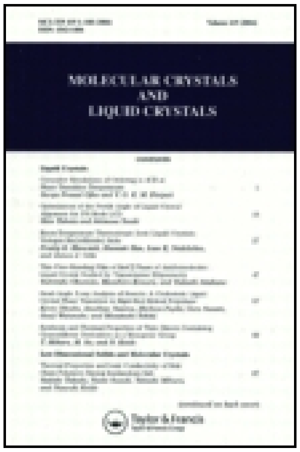

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Liquid Crystal Formulations

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LIQUID CRYSTAL FORMULATIONS

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Abstract: Chiral-Nematic Dispersions and Encapsulations were investigated for different mixture concentrations of the nematic liquid crystal E7 and E48 and the cholesteric liquid crystals TM74A and TM75A in the Infrared and Visible regime. Liquid crystal (E7:TM74A) dispersions as stand alone systems and as polymer dispersed materials were found to be bistable in the near IR region.[‡] Chiral-nematic dispersion of E48:TM74A displayed different bright colors in the 400-760 visible range and exhibited thermochromic properties at room temperature. The PVA encapsulated E48:TM74A mixture (60:40) also showed thermochromicity between 30°C to 43°C. A ternary system was formulated from TM74A:TM75A:E48. Mixtures with high cholesteric concentration exhibited thermochromicity whereas systems with low cholesteric concentration showed electro-optic properties. Gel dispersion was done on mixtures with low cholesteric concentration using a liquid crystal polymer cinnamate. The polymer network effected stabilization on the liquid crystal molecules. Electro-optic tests showed that threshold voltage increases as the cholesteric amount increases in the different LC mixtures. Polymer and gel dispersions also increased the threshold voltages.

INTRODUCTION

For the last decades, researches in LCs have increased tremendously resulting in new methods of fabrication, wider areas of application, more accurate characterization techniques and in-depth theoretical analyses. In the 1980's, LCs were combined with polymers to create an electrically-controllable light scattering medium. This type of

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[†] Presentor

[‡] Initial results obtained at the LCI-KSU, June 1993.

material is known as polymer dispersion[1]. Such dispersions have various forms depending on the concentration of the polymer. To date, the system most understood and extensively investigated are those with high polymer concentration (50-80 wt%) which are popularly known as PDLCs.

Because of some limitations[2], attention has shifted to systems with low polymer concentration (1-5 wt%) commonly called liquid crystal polymer dispersion (LCPD) or gel dispersion. The morphology of this system is of the gel type, forming fragile networks of crosslinked polymers responsible for the unusual electro-optic effects.

However, the most common liquid crystal type used in PDLCs of high and low polymer concentrations is a nematic which does not reflect light. Recently, Crooker and Yang developed a PDLC with reflective color display using cholesteric liquid crystal which are now commonly called PDCLCs[3]. Colorful displays are attributed to the optical properties of cholesteric liquid crystals.[4]

This research aims to investigate the properties of the different LC formulations of four different commercially available liquid crystals in the visible and IR regime. Bistability and thermochromicity of PDCLCs fabricated via different methods of polymer dispersion preparations are also verified. The research further examines the thermochromic and electro-optic properties of the ternary systems (TM74A:TM75A:E48).

EXPERIMENTAL

Materials

The binary and ternary liquid crystal formulations in this research consist of the nematics E7 and E48, and the cholesterics TM74A and TM75A (Merck). LC mixtures were sandwiched between two ITO coated glass plates with mylar strips as spacers via the capillary method. Samples that show stability at ambient temperatures were dispersed in polymethylmethacrylate (PMMA) and polyvinylpyrrolidone (PVP) via different separation techniques (TIPS, SIPS and PIPS). Cinnamate, a side-chain liquid crystal polymer which exhibits the nematic phase between 83.3°C and 111.1°C, was used in gel dispersion for ternary mixtures. Polyvinyl alcohol (PVA-98% hydrolized) was used in encapsulation of the binary liquid crystal mixture E48:TM74A.

Measurements

FT-IR spectra were recorded on a Nicolet Series II Magna-IR 750 spectrophotometer. Differential Scanning Calorimetry (DSC) was performed with a DSC-50 Shimadzu. UV-Vis spectra were obtained from U-2000 Double Beam Scanning type spectrophotometer. Textures of the different samples were obtained using a BH-2 Olympus polarizing microscope.

RESULTS AND DISCUSSION

Binary Mixtures

IR spectra of the two stable states at zero field (focal conic and planar) of E7:TM74A systems were obtained. Figure 1 shows the IR scan of the bistable E7:TM74A concentration in the near IR with low cholesteric content.

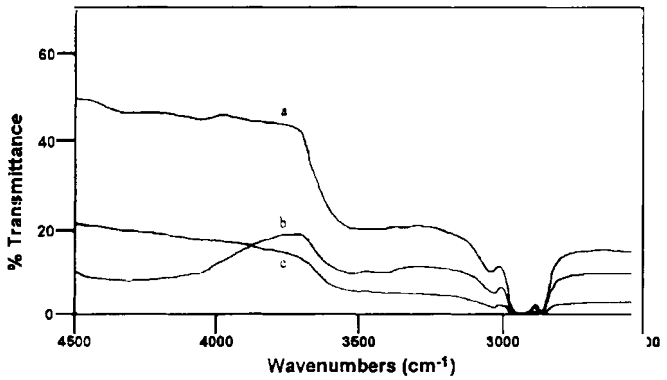

FIGURE 1 FTIR scan of E7:TM74A bistable concentration on ITO glass substrates, in (a) homeotropic texture, (b)planar texture, and (c) focal conic texture.

Transmission in the near IR region (4500-4000 cm-1) of the planar texture is higher than the focal conic texture. This is because when light is incident on the sample cell, selective reflection occurs where the wavelength of the reflected maxima is governed by Bragg's law. At normal incidence, the reflected light is strongly circularly polarized; one circular component is almost totally transmitted while the other circular component is totally reflected[5]. In the focal conic state, the cell is strongly scattering because of the random orientation of the helical axes. Towards the mid-IR region, spectra of the focal conic and the planar state cross at a particular wavelength. At shorter wavelengths (mid-IR to far IR), the focal conic texture has higher transmission than the planar texture. This is attributed to the pitch of the chiral-nematic mixture in the sample cells.

Polymer dispersion on PVP decreased the bistability contrast. The presence of the polymer greatly reduced the transmission of the focal conic and the planar state. This means that the polymer affects the orientation of the helical axis of the chiral component of the liquid crystal molecules. Random orientation of the helical axis is almost retained when the system is transformed to the planar texture. The polymer stabilizes the focal conic state.

(E48:TM74A)

Different cholesteric systems of E48 and TM74A were studied using the UV-Visible Spectrophotometer. Table 1 shows the tabulation of the reflected colors of the samples. This is in accordance with Bragg's Law,

$$\lambda_o = n_{ave}\, p, \qquad (1)$$

where λ_o is the reflected wavelength, n_{ave} is the mean refractive index of the liquid crystal and p is the pitch of the cholesteric liquid crystal. Increasing theTM74A concentration increases the pitch, thus increasing the wavelength reflected. For low concentrations of E48 (10-20%), the mixtures assume the color of the higher component, TM74A. Similarly, for high amounts of TM74A (80-90%), the mixtures assume the color of the cholesteric system.

Among the mixtures, 40:60 E48:TM74A was chosen for encapsulation because of its thermochromic properties.

TABLE I Summary of colors reflected by E48:TM74A at different concentrations.

E48(TM74A)	WAVELENGTH REFLECTED (nm)	OBSERVATIONS
30 (70)	420	violet
35 (65)	450	blue
40 (60)	500	green
45 (55)	560	yellow
50 (50)	610	orange
55 (45)	670	light orange

PVA Encapsulation

Encapsulation using polyvinyl alcohol (PVA) resulted in droplet formation. Table 2 summarizes the color change of the 40:60 (E48:TM74A) LC mixture and encapsulated LC mixture upon heating. Encapsulation did not alter the thermochromicity of the liquid crystal mixture. The white appearance in both systems is due to the strong scattering property of the focal conic texture. The colorless appearance is due to the twisting of the pitch upon application of heat. The pitch becomes so short such that the wavelength reflected is that of the visible light.

TABLE II Color change upon heating of 40:60 (E48:TM74A) and the encapsulated mixture.

Temperature °C	Color of Pure LC Mixture	Color of Encapsulated LC
30	blue green	blue green
37	blue	blue
39	white	faint blue/violet
41	colorless	white
>43	colorless	colorless

Ternary System (E48:TM74A:TM75A)

Ternary systems with low cholesteric concentration exhibited thermochomicity whereas systems with high cholesteric concentration showed electro-optic responses. No phase separation occured with gel dispersion using the liquid crystal polymer cinnamate of the thermochromic ternary system, thus, less viable for shutters. Instead, the polymer network stabilized the liquid crystal molecules. The solidification of the polymer enhances its volume stabilization effect. Switching voltage was about 20 volts.

PDLCs in low (LCTS) and high cholesteric ternary systems (HCTS) with PMMA were also fabricated. Phase separation occurred and the measured switching voltages were greater than that of gel dispersions (Fig. 2). This is expected as the ternary system has higher polymer content.

Threshold voltages increase as the cholesteric component increases in the different LC mixtures. This is expected as the pitch decreases upon addition of cholesteric liquid crystal in the mixtures. The voltage needed to untwist the helix also increases. Polymer and gel dispersions also increased the threshold voltages, which is expected, as the polymer stabilizes the orientation of the liquid crystals.

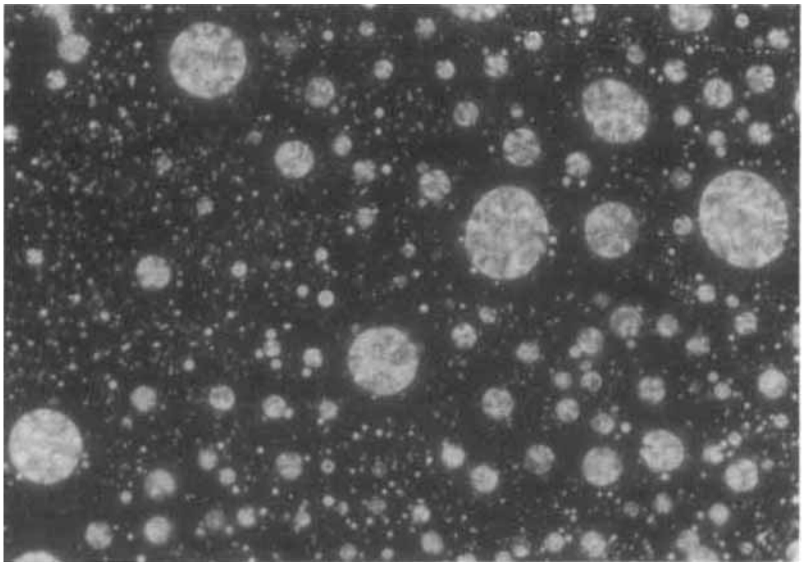

FIGURE 2 Photomicrograph of a PDCLC (PMMA: LCTS) at 30:70 weight ratio. (See Color Plate II).

CONCLUSION

We have investigated the properties of different LC formulations of E7, E48, TM74A and TM75A liquid crystals. Liquid crystal (E7:TM74A) dispersions as stand alone systems and as polymer dispersed materials were found to be bistable in the near IR region. Chiral-nematic dispersion and encapsulation of E48:TM74A exhibited thermochromic properties in the 400-760 visible at ambient temperatures. Ternary systems with high cholesteric concentration showed thermochromicity whereas systems with low cholesteric concentration exhibited the electro-optic properties, making them suitable for electro-optic devices. In the gel dispersion with cinnamate and PMMA, the liquid crystal molecules, both in low and high cholesteric concentration were stabilized. Polymer and gel dispersions increased the threshold voltages.

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