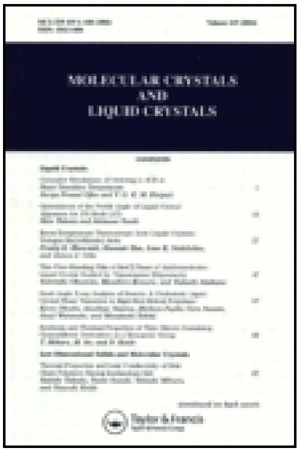

Molecular Crystals and Liquid Crystals Science and Technology. Section A. Molecular Crystals and Liquid Crystals
Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/gmcl19

Influence of Liquid Crystal Concentration on the Electro-Optical Behavior of Polymer Dispersed Liquid Crystal Films Prepared by Electron Beam Processing

U. Maschke [a], A. Traisnel [b], J.-D. Turgis [a] & X. Coqueret [a]

[a] Laboratoire de Chimie Macromoléculaire, CNRS (URA N°351) Université des Sciences et Technologies de Lille, 59655, Villeneuve, ďAscq, France

[b] Ecole Nationale Supérieure de Chimie de Lille Université des Sciences et Technologies de Lille, 59655, Villeneuve, ďAscq, France

Version of record first published: 04 Oct 2006

Mol. Cryst. Liq. Cryst., 1997, Vol. 299, pp. 371–378
Reprints available directly from the publisher
Photocopying permitted by license only

INFLUENCE OF LIQUID CRYSTAL CONCENTRATION ON THE ELECTRO-OPTICAL BEHAVIOR OF POLYMER DISPERSED LIQUID CRYSTAL FILMS PREPARED BY ELECTRON BEAM PROCESSING

U. MASCHKE, A. TRAISNEL+, J.-D. TURGIS AND X. COQUERET
Laboratoire de Chimie Macromoléculaire, CNRS (URA N°351)
+ Ecole Nationale Supérieure de Chimie de Lille
Université des Sciences et Technologies de Lille, 59655 Villeneuve d'Ascq, France

Abstract
Polymer dispersed liquid crystal (PDLC) films can be switched electrically from a light scattering off-state to a highly transparent on-state. Polymerization induced phase separation (PIPS) initiated by electron beam irradiation has been used as a powerful method to obtain defined PDLC films. Blends of an aromatic polyester acrylate in additional monomers were prepared as polymer matrix precursors. The eutectic nematic mixture E7 was used as liquid crystal material in this work. Mixtures including different amounts of these materials were exposed to the electron beam radiation. The optical transmission properties of the obtained PDLC films were investigated as a function of composition and amplitude of the applied AC voltage. The electro-optical curves strongly depend on the liquid crystal concentration and are highly reproducible.

INTRODUCTION

Polymer dispersed liquid crystal (PDLC) films consist commonly of micron sized droplets of low molecular liquid crystal (LC) dispersed in a solid polymer matrix.[1,2] The starting materials are chosen so that an externally electric field applied on the PDLC film align the LC in the droplets and switches the film from a cloudy light scattering off-state to a highly transparent on-state. These new materials are of considerable interest for display applications and light control devices like optical shutters. Polymerization induced phase separation (PIPS) initiated by electron beam (EB) radiation was used to obtain well defined PDLC films.[3-5] High conversion of monomers, controlled degree of crosslinking, fast cure rate and no thermal activation can be achieved by EB processing. Compared with the PIPS process by ultraviolet light,[6] EB curing results in completely crosslinked polymer matrices without the use of any initiating compound.

The electro-optical properties of PDLC films are controlled by several factors including the type of LC and polymer precursor of the initial reactive mixture, film thickness and droplet morphology. To our knowledge, the effects of the LC concentration on the formation and electro-optical behavior of the obtained PDLC films were studied extensively only for the conventional thiol-ene system.[7-9] The present work was focussed on the influence of the ratio of the liquid crystal content to the matrix precursors, keeping the composition of the matrix constant for each of the samples. The scattering efficiency of the PDLC films depending on the LC-content has been examined. The transmission properties of selected films of approximately identical thickness were investigated as function of driving AC voltage and sample composition. The results are discussed in terms of contrast ratio, threshold- and saturation voltage.

EXPERIMENTAL

Materials

The liquid crystal mixture E7 (Merck Ltd, GB) was used during this work; it exhibits the following refractive indices at 20°C: n_o=1.5183, n_e=1.7378 (λ=632.8nm).[10] The prepolymer chosen consists of an aromatic polyester acrylate (Rahn AG, Switzerland) diluted in additional monomers including Tripropyleneglycoldiacrylate (UCB, Belgium). The refractive index of the prepolymer in the cured state in the absence of E7 is n_p=1.5120 (λ = 632.8nm).[11]

Preparation of PDLC films

(100 - x) weight-percent (wt%) of the prepolymer (x=10, 20, ...,90) and x wt% of the liquid crystals were mixed together at room temperature for several hours. The thickness and the uniform application of the reactive initial mixtures on glass plates coated with a thin transparent layer of conducting indium-tin-oxide (ITO) (Balzers, Liechtenstein) was controlled by using a wire wound rod as a bar-coater of 25µm (Braive, Belgium). For each composition, several samples have been prepared and exposed to the electron beam radiation to cure the polymerizable mixture.

Electron beam curing

The electron beam generator used to prepare the PDLC samples by a PIPS process was an Electrocurtain Model CB 150 (Energy Sciences Inc.) with an operating high voltage of 175kV. The glass plates were placed in a sample tray, which was passed under an inert atmosphere to the accelerated electron curtain on a conveyor belt. The applied dose of 60kGy was achieved by using a beam current of 4mA and a conveyor speed of 0.22m/s.

These values have not been changed during the experiments in order to apply each time the same curing conditions. The applied dose was delivered uniformly in the depth of the sample. Heat development during the radiation process could not be controlled as in corresponding experiments using UV-light. [7-9]

Film thicknesses were measured by a micrometer calliper (Mitutoyo; uncertainty: $\pm$ 1μm). To minimize errors in the determination of film thickness, eighteen different places on each plate before and after composite film preparation were taken into account.

Electro-optical measurements

The electro-optical experiments were performed at room temperature by measuring the transmission of unpolarized HeNe laser light at a wavelength of λ = 632.8nm. The glass plates with the PDLC films were oriented normal to the laser beam. The distance between the sample cell and the detector (silicon photodiode) was approximately 30cm. The collection angle of the transmitted intensity was about $\pm$ 2°, so that principally forward scattering was detected. The intensity of transmitted light was recorded on a micro-computer using an interface card (DAS 1600-2). The transmission values were corrected for the loss of transparency which results from the reversible darkening of the glass plates upon EB irradiation.

The scattering properties of the cured PDLC films in the initial off-state were measured at different places on each glass plate allowing to average the obtained transmission values. For electro-optical measurements, the composite film of uniform thickness (15±1μm) was sandwiched by another ITO coated glass substrate and an external electric field was applied across the PDLC film. The output of a frequency generator was amplified and used to drive the shutter device. Starting from the electrical off-state, the applied sinusoidal voltage of frequency 145Hz was increased continuously up to a desired maximum value U_{max}. Subsequenty it was decreased in the same way. The whole scan up and down ramp was usually performed during 120s, an additional measuring time of 60s allows to follow the relaxation behavior of the transmittance in the off-state. The same procedure was repeated twice(ramp 2,3).

RESULTS AND DISCUSSION

Optical properties

The influence of the ratio of the LC content to the polymer matrix precursors on the transmission in the initial off-state (T_0) is presented in Figure 1. In the LC weight percentage range from $0 < x \leq 20$, the transmitted intensity remains nearly unchanged. In this concentration range, the LC molecules form a homogeneous dispersion in the matrix.

This behavior is expected since one observes from the phase behavior of other PDLC systems studied[12] that the formation of micro-droplets appear usually at higher LC concentrations. Significant reduction of the transmitted intensity is obtained if the LC content increases from 20 to 80 wt%. The phase separation LC/polymer matrix gives rise to strong scattering of light for films containing 60 to 80wt% of LC. This concentration range corresponds probably to states below the spinodal curve.

The limit of miscibility of the starting reactive mixture before curing was reached at 70 wt% of LC. Blends including more than 70 wt% of LC did not form homogeneous solutions at room temperature and have not been used for electro-optical measurements.

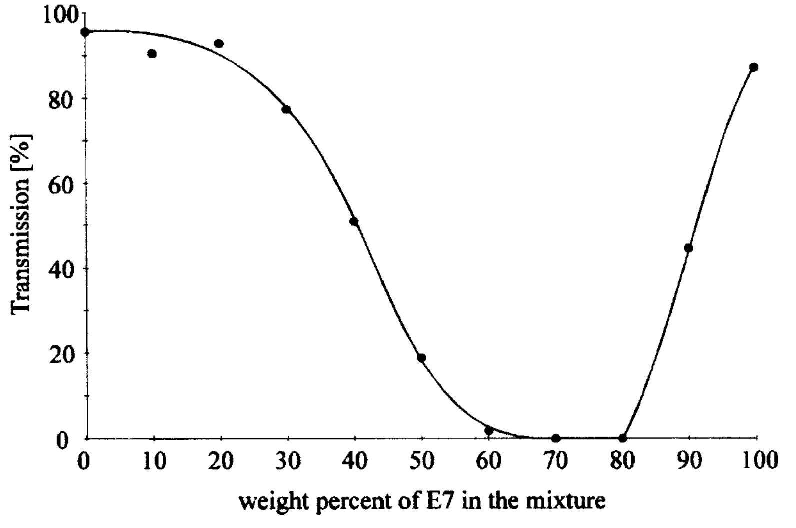

FIGURE 1 Transmission in the initial off-state of EB cured PDLC films (on single glass plates) as a function of liquid crystal content

Electro-optic behavior

Figure 2 illustrates the electro-optical response for the first voltage application (ramp 1 up), when the LC content was varied. The transmission values of all samples including 30 wt% E7 did not change even with the highest voltage (U_{max} = 120 volt) applied on the films. The corresponding data were, therefore, omitted of Figure 2. At the LC concentration of 40 wt%, upon application of a voltage ramp with a maximum of 120 volt, the transmission values only change a few percent. Starting from a high off-state transmission of 50%, the threshold voltage V_{10} (voltage required for 10% of the maximum transmission value) was estimated as high as 60 volt. Constant transmission values characterizing the on-state (T_{100}) were not obtained.

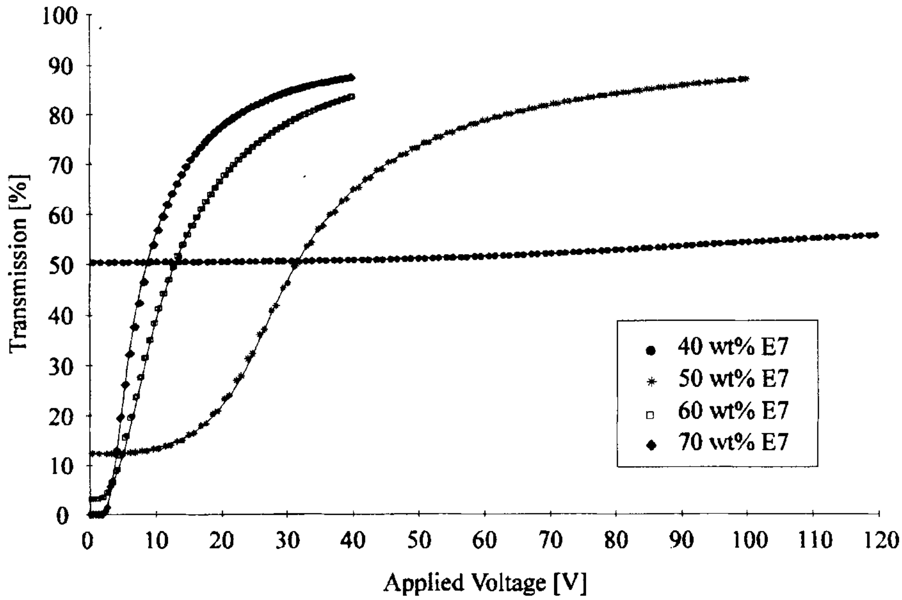

FIGURE 2 Effect of the liquid crystal content on the electro-optical response for the first voltage application (ramp 1 up, λ=632.8nm, ν=145Hz)

The electro-optic characteristics change drastically if the LC content is changed from 40 to 70 wt% : Increasing the LC concentration in this range considerably increases the off-state scattering (as already shown in Figure 1). Simultaneously, threshold and saturation voltage (V_{90}, voltage required for 90% of the maximum transmission) are reduced substantially. The electro-optical curves for samples containing 50 to 70 wt% are characterized by high transmissions in the on-state.

In the case of the 60 wt% E7 composite films, it appears that the on-state transmittance has not yet reached its maximum value with a voltage ramp of U_{max}=40 volt applied across the film. Several cells of the same compositon have been prepared and submitted to voltage ramps including a higher maximum voltage of 60 volt. It was found that the transmission vs. voltage curve remain nearly unchanged except, of course, for voltages higher than 40 volt. Characteristic results are gathered in Table I. The maximum transmission values for both 60 wt% E7 films were slightly lower (T_{100} = 83.8% and 80% for voltage maxima of 40 volt and 60 volt, respectively) than the corresponding values for the 50 and 70 wt% E7 samples. Further investigations will be necessary to clarify this dependence.

The effect of LC content on V_{10} and V_{90} is presented in Figure 3. An increase in the E7 concentration results in a decrease of the turn-on voltage region (the difference between V_{90} and V_{10}). Both V_{10} and V_{90} depend strongly on the LC concentration and seem to reach an asymptotic plateau value at 70 wt% of E7.

Composite films containing 70 wt% of LC exhibit strongly scattering in the off-state, low threshold and saturation voltages (V_{10}=3.6 volt; V_{90}=21 volt), and a high contrast ratio[13] (by calculating T_{100}/T_0). The results obtained for the different LC concentrations characterizing the electro-optical properties are summarized in Table I. The influence of the LC content on hysteresis and memory effects will be discussed in a forthcoming paper.

TABLE I Influence of the LC content on scattering properties of PDLC films (from the first ramp up cycle)

wt% of E7	40	50	60	60	70
U_{max} (volt)	120	100	40	60	40
T_0 (%)	50.5	12.3	3.1	2.7	0.06
T_{10} (%)	51.5[a]	19.8	11.2	10.4	8.8
T_{90} (%)		79.6	75.7	72.3	78.8
T_{100} (%)		87.1	83.8	80.0	87.6
$\Delta T = T_{100} - T_0$ (%)		74.8	80.7	77.3	87.54
V_{10} (volt)	60[a]	18.3	4.6	5.0	3.6
V_{90} (volt)		62.4	27.3	31.8	21.0
$\Delta V = V_{90} - V_{10}$ (volt)		44.1	22.7	26.8	17.4
$V_{H50} = \Delta V_{50}$(volt) (ramp 1 up - ramp 1 down)	30[a]	18.0	2.6	5.1	2.6
CR= contrast ratio = $\frac{T_{100}}{T_0}$	1[a]	7	27	30	1460

Note: a: estimated values

It has been shown[7-9] that the effects of the LC concentration on the electro-optical behavior for the Norland thiol-ene/E7 composite films strongly depend on droplet size and density. SEM (Scanning Electron Microscopy) analysis revealed a few droplets of small size at a concentration of 40% E7 leading to a relatively high off-state transmission and high threshold and saturation voltages. Films containing 66.4% of E7, on the other hand, were characterized by a great number of larger droplets resulting in low off-state transmission and low values for V_{10} and V_{90}. These results are in good agreement with the present observations.

Furthermore, it has been shown recently, that the 50 wt% E7 - composite film exhibits a swiss cheese morphology.[14] Monodisperse droplet size distributions with an average droplet size in the range of 0.5μm have been found by SEM analysis. The volume fraction of LC droplets in the PDLC film was around 50%. Interestingly, in spite of the relatively small number density of droplets, the corresponding electro-optical curves are characterized by quite low off-state transmission values. This might be due to the fact, that scattering is most efficient if the droplet size is in the order of the wavelength of incident light. Preliminary observations on samples containing 60 wt% E7 revealed a greater number of slightly smaller droplets as compared to the 50 wt% LC sample. These observations are in general agreement with the studies performed on the thiol-ene/E7 films. Further studies are in progress to investigate more precisely the relationship between the droplet morphology and the electro-optical behavior.

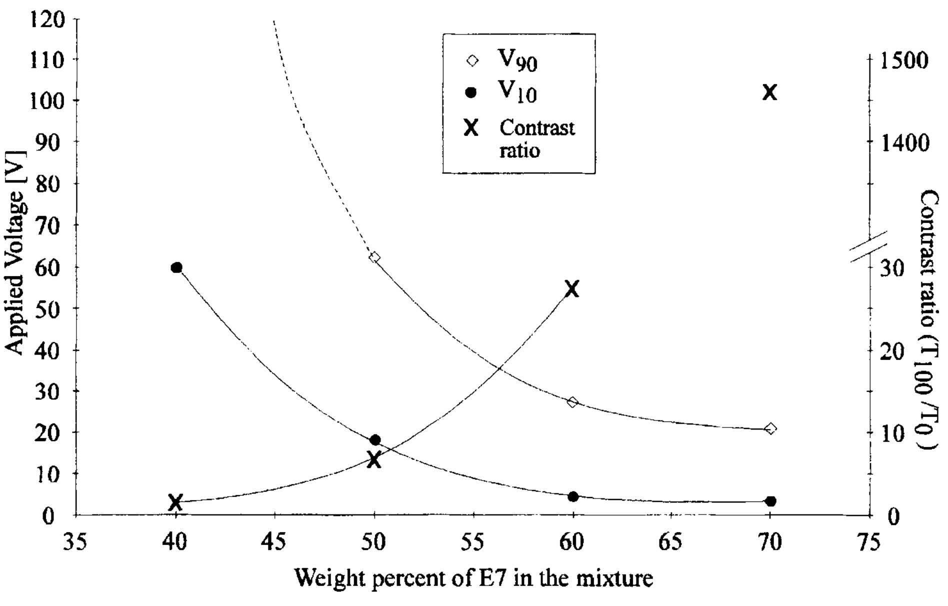

FIGURE 3 Liquid crystal concentration effect on threshold voltage V_{10}, saturation voltage V_{90} (dotted line: estimated curvature) and contrast ratio (ramp 1 up, λ=632.8nm, ν=145Hz)

CONCLUSION

Various mixtures made of LC E7 and a reactive blend of acrylate derivatives were efficiently cured by EB radiation using a polymerization induced phase separation process. The electro-optical properties of the obtained composite films are strongly related to the LC concentration. High off-state scattering was obtained for compositions containing 60 to 80 wt% of LC. The electro-optical curves for samples of 50 to 70 wt% E7 can be characterized by high transmission values in the on-state. Increasing the LC content from 40 to 70 wt% leads to substantially reduced threshold and saturation voltages. The best electro-optical performance including a high contrast ratio was found for films composed of 70 wt% of E7. Further analysis of the PDLC materials is in progress.

ACKNOWLEDGEMENTS

The authors gratefully acknowledge the support of the C.N.R.S., the Région Nord-Pas de Calais and the Ministère de l'Enseignement Supérieur et de la Recherche. The authors are indebted to C. Dérouard and Prof. Dr. M. Benmouna for their assistance.

REFERENCES

1. J.W. Doane in Liquid Crystals-Applications and Uses, edited by B. Bahadur (World Scientific, Singapore, 1990), Vol. 1, Chap. 14, pp. 361-395.
2. H.S. Kitzerow, Liq. Cryst., 16, 1 (1994).
3. N.A. Vaz, G.W. Smith, and G.P. Montgomery Jr, Mol. Cryst. Liq. Cryst., 197, 83 (1991).
4. U. Maschke, X. Coqueret, and C. Loucheux, J. Appl. Polym. Sci., 56, 1547 (1995).
5. U. Maschke, X. Coqueret, and C. Loucheux, Nuc. Instr. Meth. Phys. Res. B, 106, 262 (1995).
6. N. A. Vaz, G.W. Smith, and G.P. Montgomery Jr, Mol. Cryst. Liq. Cryst., 146, 1 (1987).
7. A.M. Lackner, J.D. Margerum, E. Ramos, and K.-C. Lim, Proc. SPIE, 1080, 53 (1989).
8. J.D. Margerum, A.M. Lackner, J.H. Erdmann, and E. Sherman, Proc. SPIE, 1455, 27 (1991).
9. J. Kelly, W. Wu, and P. Palffy-Muhoray, Mol. Cryst. Liq. Cryst., 223, 251 (1992).
10. a) Merck Liquid Crystals, Licrilite Brochure (1994); b) H.A. Tarry, The refractive Indices of Cyanobiphenyl Liquid Crystals, Merck Ltd, Great Britain (1967).
11. U. Maschke, M. Ismaili , X. Coqueret, G. Joly, to be published.
12. J.L. West, Mol. Cryst. Liq. Cryst., Inc. Nonlin. Opt., 157, 427 (1988).
13. A.M. Lackner, J.D. Margerum, E. Ramos, S.-T. Wu, and K.-C. Lim, Proc. SPIE, 958, 73 (1988).
14. U. Maschke, J.-M. Gloaguen, J.-D. Turgis and X. Coqueret, Mol. Cryst. Liq. Cryst, 282, 407 (1996).