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### Thermotropic Copolyesters. 1. Synthesis and Characterization of Liquid Crystal Copolyesters Containing the Bicyclo [2.2.2]octane Ring System

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## Thermotropic Copolyesters. 1. Synthesis and Characterization of Liquid Crystal Copolyesters Containing the Bicyclo [2.2.2]octane Ring System

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### ABSTRACT

The syntheses and characterizations of poly[oxy(2-chloro-1,4-phenylene)oxycarbonyl-1,4-bicyclo[2.2.2]octylenecarbonyl-co-oxy(2-chloro-1,4-phenylene)oxysebacoyl] and poly[oxy(2-methyl-1,4-phenylene)oxycarbonyl-1,4-bicyclo[2.2.2]octylenecarbonyl-co-oxy(2-methyl-1,4-phenylene)oxysebacoyl] are described. The resulting random copolyesters were characterized by infrared spectroscopy, proton magnetic resonance spectroscopy, solution viscosity, and differential scanning calorimetry. The random copolyesters formed birefringent fluid states in the melt.

### INTRODUCTION

In 1970, Dewar and Goldberg [1] reported the preparation of nematic liquid crystal esters which contained the bicyclo[2.2.2]octane ring system. Their objective was to study the effect of substituting the 1,4-bicyclo[2.2.2]octylene and trans-1,4-cyclohexylene saturated ring systems for phenylene in the typical liquid crystal, p-phenylene dianisate.

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The authors reported a nematic range of 152-221 °C for 1,4-bicyclo[2.2.2]octylene di-4-n-butoxyphenyl-1-carboxylate. The authors concluded that the rigid linear geometry of the 1,4-bicyclo[2.2.2]octane system was the controlling factor in stabilizing the mesophase compared to the more flexible trans-1,4-cyclohexylene system.

In 1975, Dewar and Riddle [2] reported the preparation of bis(p-alkoxyphenyl)bicyclo[2.2.2]octane-1,4-dicarboxylates, which were characterized as nematic liquid crystals. The authors once again emphasized the importance of geometrical factors in determining the stability of the mesophase. Also in 1975, Dewar and Griffin [3] reported the synthesis of bis(p-methoxyphenyl)bicyclo[2.2.2]octane-1,4-dicarboxylate with a nematic range of 152.0-268.8 °C.

In 1981, Gray and co-workers [4] reported the synthesis of 1-(4'-cyanophenyl)-4-n-pentyloxybicyclo[2.2.2]octane and 1-(4'-cyanophenyl)-4-(4'-(2''-methylbutyl)phenyl)bicyclo[2.2.2]octane. No mesophase was observed for the former substance on heating or cooling. The latter substance formed a low-temperature cholesteric mesophase. The authors reported that, generally, the clearing temperatures decreased in the series 1-(4'-cyanophenyl)-4-n-alkylbicyclo[2.2.2]octane, trans-1-(4'-cyanophenyl)-4-n-alkylcyclohexane, and 4-cyano-4'-alkylbiphenyl.

In 1981, Gray and Kelly [5] reported the synthesis of 4-n-alkylphenyl 4-n-alkylbicyclo[2.2.2]octane-1-carboxylates and 4-n-alkoxyphenyl 4-n-alkylbicyclo[2.2.2]octane-1-carboxylates, which formed smectic mesophases.

Also, in 1981, Gray and Kelly [6] reported the preparation of low-melting liquid crystal 4-n-alkylphenyl 4-n-alkylbicyclo[2.2.2]octane-1-carboxylates which contained fluoro, chloro, bromo, or cyano groups substituted into the 2-position of the phenyl ring.

Aromatic polyesters have been prepared [7] by the reaction of aromatic dicarboxylic acid chlorides with substituted hydroquinones. The polymer prepared by the reaction of terephthaloyl chloride and hydroquinone decomposed before melting. Schaeffgen et al. [8] reported that poly(oxy-2-chloro-1,4-phenyleneoxyterephthaloyl) and poly(oxy-2-methyl-1,4-phenyleneoxyterephthaloyl) form nematic melts. In those same patents, Schaeffgen et al. [8] reported that poly(oxy-2-chloro-1,4-phenyleneoxycarbonyl-trans-1,4-cyclohexylene-carbonyl) and poly(oxy-2-methyl-1,4-phenyleneoxycarbonyl-trans-1,4-cyclohexylene-carbonyl) also form liquid crystal melts. Kwolek [9] reported that a copolyester prepared from chlorohydroquinone (95 mol%), 2,3-dichlorohydroquinone (5 mol%), and trans-1,4-cyclohexanedicarboxylic acid forms a liquid crystalline melt above its DSC melting point of 300 °C.

In a 1966 patent, Watson [10] reported the syntheses and characterizations of polyesters and random copolyesters based on bicyclo[2.2.2]octane-1,4-dicarboxylic acid, suitable dihydroxy compounds, and other acid components. Among the dihydroxy compounds mentioned were dihydric phenols, such as hydroquinone, which may contain other groups, such as halogen atoms. However, no mention was made of liquid crystal properties for the resulting series of polyesters.

Since the corresponding terephthalic acid and trans-1,4-cyclohexanedicarboxylic acid polyesters of chlorohydroquinone and methylhydroquinone had been synthesized and demonstrated to form liquid crystalline melts, we set out to prepare the corresponding polyesters of bicyclo[2.2.2]octane-1,4-dicarboxylic acid. Therefore, our objectives were to prepare polyesters which contained the bicyclo[2.2.2]-octane ring system and to investigate the potential liquid crystal properties of the systems.

## EXPERIMENTAL

Inherent viscosities were measured at 30°C with a Cannon-Fenske viscometer at a concentration of 0.5 g/100 mL in *o*-chlorophenol. Thermal analysis data were determined with a differential scanning calorimeter (Du Pont 990 thermal analyzer with the Du Pont 910 differential scanning calorimeter). Polarizing optical microscopy was performed on a Leitz Laborlux 12 Pol microscope with a Leitz 350 heating stage. Proton NMR spectra were determined with a Varian EM-360 spectrometer at 60 MHz. The chemical shifts are reported relative to tetramethylsilane. Infrared spectra were obtained on KBr disks with a Beckman 4240 infrared spectrophotometer.

The *o*-dichlorobenzene solvent used in the polyesterification was purified and dried by fractional distillation and stored over Molecular Sieves. Sebacyl chloride, chlorohydroquinone, and methylhydroquinone were commercial products. Chlorohydroquinone and methylhydroquinone were purified by recrystallization from water. Bicyclo[2.2.2]-octane-1,4-dicarbonyl chloride was obtained by reaction of the dicarboxylic acid with phosphorus pentachloride in the usual way [11]. Bicyclo[2.2.2]octane-1,4-dicarboxylic acid was prepared by the method of Wood [12].

### A. Preparation of Poly[oxy(2-chloro-1,4-phenylene)oxycarbonyl-1,4-bicyclo[2.2.2]-octylenecarbonyl-co-Oxy(2-chloro-1,4-phenylene)oxysebacyl] (I)

A 100-mL three-necked round-bottom flask equipped with a condenser, a gas inlet, and a magnetic stirrer was charged with 3.90 g (0.0167 mol) of bicyclo[2.2.2]octane-1,4-dicarbonyl chloride, 4.00 g (0.0278 mol) of chlorohydroquinone, 2.65 g (0.0111 mol) of sebacyl chloride, and 30 mL of *o*-dichlorobenzene. The resulting mixture was heated at 170°C for 8 h under a nitrogen atmosphere. After cooling, the polymer was precipitated by pouring the reaction mixture into 400 mL of acetone. After filtering, washing several times with acetone, water, and methanol, and drying the polymer in a vacuum oven for 24 h at 90°C, 6.4 g of the copolyester was obtained.

The analysis results for random copolyester I were as follows. Analysis: Calculated for  $(C_{16}H_{15}O_4)_{0.6}(C_{14}H_{19}O_4)_{0.4}$ : C, 61.11; H, 5.56; Cl, 11.89. Found: C, 62.15; H, 5.50; Cl, 11.69.

The infrared spectrum of I showed peaks at 3100 (aromatic C-H stretch); 2920 and 2860 (aliphatic C-H stretch); 1750 (ester C=O stretch); 1595 and 1490 (aromatic nucleus); and 1222, 1171, and 1022 (C-O stretch)  $cm^{-1}$ .

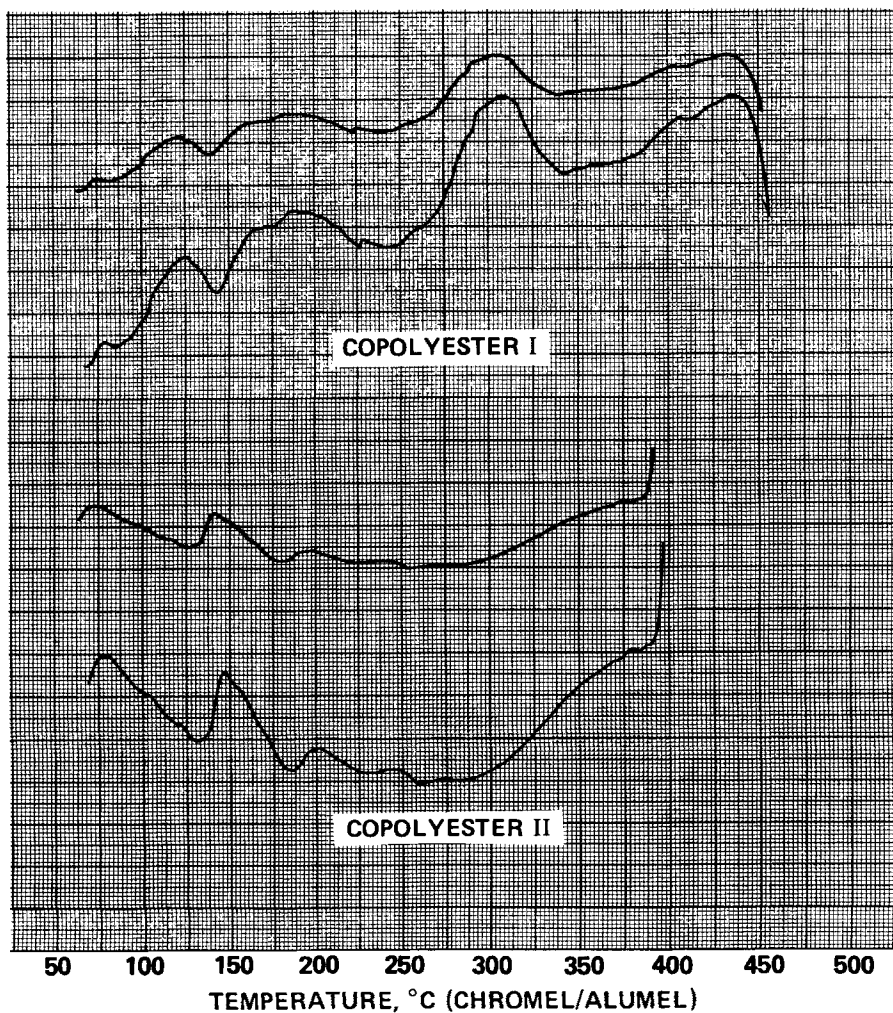


FIG. 1. DSC thermogram of copolyesters I and II.

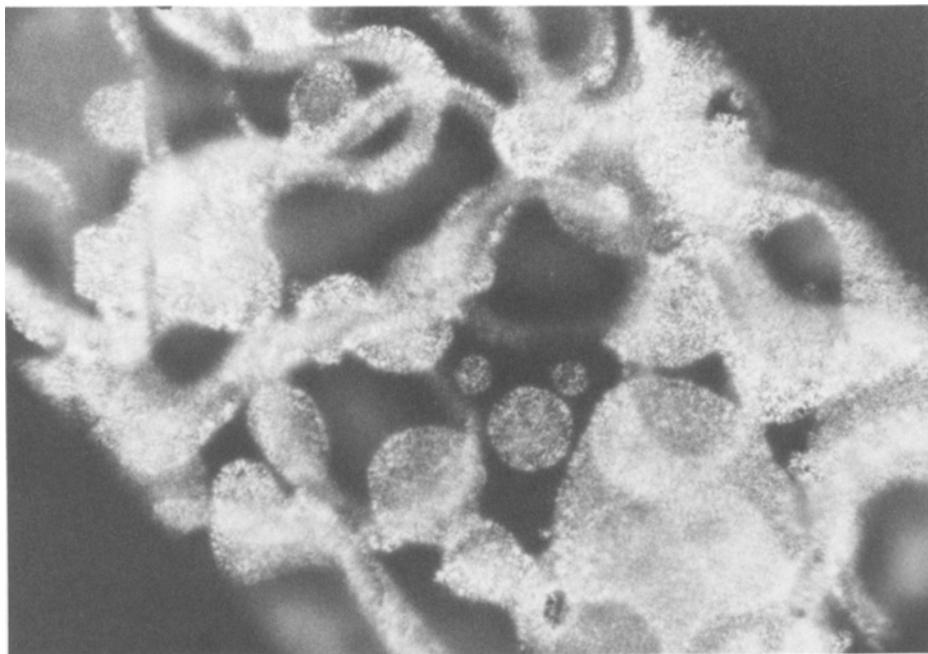


FIG. 2. Hot-stage polarizing optical micrograph of copolyester I. Magnification 32 $\times$ .

The differential scanning calorimetry thermogram of copolyester I showed an endotherm at 140°C, a broad endotherm centered at 240°C, and a decomposition endotherm centered at ~340°C (Fig. 1). Hot-stage polarizing optical microscopy (Fig. 2) established a softening temperature of 150°C, a transition to a birefringent fluid state at ~199°C, and decomposition beginning at ~317°C. The thermal properties and inherent viscosity of polymer I are shown in Table 1.

The proton nuclear magnetic resonance spectrum of I in 3:1 deuterated chloroform/trifluoroacetic acid is shown in Fig. 3. The peaks at  $\delta$  1.1, 1.4, and 2.5 represent protons on the methylene groups in the sebacyl chain. The peak at  $\delta$  2.1 represents the protons on the three methylene bridges in the bicyclo[2.2.2]octane ring system. The doublet centered at  $\delta$  7.2 represents the protons on the aromatic ring.

TABLE 1. Thermal and Inherent Viscosity Properties of Copolyesters I and II

Copolyester	$\eta_{inh}$ , dL/g <sup>a</sup>	DSC transitions, °C <sup>b</sup>	Hot-stage polarizing optical microscopy transitions, °C
1	0.90	140, 240, 340 <sup>c</sup>	150, <sup>d</sup> 199, <sup>e</sup> 317 <sup>c</sup>
2	0.60	127, 255	166, <sup>d</sup> 208, <sup>e</sup> 345 <sup>c</sup>

<sup>a</sup>The conditions were 0.5 g/100 mL polymer in *o*-chlorophenol at 30°C.

<sup>b</sup>The temperature programming rate was 50°C/min.

<sup>c</sup>This represents a decomposition temperature.

<sup>d</sup>This represents a softening temperature.

<sup>e</sup>This represents the transition temperature to a birefringent fluid state.

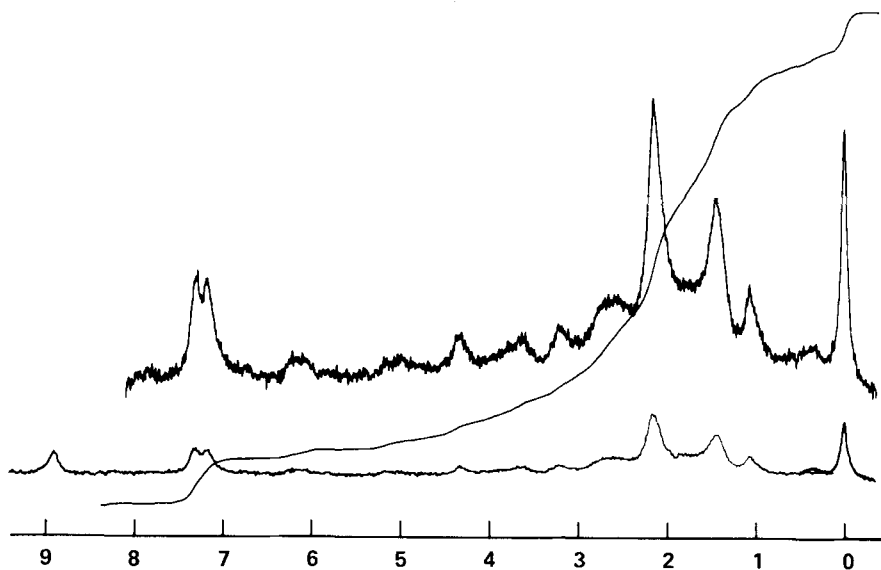


FIG. 3. Proton NMR spectrum of copolyester I.

B. Preparation of Poly[oxy(2-methyl-1,4-phenylene(oxycarbonyl-1,4-bicyclo[2.2.2]-octylenecarbonyl-co-Oxy(2-methyl-1,4-phenylene)oxysebacyl)] (II)

A 100-mL three-necked round-bottom flask, equipped with a condenser, a gas inlet, and a magnetic stirrer was charged with 1.16 g (0.00494 mol) of bicyclo[2.2.2]octane-1,4-dicarbonyl chloride, 1.02 g (0.00823 mol) of methylhydroquinone, 0.790 g (0.00329 mol) of sebacyl chloride, and 15 mL of *o*-dichlorobenzene. The resulting mixture was heated at 170°C for 8 h under a nitrogen atmosphere. After cooling, the polymer was precipitated by pouring the reaction mixture into an acetone/hexane mixture (20/80 v/v). After filtering, washing several times with acetone, water, and methanol, and drying the polymer in a vacuum oven for 24 h at 90°C, 1.69 g of the copolyester was obtained.

The analysis results for random copolyester II were as follows. Analysis: Calculated for  $(C_{17}H_{18}O_4)_{0.6}(C_{15}H_{22}O_4)_{0.4}$ : C, 69.93; H, 7.05. Found: C, 70.47; H, 6.85.

The infrared spectrum of II showed peaks at 3070 (aromatic C-H stretch); 2920 and 2860 (aliphatic C-H stretch); 1746 (ester C=O stretch); 1487 (aromatic nucleus); and 1230, 1170, and 1035 (C-O stretch)  $cm^{-1}$ .

The differential scanning calorimetry thermogram of copolyester II was quite complicated. It showed an endotherm at 127°C, followed by a broad endotherm centered at 255°C (Fig. 1). Hot-stage polarizing optical microscopy (Fig. 4) established a softening temperature of 166°C and a transition to a birefringent fluid state at 208°C which was maintained up to 345°C.

The proton nuclear magnetic resonance spectrum of II in 3:1 deuterated chloroform/trifluoroacetic acid is shown in Fig. 5. The peak at  $\delta$  1.4 represents protons on the methylene groups in the sebacyl chain. The doublet at  $\delta$  2.1 represents the protons on the three methylene bridges in the bicyclo[2.2.2]octane ring system. The broad peak centered at  $\delta$  2.5 represents the methyl group on the aromatic ring. The peak at  $\delta$  7.1 represents the protons on the aromatic ring. Spinning side bands appear at  $\delta$  0.9, 3.5, 5.1, and 8.4.

## RESULTS AND DISCUSSION

Random thermotropic copolyesters were formed by the step-reaction polycondensation of 1) chlorohydroquinone and bicyclo[2.2.2]octane-1,4-dicarbonyl chloride and sebacyl chloride and 2) methylhydroquinone and bicyclo[2.2.2]octane-1,4-dicarbonyl chloride and sebacyl chloride. The structures of the random copolyesters are shown in Fig. 6.



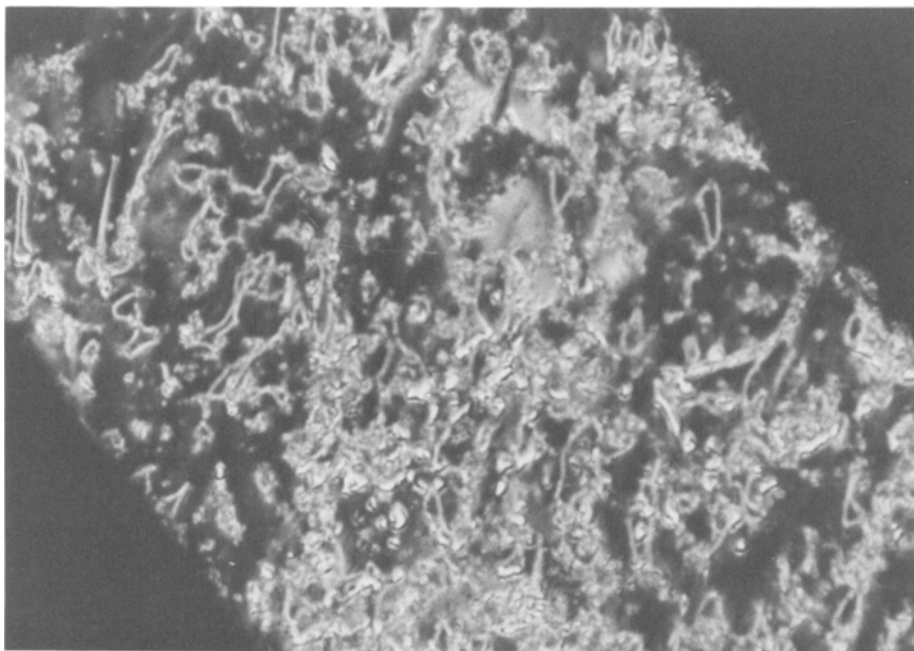


FIG. 4. Hot-stage polarizing optical micrograph of copolyester II. Magnification 32 $\times$ .

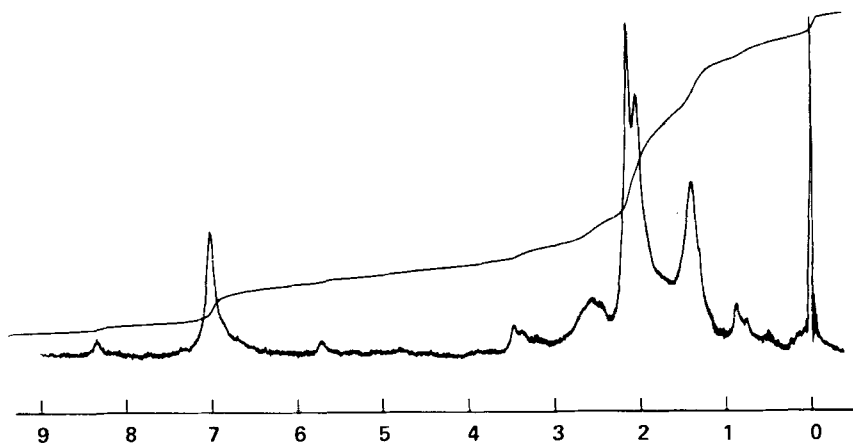


FIG. 5. Proton NMR spectrum of copolyester II.

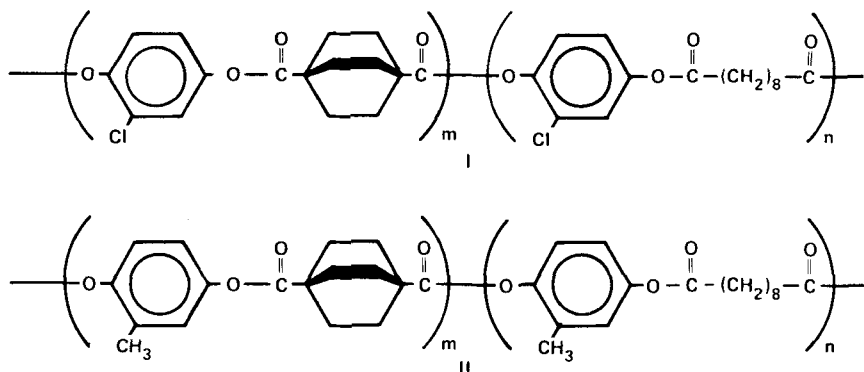


FIG. 6. Structures of random copolyesters I and II.

### CONCLUSIONS

In summary, poly[oxy(2-chloro-1,4-phenylene)oxycarbonyl-1,4-bicyclo[2.2.2]octylenecarbonyl-co-oxy(2-chloro-1,4-phenylene)oxysebacoyl] and poly[oxy(2-methyl-1,4-phenylene)oxycarbonyl-1,4-bicyclo[2.2.2]octylenecarbonyl-co-oxy(2-methyl-1,4-phenylene)oxysebacoyl] were synthesized and shown to form birefringent fluid states in the melt. It was necessary to use the flexible sebacyl spacer in order to produce a copolyester with low enough thermal transition temperatures to demonstrate thermotropic behavior.

### ACKNOWLEDGMENTS

We thank Dr Edward Samulski for suggesting that polymers which contained the bicyclo[2.2.2]octane ring system should form birefringent melts and for his encouragement during the course of the work. This work was supported in part by the Office of Naval Research.

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