Macromolecules

Volume 16, Number 7 July 1983

Liquid Crystal Polymers. 5. Liquid Crystalline Polyesters Containing Naphthalene Rings[†]

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ABSTRACT: All-aromatic copolyesters prepared with 2,6-oriented naphthalene derivatives have lower melting points than those prepared with 1,4- and 1,5-oriented monomers, and they exhibit thermotropic liquid crystalline behavior when a high proportion of the polymer chains consist of the 2,6-oriented naphthalene rings and *p*-phenylene rings connected by carboxy groups. The introduction of flexible aliphatic groups in liquid crystalline polyesters reduces the polymer relaxation times, and the introduction of rigid kinks in the polymer chains reduces the degree of extended-chain orientation that can be obtained. Consequently, substantial modification with flexibilizing or kinking components reduces the liquid crystallinity and the level of tensile and stiffness properties that can be achieved in injection-molded plastics and melt-spun fibers.

Introduction

In the preceding paper of this series,[1] an overview was given of the effect of structure on the melting points and polymer properties of liquid crystalline aromatic polyesters. The basic structure consists of benzene rings attached at para positions through carboxy groups, and the homopolyesters derived from terephthalic acid and hydroquinone, or from *p*-hydroxybenzoic acid alone, melt at about 600 °C. These high melting points can be decreased to a temperature below 400 °C, at which the polyester is sufficiently stable to be melt spun or injection molded by the introduction of flexible aliphatic units into the rodlike aromatic structures, by the introduction of rigid kinks in the rods, by the addition of certain substituents to the aromatic rings, or by modification of the polyesters with certain rodlike comonomers. An effective rodlike comonomer was 2,6-naphthalenedicarboxylic acid. The objective of this paper is to show the effect of composition on the melting points and properties of thermotropic liquid crystalline polyesters containing naphthalene rings.

Compounds that are liquid crystalline can be obtained with certain para-substituted aromatic diesters of 1,4-,[2] 1,5-,[2] and 2,6-oriented[3] naphthalene derivatives. Table I lists several of these diesters and, for comparison, similar liquid crystalline diesters of hydroquinone.[4] The bonds attached to the naphthalene rings are directly opposite each other or, if on different rings, are opposite and parallel. Liquid crystalline compounds apparently cannot be obtained when the substitution is at other positions on the naphthalene rings, because kinked structures are obtained instead of the required rigid rod structures. Since the only compound found in the literature having the fourth structure had R equal to hexyl, the other compounds containing terminal hexyloxy groups are included in the table so that the nematic ranges can be compared. The lowest melting of the naphthalene diesters contains the 2,6-disubstituted ring and remains liquid crystalline to a higher temperature (230 °C) than the other hexyloxy-terminated esters. As will be shown later, polyesters containing this 2,6-oriented structure melted lower than polyesters containing 1,4- and 1,5-oriented naphthalene rings.

Experimental Section

The aromatic polyesters were conventionally prepared from aromatic dicarboxylic acids, the diacetates or dipropionates of aromatic diols, and acetoxybenzoic acids. Specific preparations of the different types of polyesters are given in the various references. All of the polyesters exhibited shear opalescence, which is an indication of liquid crystallinity.

Inherent viscosities (IV's) were measured at 25 °C in a 25/40/35 wt % mixture of phenol/*p*-chlorophenol/tetrachloroethane at a polymer concentration of 0.1 g/100 mL. Since some of the all-aromatic polyesters were insoluble in all solvents tested, their IV's could not be determined. Therefore, melt flows were measured with a 0.04-in. capillary and 2160-g load in accordance with ASTM D1238.

A differential scanning calorimeter (DSC) (Perkin-Elmer DSC-2) was used for determining melting points (first cycle) and glass-transition temperatures (second cycle).

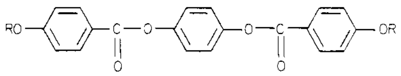
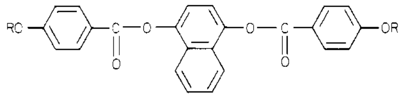
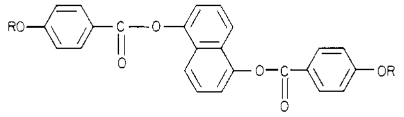
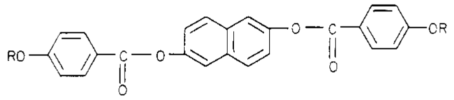
Softening points were determined on pressed films with a DuPont 941 thermomechanical analyzer having a 10-g weight on a tipped probe (0.025-in. diameter) and a scan rate of 10 °C/min.

Relaxation times were determined with a Rheometrics Model RMS-7200 mechanical spectrometer by use of the eccentric rotating-disk mode.

[†] Presented in part at the Macromolecular Symposium of the International Union of Pure and Applied Chemistry, July 12–16, 1982, Amherst, MA.

0024-9297/83/2216-1027$01.50/0

Table I
Liquid Crystalline Esters

compound	nematic range, °C	
	$R = CH_3$	$R = C_6H_{13}$
	213-297	122-211
	180-229	153-168
	216-235	169.5-170.5
		122-230

Melt viscosities were determined with an Instron capillary rheometer.

The polymers were injected into unheated molds in a 1-oz Watson-Stillman injection-molding machine to produce $2^1/_2 \times {}^3/_8 \times {}^1/_{16}$ in. bars for tensile measurements and $5 \times {}^1/_2 \times {}^1/_8$ in. bars for determination of flexural properties, Izod impact strength, heat-deflection temperature, and mold shrinkage. ASTM procedures were used for measuring tensile strength and elongation at break (ASTM D1708), flexural modulus and flexural strength (ASTM D790), notched Izod impact strength (ASTM D256 Method A), heat-deflection temperature (determined at 264 psi, ASTM D648), and mold shrinkage (ASTM D955).

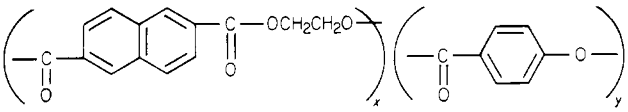
The polyesters were melt spun through a one-hole capillary on an Instron rheometer and taken up on a roll at about 2000–4000 ft/min. The fibers were then wrapped around a wire frame that was placed in a glass tube contained in an aluminum block, dried by heating under a nitrogen or argon flow at 125 °C for 1 h, and then heated at the indicated elevated temperatures and times to increase the polyester molecular weights. The tensile properties of the as-spun and heat-treated fibers were determined by averaging ten breaks of 1-in. gage length single filaments. The elastic modulus was the slope of the stress–strain curve.

Results and Discussion

So that the compositions can be directly compared with those in the preceding papers of this series and those in our patent references, the same terminology for describing the compositions is used: all acidic components (dicarboxylic acids and hydroxy acids) total 100 mol % and all diol components total 100 mol %.

Polyesters Containing Flexible Units. As discussed in our earlier publication,[1] one method of reducing the high melting points of all-aromatic, rodlike polyesters so that the polymers will be sufficiently thermally stable to be injection molded or melt spun is to introduce flexible aliphatic units into the polymer chains. Liquid crystalline copolyesters containing naphthalene rings and flexible units can be prepared by the reaction of *p*-acetoxybenzoic acid with the polyester from ethylene glycol and 2,6-naphthalenedicarboxylic acid.[5,6] Table II shows the increase in tensile strength (${}^1/_{16}$-in.-thick bars) and flexural modulus (${}^1/_8$-in.-thick bars) that are obtained in injection-molded specimens when poly(ethylene 2,6-naphthalenedicarboxylate) is modified with 60 and 80 mol % *p*-hydroxybenzoic acid (PHB, $y = 0.6$ and 0.8 in structure). The increase in strength and modulus and the zero mold shrinkage (because of a zero coefficient of linear thermal expansion) are due to the liquid crystallinity, which permitted extended-chain orientation of the polymer on injection molding. The increase in heat-deflection temperature is due to the increase in T_g and crystallinity in the copolyesters. The lower strength and stiffness obtained when $y = 0.8$ vs. $y = 0.6$ may be due to some relaxation of the polymer chains because of the high injection-molding temperature (360 °C) required when $y = 0.8$ (molding temperature 245 °C when $y = 0.6$) and to lower orientation because of the high melt viscosity. High tensile and flexural properties and a zero coefficient of linear thermal expansion are obtained only in the direction of orientation; the properties obtained in the perpendicular direction are similar to or somewhat lower than the properties of polyesters that are not liquid crystalline. It is of interest that only 20 mol % PHB ($y = 0.2$) was required to make the copolyester liquid crystalline, whereas when poly(ethylene terephthalate) (PET) was modified by the reaction of *p*-acetoxybenzoic acid with PET, 35 mol % of the PHB component was required to make the copolyester liquid crystalline.[7] The difference in the compositions, of course, is the presence of the wider, fused-ring naphthalene structure rather than the single-ring phenylene structure.

Table II
Properties of Injection-Molded Plastics



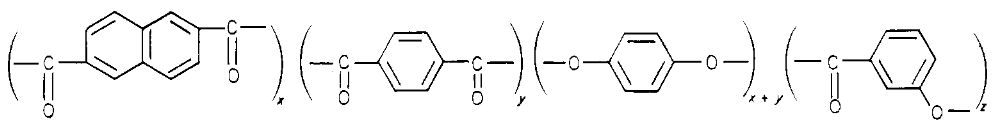
	x/y		
	1.0/0	0.4/0.6	0.2/0.8
inherent viscosity	0.80	0.55	*a*
injection-molding temp, °C	280	245	360
tensile strength, psi	12 000	24 700	22 200
elongation to break, %	16	14	14
flexural modulus, 10^5 psi	3.7	19.1	16.4
notched Izod impact strength, (ft-lb)/in.	0.7	0.7	0.6
heat-deflection temp, °C	91	120	226
mold shrinkage, %	1.0	0.0	0.0

[a] Insoluble in iv solvent; melt flow 1.0 g/10 min at 325 °C.

Polyesters Containing Rigid Kinks. Another method of reducing the high melting points of all-aromatic, rodlike polyesters so that they can be thermally processed is to introduce rigid kinks into the polymer chains. Copolyesters of 2,6-naphthalenedicarboxylic acid (N), terephthalic acid (T), and hydroquinone (*x* and *y* components in

Table III

Properties of Injection-Molded *m*-Hydroxybenzoic Acid Polyesters

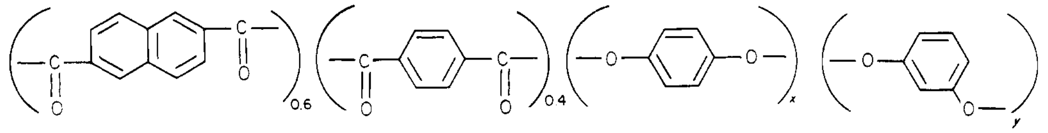


	x/y/z	
	0/0/1.0	0.40/0.25/0.35
inherent viscosity	0.50	*a*
injection-molding temp, °C	330	360
tensile strength, psi	12 600	36 100
elongation to break, %	93	11
flexural modulus, 10^5 psi	3.9	12.6
flexural strength, psi	19 800	27 100
notched Izod impact strength, (ft-lb)/in.	1.1	2.0
heat-deflection temp, °C	122	120

[a] Insoluble in iv solvent.

Table IV

Properties of Injection-Molded Resorcinol-Modified Polyesters



	x/y	
	0.6/0.4	0.4/0.6
injection-molding temp, °C	360	330
tensile strength, psi	32 000	18 600
elongation to break, %	9	7
flexural modulus, 10^5 psi	10.5	8.7
flexural strength, psi	28 600	26 700
notched Izod impact strength, (ft-lb)/in.	3.3	2.5
heat-deflection temp, °C	131	137

structure in Table III) melt too high (above 400 °C) to be injection molded or melt spun without thermal decomposition, but modification with *m*-hydroxybenzoic acid (*z* component in structure) introduces rigid kinks and reduced the melting points below 400 °C. The first composition in Table III, the homopolyester of *m*-hydroxybenzoic acid, is not liquid crystalline because of the large number of rigid kinks in the polymer chain, but the second polymer is liquid crystalline because only 35 mol % ($x + y + z = 100$ mol %) of the kinking component is present. Because of the liquid crystallinity, which permits extended-chain orientation on injection molding, the second composition has higher tensile strength, lower elongation, and higher flexural properties. The heat-deflection temperatures are similar since the polymers are noncrystalline, and therefore, the heat-deflection temperature is determined by the polymer T_g (about 140 °C). If the N component is not present and the *m*-hydroxybenzoic acid component is increased to reduce the polymer melting point below 400 °C to attain melt processability without thermal decomposition, it is necessary to add so much of the *m*-hydroxybenzoic acid that liquid crystallinity is lost. On the other hand, if a substituted hydroquinone, such as methyl- or chlorohydroquinone, is used, the N component,[8] the T component,[8] or the *m*-hydroxybenzoic component[9] can be omitted (either *x*, *y*, or $z = 0$).

When the *m*-hydroxybenzoic acid component in the structure in Table III is replaced by a different kinking component, resorcinol, the melting points in Figure 1 are obtained.[10] The copolyesters are liquid crystalline even when 60 mol % resorcinol is present (both diols total 100 mol %). Without the resorcinol component, the melting points are above 400 °C. Also, without the T (left side of graph) or N (right side of graph) components, the melting points are above 400 °C. If the N component is omitted and more resorcinol is added, liquid crystallinity is lost before the melting point is reduced below 400 °C. Therefore, all four components are needed. The N,[11] the T,[11] or the resorcinol[9] component can be omitted, however, if a substituted hydroquinone, such as methyl- or chlorohydroquinone, is used.

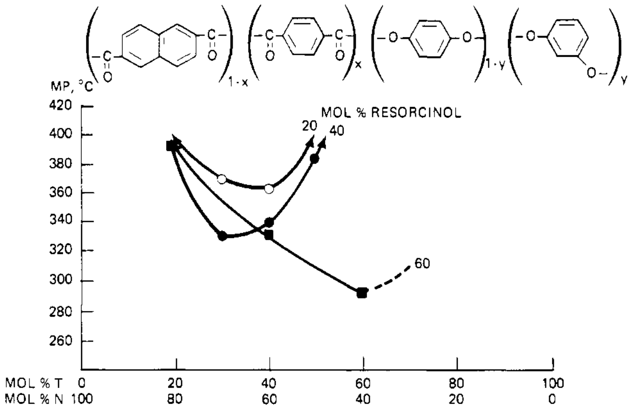
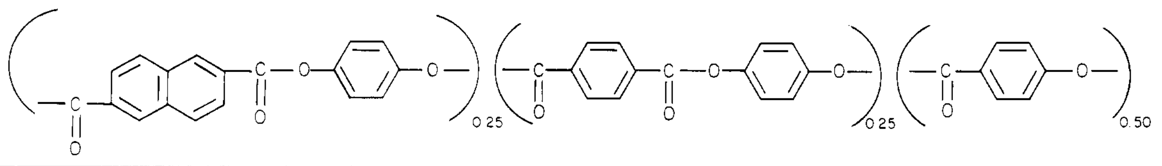


Figure 1. Melting points of copolyesters of 2,6-naphthalenedicarboxylic acid, terephthalic acid, hydroquinone, and resorcinol.

Table IV shows the decrease in tensile strength and flexural properties that occurs in these liquid crystalline copolyesters when the kinking component, resorcinol (*y*), is increased from 40 to 60 mol % ($x + y = 1.0$). If the polymer were not liquid crystalline, the tensile strength would be about 10000–12000 psi and the flexural modulus about (3.5–4.0) × 10^5 psi. Although the polymers exhibited

Table V
Fiber Properties of NT(HQ)(PHB) Copolyester



	as-spun[a]	heat-treated (320 °C, 1 h)
denier/filament	2.3	2.5
tenacity, g/denier	6.7	22
elongation, %	1.8	3.1
elastic modulus, g/denier	450	990

[a] Polymer melt flow was 50 g/10 min at 350 °C.

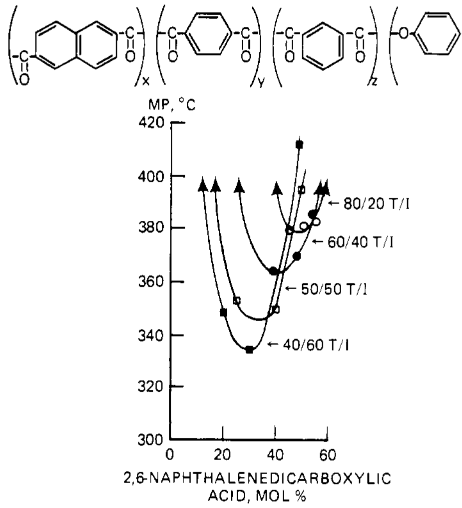


Figure 2. Melting points of copolyesters of 2,6-naphthalenedicarboxylic acid, terephthalic acid, isophthalic acid, and hydroquinone ($x + y + z = 1$).

liquid crystallinity when molten, the injection-molded bars had essentially no crystallinity in the normal sense, so the heat-deflection temperatures are based on the polymer T_g's (about 140–150 °C). The fibers were more crystalline than the plastics (probably because of their higher orientation), and fibers of the first composition (coated with talc to minimize sticking) were heat treated for 1 h at 320 °C under nitrogen to increase the polymer molecular weight and thereby give tenacities of 10 g/denier or higher.

When the resorcinol component in the structure in Figure 1 is replaced by a dicarboxylic acid kinking component, isophthalic acid, the melting points in Figure 2 are obtained.[12] All of the polymers are liquid crystalline. If no N component ($x = 0$) is present, so much isophthalic acid (z component in structure) must be added to reduce the melting point below 400 °C that the resultant copolyester is not liquid crystalline. As would be expected, the melting points decrease as the isophthalic acid content increases. The arrows indicate melting points above 400 °C. Even when 45 mol % isophthalic acid was present, along with 20 mol % T (30/70 T/I ratio) and 35 mol % N, a fiber tenacity of 5 g/denier was obtained (as-spun fiber) that was 12 g/denier after heat treatment at 260–290 °C. As in the preceding compositions containing rigid kinking components, if a substituted hydroquinone (such as methyl- or chlorohydroquinone) is used instead of hydroquinone, either the N[13] or the isophthalic acid[9] component can be omitted (x or $z = 0$) and melt-processable liquid crystalline copolyesters obtained.

Polyesters Modified with *p*-Hydroxybenzoic Acid. The various types of kinking components in the copolyesters just discussed can be omitted and replaced, surprisingly, with a para-oriented nonkinking component, *p*-hydroxybenzoic acid, (PHB) to give polymers with melting points below 400 °C.[14,15] Figure 3 shows the effect of composition on the melting points of polyesters of N, T, PHB, and hydroquinone ($x + y + z = 100$ mol %). At a given PHB level, the melting points decreased as the T content increased, relative to N, until a eutectic was reached (at about 25 mol % T on the 70 mol % PHB curve and 60 mol % T on the 20 mol % PHB curve). When no PHB is present, the melting points are above 400 °C. When no N is present, the melting points are above 500 °C.[16] Graphs that compare the melting points of these copolyesters when either the T component or N component is omitted are given in our earlier paper.[1]

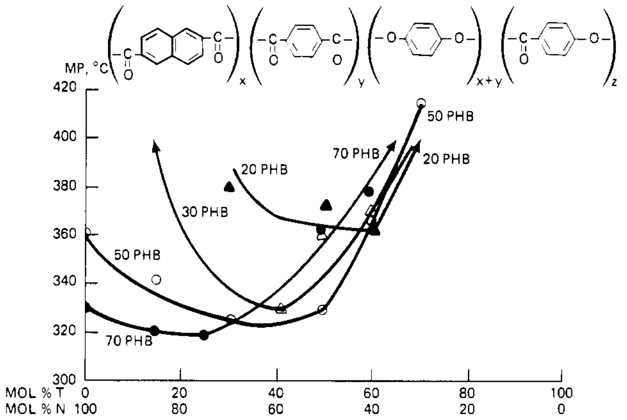
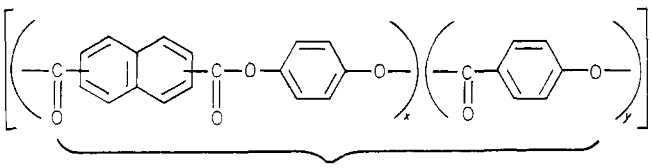
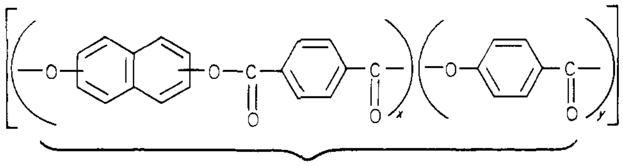


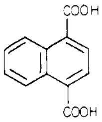
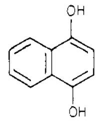
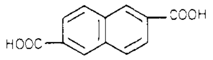
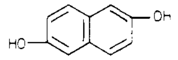
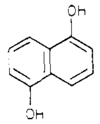
Figure 3. Melting points of copolyesters of 2,6-naphthalenedicarboxylic acid, terephthalic acid, hydroquinone, and *p*-acetoxybenzoic acid.

When the proportions of $x/y/z$ in the formula in Figure 3 were 25/25/50, a TGA curve showed no weight loss until about 450 °C (polymer heated under nitrogen at a rate of 20 °C/min), and the loss was about 1% at 500 °C. When the polymer was heated isothermally at 400 °C in either nitrogen or air for 1 h, however, about 2% weight loss occurred. This temperature is about the upper stability limit for aromatic polyesters.

Table V shows the fiber properties that were obtained when this composition was melt spun at 350 °C at about 2500 ft/min. (For comparison, PET has a fiber tenacity of about 1.5 g/denier when spun at a similar rate, and the tenacity is increased to about 5–6 g/denier when the fiber is oriented by drafting.) When the liquid crystalline fibers were heated in an argon atmosphere for 1 h at 320 °C, the tenacity tripled, the elongation almost doubled, and the modulus doubled. [The high values obtained for the elastic moduli (slope of the stress–strain curve) are due to the use of single filaments (average of 10 breaks) with a 1-in. gage length. The use of longer gage lengths, which were unavailable to us, or plied yarn results in appreciably lower

Table VI
Melting Points of Polyesters Containing Naphthalene Rings

acid	PHB, mol %	mp, °C	diol	PHB, mol %	mp, °C
	70	>380		50-60	>380
	50-85	330 360		40-85	295 357
				50-75	>380

values.] The molecular weights of these copolyesters could not be determined by solution methods because of insolubility, but a log–log plot of fiber tenacity vs. melt viscosity showed a linear relationship. The fiber tenacity increased as the melt viscosity (determined from the fibers) increased, thereby indicating that the higher tenacities of the heat-treated fibers are due to increased molecular weights.

Significance of Polyester Relaxation Times. Relaxation times help explain the high properties that can be obtained with liquid crystalline polyesters. In Figure 4 the relaxation times are plotted against frequency in rad/s (identical with shear rate in s^{-1}). The upper solid plot is that of the liquid crystalline NT copolyester that has just been discussed, and the relaxation times were determined at 360 °C, a typical processing temperature. Intersecting this plot is one of a polyester that is not liquid crystalline because of the kinks in its chain from isophthalic acid (I) and bisphenol A (BPA); the polyester (IV 0.62) was prepared from 50 mol % N acid, 50 mol % I acid, and BPA diacetate. These data show that long relaxation times are not unique to liquid crystalline polyesters. Modification of an all-aromatic polyester with an aliphatic component reduces its relaxation time, as is shown for poly(ethylene 2,6-naphthalenedicarboxylate) (PEN) (IV 0.74, processing temperature 300 °C) and PEN modified with 25 mol % PHB (IV 0.6, processing temperature 325 °C). As would be expected, increasing amounts of PHB in copolymers with PEN give longer relaxation times and higher levels of liquid crystallinity. (Modification of PEN with 20 mol % PHB is just sufficient to make the copolyester liquid crystalline.) The lowest curve, included for comparative purposes, is PET (IV 0.60) measured at its processing temperature of 275 °C. (Relaxation times of PET at frequencies of 10 rad/s or less could not be determined because the modulus was too low to measure.) The lower relaxation times of PET, compared to those of PEN, are due to the presence of the smaller aromatic ring component in the polymer (phenylene instead of naphthalene). Reduction of the flexibility of PET by modification with about 60 mol % PHB, however, increases the relaxation times at 275 °C to those of 25N25T(HQ)50(PHB) at 360 °C. The cooling of a melt-spun fiber or injection-molded bar is a low-rate process, and extrapolation of the upper solid curve of the liquid crystalline polyester to a frequency (shear rate) of 0.01 rad/s gives a relaxation time of several seconds. What is needed is a relaxation time long enough for the extended-chain orientation obtained on melt spinning or injection molding to be locked in when the fiber or plastic cools below its crystallization temperature (or T_g, if not crystalline). Of the compositions in Figure 4, 25N25T(HQ)50(PHB) gives the highest tensile and flexural properties on injection molding because of its long relaxation times at low shear rates and its extended chain orientation.

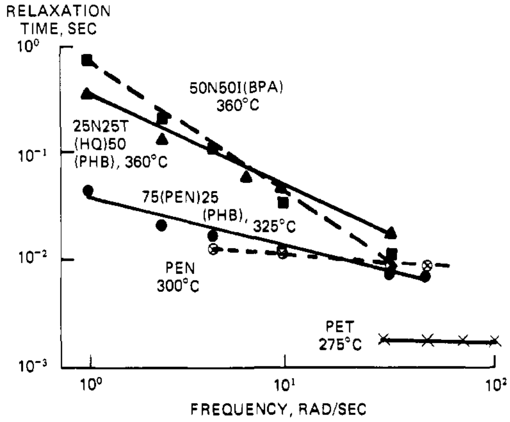


Figure 4. Relaxation times of polyesters. N = 2,6-naphthalenedicarboxylic acid, I = isophthalic acid, T = terephthalic acid, BPA = bisphenol A, HQ = hydroquinone, PHB = *p*-hydroxybenzoic acid, PEN = poly(ethylene 2,6-naphthalenedicarboxylate), PET = poly(ethylene terephthalate).

Polyesters from Various Naphthalene Monomers. Since we had found that copolyesters of 2,6-naphthalenedicarboxylic acid, hydroquinone, and *p*-hydroxybenzoic acid melt sufficiently low to be melt processed without thermal stability problems, it was of interest to determine the effects of other naphthalene monomers on PHB copolyester melting points and properties. In addition to the 2,6-isomers, we expected the 1,4- and 1,5-isomers also to give liquid crystalline polyesters. The 1,5-naphthalenedicarboxylic acid was not available, and we found that the 1,4-acid gave PHB copolyesters that melted too high (solidified during polymerization at 380 °C) to be processed. The 1,4- and 1,5-naphthalenediols (used as the diacetates) also gave high-melting PHB copolyesters with terephthalic acid, but the 2,6-isomer gave lower melting points than the 2,6-dicarboxylic acid compositions. These results are summarized in Table VI with the copolyesters prepared from the naphthalenedi-

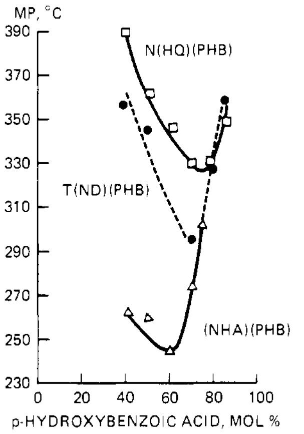


Figure 5. Melting points of PHB copolyesters containing naphthalene rings. PHB = *p*-hydroxybenzoic acid, N = 2,6-naphthalenedicarboxylic acid, HQ = hydroquinone, T = terephthalic acid, ND = 2,6-naphthalenediol, NHA = 6-hydroxy-2-naphthoic acid.

carboxylic acids listed on the left side of the table and those obtained from the naphthalenediols on the right side of the table. The two melting points listed for each of the 2,6-isomers show the melting point ranges of the copolyesters containing 50–85 mol % and 40–85 mol %, respectively, of PHB (y component); lower and higher levels of PHB gave higher melting points (Figure 5). Fisher–Hirschfelder–Taylor models showed that the repeating unit length of the 1,5-diol is similar to that of the 1,4-diol and of hydroquinone, whereas that of the 2,6-isomer is significantly longer and, thereby, may prevent this moiety from fitting into the crystalline lattice with the one-ring hydroquinone and PHB comonomers, thus reducing the melting point. The homopolyester of 2,7-naphthalenediol and terephthalic acid melted at 418 °C and apparently was not liquid crystalline (pressed film was clear). Since the low molecular weight diesters of 1,4- and 1,5-naphthalenediol in Table I are liquid crystalline, high molecular weight polyesters undoubtedly would be thermotropic liquid crystalline polymers if the high melting points were decreased by the addition of substituents to the aromatic rings and introduction of flexibility or kinking in the polymer chains.

The melting points of PHB copolyesters containing 2,6-oriented naphthalene rings [dicarboxylic acid, diol (ND), and hydroxy acid (NHA)] are compared in Figure 5. The compositions of the two upper curves are also disclosed in two Celanese patents,[14,17] and the melting points in the lower curve were taken from a Celanese patent.[18] Melt-spun fibers and injection-molded plastics of these compositions exhibit the high strength and stiffness properties that are characteristic of liquid crystalline copolyesters. Specific properties of injection-molded N(HQ)(PHB) copolyesters are given in our earlier paper.[1] Wissbrun[19] has studied the effect of thermal history, temperature, and shear rate on the melt viscosity of compositions very similar to those in Figure 5.

Significance of Polyester Softening Points. When fibers of liquid crystalline polyesters are heat treated to increase their molecular weights, and thereby their tensile properties, it is important that the fibers do not soften sufficiently to stick together during the heat-treatment process. The softening points of the polymers give an indication of the temperatures to which the fibers can be heated before sticking will occur (unless during the heat-treatment process further crystallization of the fiber occurs, which then allows higher temperatures to be used). In Figure 6, the melting points (T_m), determined by differential scanning calorimetry, are compared with the softening points (T_s), determined by thermomechanical analysis. Since the softening points of the upper N(HQ)(PHB) compositions are only about 5–10 °C below the melting points, the fibers can be heat treated to about 320 °C or higher, depending upon the composition and T_s, before fiber sticking will occur. The similar lower compositions,[20] prepared with phenylhydroquinone instead of hydroquinone, had very low softening points, and the crystallinity was so low that no crystalline melting points were detected at 50 and 80 mol % PHB contents (y = 0.5 or 0.8). The advantage of the relatively low softening points of these polyesters is that extruded sheets can be thermally formed into various shapes at temperatures near the polymer softening points or, if little or no crystallinity is present, at temperatures near the heat-deflection temperatures, which are lower than the softening points. When the naphthalene and phenylene rings were reversed in the upper composition to give copolyesters of terephthalic acid, 2,6-naphthalenediol, and PHB, the melting points were a little lower than those of the N(HQ)(PHB) compositions (Figure 5), and the softening points were about 20–25 °C below the melting points. Therefore, fibers of these compositions can be heat treated to give high tensile properties, but because their softening points are lower than those of the upper compositions, longer heat-treatment times are required.

When the PHB component in the lower structure of Figure 6 was omitted and terephthalic acid added to the composition, the melting and softening points in Figure

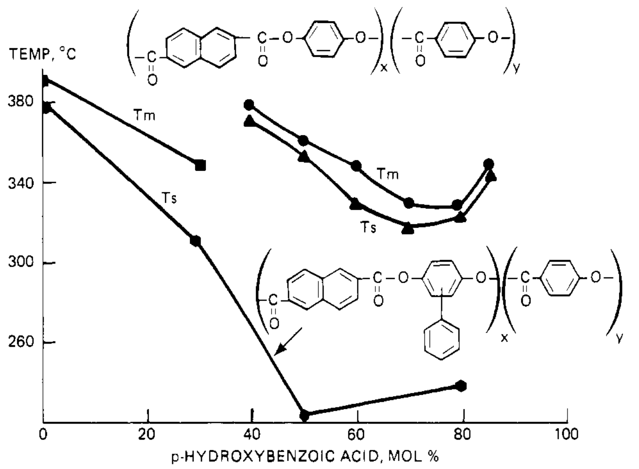


Figure 6. Melting and softening points of *p*-hydroxybenzoic acid copolyesters. T_m = DSC melting point, T_s = TMA softening point.

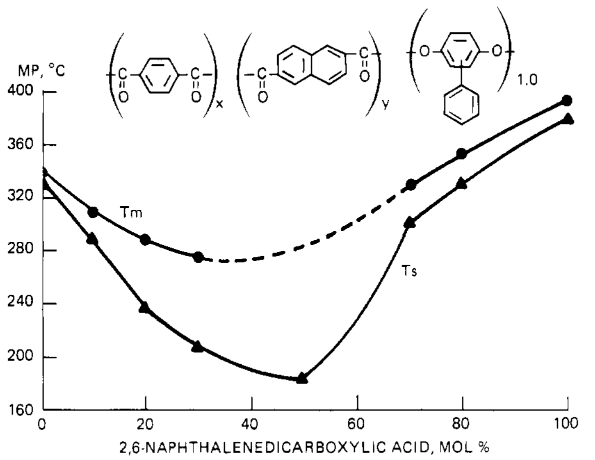


Figure 7. Melting and softening points of phenylhydroquinone copolyesters.

Table VII
Effect of 2,6-Naphthalenedicarboxylic Acid on Fiber Properties of Phenylhydroquinone Polyterephthalate

	naphthalene diacid, mol %			
	0		10	70
as-spun[a]				
denier/filament	1.2	1.4	1.9	1.9
tenacity, g/denier	4.8	4.5	6.9	7.3
elongation, %	1.3	1.1	2.8	3.2
elastic modulus, g/denier	500	470	380	330
heat-treated[a]				
tenacity, g/denier	18	28	20	23
elongation, %	3.0	3.7	5.2	6.3
elastic modulus, g/denier	900	810	350	370
toughness, g/denier	0.25	0.44	0.48	0.65

[a] See text for spinning and heat-treating conditions.

7 were obtained. No DSC crystalline melting point was observed at 50 mol % N because of lack of crystallinity, and the softening points in the middle of the modification range were greatly depressed, as they were with the phenylhydroquinone copolyesters containing PHB instead of T.

The large depression of the softening points of some of the polymers in Figure 7 limited the compositions that could be heat treated without the problem of individual filaments fusing together. Table VII shows the effects on the fiber properties of 10 and 70 mol % N modification of phenylhydroquinone polyterephthalate. The polyesters (IV's about 2.0) were spun from a one-hole capillary at 350–360 °C. Data are also given for two homopolyesters to show the effects of tenacity and elongation on the fiber toughness (determined by measuring the area under the stress–strain curve). The heat-treated sample having the higher tenacity (obtained by a slightly longer heat-treatment time at 340 °C) also has a somewhat higher elongation and, of course, higher toughness. Because of the lower softening points of the N-modified copolyesters, it was not possible to heat fibers of these compositions directly to 340 °C, and the fibers, wrapped on a metal frame and inserted in a tube, were heated with a slow argon sweep for 1 h each at 180, 220, 260, and 280 °C and then 2 h at 300 °C. The sample modified with 70 mol % N and having the higher softening and melting points was also heated for 2 h at 320 °C. These two copolyesters had lower elastic moduli and higher elongation and toughness values than the two homopolyesters, particularly when fibers of similar tenacity are compared. Elongation and toughness are important properties in many industrial fiber applications.

Conclusions

Although compounds that are liquid crystalline can be obtained with certain para-substituted aromatic diesters of 1,4-, 1,5-, and 2,6-oriented naphthalene derivatives, the all-aromatic homopolyesters with similar structures melt too high to be thermally processed without thermal decomposition. All-aromatic copolyesters prepared with 2,6-oriented naphthalene monomers have lower melting points than those prepared with 1,4- and 1,5-oriented monomers, and they exhibit thermotropic liquid crystalline behavior when a high proportion of the polymer chains consist of the 2,6-oriented naphthalene rings and *p*-phenylene rings connected by carboxy groups. Their injection-molded plastics have very high strength and stiffness properties and very low coefficients of thermal expansion in the direction of orientation, and their melt-spun fibers have high tenacities and moduli.

The polymer softening points, which can be determined by thermomechanical analysis, give an indication of the temperature to which the fibers can be heated (to increase their molecular weights and tensile properties) before sticking of the individual filaments occurs. Low softening points, however, permit the thermal forming of shapes at relatively low temperatures compared to the melting points and also permit the retention of the strength and stiffness properties. Reduction of softening points and crystallinity without reduction of liquid crystallinity or reduction of tensile strength can be accomplished by modification of phenylhydroquinone polyterephthalate with 2,6-naphthalenedicarboxylic acid.

The introduction of flexible aliphatic groups in liquid crystalline polyesters reduces the polymer relaxation times, and the introduction of rigid kinks in the polymer chains reduces the degree of extended-chain orientation that can be obtained. Consequently, substantial modification with flexibilizing or kinking components reduces the liquid crystallinity and the level of tensile and stiffness properties that can be achieved in injection-molded plastics and melt-spun fibers.

Acknowledgment. I acknowledge the numerous contributions of J. C. Morris and H. F. Kuhfuss, who also prepared the polyesters. I am also indebted to R. M. Schulken and R. H. Cox for determination of the relaxation times and to J. T. Moore for determination of the softening points.

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