Thermoplastic and Thermoset Main Chain Liquid Crystal Polymers Prepared from Biphenyl Mesogen

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SYNOPSIS

Main chain liquid crystal thermoplastic polyesters and thermosetting epoxy resins were prepared using biphenyl mesogens. The melting points of the polyesters were effectively decreased by incorporating flexible methylene spacers into the polymer main chain. The liquid crystal epoxy resins exhibit high glass transition temperature, low thermal expansion coefficients, high dielectric strengths, and low dielectric loss. They are suitable for the preparation of self-reinforcing molecular composites. © 1993 John Wiley & Sons, Inc.
Keywords: liquid crystals • polymers • thermoplastic • thermosetting • epoxy • polyesters • self-reinforcing • molecular • composites • nematic • smectic

INTRODUCTION

In the realm of high-performance polymers, there is a never-ending quest for materials with higher thermal and dimensional stability, higher modulus and tensile strength, lower coefficient of thermal expansion, and lighter mass. Liquid crystal polymers have been developed recently to meet these demands.[1]

While large numbers of thermoplastic liquid crystal polymers have been synthesized, relatively few thermoset liquid crystal polymers have been prepared.[2-6] With mesogenic groups along the main chain of the polymer, and crosslinking capability between chains, thermosetting liquid crystal polymer would exhibit desirable properties in both the uniaxial and transverse directions and should be good candidates for self-reinforcing composite materials. In this article, we present the synthesis of thermoplastic and thermoset liquid crystal polymers from biphenyl mesogens, and discuss the structure-property relationships of the prepared polymers.

EXPERIMENTAL

Materials

Monomers (4,4'-biphenol, 4,4'-oxydibenzoic acid, thionyl chloride, adipoyl chloride, pimeloyl chloride, suberoyl chloride, sebacoyl chloride, and epichlorohydrin) were purchased from Aldrich. The chemicals were used as received without further purification. Samples of bisphenol A epoxy (Epon 828) were obtained from Shell Co. and used as received. Curing agents (diaminodiphenylsulfone and trimellitic anhydride) were purchased from Aldrich and used as received.

### Synthesis of Rigid-Rod Aromatic Polyesterether Copolymers (Scheme I of Figure 1)

Preparation of 4,4'-Dichloroformyldiphenylether. The acid chloride was prepared by refluxing 4,4'-oxydibenzoic acid (0.02 m) with excess thionyl chloride (0.14 m) in the presence of 1 drop of dry N,N-dimethylformamide for 3 h. Excess thionyl chloride was removed under reduced pressure. The solid product was recrystallized from hexane/heptane mixture (5 : 1 by volume). Recrystallized solids gave a melting point of 87.5–88°C (lit.[7] 87–89°C). IR (KBr): 1720 cm^{-1}.

Preparation of Aromatic Polyesterether Copolymer (Polymer I). The polymer was synthesized using interfacial condensation. A mixture consisting of sodium hydroxide (20 mmol), water (100 mL), 4,4'-biphenol (10 mmol), and benzyltrimethylammonium chloride (1.63 g of a 10% aqueous solution) was prepared. The mixture was transferred to a Waring blender and stirred while a second solution

Scheme I   Synthesis of Liquid Crystal Aromatic Polyester- ether Copolymer
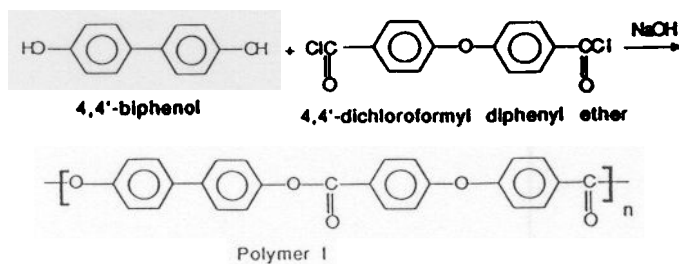
Scheme II   Synthesis of Liquid Crystal Aromatic-Aliphatic Polyester
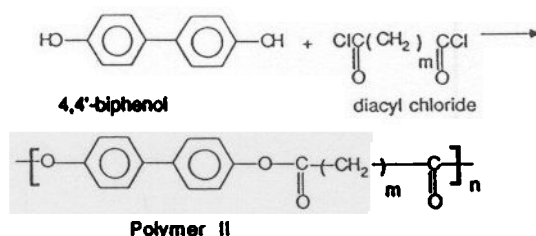
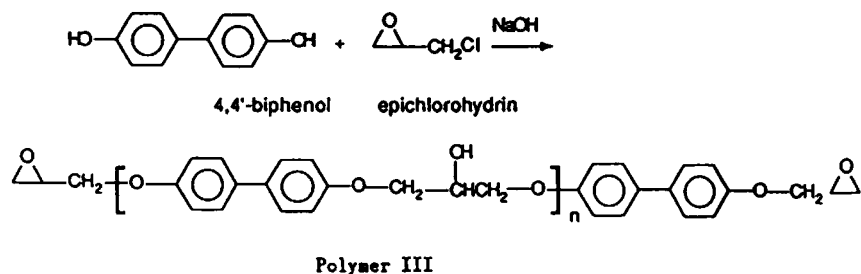## Scheme III   Synthesis of Liquid Crystal Epoxy Resin

Figure 1. Reaction schemes.

consisting of 4,4'-dichloro-formyl diphenyl ether in chloroform (10% solution) was added rapidly. The thick white slurry was stirred at high speed for 10 min and then poured into acetone to coagulate the product. The precipitated polymer was washed with acetone, water, and methanol in sequence; the white powdery solid was then dried in a vacuum oven at 70°C overnight. IR (KBr): 1720, 1580, 1480, 1240, 1190, 750 cm^{-1}. mp > 500°C.

Preparation of Aromatic Aliphatic Polyesters (Scheme II of Figure 1)

The same procedure described in the previous section was followed. The polyesters were prepared by interfacial condensation using 4,4'-biphenol (10

mmol) and an aliphatic diacyl chloride (10 mmol). The aliphatic acid chlorides used were adipoyl, pimeloyl, suberoyl, and sebacoyl chlorides.

Preparation of Liquid Crystal Epoxy from Biphenol and Epichlorohydrin (Scheme III of Figure 1)

To 0.01 m 4,4'-biphenol, 0.1 m epichlorohydrin, and 1 drop of water was added. The mixture was stirred and heated to 100°C followed by cooling to 95°C. Then sodium hydroxide (0.02 m) was added and the mixture was maintained at 100°C for 30 min. The excess epichlorohydrin was removed at reduced pressure. The white residue was washed twice with toluene. The toluene washings were combined and

the solvent evaporated under reduced pressure to yield the polymer as a white solid which melted at 140–142°C.

Characterization of Liquid Crystal Properties of Synthesized Polymers

The thermotropic property of synthesized polymers were studied via Perkin-Elmer DSC-2 for phase transition and via Leitz Ortholux II POL-BK microscope equipped with polarizing light and heating stage for birefringence.

Preparation of Cured Liquid Crystal Epoxy and Bisphenol a Epoxy Samples with Diaminodiphenylsulfone (DDS) and Trimellitic Anhydride (TMA) Curing Agents

A molar equivalent of DDS to both epoxies was used. The liquid crystal epoxy was cured at 170°C, 0.25 mm Hg, for 2 h, then 180°C, 1 atm for 2 h. The bisphenol A epoxy (Shell, Epon 828) was cured at 180°C, 1 atm for 4 h.

A molar equivalent of TMA to both epoxies was used. The curing conditions were the same for liquid crystal epoxy and Epon 828. The samples were cured at 150°C/2 h, 200°C/2 h, 250°C/2 h.

The completeness cure of samples was checked by IR. All samples show the absence of the epoxide ring IR absorption (ca. 910 cm^{-1}); thus, they were well cured.

Thermal and Electrical Properties of Cured Liquid Crystal Epoxy

The glass transition temperatures and Z-axis thermal expansion coefficients of the samples were determined by thermal mechanical analysis (TMA) using a Perkin-Elmer TMS-2 analyzer.

The dielectric strength and dielectric loss of the

Table I. Effect of Flexible Spacer Length on the Melting Point of Liquid Crystal Polyesters

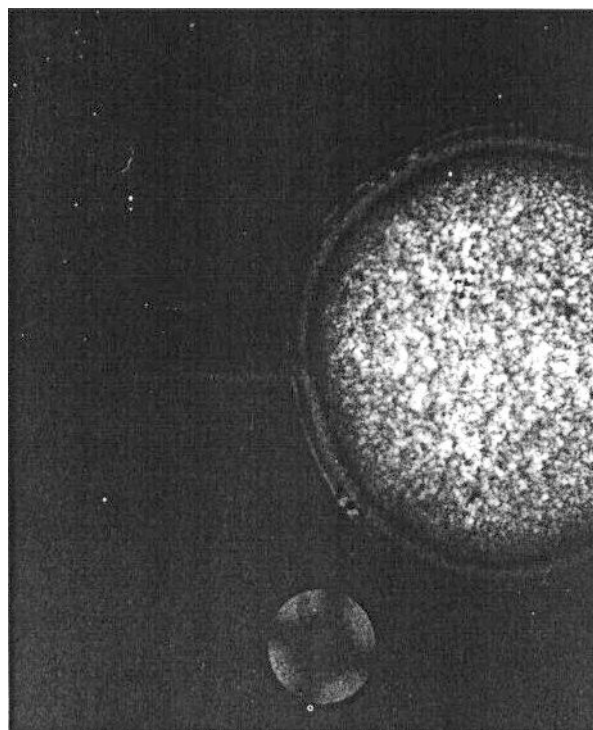| Number of Methylene Units (m)	Melting Point (T_m) (°C)
4	320
5	229
6	225
8	196

Figure 2. Optical micrograph of liquid crystal polyester (polymer II, m = 8) under crossed polars (50X).

cured samples were measured according to ASTM D149 and ASTM D150, respectively.

RESULTS AND DISCUSSION

An aromatic rigid-rod polyesterether copolymer (polymer I) was prepared in quantitative yield according to Scheme I of Figure 1 by interfacial polycondensation via the Schotten–Bauman reaction. However, the polymer melted above 500°C. To lower the melting point of polymer I, we replaced its biphenol ether moiety in polymer I with flexible methylene units as shown in Scheme II of Figure 1.

The effect of the length of flexible spacers on the melting point of polymer II is shown in Table I.

The synthesis and characterization of polymer II has been studied extensively by Blumstein et al.[8] and Asrav et al.[9] Our results are consistent with their results. The highlights of our observation are discussed here.

The melting point of polymer II decreases with increasing methylene unit length. Except for polymer II, where m is equal to 4, all the other molecules, when observed under crossed polars in a hot-stage
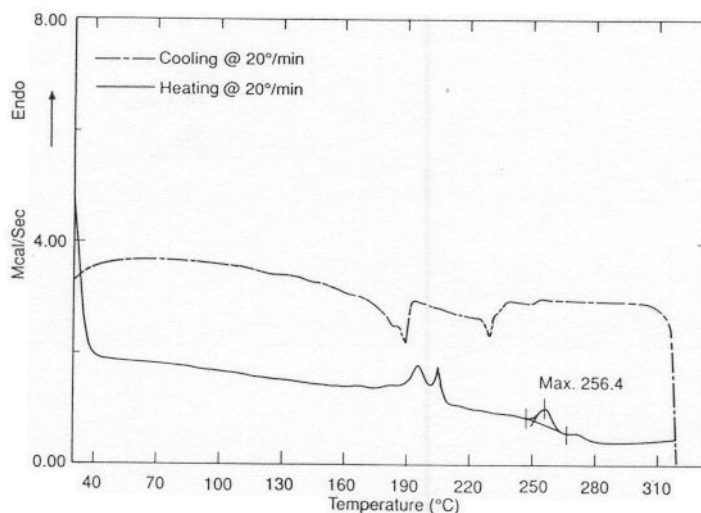
Figure 3. DSC thermogram of liquid crystal polyester (polymer **II**, m = 8).

microscope, exhibit nematic (m = 5) and smectic (m = 6 and m = 8) birefringences. Figure 2 shows a smectic birefringence and Figure 3 gives the DSC thermogram of polymer **II** containing 8 methylene units. The DSC curve shows double melting at 197°C and 204°C, a characteristic of rigid flexible polyesters.[10] Annealing effects were observed during the cooling cycle, involving loss of some solid-solid transition and changes in temperature, shape, and area of exothermic/endothermic peaks.

A thermoset liquid crystal epoxy (polymer **III**) was prepared according to Scheme III of Figure 1. The IR spectrum (Fig. 4) shows the characteristic

bands for epoxy resins at 916 and 863 cm^{-1}. The DSC study of this epoxy is shown in Figure 5. Two transition temperatures were exhibited upon heating. The epoxy started to melt at 115°C and became isotropic at 152°C. The optical micrograph of the epoxy is shown in Figure 6. Smectic birefringent patterns were obtained when the epoxy was observed under the polarized microscope at 135°C.

The liquid crystal epoxy was cured with diaminodiphenyl sulfone (DDS) and trimellitic anhydride (TMA) separately. The properties of cured samples were compared with those of conventional bisphenol A epoxy (Epon 828) cured with the same curing
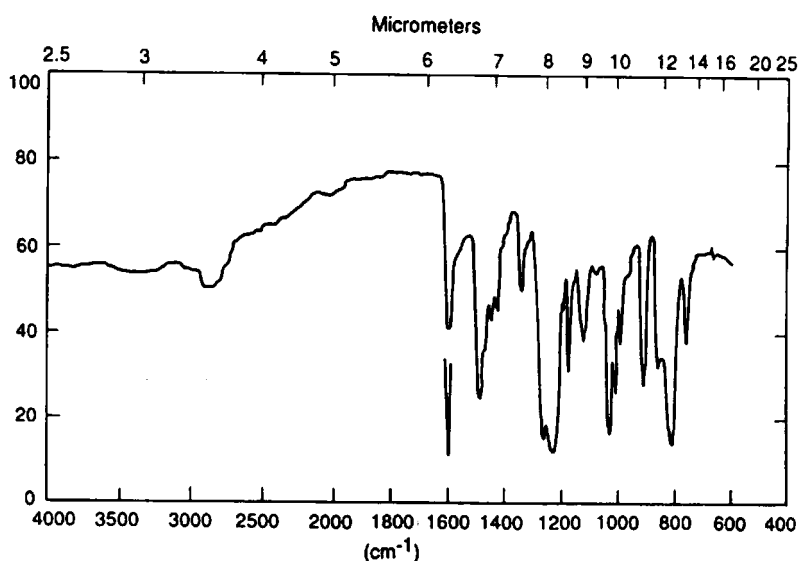

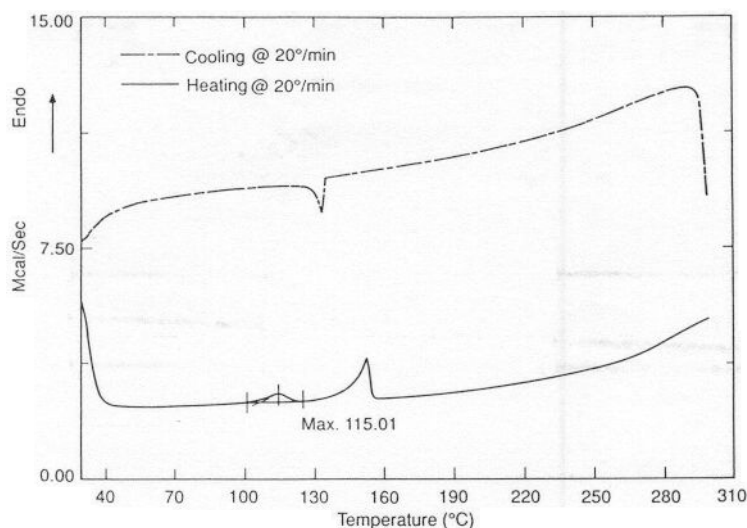**Figure 4.** IR spectrum of liquid crystal epoxy (polymer **III**).

Figure 5. DSC thermogram of liquid crystal epoxy (polymer III).

agents. As shown in Tables II and III, the liquid crystal epoxy exhibits better thermal and electric properties than does bisphenol A epoxy. In the case of thermal properties, the liquid crystal epoxy showed increased glass transition temperature (15.5% for DDS curing agent and 44% for TMA

Figure 6. Optical micrograph of liquid crystal epoxy (polymer III) under crossed polars (50X).

curing agent) and reduced coefficient of thermal expansion (18.9%, DDS curing agent). Ochi et al.[11] reported the glass transition temperature was increased and internal stress was decreased by introducing the tetramethyl biphenyl structure to the epoxy resin networks, i.e., diglycidylether tetramethyl biphenyl (DGETMB). Our results were consistent with their observation, although they didn't describe any liquid crystal property of DGETMB. When the liquid crystal epoxy was cured with trimellitic anhydride, the cured material showed increased dielectric strength (13.7%) and decreased dissipation factor (14.2%). The results are expected because of the highly ordered rigid rod structure of the liquid crystal epoxy. Although the reactivity of liquid crystal epoxies versus curing agents was not quantitatively evaluated, a shorter gel time than that of bisphenol A epoxy was observed.

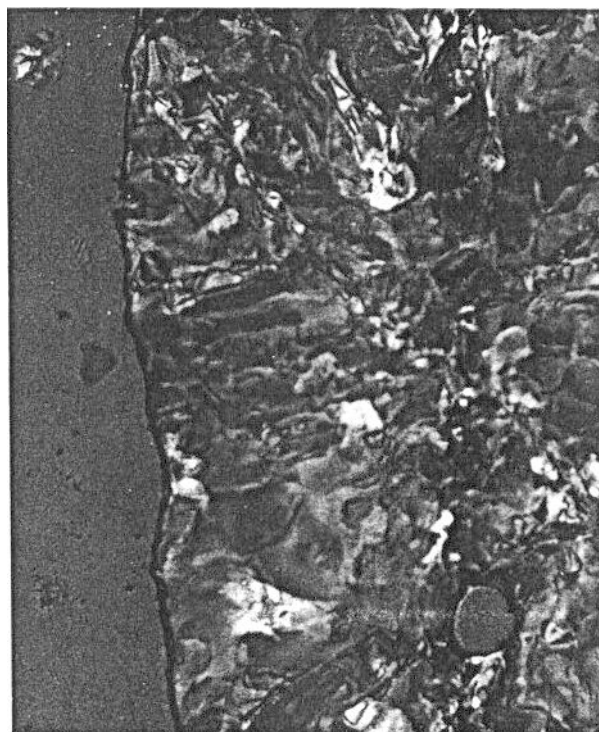The possibility of using liquid crystal epoxies for molecular composites is currently under investiga-

Table II. Comparison of Thermal Properties between Liquid Crystal Epoxy and Bisphenol A Epoxy (Epon 828), Both Cured with Molar Equivalents of Diaminodiphenylsulfone (DDS)

Sample	T_g (°C)	CTE (ppm °C^{-1})
LC Epoxy/DDS	231	56.9
Epon 828/DDS	200	67.7

Table III. Comparison of Thermal and Electrical Properties between Liquid Crystal Epoxy and Bisphenol A Epoxy (Epon 828), Both Cured with Molar Equivalents of Trimellitic Anhydride (TMA)

Sample	T_g (°C)	Dielectric Strength (kV/10 mil)	Dissipation Factor (@ 1 MHz)
LC Epoxy/TMA	183	12.38	0.0319
Epon 828/TMA	127	10.89	0.0372

tion. Crosslinked liquid crystal epoxy resins can eliminate the anisotropic properties of conventional liquid crystal polymers. The mechanical properties of liquid crystal epoxy could be improved further by using rigid rod curing agents instead of conventional curing agents.

CONCLUSIONS

Thermotropic main chain liquid crystal polyester and epoxy resins have been prepared using biphenyl mesogen. The melting point of the polyester was reduced by introducing flexible methylene units into the polyester main chain. The liquid crystal epoxy resin exhibited better thermal and electrical properties than did conventional bisphenol A epoxy resins when cured with conventional curing agents. The liquid crystal epoxy is suitable for the preparation of self-reinforcing molecular composites.

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