Enhanced electro-optical characteristics of dispersed Azo dye doped polymer-liquid crystal display

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The purpose of the current study was to examine the electro-optical characteristics of polymer-dispersed liquid crystals (PDLC) films based on doping of Azo black dye ($C_{36}H_{37}N_7$). The following dye doped PDLC devices have been prepared using various ratios of nematic liquid crystal (LC) TL203, prepolymer PN393 and black dye by adopting the photo induced phase separation technique. For this study, Azo dye was doped into them with 0.5 – 1.5 wt%. The findings of the study revealed that this Azo dye could be employed into the PDLC films as colored optical devices and windows shutters, hence its doping significantly improve the electro-optical characteristics.

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1. Introduction

Polymer-dispersed liquid crystals (PDLCs) films demonstrate a key new class of materials, which contain useful electro-optical characteristics and are being employed in various display applications like as flexible displays, large-area devices projection displays, electrically switchable windows etc. Such PDLC films provide an advantageous feature over conventional liquid crystal (LCD) display, which is they do not require additional polarizers [1-5]. These films are formed within a self-supporting and mechanically stable polymer matrix, that do not need the optical elements and alignment layers to modify the path of light likewise needed for the other LC technologies [6–9]. Additional benefits of PDLC films include the quick response time, low production cost, no leakage of materials and their simple fabrication procedures, which give them an edge over other display technologies [6–9]. Generally, the PDLCs are fabricated with phase separation method with varying conditions that produce micron sized domains of liquid crystals that are randomly dispersed in a polymer matrix [7-9].

Later, to produce color display films for the applications of color optical shutters and projection windows the dichroic dyes have been added in following PDLC devices; that produce dye doped PDLC (D-PDLC). These devices demonstrate a higher reflectivity, a wide viewing angle and low power consumptions (as shown in Fig. 1). Nevertheless, such D-PDLC devices have shortcomings such as formation of larger LC droplets at higher dye contents, low contrast ratio (CR) at higher dye contents, and higher affinity towards polymer molecules of dye [10-15].

The purpose of the current study was to examine the new compound as Azo black dye (C36H37N7) (G-241, Hayashibara-Japan) which has non-polar, stable and inactive molecular properties. To evaluate the characteristics of following dye inside the polymer dispersed liquid crystal (PDLC) films, a nematic liquid crystal (LC) TL203 and commercial monomer PN393 was selected. To evaluate the optimum characteristics of D-PDLC various compositions per weight percentage of LCs and dye have been selected. For the purpose, the following characteristics like absorbance, contrast ratio, dichroic ratio, transmittance-volt, contrast ratio-volts and morphologies have been explored for D-PDLC and have been discussed in details.

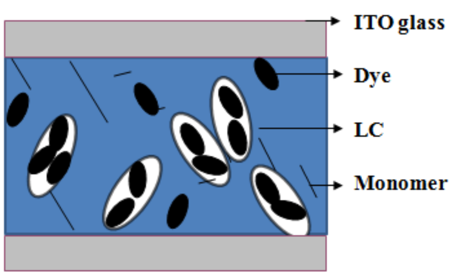

Fig. 1. A schematic view of dye doped PDLC display film

2. Experimental

2.1. Materials and methods

Here, the dye doped PDLC (D-PDLC) films were prepared by introducing a mixture of liquid crystal and pre-polymer between the transparent indium tin oxide (ITO) coated glass plates with a 10 µm cell gap thickness. The mixtures of LC, pre-polymer and dye was formed by using TL203 (Merck) as liquid crystal (LC), PN393 (Merck) as prepolymer and G-241 (Hayashibara-Japan) as azo black dye ($C_{36}H_{37}N_7$) with different compositions of LC/prepolymer 77:23, 78:22 and 80:20 by weight. The dye ratio was varied from 0.5 wt% to 1.5 wt%.

In order to make the D-PDLC device the LC, prepolymer and dye mixture was inserted into the two ITO glass cell using the capillary rise method. The cells were polymerized by illuminating them with a UV lamp (λ ~365 nm) by keeping the intensity of 1 mW/cm^2 for 10 minutes at 24^{o}C temperature. The polymer induced phase separation (PIPS) method using the UV irradiation was adopted for the preparation of D-PDLC films.

2.2. Experimental measurements

For the estimation of electro-optical characteristics such as the transmittance (T) and contrast ratios (CR) against voltages experiments were conducted at room temperature by finding out the transmission of un-polarized HeNe laser light by Minolta UV–Vis spectrophotometer (model UV-3500d, Japan). For dichroic ratios (R) and contrast ratios (CR) the absorbance measurements at wavelength in the ranges of λ = 400-600 nm by Minolta UV–Vis spectrophotometer has been used. The sample D-PDLC films were kept normal to the laser beam. The collection angle of the transmitted intensity was around 0^o, and according to it the principally forward scattering was detected. The transmission/absorbance quantities were corrected by fitting suitable calibration standards.

The surface morphologies of the D-PDLC films were observed via polarized optical microscope (Olympus Model BX-60) at 10X magnification adjusted with a digital camera connected to a PC workstation.

3. Results and discussion

3.1. Measurement of maximum absorption of dye, contrast ratio, dichroic ratio

In order to find the appropriate optical properties of following Azo dye G-241 the contrast ratio ($CR = A_{OFF} / A_{ON}$) and dichroic ratio ($R = A\| / A\perp$) of following dye in TL203 was important to determine. Here the properties A_{OFF}, A_{ON}, $A\|$ and $A\perp$ are the absorbance at OFF, ON state of electricity and absorbance at polarized parallel and perpendicular to the polarizer. For the purpose initially three different dye contents (0.5 wt% -1.5 wt%) in the TL203 LC were mixed and filled in 10 µm cell gap of two ITO glasses.

In order to find following properties, initially the maximum absorbance of the dye has been determined. For the purpose the absorbance spectra of TL203/dye ITO device at different dye contents from 400-600 nm wavelengths at voltage off state has been determined. Further, the following spectra of the dye in visible range were plotted in Fig. 2. The dye G-241 showed two maximum absorption peaks at two different regions for all dye contents. The higher absorption band was observed from 400-440 nm with maximum absorbance at 400 nm. The largest absorption peak for 1.5 wt% of dye at 400 nm was observed as 1.15%. However, second absorption peak was observed at 540 nm. For further studies such as dichroic ratios and contrast ratios, the 400 nm wavelength has been chosen. Moreover, such spectra showed an increase in absorption intensities with the addition of dye contents. The maximum absorption of dye was observed for 1.5 wt% LC-dye device.

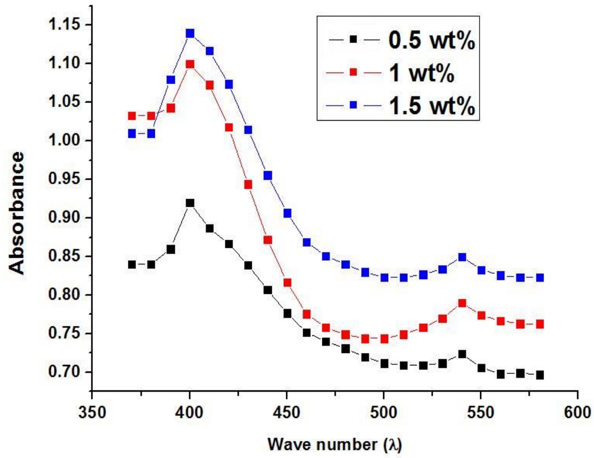

Fig. 2. Absorbance spectra of dye G-241 with varying dye contents in TL203 Liquid crystal

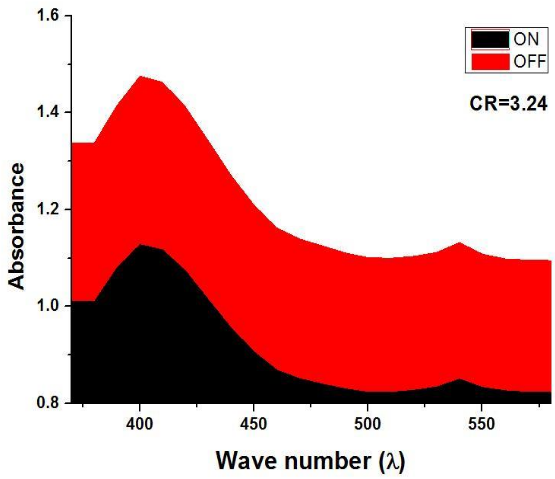

Fig. 3 (a). Absorbance spectra of dye having 1.5 wt% in LC at voltage OFF/ON state showing Contrast ratio

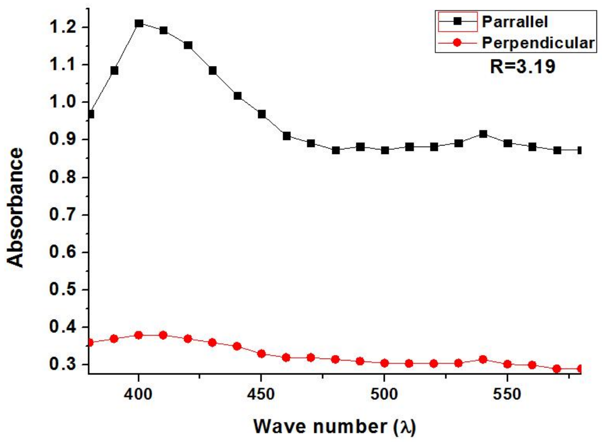

Fig. 3 (b). Absorbance spectra of dye having 1.5 wt% in LC at polarized parallel/perpendicular showing dichroic ratio

In the next step, the contrast ratio (CR) and dichroic ratio (R) of dye was observed at 400 nm at 1.5 wt% of dye. To calculate the CR the polarized parallel absorption spectra of the LC/dye mixtures at 400 nm at zero and 30 voltage were determined. Fig. 3(a) illustrates the absorption spectra of G-241 dye at zero and 30 the saturated applied voltage. The contrast ratio of the dye was calculated by using the formula, CR = A_{OFF} /A_{ON}. Here A_{OFF} is the absorption of light at zero electric field and A_{ON} is the absorption of light at 30 volts. On following this equation, the CR was observed as 3.24. It was believed that with zero electric field the liquid crystal molecules were in a uniform parallel orientation and the dye molecules were oriented with the long molecular axis parallel to the electric field vector of the polarized light (i.e. parallel to the nematic director) [15-16]. To find the dichroic ratio of dye, the absorption spectra of LC-dye device was observed at polarized parallel and perpendicular positions and following spectrum was shown in Fig. 3(b). The dichroic ratio of dye was calculated by observing the absorbance ratio of polarized parallel ($A_\parallel$) and perpendicular ($A_\perp$) to the light for 1.5 wt% of dye [15-16]. Fig. 3(b) showed that the absorption at polarized parallel ($A_\parallel$) and at perpendicular ($A_\perp$) was observed as 1.21, 0.38 respectively. The dichroic ratio was observed as 3.19. The CR was directly related to order parameter for the transition moment, while the molecular structure was considered to relate with order parameter for the molecular axis [16].

3.2. The morphologies of D-PDLCs

It is known earlier that for the enhanced light-scattering efficiency from the D-PDLCs, the better droplet uniformity and smaller size formation is essential. This situation enhances further if the droplet size remain comparable to the wavelength of scattered light [17]. Hence, to inquire the favorable composition for the D-PDLC display with G-241 dye three different compositions with varying the LC weight percentage were prepared. Following compositions 80:20, 79:21, 78:22 wt% were selected as per LC/prepolymer weight percentage. To examine the appropriate dye concentrations to achieve the valuable electro optical properties and morphologies; three different dye concentrations have been selected. For this reason, the following concentration of dye 0.5 wt%, 1.0 wt% and 1.5 wt% have been used. The morphologies of the subsequent D-PDLC as observed from polarized optical microscope under 10X magnifications were shown in Fig. 4 (a,b,c).

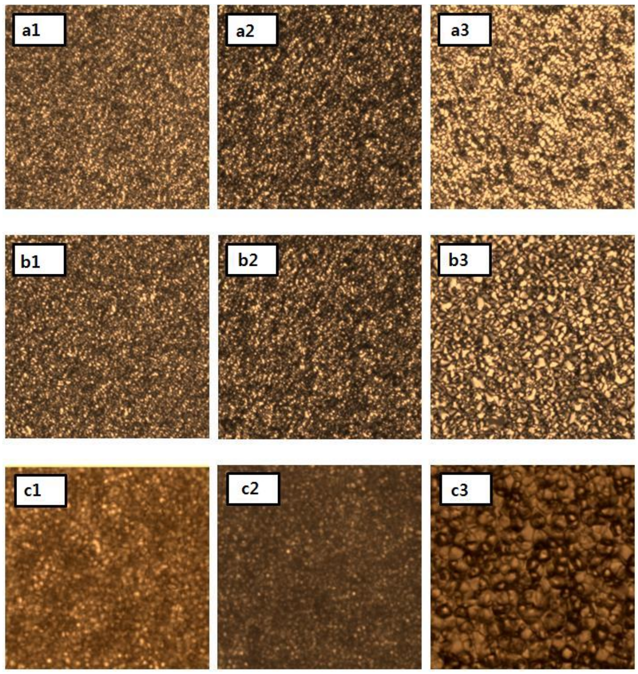

Fig. 4. (a,b,c). Polarized optical microscope images of D-PDLC having (a) 78 wt% LC and dye G-241 (1) 0.5wt%, (2) 1.0 wt%, (3) 1.5 wt%, (b) 79 wt% LC and dye G-241 (1) 0.5wt%, (2) 1.0 wt%, (3) 1.5 wt%, (c) 80 wt% LC and dye G-241 (1) 0.5wt%, (2) 1.0 wt%, (3) 1.5 wt%

Fig. 4(a-c) showed smaller droplets formation for all LC contents while dye contents were fixed as 0.5 wt%. However, an increase in droplet size of D–PDLC with the addition of LC contents (from top to bottom) and with increase of dye contents (from left to right) have been observed. This increase in droplet size was obvious for 80 wt% LC contents at higher dye contents (1.5 wt%) only. The Fig. 4(a) displayed smaller droplet size formation at almost all LC concentrations (except 80 wt %) and dye 0.5-1.5 wt% contents. This was considered as the achievement for the D-PDLC as fabricated with G-241 dye. Since previously with the increase in dye contents, the increase in droplet size was a major drawback. Moreover, the D-PDLC showed coalescence and random size distribution of LC droplets with the increase in dye and LC contents [18]. Such situation further deteriorates the electro optical properties. The reason for that increase in droplet was considered as absorption of UV light and solubility with polymer matrix of dye molecules [18].

In addition to this, larger LC droplets were observed only for LC concentrations of 80 wt % especially at 1.5 wt% of dye. However, collectively G-241 showed fine droplet morphology with regular LC droplets size and with no coalescence observed. The higher contrast ratio, dichroic ratio and the formation of smaller LC droplet size formed by this dye made it superior to other dyes.

3.3. Electro-optical properties

Keeping in mind the droplet morphology, it was expected a better electro optical properties with the voltage. For the purpose, the electro optical properties the transmittance and contrast ratio was observed against the applied voltages. The electro-optical properties like transmittance and contrast ratio were observed at various voltages and were plotted in Fig. 5. The voltage-transmittance (V-T) characteristic was measured for various LC and dye concentrations for D-PDLC display. Fig. 5 showed a general trend of increase in transmittance with the increase in voltage. Moreover, an increase in transmittance at OFF state was observed as the dye contents increased from 0.5 wt% to 1.5 wt%. However, due to formation of smaller drop morphologies the scattering for the D-PDLC device was found still better. However, with the increase in LC contents (from 78 wt% to 80 wt%) an increase in OFF transmittance and decrease in OFF scattering was observed. These results were expected due to increase in droplet size with the increase in LC contents. Moreover, this behavior was observed earlier due to higher absorption of light at higher dye contents that produced low transmission of light [19].

That might produce further poor electro optical properties such as threshold voltages and saturation voltages. However, contrary to the previous findings, following dye-PDLC showed V_{th} >10 volts and saturation voltage less than 30 volts. Following results lead to a higher contrast dye PDLC with increase in voltage. However, in addition to this, Fig. 5 showed increase in ON state transmittance with the increase of LC and dye contents. This behavior was related to the anchoring energies and intermolecular forces that can be decreased when the droplet size was essentially large [18-19]. Hence, the higher LC contents D-PDLC device showed higher transmittance due to larger droplet size.

The contrast ratio (CR), of a dichroic PDLC film was an important parameter to measure the performance of any electro-optical devices. The contrast ratio of following dye PDLC was shown in bottom of Fig. 5. The obtained graphs showed a higher CR for the 78 wt% of LC contents. The maximum contrast ratio was observed for the 0.5 wt% of dye contents as 1:7.5%. However, as the dye contents were increased, a little decrease in CR was seen for 78 wt% of LC contents. This behavior was probably due to randomly distribution of dye inside the polymer matrix out of LC droplets that may absorb the UV light. Hence, it may lead to increase in droplet size and OFF transmittance [18-19].

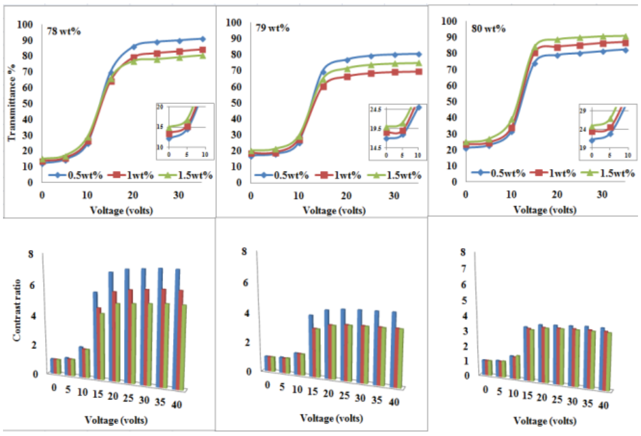

Fig. 5. Electro-optical transmittance and Contrast ratio (CR) of D-PDLC fabricated with 78 wt%, 79 wt% and 80 wt% of liquid crystals contents with varying dye contents (0.5wt%, 1.0 wt% and 1.5 wt%)

4. Conclusions

Here in the reported work, a new Azo black dye (G-241, Hayashibara-Japan) was selected to produce D-PDLC due to its chemically stable, inactive and non-polar structure. This dye was used with the mixture of TL203 as nematic liquid crystal and PN393 as monomer to produce a high contrast black dye-doped PDLC display. For the purpose, various concentrations of LC and dye have been chosen. Prior to characteristics study of dye PDLC the optical contrast and dichroic ratio in LC was observed that was found as 3.24 and 3.19 respectively. The results of this study produced smaller size droplet morphologies with different compositions of dye. Moreover, following D-PDLC showed reasonable small threshold and saturation voltages at small LC and higher dye contents.

Such results are novel and promising due to use of new Azo black dye that produced enhanced electro optical properties such as threshold voltages, saturation voltages, OFF transmittance, contrast ratios, and dichroic ratios properties at higher dye contents. This is an additional achievement as the electro optical properties reached to the maximum as the new material of dye contents are increased.

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