

# Influence of Different Polyesters and Their Molecular Weight on the Textural and Electrooptical Behavior of Polymer-Dispersed Liquid Crystals

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**ABSTRACT:** The textural and electrooptical behavior of a nematic liquid crystal (LC) dispersed in a flexible and rigid polyester was studied. The dispersion of LC in the polymer matrix and light transmission through the polymer-dispersed liquid crystal (PDLC) is governed by the nature of the polymer, its molecular weight, and the applied voltage. It was observed that the transmission of light and the dispersion of LC maximizes their respective values at the minimum molecular weight irrespective of the nature of the polymer and at the maximum voltage. The reason is the predominance of chain alignment over entanglement at the

minimum molecular weight. As molecular weight increases, the transmission of light as well as the dispersion of LC in the polymer may increase or decrease depending on the predominance of chain entanglement or chain alignment. The alignment of LC droplets in the direction of the applied voltage is increased by an increase in the applied voltage, causing enhancement of the light transmission. © 2002 Wiley Periodicals, Inc. *J Appl Polym Sci* 87: 284–289, 2003

**Key words:** polyesters; liquid crystalline; polymers (LCP); transparency

## INTRODUCTION

Polymer-dispersed liquid crystals (PDLCs) are defined as a dispersion of liquid crystals (LCs) in the form of droplets in a polymer matrix.<sup>1,2</sup> These can be prepared by a variety of techniques, all involving (macroscopically) incomplete phase separation (“microphase separation”) of an initially homogeneous mixture.<sup>3</sup> Some of the potential applications of PDLCs are switchable windows, display devices, infrared shutters, angular-discriminating filters, thermoelectrooptic switches, memories, gas-flow sensors, optical sensors, and optical gratings.<sup>4</sup> Scientists have found considerable interest in PDLCs as a subject of both fundamental and applied research. Fundamentally, they address challenging questions like the dynamics of phase separation, ordering and structure selection, as well as finite size and surface effects at equilibrium. On the applied side, the technologists tailored these PDLCs into useful devices for potentially electrooptic application. By matching the refractive index of the polymer and the ordinary refractive index of the LC, PDLC films can be switched from a translucent “off”

state to a transparent “on” state by application of an electric field. In the field-off state, the balance between the nematic elasticity and the surface anchoring determines the director field inside each droplet; the orientation of the director varies randomly from droplet to droplet—hence, the film scatters light strongly and is opaque. If an electric field is applied perpendicular to the film, the director will align along the field direction, and for normal light incidence, the film becomes transparent.<sup>4</sup>

Unlike conventional LC displays, these films are flexible and very easy to prepare, since no orienting glass plates, and, hence, no complex surface treatments, are required. In addition, their light transmittance is much higher than that of the more conventional twisted- or supertwisted-nematic devices, owing to the absence of polarizers.<sup>5</sup> The morphology, and, in particular, the droplet size and density, has a major influence on the optoelectronic response of these materials and on the scattering efficiency of their films,<sup>6,7</sup> which is maximized when the droplet size is on the order of the wavelength of light. Both the threshold voltage and the switching speed of the resulting display decrease with increasing droplet size.<sup>4</sup> Smith and coworkers<sup>8–10</sup> reported on the PDLC morphology, such as the relationship between the droplet diameter and the droplet number density and the fractional amount of LC contained in the droplets. The quantity was later related to solubility parameters in

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the context of a thermodynamic treatment<sup>11</sup> based on the Flory–Huggins theory of polymer mixtures,<sup>12</sup> neglecting the nematic character of the LC droplets. Although much empirical knowledge has been gathered on the fabrication of PDLCs, a detailed understanding of the underlying physical mechanisms leading to specific electrooptic properties is still lacking. The present report aimed at understanding the dispersion mechanism of a nematic LC in a different polymer matrix having different molecular weights with respect to their electrooptic behavior.

Several recent developments on the functioning<sup>13–15</sup> of the PDLCs as well as their applications<sup>16–19</sup> were reported. Bloisi et al.<sup>13</sup> devised a mathematical model for light transmittance and tested it experimentally. Vicari<sup>14</sup> presented another model to describe the optical phase shift induced by polymer-dispersed LCs on light impinging transversely on the PDLC. Ambrozic et al.<sup>15</sup> studied surface anchoring and LC droplet deformation in PDLCs. They found that the applied electric field with variable strength and a direction orthogonal to the NMR field was confined to the sub-micrometer quasi-spherical cavities with planar surface anchoring. All these reports indicate that the electrooptical properties are dependent on the functioning of LCs in PDLCs. The composition of the polymer matrix in PDLCs is another important factor affecting electrooptical properties.<sup>20</sup> The present investigation reports a new type of PDLC based on the polyester matrix and studied the influence of different polyesters and their molecular weight on the textural and electrooptical behavior of PDLCs.

## EXPERIMENTAL

### Synthesis of polyesters

Rigid polyesters were synthesized from phthalic anhydride and ethylene glycol in a stoichiometric ratio of 1:0.9 using *para*-toluenesulfonic acid as a catalyst, whereas flexible polyesters were made from adipic acid and ethylene glycol in the same stoichiometric ratio as that of the rigid polyester using an alkali initiator. The reactants were refluxed at 70°C for 1 h; then, water vapor was distilled off directly for the former one and after neutralization with succinic acid for the latter one. During distillation, intermittent samples were taken out at definite intervals (10 min for the rigid and 15 min for the flexible polymer). The viscosity-average molecular weights of the polymer samples were measured from the increase in torque during the measurement of the viscosity. The intermittent samples were further used as a dispersion medium for LCs for the preparation of PDLCs.

### Preparation of PDLCs

The standard procedure<sup>20</sup> was adopted for the preparation of the PDLCs. A room-temperature eutectic LC

mixture E 38 (obtained from M/S E-Merck, Darmstadt, Germany) was dispersed in the polymer matrix. E-38 shows a nematic LC range at 57°C. The solvent-induced phase-separation (SIPS) technique was adopted to prepare the PDLC films. Both the polymer and the LC were dissolved in chloroform (supplied by Ranbaxy Chemicals, Chandigarh, India) to obtain a homogeneous solution. The sample was then spread onto a clean glass substrate. The solvent was removed by placing the sample in an oven at 50°C for about 1 h. The accuracy of the oven was  $\pm 0.5^\circ\text{C}$ . A thin film (25  $\mu\text{m}$ ) of the dispersed system was then peeled off and sandwiched between two indium tin oxide (ITO)-coated glass substrates. These were sealed using a NORLAND NOA 65 optical adhesive.

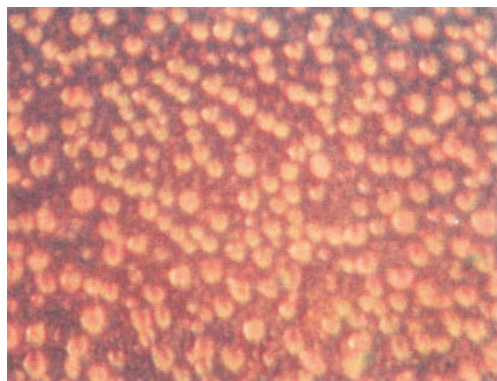
### Electrooptical measurements

Electrical connections were applied to the sample across the ITO-coated substrates using an indium solder. The sample cell was placed in a LINKAM temperature cum hot-stage programmer (Model TP 92 and TMHS 600) whose accuracy was 0.1°C. The optical textures of the dispersed films were studied through an Olympus polarizing microscope (Model BX 51P) fitted with a photodetector and a CCD interface under a magnification of 100 $\times$ . The electrooptic and transmission characteristics of the PDLCs were studied at room temperature and at a constant ac frequency by varying the voltages across the PDLC cell and acquired on a Tetronix digitizing storage oscilloscope (Model TDS 210). All PDLC specimens were tested three times to ensure the repeatability of the measurement.

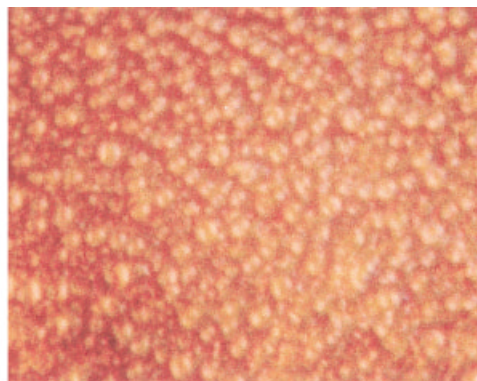
## RESULTS AND DISCUSSION

The optical textures of the nematic LC dispersed in a rigid polymer matrix of the same molecular weight were viewed at 10 and 30 V and are shown in Figure 1(a,b), respectively. It is evident from the photographs that the dispersion of nematic LC increases with increase in the applied voltage. This is due to more alignment of LC droplets in the direction of the applied voltage. This ordering of the LC may have helped in enhancing its dispersion in the polymer matrix.

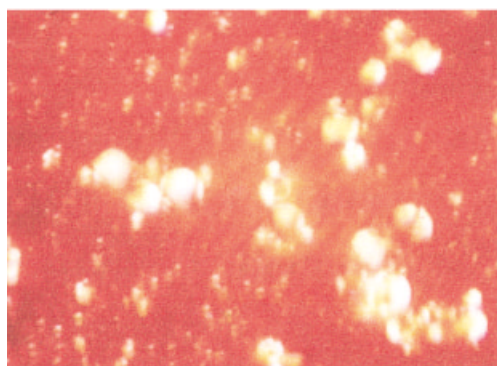
The changes in texture of the nematic LC at a constant voltage (10 V) with an increase in molecular weight of the rigid polymer matrix are shown in Figure 1(a–f). Figure 1(a), which represents a low molecular weight (500) polymer matrix, shows better dispersion of the LC. The dispersion of the LC is reduced with increase in the molecular weight up to 1000 of the polymer matrix [Fig. 1(c,d)], whereas it is increased beyond this molecular weight [Fig. 1(e,f)]. The rigid polymer matrices that contain the polar benzene ring



**Figure 1a**



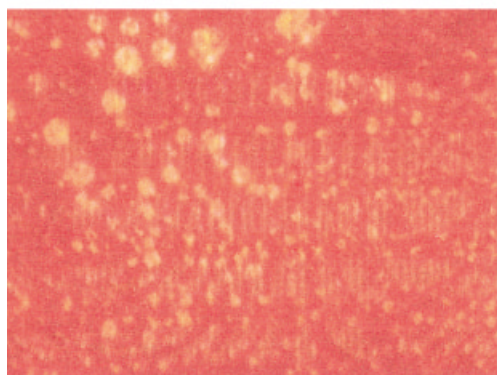
**Figure 1b**



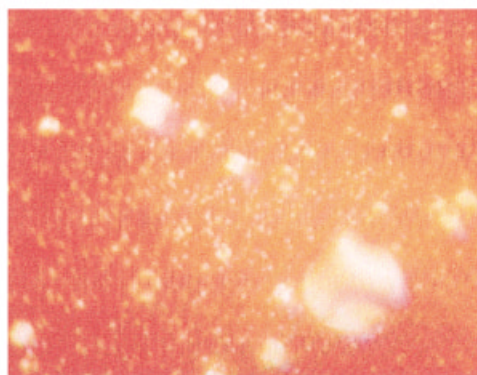
**Figure 1c**



**Figure 1d**



**Figure 1e**

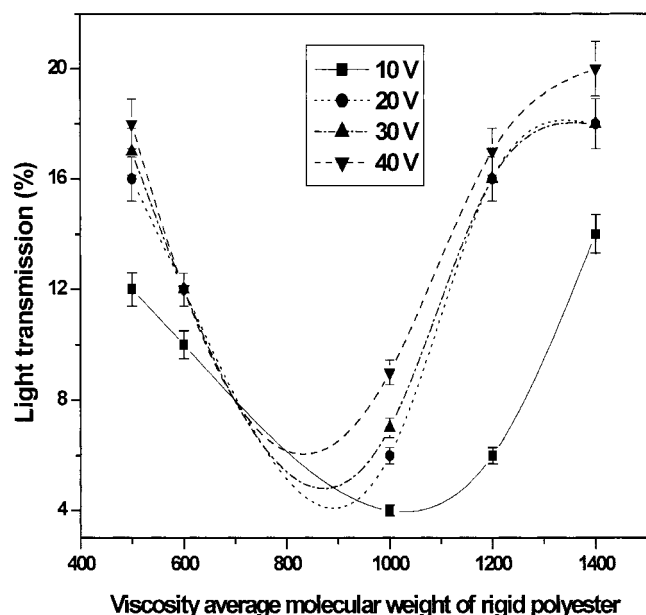


**Figure 1f**

**Figure 1** Photographs of LC dispersed in a rigid polyester [poly(ethylene phthalate)]; (a,b) represent the same average molecular weight (500) of the polymer used for the dispersion of LC but photographs viewed at 10 and 30 V, respectively; (c–f) represent PDLCs having a rigid polyester of a viscosity-average molecular weight of 600, 1000, 1200, and 1400, respectively.

in their chain can be aligned more in the direction of the applied voltage with increase in the molecular weight. This helps in the enhancement of the dispersion of the LC in the rigid polymer. On the other hand, the increasing molecular weight induces an increase in chain entanglement as well as the inherent viscosity of the polymer. This causes a reduction in the dispersing capability of the rigid polyester. These two opposing

factors dictate the dispersing capability of the rigid polymer. It seems that the maximum entanglement occurs up to the molecular weight of 1000, beyond which entanglement remains almost the same. Thus, below a molecular weight of 1000, the effect of entanglement is prominent, causing a reduction in the dispersion of the LC, whereas beyond the molecular



**Figure 2** Variation of percent transmission of light with the viscosity-average molecular weight for LC dispersed in rigid polyester at 10, 20, 30, and 40 V.

weight of 1000, the alignment effect is more dominant, leading to an increase in the dispersion of the LC.

The variation of the percent transmission of light against the molecular weight (viscosity average) of the rigid polymer at 10, 20, 30, and 40 V is shown in Figure 2. During their plotting, the percent error and the standard deviation of each data point were recorded (Table I). The percent error is the deviation of each data point about the mean of the data set of the transmission of light. These values were also shown as error bars in Figure 2. The very low percent error (below 2%) is indicative that the data set is statistically

sound. The standard deviations of all data sets corroborate well the above statistical soundness, as all data points will lie within three standard deviations in any distribution (Chebyshev's rule and empirical rule).<sup>21,22</sup> From Figure 2, the transmission of light decreases with increase in the molecular weight up to 1000, beyond which it increases. The transmission of light will be more if the LC is better dispersed in the rigid polymer. So, the change in percent transmission with an increase in the molecular weight at 10 V corroborates the change in the dispersion of the LC in a rigid polymer, which was explained in the discussion of Figure 1. It is evident from Figure 2 that the transmission increases with increase in the applied voltage. When the voltage is applied, the helical structure of the LC opens up, that is, the droplets expand, instability sets in, and the droplets break up, leading to better dispersion in the polymer matrix. But when the field is withdrawn, these droplets tend to coalesce. But due to opposing polarities at the interphase of the LC droplets and rigid polyester matrix, the droplets do not coalesce; moreover, the effect of the rigid matrix also hinders the movement of energy-deficient LC droplets.

Figure 3(a–d) show photographs (at 10 V) containing the microstructure of the LCs dispersed in the samples of different molecular weights of the flexible polyesters. As one moves from Figure 3(a) to (d), the molecular weight of the polymer matrix increases. The dispersion of LC in the polymer matrix is the highest in Figure 3(a) and it decreases with increase in the molecular weight of the polymer matrix. The increase in molecular weight increases the chain entanglement as well as the inherent viscosity, which reduce the dispersing capability of the flexible polymer. The flexible chains of poly(ethylene adipate) are less polar

**TABLE I**  
Standard Deviation (SD) and Percent Data Error from Figures 2 and 4

| Molecular weight of the polyester  | SD and percent data error of the plotted percent transmission of light against molecular weight at the applied voltage of |         |       |         |       |         |       |         |
|------------------------------------|---|---------|-------|---------|-------|---------|-------|---------|
|                                    | 10 V  |         | 20 V  |         | 30 V  |         | 40 V  |         |
|                                    | SD  | % Error | SD    | % Error | SD    | % Error | SD    | % Error |
| <b>Rigid polyester (Fig. 2)</b>    |   |         |       |         |       |         |       |         |
| 500                                | 4.147   | 0.60    | 4.775 | 0.80    | 4.528 | 0.85    | 4.550 | 0.90    |
| 600                                | 4.147   | 0.50    | 4.775 | 0.60    | 4.528 | 0.60    | 4.550 | 0.60    |
| 1000                               | 4.147   | 0.20    | 4.775 | 0.30    | 4.528 | 0.35    | 4.550 | 0.45    |
| 1200                               | 4.147   | 0.30    | 4.775 | 0.80    | 4.528 | 0.80    | 4.550 | 0.85    |
| 1400                               | 4.147   | 0.70    | 4.775 | 0.90    | 4.528 | 0.90    | 4.550 | 1.00    |
| <b>Flexible polyester (Fig. 4)</b> |   |         |       |         |       |         |       |         |
| 400                                | 2.986   | 0.70    | 4.397 | 0.90    | 4.083 | 1.00    | 4.573 | 1.10    |
| 600                                | 2.986   | 0.45    | 4.397 | 0.55    | 4.083 | 0.65    | 4.573 | 0.70    |
| 900                                | 2.986   | 0.45    | 4.397 | 0.75    | 4.083 | 0.95    | 4.573 | 0.95    |
| 1200                               | 2.986   | 0.45    | 4.397 | 0.40    | 4.083 | 0.60    | 4.573 | 0.60    |

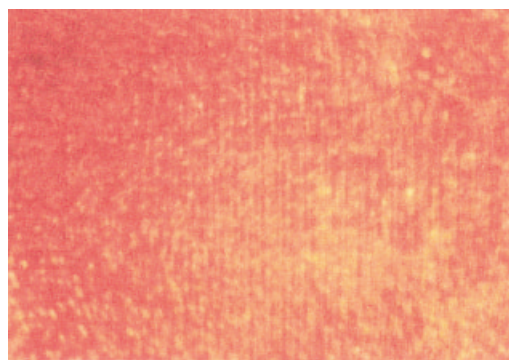


Figure 3a

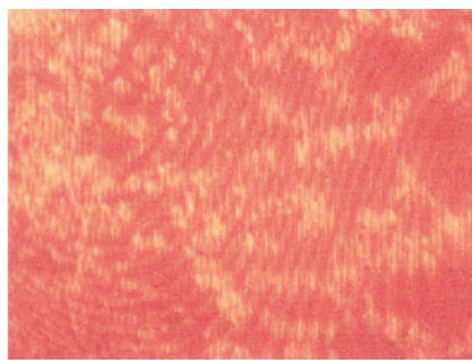


Figure 3b

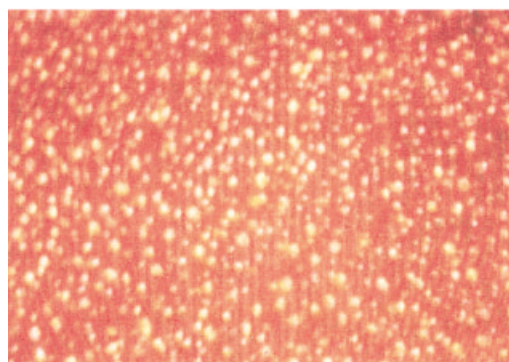


Figure 3c

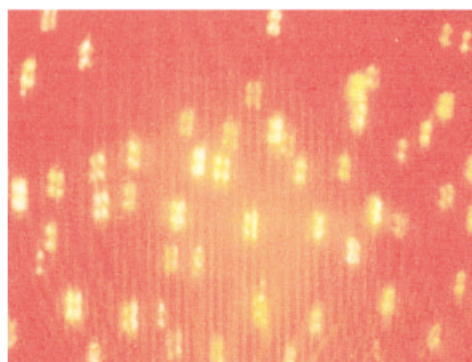
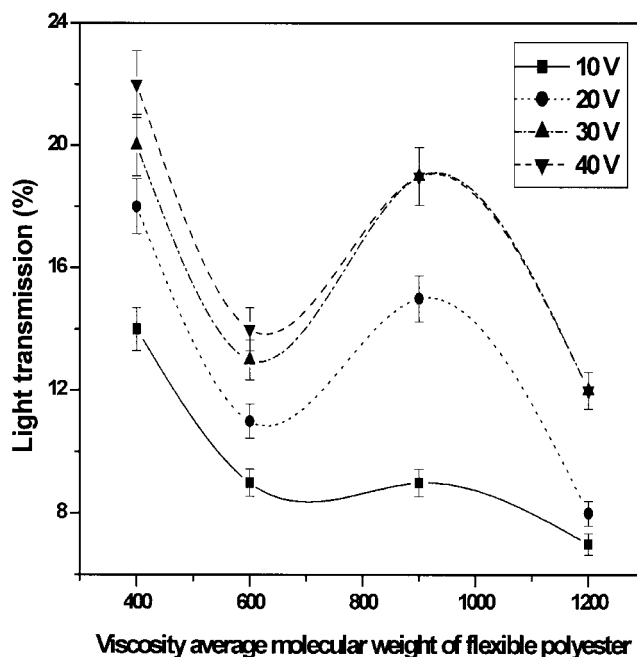


Figure 3d

**Figure 3** Photographs of LC dispersed in a flexible polyester [poly(ethylene adipate)]; (a–d) represent PDLCs having flexible polyester of a viscosity-average molecular weight of 400, 600, 900, and 1200, respectively.

compared to the rigid backbone. Thus, polymer chain alignment in the direction of the applied voltage is minimum for the lowest molecular weight matrix [Fig. 3(a)] and it is increased in an appreciable proportion, as an increase in the molecular weight of the polymer matrix leads to an increase in its polarity. The increase in dispersion of LC in Figure 3(c) can be explained by the predominance of the polymer chain alignment compared to the chain entanglement. The reason behind the decrease in the dispersion in Figure 3(d) compared to Figure 3(c) is not well understood. Probably, this may be explained by the presence of extra networks in the polymer matrix, which are formed during the latter phase distillation of the polymer precursor at a high temperature for the removal of water vapor.

The variation of the percent transmission of light against the molecular weight (viscosity average) of the flexible polymer at 10, 20, 30, and 40 V is shown in Figure 4. The standard deviation and percent error values for the whole data set of light transmission are recorded in Table I. The low percent error (below 2%) and the lying of all data points within three standard deviations to either side of the mean supports the statistical soundness of the data set.<sup>21,22</sup> It is evident



**Figure 4** Variation of percent transmission of light with a viscosity-average molecular weight for LC dispersed in a flexible polyester at 10, 20, 30, and 40 V.

from Figure 4 that the percent transmission decreases initially up to a molecular weight of 600, starts increasing at a molecular weight of 900, followed by its decrease, leading to anti-Z or S plots. The initial decrease in the transmission may be explained by the predominant entanglement of the polymer chains compared to the alignment of chains in the direction of the applied voltage, causing better dispersion and, hence, better transmission, whereas the alignment of polymer chains along with the LCs in the direction of the applied voltage is predominant over the chain entanglement, causing a subsequent decrease in the transmission in the molecular weight range of 600–900. The decrease in transmission beyond a molecular weight of 900 may be caused by predominant networks formed during the preparation of poly(ethylene adipate) from the polymer precursor. It is evident from the plots that the transmission increases with increase in the voltage at any molecular weight of the polymer. As the applied voltage increases, the helical structure of the LC expands much faster compared to the chains of the flexible polyester matrix. This causes rupturing of the polymer layers embedded around the LC and induces coalesce by the direct contact of LC droplets among themselves. This happens much before the point of instability of LC sets in. At the point of instability, the LC droplets break up but they coalesce when the applied voltage is withdrawn.

### CONCLUSIONS

The dispersion of LC in the polymer matrix as well as the light transmission through the PDLC is governed by the nature of the polymer, its molecular weight, and the applied voltage. The light transmission as well as dispersion of LC is maximum at a minimum molecular weight irrespective of the nature of the polymer and at maximum voltage. This is caused by the predominant chain alignment over entanglement at its minimum molecular weight. With increase in the molecular weight, the transmission in light as well as the dispersion of LC in the polymer may increase or de-

crease depending on the predominance of chain entanglement or chain alignment. With increase in the applied voltage, the LC droplets align more in the direction of the applied voltage, causing more dispersion of LC in the polymer matrix and, hence, more light transmission.

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