**Guest-Host Polymer Dispersed Liquid Crystal Display Device: Role of Dichroic Dye**

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**Abstract:** Guest-host polymer dispersed liquid crystals or dye doped polymer dispersed liquid crystals (PDLC) samples were prepared using a nematic liquid crystal, UV curable polymer and a dichroic dye (anthraquinone blue) in equal ratio [liquid crystal/polymer] by polymerization induced phase separation (PIPS) technique. Non-ionic dichroic dye (1%, 2% and 4% wt./wt. ratio) was taken as guest in PDLC host. In the absence of electric field, liquid crystal droplets exhibited bipolar configuration, however relatively at higher field, maltese type crosses were observed. Our results indicated that ~1% dye doped PDLC sample shows better transmission and faster switching response over higher dye concentrated 2% and 4% dye doped PDLC samples.

**Keywords:** Nematic liquid crystal; Guest-host polymer dispersed liquid crystal; Polymerization induced phase separation; Droplet morphology; Anthraquinone dye

**Introduction**

PDLC composite films constitute a novel class of optical materials. They usually consist of micron-sized liquid crystals (LCs) droplets dispersed in optically transparent polymer matrix [1-6]. These materials have been the subjects of much interest due to their wide applications ranging from switchable windows to large area LCD devices [2, 7-10]. Colored PDLC are formed by incorporating dyes in the PDLC material. Dichroic dye employed in a PDLC film produces higher contrast than isotropic dye. The orientation of the elongated dye molecule is governed by the nematic director configuration inside the droplet. Therefore, the dye absorbance is modulated by the alignment of the nematic director with an external electric field. In the off state, LC droplet director and hence dye molecules are randomly are randomly distributed inside the polymer matrix. However, in the ON state, the droplet director and the dichroic dye molecules dissolved in the droplet are aligned normal to the surface of the film.

Several research groups [11-14] have made experimental studies on the infrared absorption spectroscopy, method for improving the contrast ratio, optical properties in dye doped PDLC films in unaligned and aligned configurations etc but not much effort has been made on the study of dye doped LC droplet morphology and their electro-optic responses. Recently Raina et al. investigated in detail the LC droplet orientation phenomena and influence of dye dispersion in PDLC films [15-16]. Guest-host polymer dispersed liquid crystal (GHPDLC) samples were prepared by a standard PIPS [3-5] technique.

In the present work, we report some interesting results, made on the basis of electro-optic responses of GHPDLC samples as a function of different dye concentration. The role of dye concentration on LC droplet morphological behavior, thermo-optic and switching responses has been investigated in detail.

**Experimental**

A room temperature nematic liquid crystal (NLC) BL036 (Merck, UK) [17], UV curable polymer NOA–65 (NORLAND, NJ) [18] and blue anthraquinone dye [19] were used as a base materials for sample preparations. The NLC shows a wide nematic phase up to 95°C. Guest-host polymer dispersed nematic liquid crystal (GHPDNLc) samples were prepared by first dissolving the dye (1%, 2% and 4%) wt./wt. ratio in NLC and then dispersed into the polymer material. The NLC and polymer were taken in equal (1:1) wt. /wt. ratio. We call this homogenous mixture as GHPDNLc mixtures. The mixture was then filled between two indium tin oxide (ITO) coated glass substrates by capillary action after heating the material to its isotropic temperature. The cell gap was controlled by a mylar spacer of thickness 10µm. The sample cells were sealed by optical adhesive and exposed under UV light (intensity~ 2mW/cm²) for one hour. The samples were placed in a hot stage coupled with programmable temperature controller (Model TP94 and THMS 600) and then cooled down to room temperature @0.1°C/ min. Uniform dispersion of LC droplets were viewed under crossed polarizers at a magnification of 10X through Olympus polarizing microscope (Model BX-51P). Output responses were detected using a photomultiplier tube (Model RCA 931-A). The data was acquired in the computer interfaced with digital storage Oscilloscope (Model-Tektronix Model TDS 2024).

**Results and Discussions**

**Droplet Morphology:** The effect of dye concentration (1%, 2% and 4%) on LC droplet morphology matrix at zero fields is shown in Fig.1. Here we noticed that with increasing dye concentration (from 1% to 4%), the absorbance in 4% GHPDNLc sample is higher than 2% and 1% samples respectively. We believe that the higher absorption on 4% concentration leads to lower transmission of the guest host device. Fig.2 shows the UV-VIS spectra in GHPDNLc samples. The spectra shows a maximum absorbance in 4% GHPDNLc sample and lead to lower transmission. Thus 1% dye
doped sample give better transmission properties than higher dye concentrated samples. Optical texture shows that bipolar configuration is dominant in comparison to others configurations (radial, axial).

![Image](a) ![Image](b) ![Image](C)

**Figure 1.** Influence of dye concentration (a) 1% (b) 2% and (c) 4% on LC droplet morphology

![Image](a) ![Image](b)

**Figure 2.** Absorbance of dye molecules in (a) 1% (b) 2% and (c) 4% GHPDNLC samples

At relatively low voltage (~<10V<sub>p-p</sub>) we observed that the droplet orientation does not change much vary, however, at higher voltage (~>80V<sub>p-p</sub>) maltese type crosses [Fig.3] were appeared in the 1% dye concentration. Similar droplet behavior was also observed for 2% and 4% samples but relatively at higher voltage.

![Image](a) ![Image](b) ![Image](c) ![Image](d)

**Figure 3.** Optical textures of GHPDNLC sample at various applied voltage (f = 500Hz) (a) 0V<sub>p-p</sub> (b) 10V<sub>p-p</sub> (c) 30V<sub>p-p</sub> and (d) 100V<sub>p-p</sub> at room temperature for 1% sample

The increase in applied voltage with increasing dye concentration may be due to the partial increase of viscosity of the composite, change in morphology, increase in conductivity of LC droplet and strong anchoring with the polymer walls. The optical transmission as a function of applied voltage dependence at different dye concentration at 40°C is shown in Fig. 4. It shows that nearly 50% transmission can be achieved in ~1% over 2% and 4% GHPDNLC samples. It can be concluded from the Fig. 4 that ~ 1% dye concentrated sample shows higher transmission than 4% sample.

![Image](a) ![Image](b) ![Image](c) ![Image](d)

**Figure 4.** Variation of applied voltage (f = 500Hz) on optical transmission at different dye concentration at 40°C

**Thermo-optic responses:** Considering the isolated partially spherical nematic liquid crystal droplet consisting small amount of dichroic dye in a polymeric material and assuming that the nematic LC behaves as an isotropic LC medium, the effective electric field (E<sub>eff</sub>) across a nematic LC droplet can be computed by
considering both conductivity and dielectric terms at different frequencies and can be written as [20].

\[ E_{\text{eff}} = E_a \frac{3\sigma_{\text{pol}}}{2\sigma_{\text{pol}} + \sigma_{\text{LC}}} \]  
\((\text{For conductive terms})\) (1a)

and

\[ E_{\text{eff}} = E_a \frac{3\varepsilon_{\text{pol}}}{2\varepsilon_{\text{pol}} + \varepsilon_{\text{LC}}} \]  
\((\text{For dielectric terms})\) (1b)

Where \( E_a \) refer to the applied electric field, \( \varepsilon_{\text{pol}} \) and \( \varepsilon_{\text{LC}} \) are the dielectric constants and \( \sigma_{\text{pol}} \) and \( \sigma_{\text{LC}} \) are the conductivities of the polymer matrix and the LC respectively. Eq. 1(a) is valid at very low frequencies (\( \omega \to 0 \)) where conductivity terms are dominant whereas Eq. 1(b) is significant at higher frequencies (\( \omega \to \infty \)). We feel that at high frequencies (\( \omega \to \infty \)), conductivity effect will become insignificant relative to dielectric effects, where ionic motion can be considered to be frozen out. Thus very few mobile ions generate a significant depolarization in the composite films. The threshold field \( E'_{\text{eff}} \) for bipolar droplets broadened by their random orientation can be as given by the expression [21];

\[ E'_{\text{eff}} = \frac{1}{R} \left[ \frac{K(l^2 - 1)}{\varepsilon_0 \Delta \varepsilon} \right]^{1/2} \]  
(2)

Where \( R \) denotes droplet radius, \( l \) its anisotropy. \( K \) is effective elastic constant, \( d \) the film thickness and \( \Delta \varepsilon \) the dielectric anisotropy of the LC.

Applying Eq. (2) and Eq. 1(a, b) the threshold voltage \( V_{th} \) for a bipolar droplet was computed using the equation;

\[ V_{th} = \frac{d}{c} \frac{K(l^2 - 1)}{\varepsilon_0 \Delta \varepsilon} \]  
(3)

1/c is related to the effectiveness of the field across the droplets due to a dielectric or conductivity mismatch between the LC droplets and surrounding polymer matrix [20]. The prefactor ‘c’ is given by

\[ \frac{3\sigma_{\text{pol}}}{(\sigma_{\text{LC}} + 2\sigma_{\text{pol}})} \]

Separating out the temperature dependent terms, Eq. (3) can be written in the form [22]

\[ V_{th} \propto \left( \frac{K}{\Delta \varepsilon} \right)^{1/2} \]  
(4)

Both \( K \) and \( \Delta \varepsilon \) are the function of the LC order parameter and they decrease with increasing temperature and thus \( V_{th} \) also behaves in the same manner as predicted by the theory [23].

In the present study, we observed an unusual behavior of \( V_{th} \) as a function of temperature (i.e. \( V_{th} \) increases with increasing temperature). We have tried to explain this behavior on the basis of average LC droplet size distribution in the matrix and reduction of effective voltage across the NLC droplets in a dielectric film when subjected to an alternating electric field. We believe that the external field may not act directly on the LC droplet, thus giving rise to generation of extra-charges stored at the polymer liquid crystal interface and other disclination sites.

From Eq. 1(a, b) and Eq. 3 it can be seen that \( V_{th} \) is inversely proportional to \( E_{\text{eff}} \). In PDLC films, the ionic movements can set up a depolarization field with the application of electric field. Depolarization field opposes the applied field and reduces the \( E_{\text{eff}} \). The competition between the depolarization field and the applied field at higher voltage may in turn reduce the total effective field across the LC droplet thus contributing to the higher \( V_{th} \). The voltage dependence of the output transmission at different temperatures for 1% GHPDNLCl sample is shown in Fig.5. It depicts that as temperature increases, the transmission increases and slightly shifts to higher applied voltage. Primarily it may be due to the decrease in order parameter with an increase in temperature. Another possible reason may be due to decrease in anchoring energy of LC with polymer network resulting in a large amount of small LC droplets and aligned at higher temperature produces higher transmission.

![Figure 5. Variation of applied voltage (f = 500Hz) on optical transmission at different temperatures for 1% dye doped sample](image)

**Electro-optic responses:** The optical response such as rise time (\( \tau_r \)) defined as the time required for transmission change from 10% to 90% upon switching the film ON. The rise time is computed as [24]

\[ \tau_r \propto \frac{\gamma_1}{\Delta \varepsilon E^2} \]  
Or \( \tau_r \propto \frac{1}{E^2} \)  
(5)

Where \( \gamma_1 \) denotes rotational viscosity coefficient. Fig.6 shows the voltage dependence of the magnitude of rise time at different dye concentration.

![Figure 6. Variation of applied voltage (f = 500Hz) on rise time at different dye concentration](image)
predicted by the theory (Eq.5). A fluctuating behavior in 2% GHPNLC sample was noticed but follows the similar behavior as for 1% and 4% Samples. It was found that ~1% GHPDNLC sample shows faster response time than 4% GHPDNLC.

Conclusions
The influence of dye concentration on droplet morphology and their optical responses as a function of applied voltage and temperature has been investigated. The electric field strongly influences the LC droplet orientation and maltese type crosses were observed at much higher field. Our result indicates that ~1% dye concentration GHPDNLC sample shows higher transmission (~50%) and faster switching responses. The optical transmission and $V_{th}$ increases with increasing temperature due to increasing in conductivity of the composite films and hence reduction in effective electric field across the dye doped liquid crystal droplets.

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