and melting point by virtue of two effects: firstly, by the steric hindrance of having a large phenyl substituent, and secondly, by the random head-to-head or head-to-tail addition of this monomer along the polymer chain.

In contrast to mono-substitution, *symmetrical di-substitution* of the hydroquinone with even large substituents such as phenyl groups does not appear to reduce crystallinity in the homopolymers (compare polymer III with VIII–X, Table I) and hence these polymers did not melt. In the case of the 2,5 di-substituted polymers (VIII and IX in Table I), there is no differentiation between head-to-head or head-to-tail additions. However, in the case of the 2,6 di-substituted polymer (X, Table I), such a differentiation is possible, yet it was not sufficient to destroy the geometrical regularity and suppress crystallization.

The copolyesters IV–VII can be considered to be similar to the homopolymer III, except that a third monomer (the di-substituted hydroquinones in IV–VI or hydroquinone in polymer VII) has been added in small amounts to create a random copolymer.

Whereas the homopolymer III of hydroquinone and terephthalic acid had a crystal–nematic transition at 333°C, all the copolymers IV–VII had the crystal–nematic transition at a lower temperature (in the vicinity of 300°C, Table IV). The homopolymer III had a clearing temperature of 450°C. Interestingly, all the copolyesters (except the lower molecular weight IV A) also had isotropization temperatures in the vicinity of 450°C, but in two cases the N–I transition was actually higher. Thus, the addition of the di-substituted hydroquinone comonomer depresses the crystal–nematic transition while not having the same effect on the nematic–

isotropic transition, when compared with the homopolymer III.

Comparing the data for the low and high molecular weight polyesters IV A and IV B, it is interesting to notice that the crystal–nematic transition is almost invariant at about 275–295°C but the clearing temperatures were drastically different (about 380°C for IV A vs. 480°C for IV B). Thus, molecular weight seems to have a significant impact on the clearing temperature but not on the crystal–nematic transition.

Compared with the homopolymer, random introduction of a third monomer to form a copolymer introduces further disruption of chain regularity (apart from that caused by the bulk of the substituent, and head-to-head or head-to-tail addition where applicable). This also reduces crystallinity, even if the third monomer is the unsubstituted hydroquinone (polymer VII, Table I) or the symmetrically di-substituted hydroquinones as in polymers IV–VI. The latter is effective in disrupting chain packing when incorporated in small amounts due to the greater bulkiness of two substituents and the randomness of the inclusions. Though the copolymers IV–VI have lower crystal–nematic transition temperatures than the homopolymer III when the comonomer is added randomly in small amounts, it may be anticipated that in larger quantities, the incorporation of the di-substituted hydroquinone may create blockiness that would again increase the crystallinity and the melting point.

Generally, it appears that the polyesters made from the frustrated chain packing method will always tend to be nematic. This seems to be the case here. Polyesters made from a similar concept reported in other studies also appear to be exclusively nematics.^{10,12–14} In contrast, smectic mesophases are often formed from main-chain aromatic polyesters containing flexible spacers between mesogens.^{16,32} This is because in the former, the mesophase is stabilized by disrupting the regularity of the chain by unsymmetrical substitution, whereas in the latter, it is created by reducing the rigidity of the backbone while keeping a chain structure that is symmetrical. Nematics would be preferred to smectic polyesters for applications such as injection molding and fiber spinning owing to the lower viscosity of the former.

CONCLUSIONS

The copolyesters of terephthalic acid, phenylhydroquinone, and di-substituted hydroquinones melted and formed a liquid crystal phase. Optical microscopy was used as the primary tool to evaluate the

nature of the mesophases. All the copolyesters showed a nematic liquid crystal phase; there was no multiple mesophase behavior. The classical features of the nematic phase, such as the marbled and the schlieren textures, as well as surface inversion walls, were observed with these polyesters. The droplet texture of the nematic phase and homeotropic alignment was observed only with a low molecular weight polymer.

The crystal–nematic transitions were generally in the vicinity of 300°C. A clearing temperature, which is not always observed with aromatic polyesters, was found with all the copolyesters. The clearing temperatures were generally above 400°C. The thermal stability in air at temperatures near or above the clearing point over a prolonged period was relatively poor, but as the nematic-to-isotropic range was over a 100°C in all the cases, a useful working range is still available with these copolyesters. To observe a crystal–nematic–isotropic sequence and the reverse isotropic–nematic–crystal (or glass) transition, fast heating and cooling rates had to be used.

The DSC results also confirmed the presence of first-order phase transitions that were in general accord with those observed by microscopy. Endothermic transitions corresponding to crystal–nematic and nematic–isotropic phase changes were recorded on the first heating run, with a fast heating rate. The observation of the reverse exothermic isotropic–nematic transition was not always possible due to degradation after isotropization.

REFERENCES

1. S. G. Cottis, J. Economy, and B. E. Nowak, U.S. patent 3637595 (1972) to Carborundum.
2. B. P. Griffin and M. K. Cox, *Br. Polym. J.*, **12**, 147 (1980).
3. M. Ballauf and G. F. Schmidt, *Mol. Cryst. Liq. Cryst.*, **147**, 163 (1987).
4. W. J. Jackson, Jr., *Contemporary Topics Polym. Sci.*, **5**, 177 (1984).
5. C. R. Payet (to Dupont) U.S. patent 4, 159, 365 (1979).
6. W. Jackson, Jr., *Br. Polym. J.*, **12**, 154 (1980).
7. R. R. Luise, U.S. patent 4 183 895 (1980).
8. W. R. Krigbaum and T. Tanaka, *Macromolecules*, **21**, 743 (1988).
9. J. F. Harris, Jr., U.S. patent 4, 294, 955 (1981).
10. R. O. Garay, P. K. Bhowmik, and R. W. Lenz, *J. Polym. Sci., Part A, Polym. Chem.*, **31**, 1001 (1993).
11. C. K. S. Pillai, D. S. Sherrington, and A. Sneddon, *Polym. Commun.*, **33**, 3968 (1992).
12. P. K. Bhowmik, E. D. T. Atkins, and R. W. Lenz, *Macromolecules*, **26**, 447 (1993).
13. R. L. Johnson and S. Z. D. Cheng, *Macromolecules*, **26**, 94 (1993).
14. D. Dainelli and L. L. Chapoy, *Macromolecules*, **26**, 385 (1993).
15. P. J. Stenhouse, E. M. Valles, S. W. Kantor, and W. J. MacKnight, *Macromolecules*, **22**, 1467 (1989).
16. P. Meurisse, C. Noel, L. Monnerie, and B. Fayolle, *Br. Polym. J.*, **13**, 55 (1981).
17. S. W. Kantor and Ta-Cheung Sung, *Macromolecules*, **26**, 3758 (1993).
18. P. K. Bhowmik, E. D. T. Atkins, and R. W. Lenz, *Macromolecules*, **26**, 440 (1993).
19. A. M. Ghanem, L. C. Dickinson, R. G. Porter, and A. E. Zachariades, *J. Polym. Sci., Part B, Polym. Phys.*, **28**, 1891 (1990).
20. P. Le Barney, J. C. Dubois, C. Friedrich, and C. Noel, *Polym. Bull.*, **15**, 341 (1986).
21. G. Galli, M. Laus, A. S. Angeloni, P. Ferruti, and E. Chiellini, *Eur. Polym. J.*, **21**, 727 (1985).
22. C. Noel, C. Friedrich, F. Laupretre, J. Billard, L. Bosio and C. Strazielle, *Polymer*, **25**, 263 (1984).
23. D. Demus and L. Richter, *Textures of Liquid Crystals*, Verlag Chemie (Weinham), New York, 1978.
24. J. Nehring and Saupe, *J. Chem. Soc. Faraday Trans.*, **II 68**, 1, (1972).
25. a) E. Dubois-Violette, O. Parodi, *J. Phys. Colloq.*, **30**, C4-57 (1969). b) R. B. Meyer, *Phys. Rev. Lett.*, **22**, 918 (1969).
26. R. B. Meyer, in *Polymer Liquid Crystals*, A. Ciferri, W. R. Krigbaum and R. B. Meyer (eds.), Academic Press, New York, 1982.
27. R. W. Lenz, A. Furukawa, P. Bhowmik, R. O. Garay, and J. Majnusz, *Polymer*, **32**, 1703 (1991).
28. J. Runt and I. R. Harrison, in *Methods of Experimental Physics*, vol. 16, part B, R. A. Fava (ed.), Academic Press, New York, 1980, p. 287.
29. Z. Bashir, *J. Mater. Sci. Lett.*, **12**, 598 (1993).
30. Z. Bashir, J. A. Odell, and A. Keller, *J. Mater. Sci.*, **21**, 3993 (1986).
31. M. E. Nichols and R. E. Robertson, *J. Polym. Sci., Phys. Ed.*, **30**, 755 (1992).
32. W. R. Krigbaum and J. Watanabe, *Polymer*, **24**, 1299 (1983).

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