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Influence of a guest dichroic azo dye on a host liquid crystal dispersed in polymer matrix

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Abstract: Guest dichroic azo dye doped in a host liquid crystal, embedded in acrylate polymer matrix called as Guest –Host Polymer Dispersed Liquid Crystal (G-HPDLC), prepared from polymer induced phase separation (PIPS) technique is a subject of present study. Transmittance properties of such G-HPDLC have been studied at various conditions (0-100 V, 200 Hz, 25 °C-50°C). Morphological transformation arising during polymerization of pre-polymer and due to application of voltage has been recorded with polarizing optical microscope (POM). It was further observed that the dye concentration has significant effect on the morphological and electro-optical properties of the composite films. Dielectric relaxation characterization of samples studied using precision impedance analyzer (20 Hz-20 MHz, 25 °C-90 °C) modeled with Debye and Cole-Cole methods indicate mono-dispersive nature of G-HPDLC films.
Key words: Guest-Host, Dichroic dye, PDLC, Cole-Cole.

1. Introduction and Experimental:

1.1. Introduction: Liquid crystal (LC) is an intermediate phase of matter in between conventional liquid and solid crystal. For the best utilization of overwhelming properties of LC, polymer dispersed liquid crystal (PDLC) films consist of randomly dispersed micron sized LC droplets embedded in solid polymer matrix. PDLC films can be used as switchable windows, flat panel displays, optical shutters, light modulators etc. Dispersion of droplets has been achieved by polymer induced phase separation (PIPS) technique. The PDLC system in which guest dye is doped in a host LC is named as guest-host polymer dispersed liquid crystal (GHPDLC). Very small amount of these guest molecules dissolved in host can enhance the optical nonlinearity of the material. From recent studies it has been predicted that doping of dye in PDLC provides vivid color, high brightness, excellent hues, large viewing angle and enhances optical response. Dye used for liquid crystalline media must have high: order parameter, purity, dichroic ratio and solubility & compatibility with LC. Orientation of LC and dye dipoles under an external electric field influences dielectric parameters of films therefore dielectric relaxation spectroscopy has been used as a tool to investigate molecular dynamics of LC and dichroic azo dye [1-3].

1.2. Experimental work: 23 µ PET film spacers were sandwiched between two indium tin oxide (ITO) coated transparent electrode with to fabricate cell with effective cell area 3 cm^2.To prepare GHPDLC, initially host LC BL036 (T_{N-I}=96.8 °C, Merck Ltd, Japan) is doped with guest disperse orange 25 dye (melting point

170 ºC, molecular formula $C_{17}H_{17}N_5O_2$ and UV-Vis absorption λ_{max} at 457 nm, Sigma Aldrich) in various concentrations from 0%-1%. This guest host system is homogenized with photo-curable pre-polymer SAM-114 in ratio of 45/55 wt/wt % of polymer/LC heating up to the isotropic temperature of LC. This mixture was filled into cells by capillary action and cured in UV chamber under 8 mW, UV light of wavelength 354 nm.

2. Results and Discussion:

2.1. Morphological Study: Study of significant morphological changes arise in GHPDLC films by the addition of guest dichroic dye molecule into the host LC was done by POM (Olympus BX53). Figure 1 clearly depicts that with the increase in dye concentration from 0% to 1% there is significant increase in droplet size from submicron to ~10 µ. Presence of dye molecules reduces polymerization rate as dye molecules absorb some of the UV radiations provided for photo-polymerization results in increased droplet size with bipolar configuration[4, 5]. Upon application of small electric field (~10 V) there is substantial difference in the director direction of molecules which are inside LC droplet and which are near the polymer-LC interface. With the further increase in electric field (30 V and above), small LC droplets acquire maltese type structure where as bigger droplets attain twisted arrangement as shown in figure 2 (e) &(f).

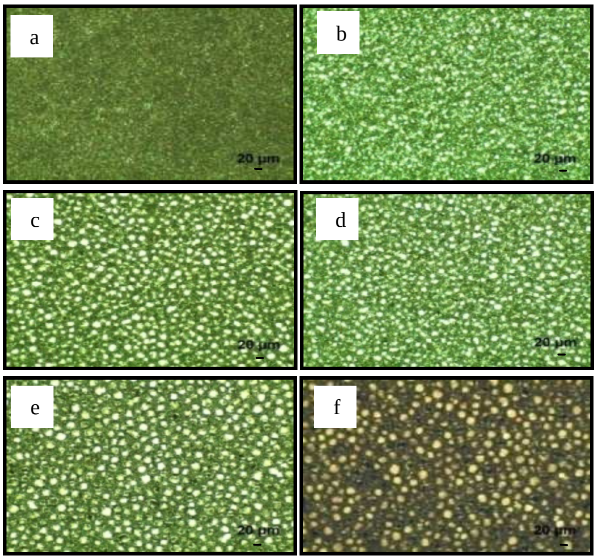

Figure 1: Effect of dye concentration (a) 0%, (b) 0.007%, (c) 0.015%, (d) 0.0625%, (e) 0.25%. (f) 1 % on droplet morphology of GHPDLC films.

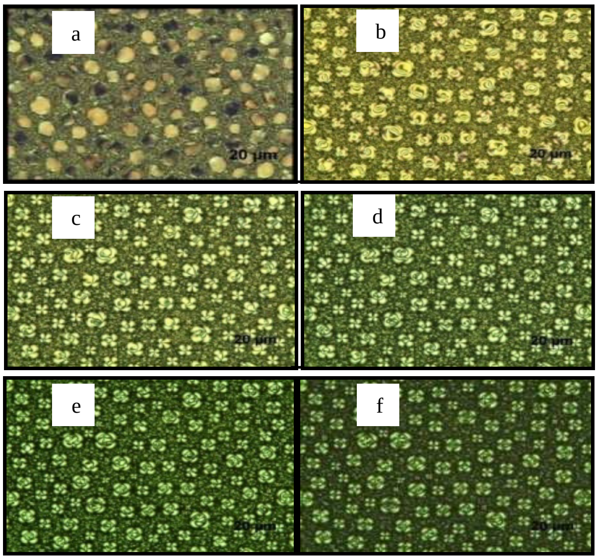

Figure 2: Effect of voltage (a) 0 V, (b) 10 V, (c) 20 V, (d) 30 V, (e) 60 V, (f) 90 V on droplet morphology of GHPDLC film with 1% dye concentration.

2.2 Electro-optical and Dielectric Study: The electro-optical properties of GHPDLC films were studied in terms of change in transmittance with respect to a.c. electric field. Details of experimental set up are reported elsewhere [6]. Voltage–transmittance curve was obtained by increasing voltage in steps of 10V up-to 100 V at optimized frequency 200 Hz and temperature 25 °C is shown in figure 3. Initially GHPDLC film is opaque in the OFF state (T_0). On increasing voltage, transmission reaches 10% of its OFF state value termed as threshold voltage (V_{th}). With the further increase in voltage the transmittance of film saturates (T_{sat}), corresponding voltage is termed as saturation voltage V_{sat}, and it is called as ON state. Difference in ON and OFF state transmittance is termed as transmission difference ($\Delta T = T_{sat} - T_0$). Mathematical expressions of V_{th} and V_{sat} for droplet were given elsewhere [7, 8]. Values of various electro-optic parameters are summarized in table 1.

Table 1: Electro-optic and dielectric data of GHPDLC with various dye concentration.

Dye conc. (Wt %)	***Electro-optic Parameters***					***Dielectric Parameters***		
	T_0 (%)	T_{sat} (%)	ΔT(%)	V_{th}	V_{on}	*Frequency*	$\delta\varepsilon'$	α
0.0%	1.12	95.1	93.97	10.4	60	20MHz	9.031	0.04
0.007%	**1.83**	**98.97**	**97.59**	**1.3**	**33**	**15.1MHz**	**5.993**	**0.04**
0.015%	6.12	96.93	90.81	1	33	20 MHz	8.222	0.02
0.0625%	9.59	97.85	88.26	1.4	25	17.4MHz	8.636	0.03
0.25%	28.57	97.24	68.67	4.4	23	17.4MHz	9.671	0.04
1%	38.36	97.34	58.97	5.6	22	20 MHz	10.06	0.05

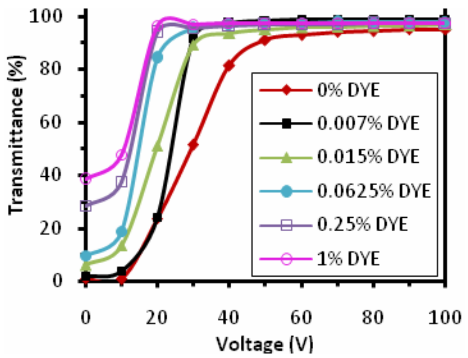

Figure 3: Transmittance vs voltage curves of GHPDLC films with various dye concentration at 200 Hz and 25 ºC.

The complex dielectric permittivity of GHPDLC film is: $\varepsilon^*(\omega) = \varepsilon'(\omega) - i\varepsilon''(\omega)$ (1)

According to Cole-Cole model $\varepsilon^*(\omega)$ is given by: $\varepsilon^*(\omega) = \varepsilon_\infty + \frac{(\delta\varepsilon')}{1+(i\omega\tau)^{1-\alpha}}$ (2)

where, $\delta\varepsilon' = \varepsilon_s - \varepsilon_\infty$ is dielectric strength, ε_s and ε_∞ are the static and infinite frequency dielectric constants respectively, ω is the angular frequency and τ is an average relaxation time, α is distribution parameter ranges from 0 to 1. When α=0, the Cole-Cole model reduces to the Debye Model. For the qualitative evaluation, Cole-Cole plot is drawn between the ε' and ε'' of the complex dielectric permittivity. The parameter α is expressed as: $\varphi = \frac{\alpha\pi}{2}$, Where φ is an angle between arc radius and ε'-axis. If the center of the semicircle lie on the ε'-axis then the distribution parameter α=0 (Debye type) and if the centre is below the ε'-axis then α≠0 (non-Debye type) [6,9,10]. Parameters obtained from the Cole-Cole plot is given in table 1.

2.4. Conclusions:

From the morphological study we found increase in droplet size and majority of bipolar configuration with the increase in dye concentration. Electro-optic study suggest that GHPDLC film with low dye content (0.007 %) has low V_{th} = 1.3 V, low V_{sat}=33 V and high ΔT=97.59%. α≠0 calculated from Cole-Cole model confirm non-Debye type relaxations.

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