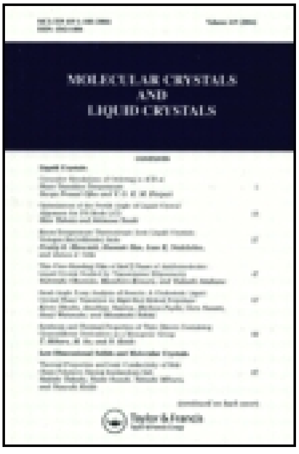

Molecular Crystals and Liquid Crystals Incorporating Nonlinear Optics
Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/gmcl17

Electro-Optic Studies on Polymer Dispersed Liquid Crystal Films Prepared by Solvent- Induced Phase Separation Technique

S. C. Jain [a] , D. K. Rout [a] & S. Chandra [a]
[a] National Physical Laboratory, Dr. K. S. Krishnan Road, New Delhi, 110012, India
Version of record first published: 04 Oct 2006.

Mol. Cryst. Liq. Cryst., 1990, Vol. 188, pp. 251–259
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Printed in the United States of America

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S. C. JAIN, D. K. ROUT and S. CHANDRA
National Physical Laboratory, Dr. K. S. Krishnan Road, New Delhi 110012, India

(*Received March 6, 1990; in final form June 18, 1990*)

The electro-optic performance characteristics of PDLC films using two different polymers, namely, poly (methyl methacrylate) (PMMA) and poly (vinyl chloride:vinyl acetate 17%) (PVC:VAC-17) and liquid crystal mixture E-8 (BDH, England) have been studied. It is found that the PMMA-based PDLC films have more superior mechanical and electro-optical properties than the PVC:VAC-17-based PDLC films. The performance characteristics of PDLC films, in general, improve significantly with increasing temperature. An optimum weight fraction of liquid crystal mixture is to be added in the polymer for good performance of the PDLC films. The finite solubility of liquid crystal mixture in the polymer affects the properties of the polymer matrix and hence the electro-optic performance characteristics significantly.

Keywords: polymer dispersed liquid crystal (PDLC), PMMA, PVC:VAC-17

1. INTRODUCTION

Polymer-dispersed liquid crystals (PDLCs) are emerging as an important class of new materials which are very interesting systems both from a basic[1] as well as an application[2–4] point of view. They are likely to be one of the most potential candidates for the fabrication of large-scale displays for outdoor applications and light shutters for controlling solar energy. In a PDLC film, a liquid crystalline material with large positive dielectric anisotropy and large birefringence is imbedded in an isotropic polymer matrix in the form of very fine droplets of micron and sub-micron sizes. The direction of the liquid crystal director varies from droplet to droplet. The interface between the polymer and the liquid crystal droplet provides optical discontinuity due to the mismatch of the refractive index of the polymer and that of the liquid crystal. So, when white light is incident on such a film, it is strongly scattered in the forward direction and renders the film a milky white appearance. However, on application of an appropriate electric field, the liquid crystal molecules within the droplets realign themselves in the direction of the field and if the ordinary refractive index n_o of the liquid crystal matches with that of the polymer, n_p, an opaque state becomes transparent. The electro-optic characteristics of a PDLC film depend on a variety of material and fabrication parameters such as (a) choice of polymer, (ii) choice of liquid crystal, (iii) solubility of liquid crystal in polymer, (iv) shape, size and density of the liquid crystal droplets, (v) temperature etc.

We have carried out detailed electro-optic studies on PDLC films prepared by the solvent-induced phase separation technique[4] using two different polymers. The salient features of these investigations are reported herewith.

2. EXPERIMENTAL

In the present investigation, PDLC films were prepared using two different polymers, namely, poly (methyl methacrylate (PMMA) and poly (vinyl chloride:vinyl acetate-17%) (PVA:VAC-17), obtained from M/s Polysciences Inc., USA and liquid crystal mixture, E-8 from M/s B.D.H. England. The polymers PMMA and PVC:VAC-17 have the refractive index, n_p = 1.49 and 1.52 respectively at room temperature (23°C), which is very close to the refractive index, n_o, of the liquid crystal mixture, E-8 (n_o = 1.52 at 23°C). Each polymer has low solubility of the liquid crystal mixture. The PDLC films were prepared using the solvent induced phase separation technique. Appropriate quantities of the liquid crystal mixture and of the polymer were dissolved in a common solvent (chloroform/acetone) in various weight proportions. The homogeneous solution of each concentration was spread in the form of a film in a suitable cast. On solvent evaporation a strongly scattering white film was obtained. The thickness of the prepared film was measured by a Surfometer SF-200 (M/s Planer industrial, UK). Films of various thicknesses ranging from 10–50 μm were prepared. The PDLC film was peeled-off from the substrate and was sandwiched between two transparent conducting glass plates under simultaneous application of heat and pressure. The scattering and electro-optic characteristics of the PDLC films depended strongly on the thermal history of the films. The electro-optic transmission properties were measured by a simple set-up in normal transmission geometry using a He-Ne laser light source (λ = 632.8 nm) along with a RCA-931A photomultiplier tube. The temperature of the cell was controlled by a water circulator (Julabo HC-40, W. Germany) to an accuracy of ±0.1°C. The refractive index measurements were carried out using an Abbe refractometer. It was ensured that the polymer films were completely solvent-free before making the refractive index measurements.

3. RESULTS AND DISCUSSION

Electro-optic transmission characteristics of the various PDLC films of different thicknesses using PMMA and E-8 in a fixed weight proportion were studied. It was seen that the films had a threshold field behaviour. The OFF state transmission decreased strongly with increasing thickness. The electro-optic transmission properties vary significantly with temperature. Figure 1 shows the variation in trans-

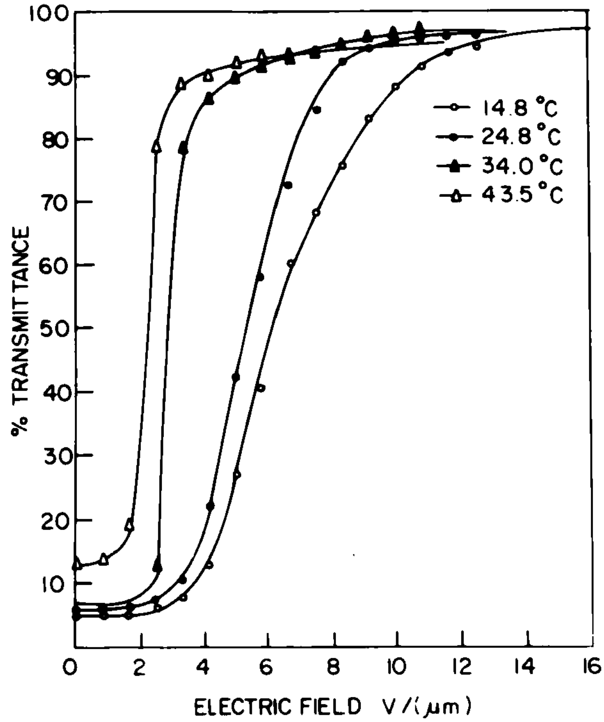

FIGURE 1 Transmittance vs. electric field characteristics of (PMMA: E8) at different temperatures.

mittance as a function of applied ac field (f = 50Hz) in a PMMA E-8: 1:1.5 weight proportion, 12 μm thick film at various temperatures. It is immediately seen that the threshold field decreases and the threshold sharpness increases with increasing temperature. The threshold field, E_{th} decreases from 3.6 (V/μm) to 1.6 (V/μm) and ΔE (difference in the electric field required to change the transmittance from 10% to 90%) decreases from 6.4 (V/μm) to 1.4 (V/μm) as the temperature increases from 14.8 to 43.5°C. It is further seen that the OFF state transmission increases considerably with increasing temperature and at the nematic-isotropic (N-I) transition temperature, the PDLC film becomes fully transparent. The highly transparent state of the PDLC films beyond the nematic-isotropic transition temperature cannot be accounted for on the basis of the refractive index matching hypothesis. As such, there is relatively a large difference between the refractive index of the polymer and of the liquid crystal, beyond the N-I transition temperature (Figure 4). The transparent state may arise due to the dissolution of the LC mixture in the polymer matrix and thus leaving no scattering sites. However, detailed studies are underway so as to clearly bring out the role of birefringence and refractive index mismatch on the scattering properties of the PDLC films. Depending upon the rate of cooling from the N-I transition temperature, the OFF state transmission and the electro-optic transmission characteristics are affected considerably. Very rapidly-cooled films showed a higher scattering OFF state and a relatively larger threshold field in comparison to the slowly-cooled films. The difference in transmission characteristics arises mainly because of variation in the droplet sizes due to the different cooling rates. The rapidly-cooled films have a much smaller droplet size than the slowly-cooled films. The size of the droplets was determined by Scanning Electron Microscopy.

The role of liquid crystal concentration on the performance characteristics of PDLC films has also been investigated. PDLC films having a different weight proportion of PMMA: E8 ranging from 1:0.8 to 1:2.5 were prepared. It was observed that in the PDLC films with the concentration of E-8, ≲ 40%, the OFF state transmission was rather high and the films did not exhibit good electro-optic transmission behaviour. Figure 2 shows a set of transmittance versus applied field curves of PDLC films with three different concentrations of E-8 in PMMA at 25°C for 20 μm thickness. It was found that the transmission characteristics did not show any significant variation in PMMA: E8 films in the range, 1:1.5 to 1:2.5. However, the 1:1 PDLC films showed higher OFF state transmission and also lower threshold field. The 1:1.5 PDLC films showed good performance characteristics. An excessive amount of E-8 in PDLC film (≳ 70%) was also undesirable, as it could not be contained in the micro-pores. The different concentrations of E-8 in PDLC films also affected the transmission-versus-temperature behaviour significantly. Figure 3 shows the variation in transmittance-versus-temperature for various PMMA: E8 films. It can be seen that the OFF state transmission increases with increasing temperature and at the N-I transition temperature, the transmission becomes 90%.

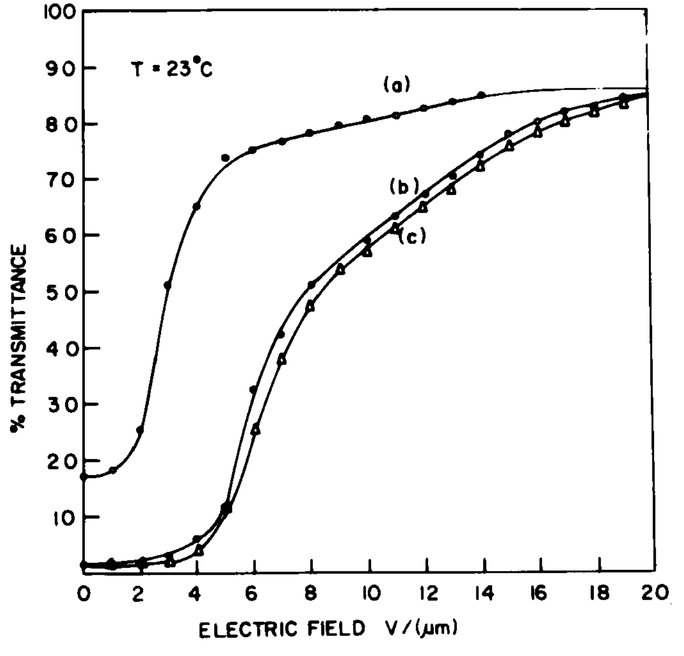

FIGURE 2 Transmittance vs. electric field characteristics of PDLCs with various liquid crystal compositions (a) PMMA: E8 = 1:1, (b) PMMA:E8 = 1.1.5, (c) PMMA: E8 = 1:2.5.

However, the N-I transition temperature is influenced by the concentration of polymer with respect to that of E-8. When the concentration of PMMA is large (>50%) (Figure 3a), not only is the N-I transition temperature lowered but also the OFF state transmission starts increasing just beyond 35°C. However, for lower concentration of PMMA (<40%), the N-I transition temperature approaches the N-I value of the pure E-8 and the OFF state transmission also remains practically constant up to 50°C (Figure 3c,d). As the lowering of the N-I transition temperature is governed by the solubility of E-8 in PMMA, it is concluded that the solubility of E-8 in PMMA is not high. It is further concluded from these studies that an optimum radio of PMMA:E-8 in the range of 1:1.5 to 1:2.0 results in PDLC films with good electro-optic performance characteristics.

We have also done detailed investigations on PDLC films using PVC:VAC-17 polymer and E-8. PVC:VAC-17 was chosen as its refractive index (n_p = 1.52) matches very well with that of E-8 at 23°C (Figure 4). The refractive index n_p of PMMA is 1.49 at 23°C.

It was found that PVC:VAC-17-based PDLC films were much more flexible (i.e., they could be easily stretched and deformed) than the PMMA-based PDLC films. Their dimensional stability during handling was not very good. The electro-optic characteristics did not show any significant improvement over PMMA-based films despite the better matching of the refractive index. Figure 5 shows the electro-optic transmission curves of a (PVC:VAC-17): E8: :1:1.5 weight proportion, 10

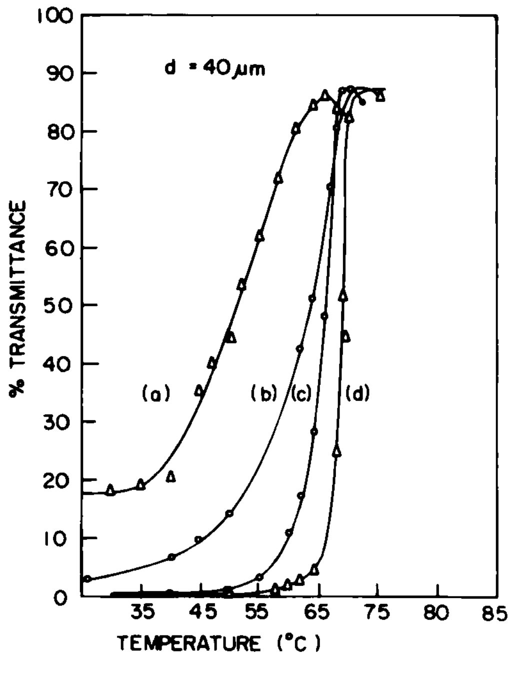

FIGURE 3 Transmittance as a function of temperature of PDLCs with various liquid crystal compositions; PMMA: E8 = 1:0.8 (a), 1:1 (b), 1:1.5 (c) 1:2.5 (d).

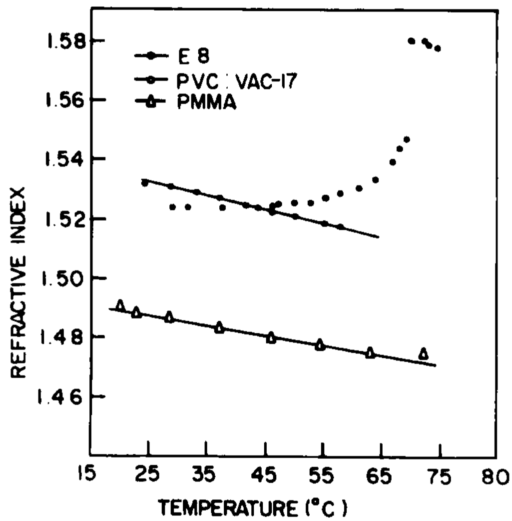

FIGURE 4 Variation of refractive index (n_p) of PMMA, PVC:VAC-17 and n_o of E8 with temperature.

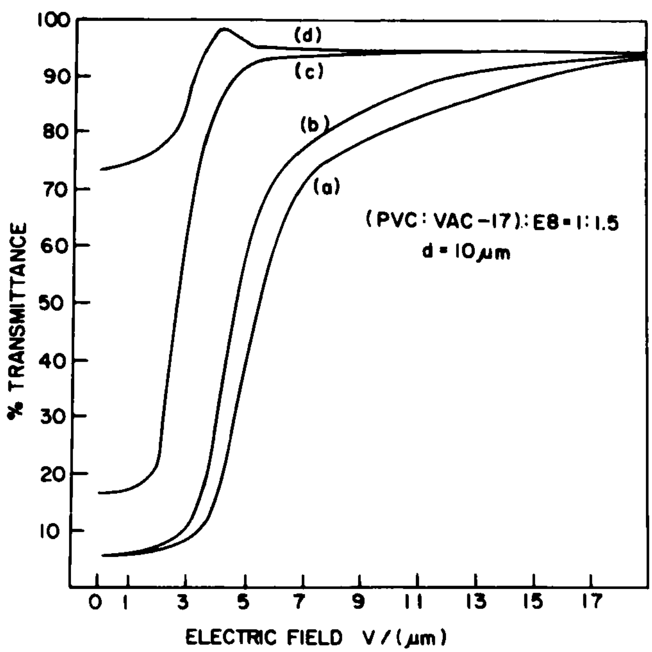

FIGURE 5 Transmittance vs. electric field characteristics of PDLC: E8: (PVC:VAC-17) at different temperatures: (a) 15.5°C, (b) 24°C, (c) 35°C, (d) 40°C.

μm thick film at various temperatures. The qualitative behaviour of these films with respect to the threshold field and its sharpness behaviour were similar to those of PMMA:E8 films. It was also observed that at 25°C, the threshold field value and % transmission behaviour versus applied ac field were nearly identical for PMMA as well as PVC:VAC-17-based PDLC films (Figure 6). However, the temperature dependence of these films did show sufficient variation quantitatively. The N-I transition temperature T_{N-I} ~ 37°C) in PVC:VAC-17 PDLC was very much lower than that in the corresponding PMMA-based film (~ 69°C), as can be seen in Figure 7. Such a significant departure of the N-I temperature is likely to arise mainly due to the higher solubility of E-8 in PVC:VAC-17. The higher solubility of E8 in PVC:VAC-17 is also manifested as these PDLC films are more rubbery and can be easily stretched. No significant improvement in the ON state transmission in the PVC:VAC-17 based PDLC films may also be due to the higher solubility of E-8 in the PVC:VAC-17 polymer, which modifies the properties of the polymer matrix. Detailed investigation of the polymer matrix properties due to definite solubility of liquid crystals is currently underway.

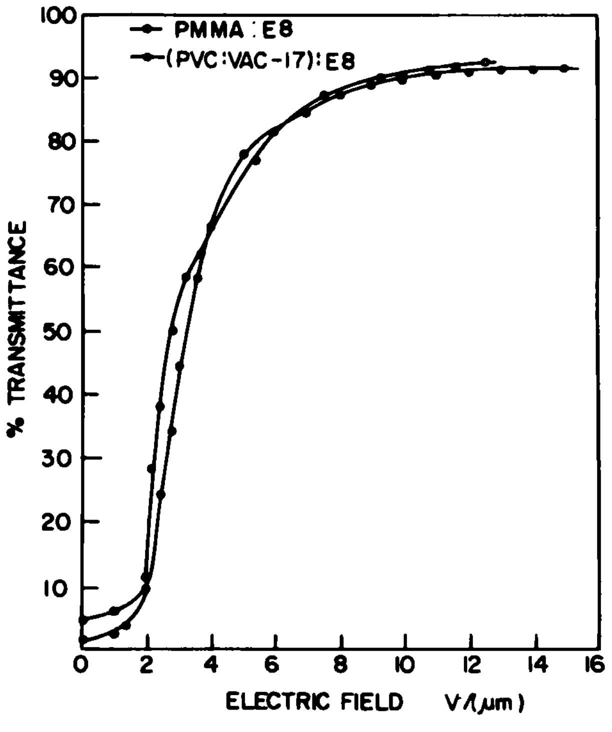

FIGURE 6 Transmittance vs. electric field characteristics of PMMA- and PVC:VAC-based PDLCs at 25°C.

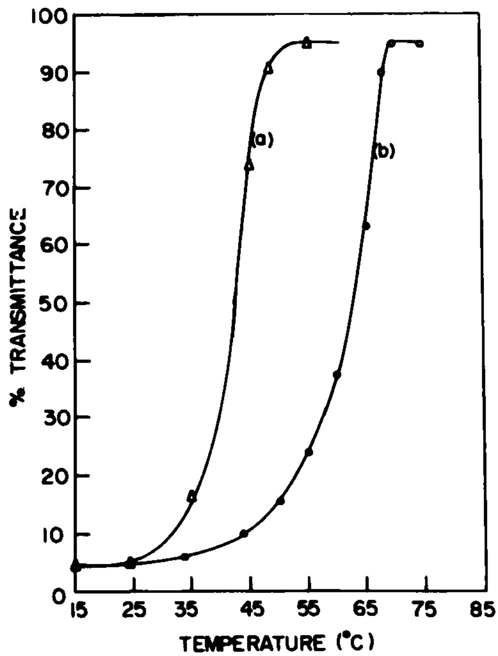

FIGURE 7 Transmittance as a function of temperature of (a) PMMA- and (b) PVC:VAC-based PDLCs with 1:1.5 liquid crystal compositions.

CONCLUSIONS

Good quality PDLC films can be conveniently made by the solvent-induced phase separation technique. The PMMA-based PDLC films are mechanically superior to the PVA:VAC-17-based PDLC films. Despite the better matching of the refractive index, n_p of PVC:VAC-17 and n_o of E-8 in contrast to that of PMMA, the electro-optic performance of PMMA-based films is either better or similar to that of PVC:VAC-17-based PDLC films. The performance of PDLC films improves with increasing temperature. The N-I transition temperature is significantly lowered in PVC:VAC-17-based PDLC films compared to corresponding PMMA-based films. There is an optimum weight fraction of liquid crystal (~ 1.5 times that of the polymer) which should be added in the polymer for good performance of the PDLC films.

Acknowledgments

The authors are grateful to Prof. S. K. Joshi, Director, NPL, for his interest in the present work and his constant encouragement. They are extremely thankful to Dr. Suresh Chand and Dr. V. S. Panwar for supplying the polymer samples.

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