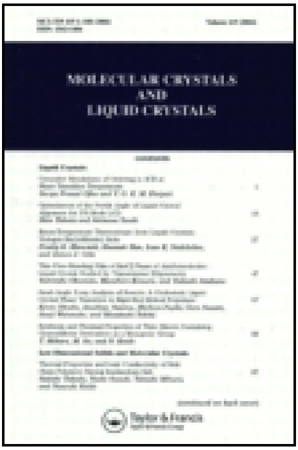

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Dispersion of Cholesteric Liquid Crystals in Side-Chain Polymer Matrix

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Cholesteric formulations (coco-cholesteryl esters:E7) were dispersed in commercial polymethylmethacrylate (PMMA) and in laboratory synthesized side-chain polymers (SCP). The side-chain copolymers were obtained via the ring opening reaction of a commercially available epon resin, ethyleneglycol diglycidyl ether, with the nematic 4-(ω-aminohexyloxy)-4'-cyanobiphenyl and the twisted nematic cholesteryl 4-aminobutyrate. Switching properties of the resulting dispersions were evaluated. Cells using PMMA as matrix exhibited distinguishable droplet with bipolar and twisted radial configuration. A maximum voltage of 60 volts was needed to transform a 70:30 by weight (LC:PMMA) composite into a transparent state. LC formulations dispersed in the SCP bearing cholesteryl and cyanobiphenyl pendant groups were found to exhibit fingerprint texture. Compared to the LC/PMMA composite, the LC/SCP dispersions required lower voltage for switching.

Keywords: cholesteric liquid crystals; side-chain polymers

INTRODUCTION

The cholesteric liquid crystals/polymer formulation is a modification of the conventional nematic-based PDLCs which utilize the electrooptical properties of liquid crystal/polymer composites. With proper refractive index-matching and good compatibilization of liquid crystals and polymer matrix, nematic-based PDLCs may be switched from an opaque OFF state to a clear ON state upon application of voltage. Switching of chiral nematic-based PDLCs, hoewever, is based on selective reflection. At the

OFF state, the cell is translucent (weakly scattering) due to a non-uniform orientation of the pitch axis. In the presence of an electric field, a uniform orientation of the pitch axis is induced along the field for liquid crystals with negative dielectric anisotropy. A planar alignment is favored and the cell selectively reflects incident light.[1] In the case of liquid crystals with positive dielectric anisotropy, the helical axis is reoriented perpendicular to the field. In higher electric fields, helical unwinding is observed.[2] This paper reports initial results of our study which aims to investigate the droplet behavior of cholesteric liquid crystal formulations obtained from mixtures of cholesteryl esters and E7 when dispersed in polymers. The ultimate goal is to explore possible effects of liquid crystal/polymer interactions on the electro-optical properties of the cell.

Methodology

Cholesteric liquid crystal mixtures were prepared by adding different amounts of cholesteryl esters derived from coconut oil to the commercially available nematic E7. The polymeric matrices used were the commercial PMMA and the epoxy-based side-chain polymers synthesized in our laboratory. Figure 1 shows the synthetic scheme for the preparation of the epoxy-based side-chain polymers with cholesteryl and cyanobiphenyl pendant groups. Copolymers containing the cyanobiphenyl and cholesteryl pendant groups were prepared by using different amounts of monomer 6 (the amine containing the cyanobiphenyl moiety), monomer 3 (the amine containing the cholesteryl moiety) and ethylene glycol diglycidyl ether (EGDE).

The PDLC cells were prepared using the SIPS method.[3] In this method mixture of polymer and low molar mass cholesteric LC is dissolved in dichloromethane. The resulting solution is then casted and sandwiched between two glass plates, using 25 micron mylar spacer. The solvent is subsequently removed by evaporation, resulting in a phase separation and polymer solidification.

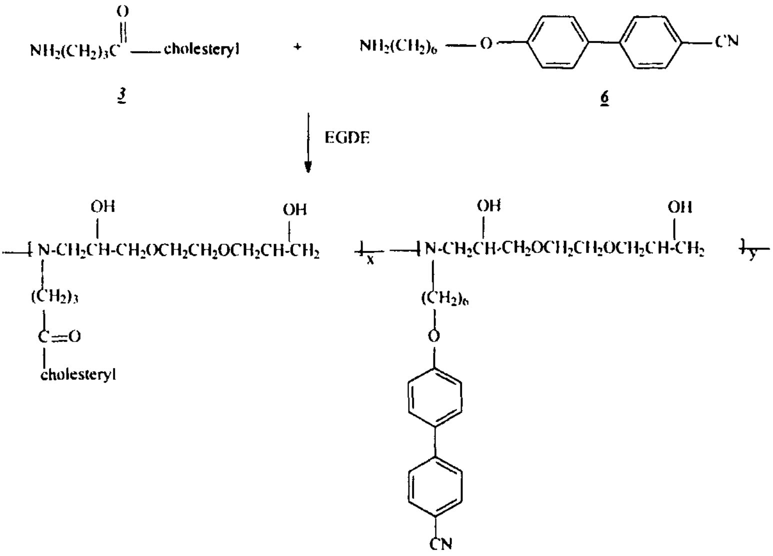

FIGURE 1 Synthesis of Side-Chain Polymers

Textures of LC mixtures as well as LC droplets were observed using the BH-2 Olympus Polarizing Microscope. Photographs of samples were taken at 200x magnification. Transitions temperatures of the samples were obtained using a Shimadzu DSC-50.

Results and Discussion

The synthesized SCP consists of both cholesteryl and cyanobiphenyl pendant groups. These functionalities were chosen to match the composition of the dispersed liquid crystal formulations obtained from cholesteryl esters and E7 (comprised mainly of cyanobiphenyls). Some of the copolymers exhibited both the planar and non-planar textures typical of cholesteric materials. No significant trend was observed in the transition temperatures of these materials based on the differential scanning calorimetric study. This may be attributed to the randomness of the composition of the copolymers and to the unpredictable extent of the destabilizing effect of the possible intermolecular/intramolecular hydrogen-bonding of the -OH groups in the polymer backbone. The latter behavior tends to disrupt the mesomorphic packing of the side group and may lead to loss of liquid crystallinity.[4]

Selective reflection exhibited by the prepared mixtures containing cholesteryl esters and E7 are shown in Table 1. Cholesteric formulations were found to exhibit planar texture before application of electric field. This texture is transformed to a highly scattering focal conic texture upon initial application of voltage. At around 120 volts, the homeotropic (highly transmitting) texture may be obtained. When these formulations are dispersed in PMMA (LC/PMMA = 70/30), droplet formation indicating phase separation was observed under the polarizing microscope. A maximum of 60 volts is required to switch this type of PDLC.

From the data gathered, it appears that the nature of the side-chain in the polymer matrix may stabilize or destabilize certain droplet configurations depending on the composition of the LC in the droplets. The SCP-dispersed droplets were larger and more irregular compared to the PMMA-dispersed droplets (Figure 2). Some of these droplets were even unstable being no longer evident under the polarizing microscope after two weeks.

Structural similarity of the polymer's pendant group with the electro-optically active component in the dispersed droplets may lead to lower or higher clearing voltages. The presence of the cholesteryl pendant group in

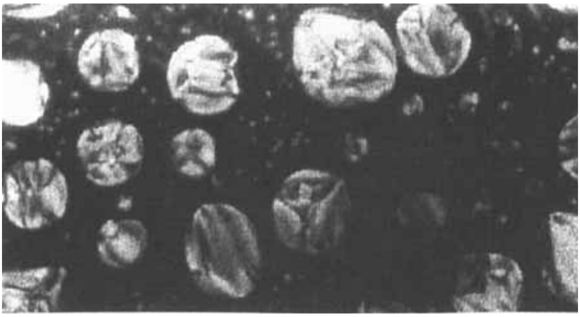

FIGURE 2 Photomicrograph of cholesteric droplets
See color plate XXII at the back of this issue.

the matrix seem to stabilize the helices in the dispersed LC thus leading to higher voltage requirement for the unwinding process. From the clearing voltages of the prepared PDLC cells using the prepared side-chain copolymers as matrix (Table 2), it is shown that lower concentration of cholesteryl esters in the LC mixture and in the polymer matrix can yield better switching property (i.e., lower clearing voltage). In the table below, **AP$_1$** samples consist of low molar mass LC formulation **A** consisting of cholesteryl esters: E7 in a weight ratio of 10:90. dispersed in a polymer matrix **P$_1$** prepared from a reaction mixture of EGDE and mesomorphic amines $\underline{\mathbf{6}}$: $\underline{\mathbf{3}}$ in a weight ratio of 90:10. **AP$_2$** samples consist of the same low molar mass LC formulation **A** but dispersed in a polymer matrix **P$_2$** prepared from a reaction mixture of $\underline{\mathbf{6}}$: $\underline{\mathbf{3}}$ in a weight ratio of 60:40. **BP$_1$** and **BP$_2$** cells consist of low molar mass LC formulation **B** which consists of cholesteryl esters:E7 in a weight ratio of 40:60 dispersed in polymer matrices **P$_1$** and **P$_2$**.

The PDLCs utilizing a low molar mass LC formulation containing 10:90 by weight ratio of cholesteryl esters and E7 have lower clearing voltages than the PDLCs containing LC formulations that have 40:60 by weight ratio of cholesteryl esters and E7. Note from the Table 2 that clearing voltages of

Weight ratio of cholesteryl ester/cholesteryl iodide/E7	Peak wavelength (nm)	Colors observed at room temp.
69.9:30.1:0.00	386.5	violet
49.0:29.0:22.0	386.5, 524.5, 545.5	green
44.6:28.5:26.9	386.5, 575.5	yellow-green
37.9:15.4:46.7	386.5, 672.5, 719.5	Red-orange

Table 1. UV-Vis Absorption data of some mixture formulations

PDLC samples	LC/Polymer weight ratio	Clearing voltages (Volts)
AP_1	70:30	15
AP_1	80:20	15
AP_1	90:10	20
AP_2	70:30	39
AP_2	80:20	25
AP_2	90:10	25
BP_1	70:30	did not clear
BP_1	80:20	60
BP_1	90:10	45
BP_2	70:30	50
BP_2	80:20	75
BP_2	90:10	45

Table 2. Clearing voltages of PDLC cells

AP_1 and AP_2 are lower than those of BP_1 and BP_2. Comparing AP_1 and AP_2, the former seems to have lower clearing voltages. AP_1 consists of a polymer matrix prepared by using a 90:10 weight ratio of monomeric amines $\underline{6}$:$\underline{3}$ in the reaction mixture, whereas AP_2 consists of a matrix prepared from a reaction mixture containing a 60:40 by weight ratio of $\underline{6}$:$\underline{3}$.

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