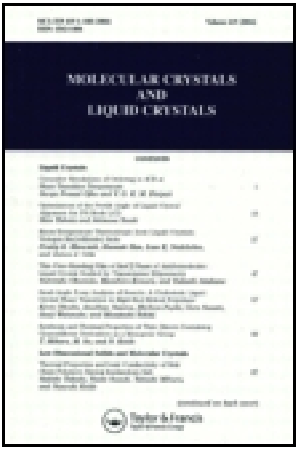


Molecular Crystals and Liquid Crystals

Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/gmcl20

Electro-Optic and Thermo-Optic Properties of Phase Separated Polymer Dispersed Liquid Crystal Films

Praveen Malik [a], A. M. Bubnov [b] & K. K. Raina [c]

[a] Department of Physics, Dr. B. R. Ambedkar National Institute of Technology, Jalandhar, Punjab, India

[b] Institute of Physics, Academy of Sciences of the Czech Republic, Prague, Czech Republic

[c] Liquid Crystal Group, Materials Research Laboratory, School of Physics and Materials Science, Thapar University, Patiala, Punjab, India

To cite this article: Praveen Malik, A. M. Bubnov & K. K. Raina (2008): Electro-Optic and Thermo-Optic Properties of Phase Separated Polymer Dispersed Liquid Crystal Films, Molecular Crystals and Liquid Crystals, 494:1, 242-251

To link to this article: http://dx.doi.org/10.1080/15421400802430430

Mol. Cryst. Liq. Cryst., Vol. 494, pp. 242–251, 2008
Copyright © Taylor & Francis Group, LLC
ISSN: 1542-1406 print/1563-5287 online
DOI: 10.1080/15421400802430430

Electro-Optic and Thermo-Optic Properties of Phase Separated Polymer Dispersed Liquid Crystal Films

Praveen Malik[1], **A. M. Bubnov**[2], **and K. K. Raina**[3]
[1]Department of Physics, Dr. B. R. Ambedkar National Institute of Technology, Jalandhar, Punjab, India
[2]Institute of Physics, Academy of Sciences of the Czech Republic, Prague, Czech Republic
[3]Liquid Crystal Group, Materials Research Laboratory, School of Physics and Materials Science, Thapar University, Patiala, Punjab, India

Polymer dispersed liquid crystal (PDLC) and guest host polymer dispersed liquid crystal (GHPDLC) films were prepared by phase separated polymerization induced phase separation (PIPS) technique. Micro-texture studies shows that the liquid crystal droplets of varying size (~5–40 μm) consists mainly of bipolar configurations at lower field (~ < 1V/μm). They develop into maltese type configuration at higher field (~8V/μm, 10V/μm for PDLC and GHPDLC). It was seen that the optical transmission increases in both cases with increasing temperature. A higher threshold voltage for GHPDLC relative to PDLC films with temperature was noticed. GHPDLC film shows faster switching time (~340 μsec) over PDLC (~510 μsec).

Keywords: anthraquinone dye; droplet morphology; polymer dispersed nematic liquid crystal; polymerization induced phase separation

PACS – 61.30

1. INTRODUCTION

Polymer dispersed liquid crystal (PDLC) composite films have attracted lot of interest due to their wide range of applications in electro-optic

---

The authors wish to thank M/S Norland, NJ and E. Merck, UK for providing the polymer and liquid crystal materials. We thank to referee for their valuable suggestions. The financial support by CSIR and DRDO New Delhi India, is gratefully acknowledged.

Author correspondence to Praveen Malik, Department of Physics, Dr. B. R. Ambedkar National Institute of Technology, Jalandhar, Punjab, India. E-mail: pmalik100@yahoo.com (Praveen Malik), or kkraina@gmail.com (K. K. Raina)

display device [1–3]. Phase separated PDLC films consists of liquid crystal (LC) micro-domains dispersed in optically transparent polymer matrix [4–8]. PDLC films have a remarkable electro-optical behavior since they can be switched from highly light scattering state (OFF) to transparent state (ON) simply by application of an electric field [1,3,5,9]. In the absence of an external electric field, the director orientation of the LC varies randomly from droplet to droplet. In this case, the LC extraordinary refractive index (n_e), ordinary refractive index (n_o) are different from polymer refractive index (n_p) and produce a strong light scattering that makes the PDLC film opaque (OFF state). While in the presence of an external electric field of sufficient intensity, the director of LC droplets align towards the direction of applied electric field and sample appears transparent. The transparency of sample is due to the matching of refractive index of LC droplets to polymer i.e. $n_o \sim n_p$.

Recently, guest-host polymer dispersed liquid crystal materials have attracted significant attention by various research groups due to its technological importance [10–12].

It has been seen observed that the dispersion of small amount of dichroic dyes (guest) into the LC (host) would enhance the optical characteristics of the liquid crystalline materials. The doped LC materials dispersed into the polymer matrix are then known as guest-host polymer dispersed liquid crystal. The morphology of the LC droplet and electro-optical properties of the guest-host PDLC and PDLC films depends on various factors, i.e. refractive index of the materials, LC/polymer concentration, amount of dye, curing rate, intensity of applied electric field, anchoring energy, cooling rate, solubility of materials relative to each other and temperature.

A schematic representation of nematic director configuration for guest-host PDLC film in different states (ON and OFF) is shown in Figure 1.

In the off state, the dye molecules and droplet director are randomly oriented and the orientation of the dye molecules is governed by the director configuration inside the droplet. In the on state, the droplet director and dye molecules are aligned in the direction of field. Therefore, the dichroic droplet structures and optical properties are modulated by the alignment of nematic director with an electric field. It was reported earlier that some amount of dichroic dye remains dissolved in the polymer binder will be unaffected by the external filed and remain randomly oriented. Therefore, only the dye dissolved in the nematic LC droplet will exhibit dichroic properties and contribute the optical responses of the film. There are various works concentrating on the electro-optical characteristics of the PDLC. However little efforts were made on the morphological analysis of guest-host systems.

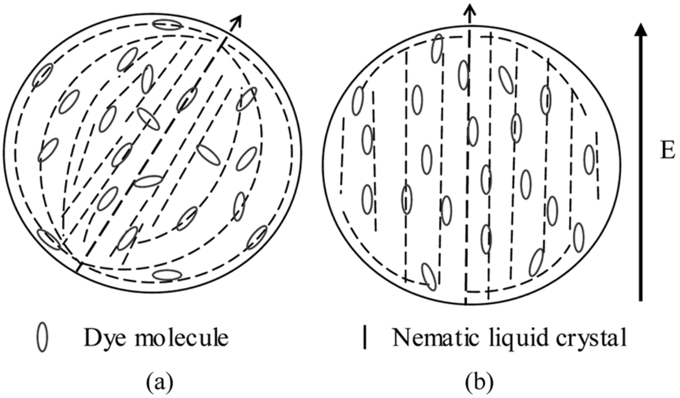


FIGURE 1 Schematic representation of nematic director configuration in PDLC droplets incorporating a dichroic dye. (a) without electric field, and (b) droplet alignment with an electric field.

Raina et al. recently studied a guest host polymer dispersed liquid crystal system (E7/NOA-65/blue anthraquinone dichroic dye) with varying the dye concentrations. It showed an enhancement in electro-optical properties even at low concentration of dye dopants [13,14].

The aim of the present work is to investigate LC droplet morphology, electro-optic and thermo-optic properties of polymer dispersed nematic liquid crystal (PDNLC) films. The effect of dichroic dye in PDNLC film on morphological and switching responses with electric field and temperature have also been investigated and compared with PDNLC film.

2. EXPERIMENTAL

Nematic liquid crystal (NLC) BL036 (purchased from E. Merck, UK) [15], UV curable polymer NOA-65 (Norland, NJ) [16] and blue anthraquinone dichroic dye (Rolic Switzerland) were used for sample preparation. Liquid crystal exhibits a nematic-isotropic transition temperature (T_{NI}) = 95°C, birefringence ($\Delta n = n_e - n_o$) = 0.267 and $n_e = 1.527$. The refractive index of the polymer material was $n_p = 1.524$. The dichroic dye was free from ionic impurities and has good solubility in the NLC. The molecular structure of dichroic dye is given in Figure 2.

Polymer dispersed nematic liquid crystal film was prepared using PIPS method [14,17,18]. In this method, first homogenous mixture of LC and pre-polymer were prepared and then polymerization was induced through the application of UV irradiation (intensity $\sim 2\,\mathrm{mW/cm^2}$) on the

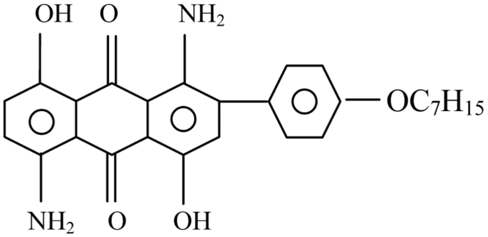


FIGURE 2 Molecular structure of anthraquinone dichroic dye.

homogenous mixture. The droplets thus formed grow in size till the polymer binder gets cured and the molecules are trapped. The NLC and NOA-65 were taken in the ratio of 1:1 wt./wt. In order to ensure proper mixing, this homogenous mixture was heated to the isotropic temperature of LC in a vacuum oven. The sample cell consists of two indium tin oxide (ITO) coated glass substrates and the cells thickness 10 μm was maintained using mylar spacer. The mixture was then filled in the empty sample cell by capillary action after heating the homogenize mixture to the isotropic temperature of LC and then sealed.

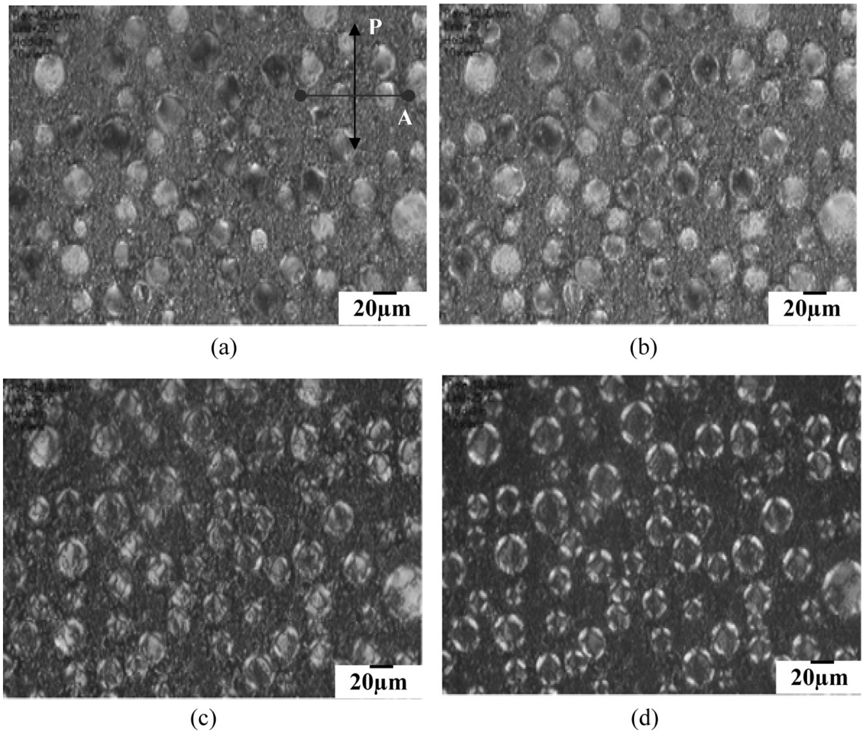
Similarly guest-host polymer dispersed nematic liquid crystal (GHPDNLC) film was prepared by first dissolving the small amount of anthraquinone dye (1% wt./wt.) in LC, and then this mixture was dispersed into the polymer matrix.

Both the sample cells were placed in a programmable temperature controller coupled to hot stage (Model TP94 and THMS 600) first heated to the isotropic temperature of LC and then cooled down to room temperature at the rate of 0.1°C/min. The morphology of LC droplets were viewed under crossed polarizers at a magnification of 10x through Olympus polarizing microscope (Model BX-51P) fitted with charge coupling device (CCD) camera and interfaced with computer. The electro-optic responses of the samples were detected and measured using a photomultiplier tube (Model RCA 931-A) under an external electric field using a function generator (Model-Scientech-4060). The data was acquired with computer interfaced digital storage oscilloscope (Model-Tektronix Model TDS 2024).

3. RESULTS AND DISCUSSION

3.1. Morphology Analysis

Morphology of LC droplets in PDNLC and GHPDNLC samples at different voltage are shown in Figures 3(a–d) and 4(a–d). It is seen that in both samples LC droplets are uniformly distributed inside



(a) (b) (c) (d)

FIGURE 3 Optical textures for PDNLC sample at various applied voltage ($f = 500\,\text{Hz}$) at room temperature (a) $0\,V_{p\text{-}p}$, (b) $10\,V_{p\text{-}p}$, (c) $30\,V_{p\text{-}p}$ and (d) $100\,V_{p\text{-}p}$.

the polymer matrix exhibit different configurations (bipolar, axial, radial, maltese). The densities of droplets in GHPDNLC sample are found higher than in PDNLC sample.

Out of these structures, bipolar configurations is dominant in comparison to others configurations. The approximate size of droplets was noticed in the range of $\sim 5\text{–}40\,\mu\text{m}$ in both samples. The droplet size was measured using Linksys software by taking the mean of major to minor axis of about 50 random droplets. It was observed that in GHPDNLC sample, at lower voltage ($\leq 10\,V_{p\text{-}p}$), LC droplet orientation does not change much vary, however at higher voltage ($\geq 80\,V_{p\text{-}p}$) bipolar configuration adopts a maltese type crosses (Fig. 4–d).

3.2. Temperature Dependence

The voltage dependence of the output transmission at different temperatures for PDNLC and GHPDNLC samples is shown in

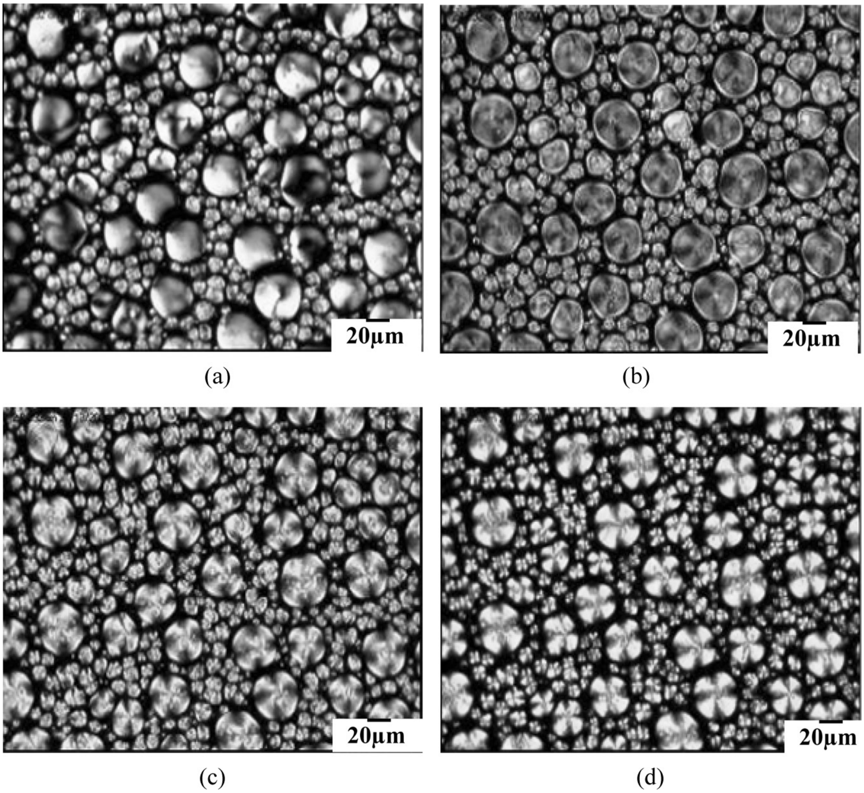
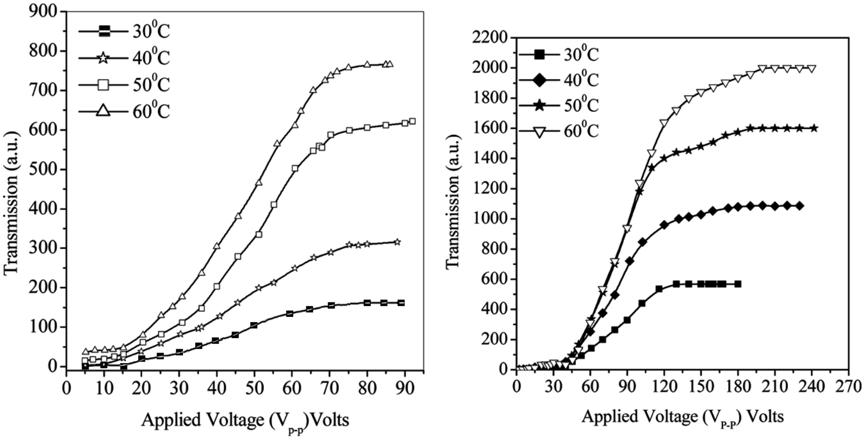


FIGURE 4 Optical textures for GHPDNLC sample at various applied voltage ($f = 500$ Hz) at room temperature (a) 0 $V_{p\text{-}p}$, (b) 10 $V_{p\text{-}p}$, (c) 30 $V_{p\text{-}p}$ and (d) 100 $V_{p\text{-}p}$.

Figures 5(a,b). It depicts that as the temperature increases (room temperature to T_{NI}), the optical transmission increases and tends to saturate at higher applied voltage. The increase in transmission with temperature may be due the decrease in order parameter and matching the refractive index of LC with polymer matrix (i.e. $n_o \approx n_p$). As the temperature of the sample increases from room temperature to T_{NI}, the extraordinary refractive index decreases, and ordinary refractive index increases and shows maximum transmission near the T_{NI}.

We observed that the threshold voltage (V_{th}) of GHPDLC is relatively higher than PDNLC. It could be due to the enhancement in relatively viscosity of dye dispersion and the steric hindrances between the LC and dye molecules.

Generally, a decrease in V_{th} with increasing temperature was noticed in PDNLC films. J. W. Han [19,20] studied the EL213/PN393



(a) (b)

FIGURE 5 Variation of applied voltage ($f = 500$ Hz) on optical transmission at different temperatures for (a) PDNLC, (b) GHPDNLC samples.

system and observed a decrease in V_{th} with increasing the temperature. A. Fuh [21] also notices a similar behavior in V_{th} with temperature for E7/EPO305 film.

We have tried to explain this behavior on the basis of reduction in effective electric field (or effective voltage) across the droplets when film is in under external electric field [17].

The effective electric field E_{eff} across a nematic LC droplet can be computed by considering both conductivity and dielectric terms at different frequencies and can be written as [22,23]

$$E_{eff} = E_a \frac{3\sigma_{pol}}{2\sigma_{pol} + \sigma_{LC}} \quad \text{(for conductive terms)} \tag{1a}$$

and

$$E_{eff} = E_a \frac{3\varepsilon_{pol}}{2\varepsilon_{pol} + \varepsilon_{LC}} \quad \text{(for dielectric terms)} \tag{1b}$$

The threshold voltage V_{th} for bipolar droplet was computed using the equation [17];

$$V_{th} = \frac{d}{cR}\left[\frac{K(l^2 - 1)}{\varepsilon_0\ \Delta\varepsilon}\right]^{1/2} \tag{2}$$

The pre-factor 'c' is given by $\frac{3\sigma_{pol}}{\sigma_{LC}+2\sigma_{pol}}$.

The used symbols in Equations 1(a,b) and (2) have usual meaning and defined earlier [17].

Separating out the temperature dependent terms, Equation (2) can be written in the form [19,20]

$$V_{th} \propto (K/\Delta\varepsilon)^{1/2} \tag{3}$$

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 [24].

From Equations 1(a,b) and (2) it can be seen that V_{th} is inversely proportional to effective field across the LC droplets. The applied electric field produces a depolarization field inside the composite film due to movement of ions. Depolarization field opposes the applied electric field and reduces the effective field across the LC droplet. The competition between the depolarization field and the applied electric field at higher voltage may in turn reduce the total effective field across the droplets thus contributing higher V_{th}.

3.3 Electro-Optic Responses

The optical response time such as rise time (τ_r) allows us to define not only the electro-optical properties of the condensed materials but also allows their performance for practical applications.

The rise term is computed as;

$$\frac{1}{\tau_r} = \frac{1}{\gamma}\left[\Delta\varepsilon\, E^2 + \frac{K(l^2-1)}{R^2}\right] \tag{4}$$

where γ is the rotational viscosity coefficient, E is the applied electric filed, and other symbols bear the same meaning defined earlier [23]. [τ_r is conventionally defined as the time required for transmission change from 10 to 90% upon switching the film].

For larger voltages, τ_r is given by

$$\tau_r \cong \frac{\gamma}{\Delta\varepsilon\, E^2} \quad \text{Or} \quad \tau_r \propto \frac{1}{E^2} \tag{5}$$

Rise time is a function of electric field, viscosity, resistivity and dielectric anisotropy. The modulation of response time is due to different dynamics when the system passes during OFF-state to ON-state and in reverse. In the ON-state of the sample, molecular orientation occurs under the action of the external electric field that competes with the elastic torque, main cause of the initial undistorted alignment.

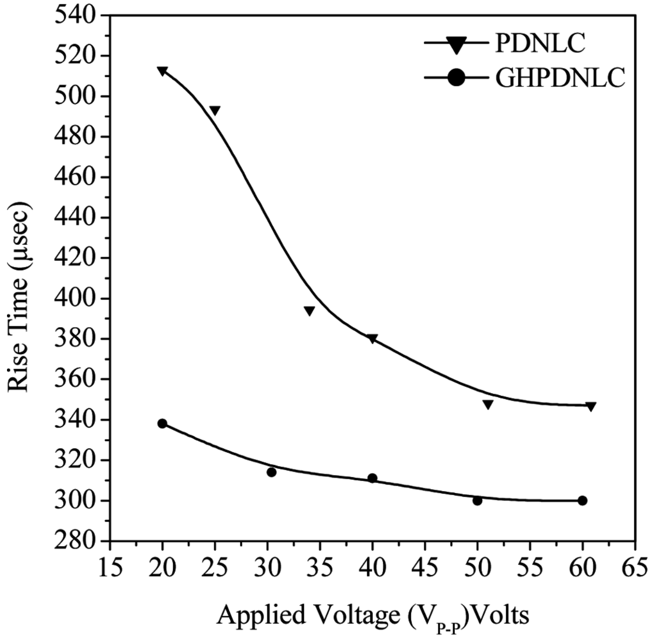


FIGURE 6 Dependence of applied voltage ($f = 500\,\text{Hz}$) on rise time for PDNLC and GHPDNLC samples at 40°C.

The voltage dependence of the magnitude of rise time for both samples is shown in Figure 6. It can be seen that τ_r decreases with increasing the applied voltage and follow the same behaviour as predicted by the theory Equation (5). It can be seen that GHPDNLC sample shows faster switching time than PDNLC.

4. CONCLUSIONS

Systematic method for phase separated PDNLC and GHPDNLC is given and their electro-optic and thermo-optic responses as a function of applied voltage and temperature have been investigated. Various LC droplet configurations were observed in which bipolar droplets dominate in both samples. It was notice that bipolar droplets were slightly unaffected at lower field (~1 V/μm) and adopts a maltese type crosses at much higher fields 8 V/μm and 10 V/μm for PDNLC and GHPDNLC samples respectively.

The optical transmission increases with increasing the temperature and then saturates at higher voltage for GHPDNLC and PDNLC films. Guest host PDNLC sample shows ~ 4 times higher transmission over PDNLC. Threshold voltage $(V_{\mathrm{th}}^{\mathrm{GHPDNLC}} \rangle V_{th}^{\mathrm{PDNLC}})$ increases with increasing the temperature due to reduction in total effective field across to LC droplets. Our result indicates that GHPDNLC sample shows faster switching time (~340 μsec) than PDNLC (~510 μ sec) at 40°C and is in good agreement with pre-defined theory.

REFERENCES

[1] Drazic, P. S. (1995). *Liquid Crystal Dispersion*, World Scientific, Singapore.
[2] Simoni, F. (1997). *Non Linear Optical Properties of LC & PDLCs*, World Scientific: Singapore.
[3] Doane, J. W., Golemme, A., West, J. L., Whitehead, J. B., & Wu, B. G. (1988). *Mol. Cryst. Liq. Cryst. 165*, 511.
[4] Fergason, J. L. (1984). *Encapsulated Liquid Crystal and Methods*, U.S. Patent, 4435047.
[5] Smith, G. W. (1993). *Mol. Cryst. Liq. Cryst.*, *225*, 113.
[6] Jain, S. C. & Rout, D. K. (1991). *J. Appl. Phys.*, *70*, 6988.
[7] Rout, D. K. & Jain, S. C. (1991). *Jpn. J. Appl. Phys.*, *30*, L1412.
[8] Doane, J. W., Vaz, N. A., Wu, B. G., & Zumer, S. (1986). *Appl. Phys. Lett.*, *48*, 269.
[9] Simoni, F. & Francescangeli, O. (2000). *Intern. J. Polymeric Mater.*, *45*, 381.
[10] Drzaic, P. S. (1996). *Pure & App. Chem.*, *68*, 1435.
[11] Zhou, J., Petti, L., Mormile, P., & Roviello, A. (2004). *Opt. Commu.*, *231*, 263.
[12] Hall, J. E., & Higgins, D. A. (1998). *Langmuir*, *14*, 1945.
[13] Kumar, P., & Raina, K. K. (2007). *Curr. Appl. Phys.*, *7*, 636.
[14] Kumar, P., Raina, K. K., & Malik, P. (2006). *Bull. Mater. Sci.*, *29*, 596.
[15] Merck, E. (2002). Data sheet.
[16] Data sheet, Norland, Cranbery, NJ, 08512, USA.
[17] Malik, P. & Raina, K. K. (2004). *Opt. Mat.*, *27*, 613.
[18] Malik, P., Ahuja, J. K., & Raina, K. K. (2003). *Curr. Appl. Phys.*, *3*, 325.
[19] Han, W. (2001). *Liq. Cryst.*, *28*, 1487.
[20] Han, J. W., Kang, T. J., & Park, G. (2000). *J. Kor. Phys. Soc.*, *36*, 156.
[21] Fuh, A. Y. G., Ko, T. C., Chyr, Y. N., & Huang, C. Y. (1993). *Jpn. J. Appl. Phys.*, *32*, 3526.
[22] Wu, B. G., Erdmann, J. H., & Doane, J. W. (1989). *Liq. Cryst.*, *5*, 1453.
[23] Kelly, J. & Seekola, D. (1990). *Proc. SPIE*, *1257*, 17.
[24] Chandrashekar, S. (1992). *Liquid Crystal 2nd edn.*, Cambridge University Press, Singapore.