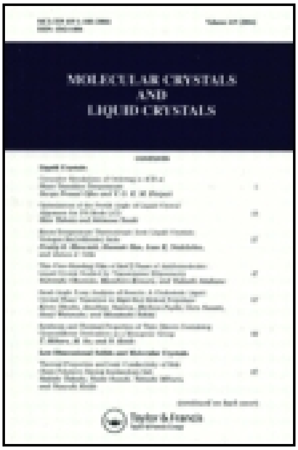

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Optical Responses of Azo Dye Doped Cholesteric Liquid Crystal-Polymer Composite System

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Liquid crystals and polymers offer unique optical and electro-optical properties which make them ideal choice for opto-electronic and sensing devices. Doping absorbing dyes into liquid crystals increase their optical responses significantly due to increased absorption in the visible region, absorption induced intermolecular and other guest host effects. In the present paper we have studied the mixture consisting of cholesteric liquid crystal, a polymer and the azo dye. The investigation was performed by (a) Studying the texture and clearing temperature of pure cholesteric liquid crystal (CLC) using Polarizing microscope, (b) The study was repeated for a mixture of CLC and Polymer taken in different proportions, (c) The change in texture at various temperature and the effect on clearing temperature was obtained by doping the CLC with azobenzene dye, and (d) The change in texture and clearing temperature was further studied for the mixture consisting of CLC and Polymer doped with azo dye.

The system was investigated further by studying the % transmission, using UV/VIS photo spectrometer, in the visible range for a pure CLC, a mixture of CLC and azo dye, a mixture of CP and MMA doped with azo dye.

Keywords: azo dye; cholesteric liquid crystal; polarizing microscopy; polymer; UV/VIS spectroscopy

I. INTRODUCTION

With the advent of digital communications, where light can be used for transmitting data, it is important to develop and study systems that can be used for optical transmission in a controlled manner. Liquid

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crystals and polymers offer unique optical and electro-optical properties which make them ideal candidate for opto-electronic and sensing devices [3]. A cholesteric liquid crystal can be considered as a one-dimensional photonic crystal with a refractive index that is regularly modulated along the helix axis because of the particular arrangement of the molecules. The result is that the propagation of light is suppressed for a particular range of wavelength [4]. The presence of a polymer network enhances the stability of structure of liquid crystal molecules aiding in the return of the liquid crystal director orientation to the desired configuration thus helping to determine and maintain the poly-domain size.

The electronic properties and process occurring in liquid crystals are decided largely by the electronic properties of the constituent molecules. Liquid crystals are found to be quite absorptive in the UV region. In the visible and near infrared regions there are fewer absorption bands and hence liquid crystals are quite transparent in these regions. It is observed that doping absorbing dyes into liquid crystals increase their optical responses significantly due to increased absorption in the visible region, absorption induced intermolecular and other guest host effects. A polymer-liquid crystal interface can be regarded as a coupled system, where the two components – the polymer and the liquid crystal mutually affect each other's structure. Earlier studies have shown that low concentration of the monomer is an important factor for good contrast between the focal conic and planar state but high concentration is of interest for the self adhering and self sustaining structure necessary for flexible devices of large area on polymer substrates.

In the studies done earlier on Polymer Stabilized Liquid Crystals (PSLC) [5], it has been observed that memory effects are introduced into the characteristics of the reflection band of the material at room temperature. Also, it has been observed that mixtures of cholesteric liquid crystals doped with high clearing temperature azobenzene nematic liquid crystals are shown to possess large, fast and reversible dynamic photo sensitive features. Selective wavelength shifts approaching 400 nm are reported [6], and depending upon the host cholesteric liquid crystal both red-shifted and blue-shifted wavelength changes have been induced.

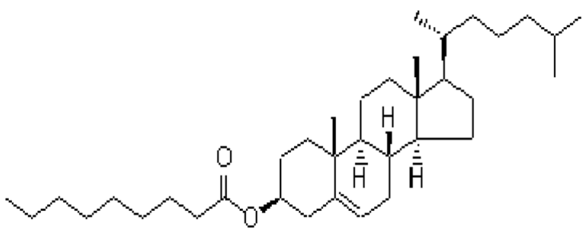
II. EXPERIMENTAL SECTION

In the present paper we have studied the mixture consisting of cholesteric liquid crystal, azo dye and a polymer. The investigation was performed by (a) Studying the texture and clearing temperature of pure cholesteric liquid crystal (CLC) using Polarizing microscope. (b) The study was repeated for a mixture of CLC and Polymer taken in different proportions. (c) The change in texture at various temperature and the effect on clearing temperature was obtained by doping the CLC with azobenzene dye. (d) The change in texture and clearing temperature was further studied for the mixture consisting of CLC and Polymer doped with azo dye.

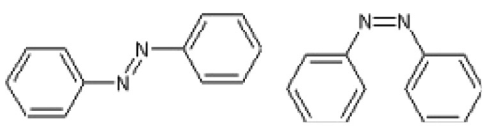
The system was investigated further by studying the % transmission in the visible range for a pure CLC, a mixture of CLC and azo dye, a mixture of CP and MMA doped with azo dye.

Starting Material

1. CLC-Cholestryl Pelargonate (CP); Molecular Formula: $C_{36}H_{62}O_2$

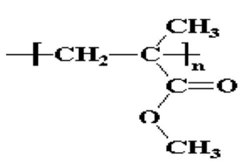


2. Azobenzene dye (orange); Molecular Formula: $C_{12}H_{10}N_2$



Trans-azobenzene (a) Cis-azobenzene (b)

3. Poly Methyl Methacrylate (PMMA);



PMMA has glass transition temperature (Tg) of 105°C and is used below the glass transition temperature in the glassy state. PMMA is more transparent than glass.

Polymerization of MMA

50 gm of monomer MMA was dissolved in 40 ml ethyl acetate. The reaction mixture was heated to reflux and 0.5 gm of catalyst, benzoyl peroxide, dissolved in 10 ml ethyl acetate was added slowly. The reflux was maintained at 80°C for three to four minutes and then cooled. The polymerized solution was thus obtained.

III. RESULTS AND DISCUSSIONS

A). PMS Studies

Samples studied are in the following proportions.

P1-100% CP (20 mg)
P2-20% CP + 80% PMMA (4 mg CP + 16 mg PMMA)
P3-50% CP + 50% PMMA (10 mg CP + 10 mg PMMA)
P4-80% CP + 20% PMMA (16 mg CP + 4 mg PMMA)
P5-CP + 1% Azobenzene(orange) Dye (18 mg CP + 2 mg Azo dye)
P6-(20% CP + 80% PMMA) + 1% Azodye (3.6 mg CP + 14.4 mg PMMA + 2 mg Azo dye)
P7-(50% CP + 50% PMMA) + 1% Azodye (9 mg CP + 9 mg PMMA + 2 mg Azo dye)
P8-(80% CP + 20% PMMA) + 1% Azodye (14.4 mg CP + 3.6 PMMA + 2 mg Azo dye)

The textures were studied using Carl Zeiss Polarizing Microscope with an automatic recording system. The textures were first taken for pure CP at various temperature. As shown [6] in earlier studies, CP has Solid to Smectic A* to Isotropic phase transitions. Textures of Smectic A* (Focal conic fan texture) and Nematic phases (thread-like structure) were obtained for pure CP.

Investigation was carried out to find the effect of forming a mixture of CP with PMMA. It was observed that the mixture of CP and PMMA taken in different proportions retained the Smectic A* (Focal conic textures) and Nematic (Thread like textures) phases.

Also TGBA* [7] phase was obtained for the mixture formed by P2 (20% CP and 80% PMMA). The texture obtained shows Smectic A phase that are broken and the molecular director of the next block is twisted abruptly by a small angle.

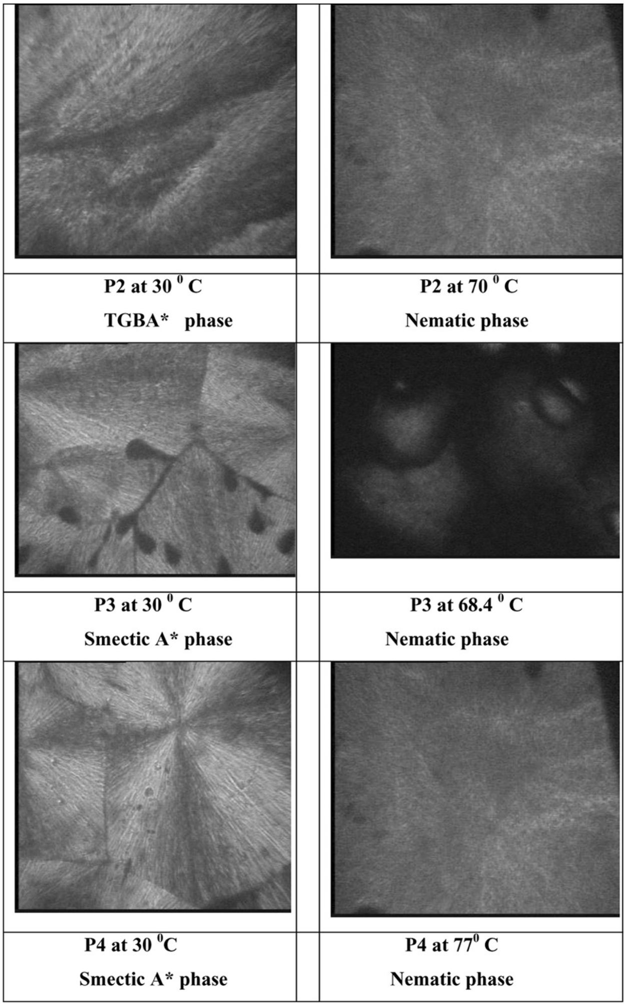


FIGURE 1 Textures of CP + PMMA taken in different proportions.

TABLE 1 Phase Transition Temperatures of the Composite System CP + PMMA

S. No.	Sample	$T(S_A{}^* - N)°C$	$T(N - I)°C$
1	P1(100% CP) [Pure CLC]	77.7	88
2	P2–20% CP + 80% PMMA	70	77
3	P3–50% CP + 50% PMMA	66	86.7
4	P4–80% CP + 20% PMMA	76.6	96.4

The textures obtained are shown in Figure 1.

The transition temperature was found to change depending on the proportion of CP and PMMA taken (Table 1).

Investigation was further carried out to study the effect of adding azobenzene (orange) dye to the mixture of CP and PMMA taken in

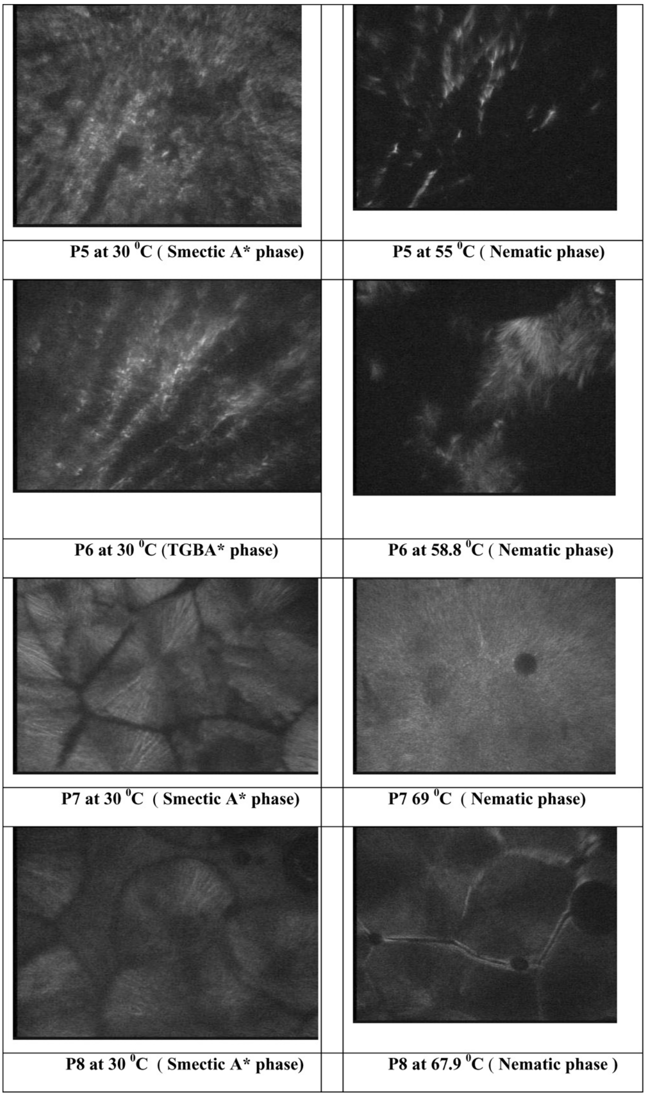


FIGURE 2 Textures of CP + PMMA + AZO dye taken in different proportions.

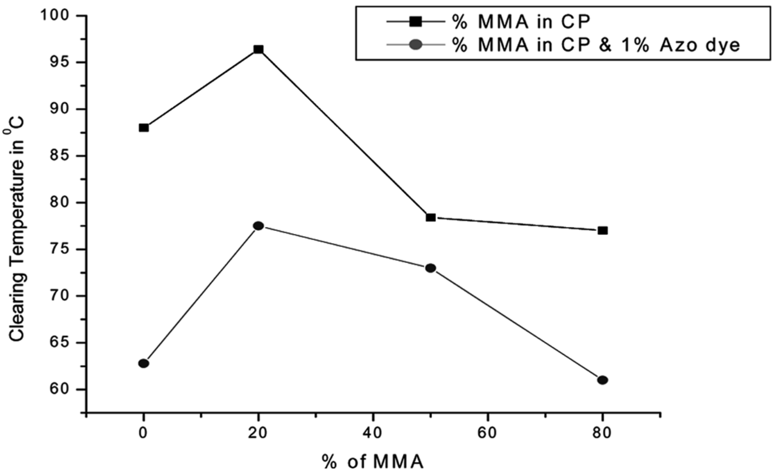


FIGURE 3 Dependence of clearing temperature for different proportions of CP, PMMA, and Azo dye.

different proportions. Textures obtained showed that the Smectic A* (Focal Conic texture) and Nematic (Thread-like texture) phases are retained for all the samples studied.

Also TGBA* [7] phase was obtained for the sample P6 (20% CP + 80% PMMA + 1% Azodye). Textures obtained are shown in Figure 2.

The clearing temperature of the composite system was found to be dependent on the concentration of the constituents (Fig. 3 and Table 2).

The clearing temperature was found to be maximum (96.4°C) for the composite system (P4-80% CP + 20% PMMA).

The effect of adding azo benzene dye was to reduce the clearing temperature (Fig. 3).

For the mixtures of CP, PMMA and azo dye, the clearing temperature was maximum for the sample P8 (80% CP + 20% PMMA + 1% Azodye).

TABLE 2 Phase Transition Temperatures of the Composite System CP + PMMA + AZO DYE

S. No.	Sample	$T(S_A{}^* - N)$°C	$T(N - I)$°C
1	P5-CP + 1% Azobenzene(orange) Dye	59.2	62.8
2	P6-20% CP + 80% PMMA + 1% Azodye	58.8	70.6
3	P7-50% CP + 50% PMMA + 1% Azodye	69	73
4	P8-80% CP + 20% PMMA + 1% Azodye	67.9	77.5

Thus it is observed that clearing temperature is highest for the mixture with constituents 80% CP and 20% PMMA.

B). Analysis in the Visible Range

UV/VIS spectroscopy involves the absorption of ultraviolet/visible range by molecules.

The intensity of the absorption band is measured by the percent of light that passes through the samples using Beer-Lambert law.

We measured the % Transmission of pure CP in the visible range and then investigated the change in the % Transmission for a mixture of CP, MMA and Azobenzene (orange) dye taken in different proportion.

It was observed that:

Pure CP has nearly 100% transmission in the range 440 nm and 600 nm (Fig. 4).

Doping CP with azo benzene dye (orange) resulted in nearly 0% transmission in the range 410 nm and 480 nm (Fig. 4).

The intensity of transmission was reduced with the addition of MMA (Fig. 4).

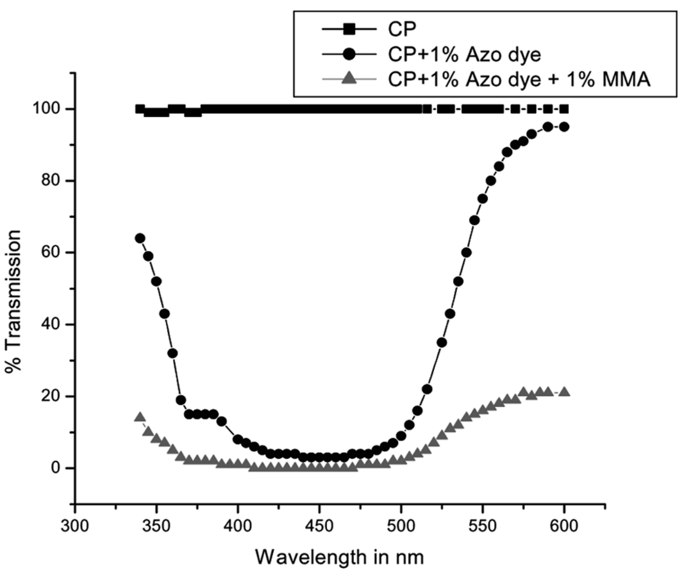


FIGURE 4 Comparison of % transmission for pure CP, CP + Azo dye & CP + MMA+ Azo dye.

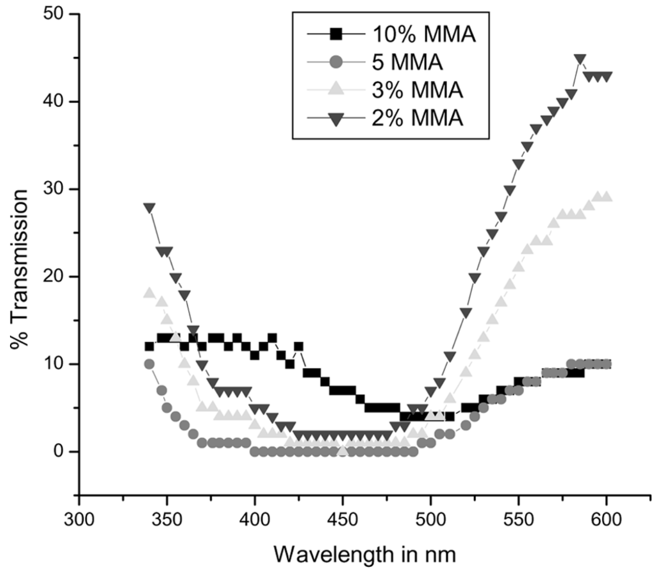


FIGURE 5 % Transmission for varying proportion of MMA and CP with a constant concentration of Azo dye.

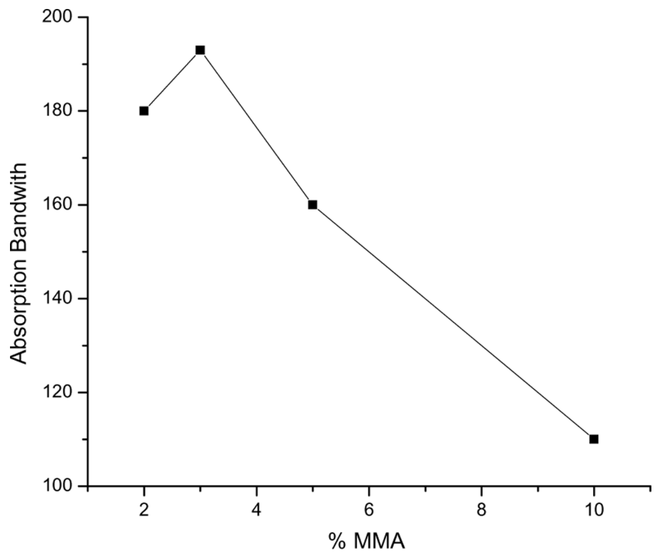


FIGURE 6 Variation of Bandwidth for varying concentration of MMA in a constant proportion of CP and azo dye mixture.

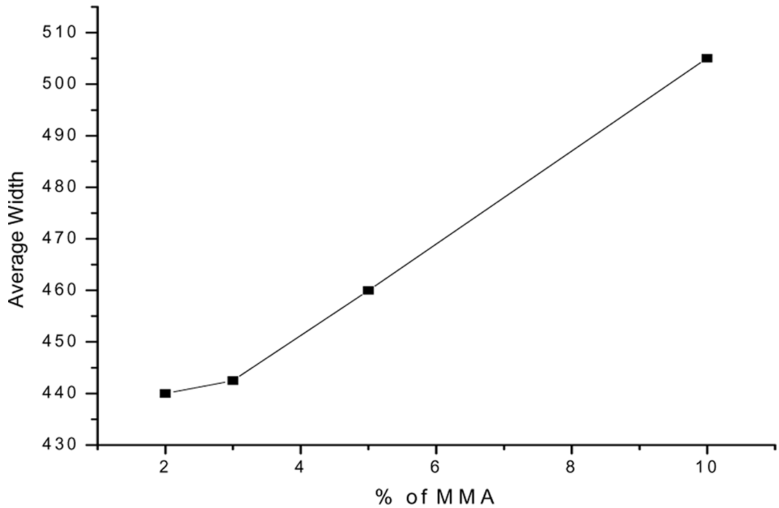


FIGURE 7 Variation of Average absorption width for varying concentration of MMA in a constant proportion of CP and azo dye mixture.

It is also observed that the intensity of transmission is inversely proportion to the concentration of MMA in the mixture (Fig. 5).

The average absorption width is found to depend upon the proportion of CP, MMA taken for a constant proportion of azo dye.

At 10% transmission the absorption bandwidth is found to decrease as the concentration of MMA is increased from 0.3% wt./vol to 1% wt./vol in the mixture of CP and MMA with a constant proportion of azo dye (1%) (Fig. 6).

At 10% transmission, the average absorption width is found to shift from 440 nm to 505 nm as the concentration of MMA is increased from 0.2% wt./vol to 1% wt./vol in the mixture of CP in MMA with a constant proportion of azo dye (1%) (Fig. 7).

IV. CONCLUSION

It can be concluded that PMMA can be used for stabilizing the CP and having controlled phase transitions by appropriately choosing the concentration of PMMA in the mixture of CP + PMMA. The important finding is that all textures exhibited by pure CP are retained, but suitable concentration of PMMA also leads to observation of TBBA* phase. This implies that the composite system of CP + PMMA can be used appropriately as per the desired application.

Addition of azo dye in small percentage was found to effectively lower the phase transition temperature for pure CP as well as for the system CP + PMMA, but retaining the phases of pure CP.

Pure CP which is found to be transparent in the visible range, was found to have nearly 100% absorption, in the range 410 nm and 480 nm, with the addition of azobenzene dye to pure CP as well as the composite system of CP + PMMA.

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