

## Mesomorphic Properties of Epoxy-Based Side-Chain Polymers with Cholesteryl and Cyanobiphenyl Pendant Groups

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Ring opening reaction of a commercially available epon resin, ethyleneglycol diglycidyl ether (EGDE) with nematic 4-( $\omega$ -aminohexyloxy)-4'-cyanobiphenyl and twisted nematic cholesteryl 4-aminobutyrate was carried out in bulk at 100°C for 10 h. The side-chain copolymers obtained were found to be mesomorphic as observed under the polarizing microscope. No trend was observed in the transition temperatures of these polymeric systems based on the differential scanning calorimetric study.

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**Key words:** liquid crystals, side-chain liquid crystalline polymers, cholesteric liquid crystals, nematic liquid crystals

### INTRODUCTION

Interest in side-chain liquid crystalline polymers (SCLCP) stems from possible applications that take advantage of the combination of the properties of liquid crystals and polymers. Cholesteric liquid crystal polymers, in particular, may exhibit the unique optical properties of cholesteric liquid crystals such as selective reflection of light in different wavelength ranges, high sensitivity of the selective light reflection to temperature, and an extreme optical activity and the most common polymer property of glass transition ( $T_g$ ) [1]. Macroscopic orientation resulting from the mesogenic group may be frozen-in below  $T_g$ . This feature makes possible the creation of the "frozen cholesteric structure" in bulk solids, films, fibers, and overcoats. Applications of SCLCP include spectrum filters, color-controlled optical elements, thermo-indicators, and colored decorative and technical overcoating [2,3].

For a polymer to form a liquid-crystalline phase, a major portion of it should be stiff and rod-like, this being the same major requisite for the low molecular weight mesogens. In SCLCP, this is often achieved by attaching a mesogenic pendant group to the polymer main chain by flexible spacer groups [4,5]. In this study, the polymer main chain was obtained from an epon resin, ethyleneglycol

diglycidyl ether (EGDE). The mesogenic groups containing cyanobiphenyl and cholesteryl, were attached to the polymer backbone via hexyloxy and butyrate spacers, respectively. Cholesteryl esters are well known for their ability to exhibit the twisted nematic phase [6]. The homopolymer containing cyanobiphenyl has been reported to exhibit the nematic phase [7]. It is hoped that in covalently introducing cholesteryl into the nematic polymeric system in different amounts, a twisted nematic or cholesteric phase would be obtained. This paper reports on the mesomorphic properties of such copolymers.

### EXPERIMENTAL

**Materials.** Ethyleneglycol diglycidyl ether (EGDE), 1,6-dibromohexane, 5% palladium on activated carbon, and tetrabutyl ammonium bromide (TBAB) were obtained from Aldrich and were used as received. 4-Bromobutyric acid, N,N-dicyclohexylcarbodiimide, 4-dimethylaminopyridine were obtained from Sigma and were used as received. Cholesterol from Fluka was used as received. 4-Hydroxy-4'-cyanobiphenyl (Tokyo Kassei) was generously donated by Professor Gen Sato of Sophia University of Tokyo, Japan.

Anhydrous sodium sulfate was used to dry all organic extracts. Molecular-sieve was used to dry organic solvents. TLC data were obtained using Anal-Tech silica gel GHLF Uniplates (Merck) with  $I_2$  as detector. Column chromatography was performed on Merck Silica Gel (70 to 230 mesh).

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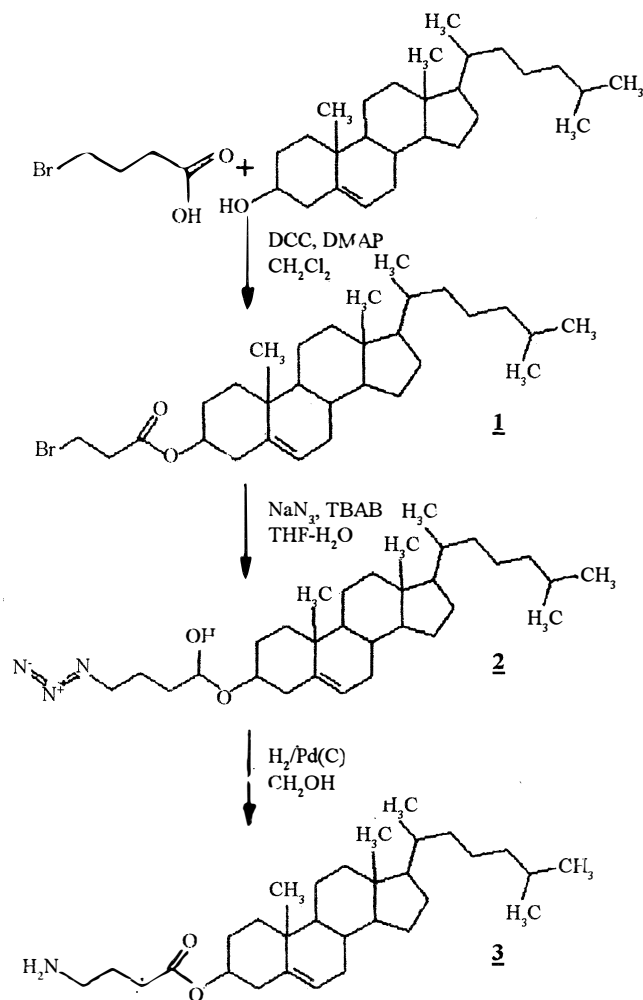


Fig. 1. Synthetic scheme for cholesteryl 4-aminobutyrate (3)

**Characterization.** A Nicolet Magna-IR Spectrometer 550 was used to obtain the infrared spectra of monomers and polymers. A Varian FT-200 spectrometer (200MHz) was used to record the  $^1\text{H}$  NMR spectra, with  $\text{CDCl}_3$  as solvent and TMS as internal standard.

A DSC-50 Shimadzu DSC equipped with thermal analyzer was used to determine thermal transitions which were reported as the maxima and minima of their endothermic and exothermic peaks, respectively. Heating and cooling scan rate of  $5^\circ\text{C}/\text{min}$  was used for the monomers, copolymers and homopolymers.

The textures of the monomers and polymers were studied using an Olympus BH-2 polarizing microscope with camera attachment.

Melting and clearing temperatures of intermediates were obtained using the capillary type melting point apparatus II equipped with Fluke 51 digital thermometer.

## Synthesis of Amines

**Cholesteryl 4-Aminobutyrate.** Cholesteryl 4-aminobutyrate (3) was prepared according to the synthetic route shown in Figure 1. The synthesis involves the preparation of cholesteryl 4-bromobutyrate (1) and cholesteryl 4-azidobutyrate (2) as intermediates.

Cholesteryl 4-bromobutyrate (1) was obtained from the reaction of 4-bromobutyric acid and cholesterol. Dicyclohexylcarbodiimide (DCC) (6.70 g, 0.0325 mol) and  $N,N$ -dimethylaminopyridine (DMAP) (0.38 g, 0.00311 mol) mixture were added to a stirred solution of 4-bromobutyric acid (5.00 g, 0.0299 mol) in sieve-dried dichloromethane. Cholesterol (13.04 g, 0.0338 mol) was added and stirring was continued for 24 h at room temperature. The resulting milky suspension was filtered, discarding the white precipitate of  $N,N'$ -dicyclohexyl urea. The filtrate was washed with 5% HCl and then water subsequently for three times. The solution was dried and the solvent was removed in a rotary evaporator. The crude product was purified by column chromatography using dichloromethane:hexane (1:1) as eluent. Yield: 11.86 g (72.4%). Melting/Clearing Temperature (Capillary method):  $T_m = 70^\circ\text{C}$ ,  $T_d = 84^\circ\text{C}$ . IR (KBr,  $\text{cm}^{-1}$ ): 1732 ( $\text{C}=\text{O}$ ).

Cholesteryl 4-azidobutyrate (2) was obtained from the reaction of the bromo-intermediate 1 and sodium azide. Compound 1 (9.58 g, 0.0175 mol) was dissolved in THF. To this was added an aqueous solution of sodium azide (3.22 g, 0.0495 mol). A pinch of tetrabutyl ammonium bromide (TBAB) was added and the mixture was refluxed for 28 h. THF was removed in the mixture and a small amount of water added to the residue. The aqueous layer was extracted with diethyl ether and the organic layer obtained was washed and dried. Ether was removed and the crude product was purified by column chromatography using dichloromethane:hexane (2:1) as eluent. Yield: 6.64 g, (74.4%). Melting/Clearing Temperature (Capillary method):  $T_m = 86^\circ\text{C}$ ,  $T_d = 96^\circ\text{C}$ . IR (nujol,  $\text{cm}^{-1}$ ): 2080 ( $\text{N}_3$ ); 1736 ( $\text{C}=\text{O}$ ).

Cholesteryl 4-aminobutyrate (3) was obtained by the reduction of the azido intermediate. Compound 2 (5.44 g, 0.0109 mol) was dissolved in methanol. Trace amount of 5% Pd on C (0.1243 g) was added and the resulting mixture hydrogenated for 36 h at room temperature in a Parr Pressure Reaction apparatus. Extent of reaction was monitored by TLC. After reaction, the mixture was filtered and the filtrate was rotavapored to remove solvent. Purification of crude product was carried out by recrystallization in ethanol. Yield: 4.12 g (79.9%). Melting/Clearing Temperature (Capillary method):  $T_m = 102^\circ\text{C}$ ,  $T_d = 110^\circ\text{C}$ . IR (Nujol,  $\text{cm}^{-1}$ ): 3300, 3175 ( $\text{NH}_2$ ); 2250 (CN); 1610, 1500 (Aromatic C-C); 1260 (C-O-Ph).  $^1\text{H}$  NMR ( $\text{CDCl}_3$ , ppm): 5.3 (broad m,  $\text{C}=\text{CH}$ , 1H), 3.35-5.65 (m,  $\text{N}-\text{CH}_2$ - and  $-\text{CH}_2-\text{C}=\text{O}$ , 4H), 0.65-2.35 (multiple signals for the cholesteryl protons,  $-\text{NH}_2$ , and  $\text{N}-\text{C}-\text{CH}_2$ , 48 H).

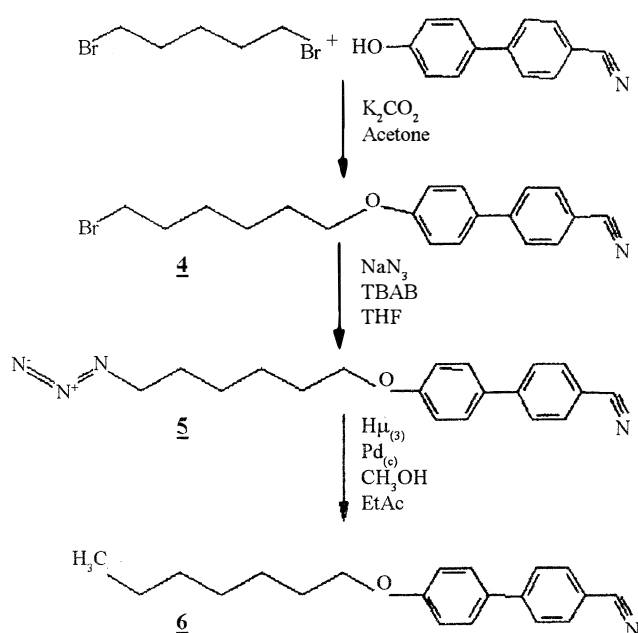


Fig. 2. Synthetic scheme for 4-(6-bromohexyloxy)-4'-cyanobiphenyl (**6**).

**4-(6-Aminohexyloxy)-4'-cyanobiphenyl (6).** The synthetic route for monomer **6** involves the synthesis of the bromo-(**4**) and azido-(**5**) intermediates as shown in Figure 2.

**4-(6-bromohexyloxy)-4'-cyanobiphenyl (4)** was prepared by refluxing 4-hydroxy-4'-cyanobiphenyl (5.00 g, 0.025 mol) and potassium carbonate (3.88 g, 0.0281 mol) with the 1,6-dibromohexane (6.13 g, 0.025 mol) for 24 h. The resulting mixture was filtered while hot and the solvent evaporated in vacuo. Chloroform was added to dissolve the residue. The organic layer was washed with 5% KOH then with water and was dried. The solvent was removed and the crude product was purified by column chromatography using dichloromethane:hexane (1:1) as eluent. Yield: 7.84 g (83.5%). Melting/Clearing Temperature (capillary method):  $T_m = 64^\circ C$ ,  $T_{cl} = 72^\circ C$ . IR (Nujol,  $cm^{-1}$ ): 2220 (CN); 1600, 1490 (Aromatic C-C); 1260 (C-O-Ph)

**4-(6-Azidohexyloxy)-4'-cyanobiphenyl (5)** was obtained from the reaction of **4** (6.56 g, 0.0175 mol) in THF and sodium azide (2.20 g, 0.0339 mol) in water, in the presence of TBAB. The mixture was refluxed for 24 h. THF was removed by rotavapor and small amount of water was added to the residue. The aqueous layer was extracted with ethyl ether. The organic layer was washed and dried. The ether was evaporated in vacuo and the crude product was purified by column chromatography using dichloromethane:hexane (1:1) as eluent. Yield: 4.86 g (85.7%). Melting/Clearing Temperature (Capillary method):  $T_m = 76^\circ C$ ,  $T_{cl} = 88^\circ C$ . IR (Nujol,  $cm^{-1}$ ): 2230 (CN); 2090 ( $N_3$ ); 1600, 1490 (Aromatic C-C); 1260 (C-O-Ph).

**4-(6-Aminohexyloxy)-4'-cyanobiphenyl (6)** was obtained by the reduction of compound **5**. To a solution of **5** (1.70 g, 0.00525 mol) in methanol, trace amount of 5% Pd on C (0.0388 g) was added and the mixture hydrogenated in a Parr pressure reaction apparatus at room temperature for 32 h. After reaction, the mixture was filtered and the filtrate was evaporated in vacuo to give a faint yellow waxy solid product. Purification was achieved by recrystallization in toluene. Yield: 1.28 g (82.6%). Melting/Clearing Temperature (Capillary method):  $T_m = 92^\circ C$ ,  $T_{cl} = 98^\circ C$ . IR (Nujol,  $cm^{-1}$ ): 3420, 1665 (N-H); 1736 (C=O).  $^1H$  NMR ( $CDCl_3$ , ppm): 1.46-1.54 (m,  $(CH_2)_3$ , 6H), 1.68 (s,  $NH_2$ , 2H), 1.79-1.86 (m,  $CH_2CH_2O$ , 2H), 2.72 (t,  $CH_2NH_2$ , 2H), 4.01 (t,  $CH_2OPh$ , 2H), 7.22 (d, ortho Hs to  $OCH_2$ , 2H), 7.53 (d, ortho Hs to CN, 2H), 7.65 (m, meta Hs to  $OCH_2$  and CN, 4H).

### Synthesis of Polymers

The epoxy homopolymers and copolymers were prepared by a ring-opening reaction shown in Figure 3. Equivalent amounts of mixtures of amines **3** and **6** (% mol of **3** in amine mixture = 10, 30, 40, 50, 90) and EGDE were charged into a polymerization vessel purged with dry  $N_2$ . The reaction vessel was sealed and heated in an oil bath at  $100^\circ C$  for 16 h. The obtained polymers were purified by multiple precipitation from a THF solution into cold petroleum ether. The polymers were dried in a vacuum desiccator for 48 h. The resulting polymers were characterized using FTIR spectroscopy, DSC and polarizing microscopy.

## RESULTS AND DISCUSSION

### Synthesis and Properties of Monomers

**Cholesteryl 4-aminobutyrate (3).** Esterification of 4-bromobutyric acid using excess cholesterol resulted in a crude cholesteryl 4-bromobutyrate (**1**) composed of white and yellow crystalline residue which upon purification using gravity column chromatography yielded white semi-opaque crystals. The crystals were then dissolved in THF and reacted with sodium azide in water, in the presence of a phase transfer catalyst (TBAB). Extended refluxing produced a cloudy white slurry. From this was extracted the solid cholesteryl 4-azidobutyrate (**2**) which was hydrogenated to yield the amine **3**. The amine was obtained as a white solid after recrystallization in ethanol. Discoloration of this compound has been observed upon aging. This may be a possible sign of degradation.

By combined differential scanning calorimetry and polarizing microscopy, the amine was found to exhibit an enantiotropic cholesteric mesophase. The DSC scan shown in Figure 4 reveals two distinct transitions, one at  $82.04^\circ C$  and a second one at  $92.23^\circ C$ . Upon heating the first major transition is accompanied by a large absorption of energy (43.98 J/g) typical of a fusion process, from crystalline solid to a liquid crystalline phase or a mesophase. The second

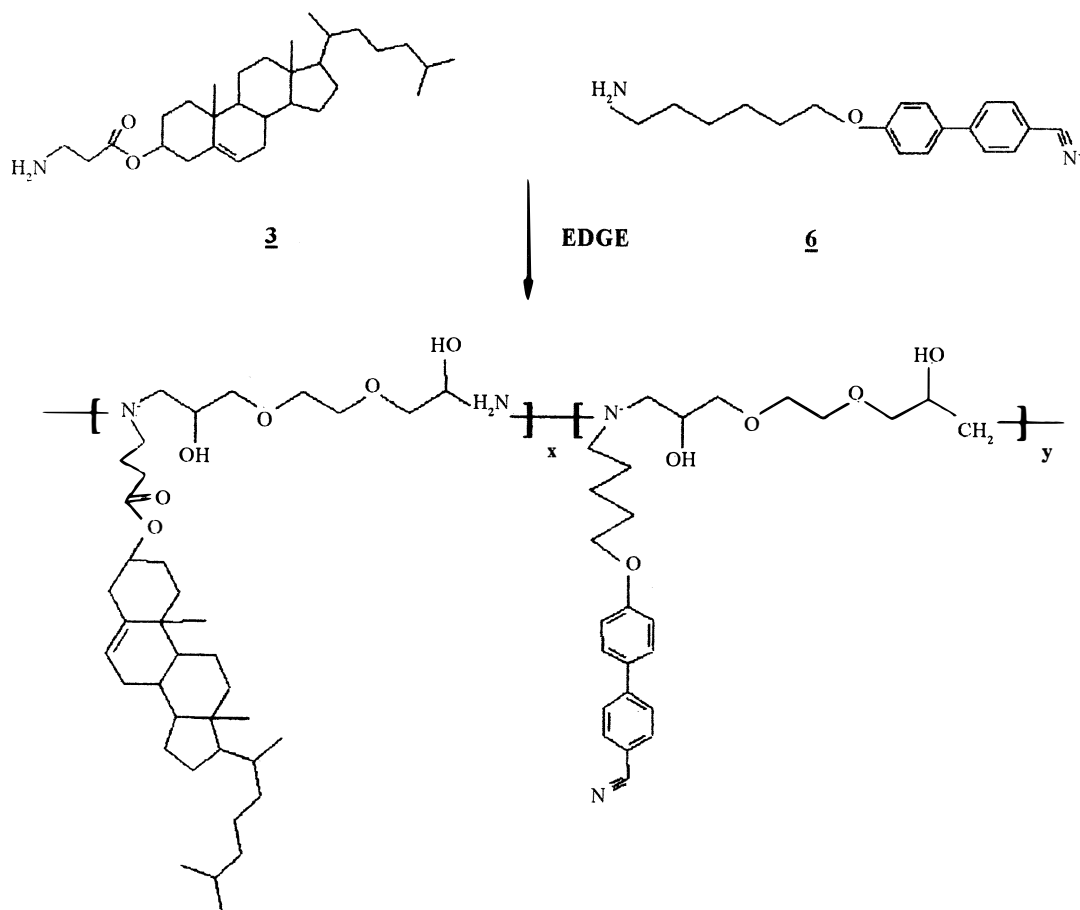
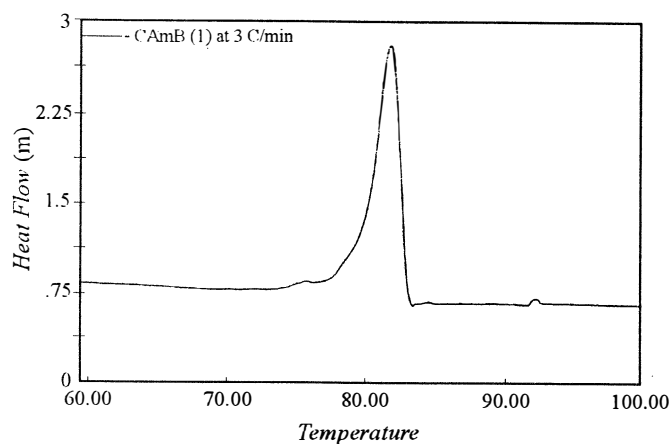


Fig. 3. Synthetic scheme for epoxy-based copolymers



Transition	$T_{\text{onset}}/^{\circ}\text{C}$	$T_{\text{peak}}/^{\circ}\text{C}$	$\Delta H/\text{J}\cdot\text{g}^{-1}$
S $\rightarrow$ Ch	79.98	82.04	43.98
S $\rightarrow$ I	92.07	92.23	0.17

C - Ch — crystal-cholesteric phase transition  
Ch - I — cholesteric-isotropic phase transition

Fig. 4. The DSC heating scan for a sample of cholesteryl 4-aminobutyrate (3).

transition displays a relatively very small and broad peak signifying a minimal enthalpy change (0.17 J/g). This represents the phase change from a mesophase to an isotropic liquid. The DSC scanning rate was set at 3°C/min in this

case to detect the low thermal activity manifested by the mesophase-isotropic transition which is otherwise undetectable with higher scanning rate.

Optical textures were observed under a polarizing microscope. The mesophase has been confirmed as cholesteric based on the grandjean texture observed for the sample amine. Figure 5 shows a net-like structure (oily streaks) typical of chiral nematic or cholesteric liquid crystals.

**4-( $\omega$ -aminohexyloxy)-4'-cyanobiphenyl (6).** The yellow phenolate slurry obtained from the 4-hydroxy-4'-cyanobiphenyl and potassium carbonate was treated with the dibromohexane. The dibromohexane was used in excess to ensure that only one of the bromo will be substituted. The resulting 4-( $\omega$ -bromohexyloxy)-4'-cyanobiphenyl (4) was converted to 4-( $\omega$ -Azidohexyloxy)-4'-cyanobiphenyl (5) by reaction with sodium azide. The desired primary amine was obtained through catalytic hydrogenation of this azido-intermediate. Just like the other amine, 4-( $\omega$ -Aminohexyloxy)-4'-cyanobiphenyl (6) was obtained as white solid which turned yellowish upon aging.

Incorporation of the cyanobiphenyl group in the intermediates and final product was confirmed by the appearance of the -CN absorption (2230  $\text{cm}^{-1}$ ), which is noted in all the

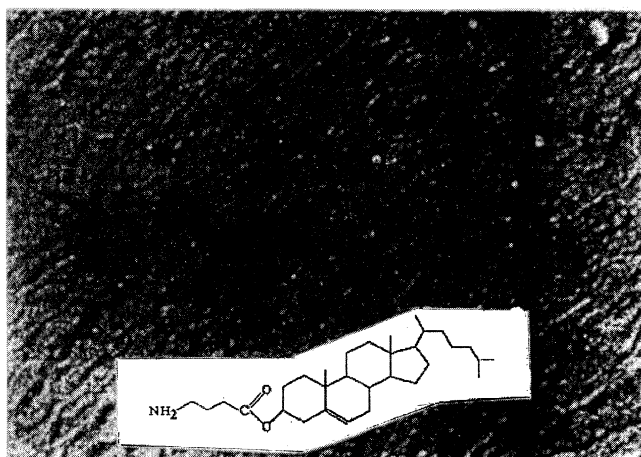


Fig. 5. The Grandjean texture observed in a sample of cholesteryl 4-aminobutyrate (**3**)



Fig. 6. The planar Schlieren texture observed in a sample of copolymer

spectra. Conversion from the bromo- to the azido-intermediate to the final amine was confirmed by the appearance of the  $\text{-N}_3$  absorption ( $2090\text{ cm}^{-1}$ ) in the spectrum of Azidohexyloxy)-4'-cyanobiphenyl, and its disappearance in the spectrum of 4-( $\omega$ -Amino-hexyloxy)-4'-cyanobiphenyl.

Based on the results of studies using the DSC and the polarizing microscopy, compound **6** was found to be nematic. Typical schlieren texture was observed for this compound. Results of the DSC scans revealed the solid to nematic transition at  $58.52^\circ\text{C}$  and the nematic to isotropic transition at  $88.32^\circ\text{C}$ .

### Synthesis of Polymers

The homopolymer containing the cyanobiphenyl pendant group was prepared by using equivalent amounts of **6** and EGDE, while the cholesteryl-containing homopolymer was prepared using **3** and EGDE, in equivalent amounts. Copolymers were prepared by varying the amounts of the two

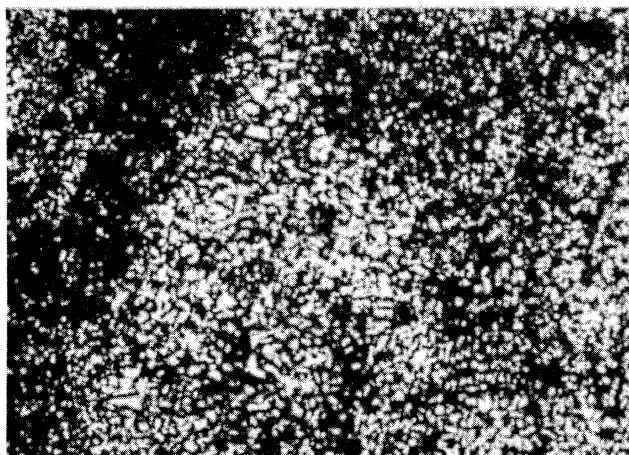


Fig. 7. The non-planar focal conic texture observed in a sample of copolymer

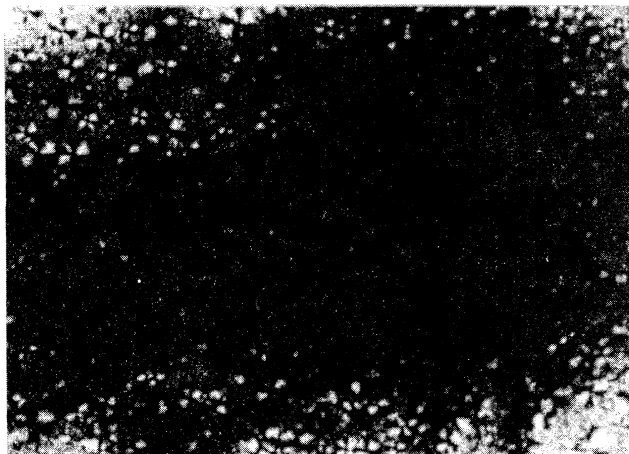


Fig. 8. Photomicrograph of a low molar mass liquid crystal formulation dispersed in the copolymer

monomers. The polymers were purified by multiple precipitation six times from a THF solution into a mixture of petroleum ether and ethyl ether.

The prepared homopolymers and copolymers vary in color, ranging from translucent white to some yellowish material. FTIR scans of the different copolymers showed the more intense absorption band of the CN group relative to the  $\text{C=O(OR)}$  group, even in systems where there are more cholesteryl-containing amines in the monomer feed. This suggests that incorporation of the cyanobiphenyl group into the polymer backbone is more favored than that of the cholesteryl ester.

### Liquid-Crystalline Behavior of Epoxy Polymers

The copolymers exhibited both the planar and non-planar structures as shown by the schlieren texture in Figure 6 and the focal-conic texture in Figure 7. These are typical textures of cholesteric materials [8]. The transition tem-

**Table 1. Phase Transition Temperatures (Mesogen to Isotropic Phase Change) of the Copolymers**

%-mol 3 in comonomer feed	%-mol 6 in comonomer feed	Isotropization temperature °C
30	70	34.67
40	60	35.04
50	50	67.62
90	10	37.57

peratures of some of these polymeric systems are shown in Table 1. The glass transition temperature was never identified because of the limitation imposed by the available DSC which was not equipped with the cooling system and the required software. Also, most of these copolymers would require annealing before a well-defined glass transition temperature can be observed. The listed transition temperatures showed a maximum isotropization temperature (the temperature at which the liquid crystalline system becomes isotropic) occurring for the system prepared from equivalent amounts of monomers 3 and 6. No significant correlation of transition temperature with monomer composition can be drawn at this point due to the unpredictable extent of the destabilizing effect on the mesophase of the intermolecular/intramolecular hydrogen bonding of the OH groups in the polymer backbone. The destabilizing effect of H-bonding has been reported to disrupt the mesomorphic packing of the side groups [9].

Since the nature of the polycondensation reaction does not provide a good control of molecular weights, completely random copolymers are expected from the comonomer pair of 6 and 3. It is known that when two monomers copolymerize, the tendency of each monomer to enter the chain can differ markedly [10]. Although the kinetic schemes for polycondensation reaction of epon resins and amines are known [11], no literature was found to report the curing kinetics for side-chain liquid-crystalline epoxy polymers. Hence, the relative reactivities of the mesogenic amine 6 and 3 and thus the type of copolymers that may be formed may not be easily predicted. The randomness of incorporation of 3 and 6 would also explain the lack of any significant trend in the observed transition temperatures for the copolymers.

### Phase Separation Study

Investigation of the phase separation of the prepared copolymers with low molar mass liquid crystals formulation based on coco-cholesteryl esters was conducted using the polarizing microscope. The method of solvent-induced phase separation (SIPS) [12] was employed in the preparation of polymer-dispersed liquid crystal (PDLC) film consisting of the select copolymers as the polymer matrix. The mixture of the copolymer and the low molar mass liquid crystals was dissolved in  $\text{CH}_2\text{Cl}_2$ . The resulting solution was then casted

and sandwiched between two glass plates, using 25 micron mylar spacer. The solvent was subsequently removed by evaporation, resulting in a phase separation and polymer solidification. Droplet formation of the low molar mass liquid crystals, which is an indication of phase separation, was observed (Fig. 8). Using lower concentration of copolymers resulted in some interesting textures and a study of their behavior in an electric field is being recommended.

### CONCLUSION

Cholesteryl- and cyanobiphenyl-containing amines which are both mesogenic were synthesized. The synthesized cholesteryl-containing amine exhibit the cholesteric (or twisted nematic) phase and the cyanobiphenyl-containing amine, the nematic phase. Attaching these as pendant groups to an epoxy backbone yields random side-chain liquid-crystalline epoxy copolymers, some of which are cholesteric. These materials are presently being studied in terms of their potential electro-optical applications.

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