

Improved Processing of Thermotropic Liquid Crystalline Polyesters

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Synopsis

A series of thermotropic liquid crystalline polyesters based on *p*-hydroxybenzoic acid, terephthalic acid, 2,6-dihydroxynaphthalene and containing small amounts of either Bisphenol A, 2,7-dihydroxynaphthalene, or polyethylene terephthalate (PET) as comonomers were prepared. The latter three materials were investigated as a means of lowering the spinning temperature of the base polymer without sacrificing properties. Samples containing 1–2.5% Bisphenol A or 2.5–5% 2,7-dihydroxynaphthalene retained most of the properties (modulus fell slightly), but spinning temperature reduction was minimal. Polymers containing 2.5–5% PET retained full properties at spinning temperatures 60–80°C below the control.

INTRODUCTION

The term “liquid crystal,” while seemingly an anomalous term, is actually a best attempt at describing a unique class of materials. A liquid crystal has the properties of a crystal yet also possesses the flow properties of a liquid. Thus, it is a highly ordered fluid. There are two classes: thermotropic, in which these properties are exhibited in the melt, and lyotropic, where the properties are attained in solution. Such properties can be observed because these materials have unique optical characteristics. Liquid crystalline compounds are optically anisotropic—they transmit light at different velocities in different directions. When observed between crossed Nicol prisms of a polarizing microscope, intense color bands are seen. These unique properties are obtained as a result of the ability of the molecules to orient themselves with respect to their longitudinal axes. Basically, compounds capable of forming liquid crystalline phases are fairly rigid along the long axis of the molecule. Both monomeric and polymeric materials are capable of exhibiting this type of order. The former types usually are symmetrical structures consisting of two substituted benzene rings connected in the para positions by a specific linking group.¹ Polymeric systems are prepared from symmetric and rigid monomers such as terephthalic acid, hydroquinone, *p*-phenylenediamine, etc. As in the monomeric systems, these rigid rod polymers will line up either in the melt or solution to give a highly ordered structure. The processing of such a polymer into a fiber, film, or molded article, from this state, results in structures that are highly ordered and exhibit superior mechanical properties over conventional folded chain polymers. Figure 1 illustrates the transition of two polymers, PET and an anisotropic polyester, from the melt into the solid phase. In this manner, liquid crystal fiber properties such as 10–30 g/d tenacity and >500 g/d modulus can be attained. PET, on the other hand, has typical properties of 9 g/d tenacity and 100 g/d modulus after drawing.

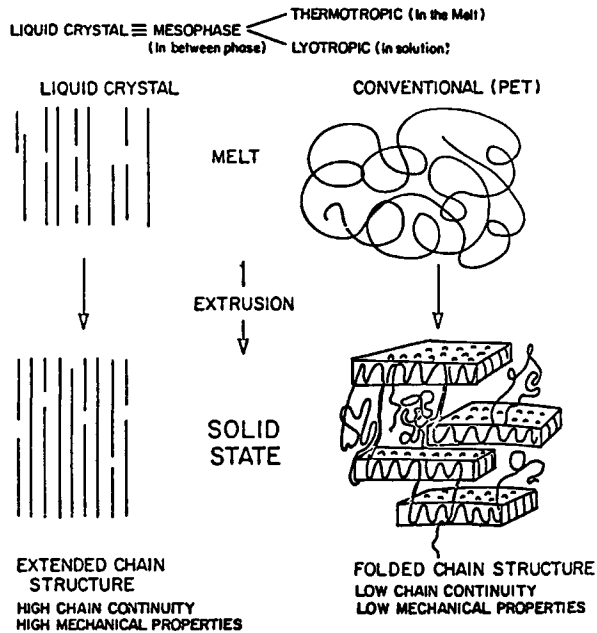
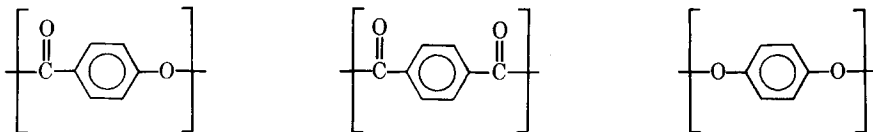


Fig. 1. Structure development of liquid crystalline vs. conventional folded chain polymers.

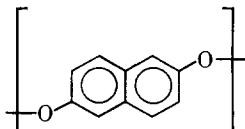
This paper will discuss thermotropic polyesters prepared via melt condensation techniques.

In order to obtain a thermotropic polymer, careful attention must be given to monomer composition. A highly rigid and symmetric polymer, such as that obtained from terephthalic acid and hydroquinone, is much too intractable for melt processing. Other monomers must be introduced that would increase tractability enough so that melt processing is possible. This can be accomplished through slight disruption of molecular order. Three approaches can be used: a flexible linkage ($-\text{CH}_2-\text{CH}_2-$); the use of a substituted benzene ring (such as chlorohydroquinone); or a molecule that would provide a kink in the chain (such as a naphthalene moiety).

The all aromatic polyester prepared from 60% *p*-hydroxybenzoic acid, 20% terephthalic acid, and 20% hydroquinone is intractable:



However, substituting 2,6-dihydroxynaphthalene for hydroquinone



results in a polyester having an anisotropic melt and as-spun fiber properties

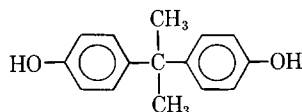
shown below²:

$$\begin{aligned} \text{tenacity} &= 5\text{--}11 \text{ g/d} \\ \text{elongation} &= 1\text{--}3\% \\ \text{modulus} &= 400\text{--}700 \text{ g/d} \end{aligned}$$

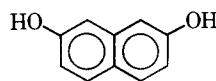
$$\text{IV} = 4\text{--}6$$

Although the polymer melts at 295°C, it is necessary to melt spin at 355–360°C to achieve optimum properties. The present paper describes an investigation that was initiated with the object of further lowering the spinning temperature of this polymer without sacrificing properties.

The approach was to partially substitute one of the monomers with a small quantity of a flexible or dissymmetric molecule to further disrupt order. Bisphenol A and 2,7-dihydroxynaphthalene were chosen as partial replacements for 2,6-dihydroxynaphthalene:



BPA



2,7-DHN

The use of poly(ethylene terephthalate) as a “monomer” in melt polymerizations was first reported by Hamb.^{3,4} It was observed that the initial high viscosity rapidly decreased, and a clear melt resulted. Continued heating and vacuum application resulted in a highly viscous melt. The proposed mechanism was an initial acidolysis of the PET followed by condensation of the carboxyl and acetate end groups to form high polymers. The technique was further applied to the synthesis of thermotropic liquid crystalline polyesters.⁵⁻⁸ As a result of these studies, PET was also investigated as a possible “monomer” in this work.

EXPERIMENTAL

Materials

***p*-Acetoxybenzoic acid** was obtained by refluxing 400 g of *p*-hydroxybenzoic acid, 800 mL of acetic anhydride, and 0.4 g sodium acetate for 2 h. Upon cooling, the white solid was filtered and recrystallized from fresh acetic anhydride; mp 195°C.

2,6-Diacetoxynaphthalene was prepared in the same manner to give a white solid; mp 177°C.

2,7-Diacetoxynaphthalene, prepared as above, gave mp 130°C.

Bisphenol A diacetate was prepared by refluxing 250 g of Bisphenol A, 500 mL of acetic anhydride, and 0.25 g of sodium acetate for 2 h. After solvent removal, the residue was poured into water in a Waring blender. The precipitated solid was filtered and continually washed with water until acid-free. Recrystallization from methanol afforded a white solid; mp 92°C.

Terephthalic acid and PET chip (0.6 IV) were obtained internally and used without further purification.

Sodium acetate was Fisher reagent grade.

Polymer Preparation

All polymers were prepared in the same manner utilizing an ester interchange technique. The following is a typical example:

57.5/2.5/20/20 *p*-hydroxybenzoic acid/PET/terephthalic acid/2,6-dihydroxynaphthalene copolymer

To a 300-mL three-necked, round-bottom flask, equipped with a mechanical stirrer, argon inlet, and distillation head/condenser, was added the following in the order given:

PET (0.6 IV)	2.88 g (0.015 mol)
terephthalic acid	19.92 g (0.12 mol)
2,6-diacetoxynaphthalene	29.30 g (0.12 mol)
<i>p</i> -acetoxybenzoic acid	62.10 g (0.345 mol)
sodium acetate	0.2 g

The system was evacuated and purged with argon four times. Under a steady flow of argon, the flask was placed in an oil bath and heated at 250°C/3 h and 280°C/2 h. At this point, 31 mL (88.5%) of acetic acid had been collected.

The temperature was then raised to 320°C. After 15 min, the argon flow was halted and a vacuum connection attached. During the next 15 min, the pressure was slowly reduced to <1 mm and then held at <0.5 mm Hg for 1 h at 320°C. Subsequently, the vacuum was released, under argon, and the flask cooled overnight. After separation from adhering glass, the polymer was ground up (liquid nitrogen) and extracted 24 h with 30°–60° petroleum ether (to remove stirrer shaft lubricant).

The resultant copolyester had an IV of 4.40 (0.1% in pentafluorophenol at 60°C) and mp = 278°C (DSC peak transition).

The polymer was melt spun into a continuous filament of approximately 26 dpf. Specifically, the polymer melt was extruded through a spinneret with a single hole jet of diameter 7 mils and length of 10 mils. The fiber was quenched in ambient air (72°F, 65% RH) and taken up at 52 m/min.

RESULTS AND DISCUSSION

A series of thermotropic liquid crystalline polyesters, containing varying amounts of Bisphenol A (BPA), 2,7-dihydroxynaphthalene (2,7-DHN), or PET were prepared in an attempt to lower spinning temperatures without sacrificing properties. Polymers containing BPA or 2,7-DHN are summarized in Table I; those containing PET, in Table II. These preparations are compared against a control sample containing 60% HBA, 20% TA, and 20% 2,6-DHN. The spinning temperature is that value at which the maximum properties were obtained.

Total mol % levels of BPA were 1%, 2.5%, and 5%. The latter sample appeared amorphous, had a high melt viscosity, and could not be spun. The lower levels exhibited crystalline melts at 293°C that were anisotropic. Both tenacity and modulus fell with increasing amounts of BPA. Although the polyester sample containing 1% BPA had reasonable properties, the spinning temperature of 335°C was still too high for further consideration.

Incorporation of the dissymmetric monomer, 2,7-DHN, into these formulations

TABLE I
Liquid Crystalline Polyesters Containing Bisphenol A (BPA) or 2,7-Dihydroxynaphthalene (DHN): HBA^a/TA^b/2,6-DHN/BPA or 2,7-DHN As-Spun Properties

Mole ratio	IV ^c	T_m (°C) ^d	T/E/M ^e	Spin temp (°C)
60/20/20/0	4.12	295	6.24/1.33/552	360
60/20/15/5 (BPA)	6.06	—	Not spinnable	—
60/20/17.5/2.5 (BPA)	3.79	293	5.32/1.53/416	340
60/20/19/1 (BPA)	4.32	293	6.03/1.46/493	335
60/20/15/5 (2,7-DHN)	3.36	275	6.24/1.76/462	331
60/20/17.5/2.5 (2,7-DHN)	4.05	282	6.37/1.54/501	340

^a *p*-Hydroxybenzoic acid.

^b Terephthalic acid.

^c 0.1% in pentafluorophenol at 60°C.

^d DSC peak transition (20°C/min scan).

^e Tenacity and modulus reported in g/denier; elongation in %.

resulted in better property retention but, again, marginal drops in spinning temperature. These results, coupled with the high price of the 2,7 isomer, precluded any further work.

The PET containing polymers are listed in Table II. Since PET has both hydroxyl and carboxyl end groups, it may be treated as an A-B type monomer. This introduces the flexibility of being able to replace any of the monomers in the formulation. Polymers were prepared in which either *p*-hydroxybenzoic acid or terephthalic acid/2,6-dihydroxynaphthalene were partially replaced. For the case shown, full property retention was achieved at spin temperatures 60–80°C below the control regardless of which monomer was replaced. Optimum properties were obtained in a sample in which 2.5% of the HBA was replaced by PET.

CONCLUSIONS

A series of thermotropic liquid crystalline polyesters, containing flexible and/or dissymmetric monomers, were prepared in an attempt to lower spin temperatures without sacrificing properties. Polymers containing 1–2.5% Bisphenol A or 2.5–5% 2,7-dihydroxynaphthalene retained most of the ambient mechanical properties (although modulus fell slightly) but still had high spin temperatures.

TABLE II
Liquid Crystalline Polyesters Containing PET: HBA/TA/2,6-DHN/PET^a As-Spun Properties

Mole ratio	IV ^b	T_m (°C) ^c	T/E/M	Spin temp (°C)
60/20/20/0	4.12	295	6.24/1.33/552	360
60/17.5/17.5/5	3.11	270	7.92/2.05/478	300
57.5/20/20/2.5	4.40	278	8.33/1.91/530	305
55/20/20/5	3.05	720	7.31/1.70/518	282

^a PET IV = 0.61.

^b 0.1% in pentafluorophenol at 60°C.

^c DSC peak transition (20°C/min scan).

Thermotropics containing 2.5–5% PET retained full properties at much lower spin temperatures. They offered the best choice of lowest spin temperatures, highest property retention, and lowest cost of the polymers investigated.

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