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

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Version of record first published: 24 Sep 2006

To cite this article: F. Gyselinck, L. Mechernene, U. Maschke, A. Traisnel & X. Coqueret (2001): Polymer Dispersed Liquid Crystal Films Prepared by Electron Beam Curing: Influence of the Nature of the Polymer Precursor, Molecular Crystals and Liquid Crystals Science and Technology. Section A. Molecular Crystals and Liquid Crystals, 368:1, 651-659

To link to this article: http://dx.doi.org/10.1080/10587250108029998

Mol. Cryst. and Liq. Cryst., 2001, Vol. 368, pp. 651-659
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Polymer Dispersed Liquid Crystal Films Prepared by Electron Beam Curing: Influence of the Nature of the Polymer Precursor

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Polymer dispersed liquid crystal (PDLC) films were prepared by a polymerization induced phase separation (PIPS) process of mixtures composed of monomers and the nematic liquid crystal (LC) E7. Electron beam (EB) radiation was employed to initiate the PIPS process. Mixtures of the LC E7 and selected well characterized di- and tri-functional acrylate monomers as polymer precursors have been exposed to a defined amount of dose of EB radiation. Tripropylene-glycoldiacrylate (TPGDA), propoxylated glyceroltriacrylate (GPTA), and a 1:1 mixture of these materials were used as monomers. The concentration of E7 in the initial mixture was kept constant at 70 weight-%. It was shown that the electro-optical properties strongly depend on the nature and the functionality of the monomers.

Keywords: Polymer Dispersed Liquid Crystal; monomer; polymer; liquid crystal; electron beam

INTRODUCTION

In recent years there has been growing interest for Polymer Dispersed Liquid Crystal (PDLC) systems particularly because they are useful for

many electro-optical applications[1-3]. These materials consist commonly of dispersions of micron-sized droplets of LC in an amorphous polymer matrix. In the so-called normal mode PDLC films can be switched from a scattering off-state to a transparent on-state, when a sufficiently high electrical field is applied. One of the most powerful methods to obtain well defined PDLC films is the polymerization induced phase separation (PIPS) mecanism. In this study the PIPS process has been initiated by electron beam (EB) curing[4-8].

In this communication electro-optical properties of PDLC films prepared by PIPS-EB will be discussed. Earlier investigations on EB-cured systems conducted in our laboratory were based on a commercially available prepolymer mixture based on an aromatic polyesteracrylate[6-8]. Unfortunately the exact composition and structure of the compounds included in this blend were not completely known. The present study involves, therefore, the use of well characterized single monomers as precursors of the polymer matrix. Monomers considered here exhibit two different functionalities, i.e. di- and trifunctional monomers. Tripropyleneglycoldiacrylate (TPGDA), propoxylated glyceroltriacrylate (GPTA), and a 1:1 mixture of these materials were used as monomers. The final mixtures including 70 weight-% (wt%) of nematic LCs E7 and 30 wt% monomer(s) were exposed to a defined amount of dose of EB radiation. The optical transmission properties of the obtained PDLC films are investigated as functions of the applied electrical field, film thickness, and sample composition. The results are discussed in terms of transmission values in the off- and in the on-state, threshold and saturation voltages (voltages required to obtain 10%/90% of the maximum transmission

value), and hysteresis effects. A particular attention was paid to the influence of the functionality of the monomers. To the best of our knowledge such an extended investigation of electro-optical properties on PIPS-EB PDLC films has not been reported before.

EXPERIMENTAL PART

Materials and sample preparation

The eutectic nematic LC E7 (Merck) was used in this work, containing essentially cyanoparaphenylene derivatives. Propoxylated glyceroltri-acrylate (GPTA) and tripropylene glyceroldiacrylate (TPGDA) as monomers were obtained from Cray Valley (France). Mixtures including 30 wt% of the monomer(s) and 70wt% of LC were used for EB-cured samples.

Samples for electro-optical studies were prepared by sandwiching the initial reactive mixture between a glass plate (Balzers, Liechtenstein) and a Polyethyleneterephthalate sheet (Renker, Germany), both coated with a thin transparent layer of conducting indium/tin oxide.

The EB generator was an Electrocurtain Model CB 150 (Energy Sciences Inc.), delivering a high voltage of 175kV. The samples prepared as mentioned above were placed in a tray which was passed under the irradiation source on a conveyor belt. Samples were exposed to a dose of 104kGy by using a beam current of 7mA and a conveyor speed of 0.19m/s. For each composition, several samples have been prepared and exposed to the electron beam radiation to cure the polymerizable mixture.

Electro-optical measurements

The electro-optical experiments were performed at room temperature by measuring the transmission of unpolarized HeNe laser light (λ=632.8nm) passing perpendicular through the PDLC film. Several voltage cycles have been applied using sinusoidal voltages of frequency 145 Hz. The transmission measurements were corrected using appropriate calibration standards.

Electro-optical measurements were performed by applying a linear increasing voltage ramp followed by a decreasing voltage ramp passing through a desired maximum value V_{max}. The whole scan up and down ramp was performed during 120 s, an additional measuring time of 60 s allowed to follow the relaxation behavior of the transmittance in the off-state. A more detailed description of the experimental conditions is given in reference[8].

RESULTS AND DISCUSSION

EB-cured PDLC films based on three different initial monomer/E7 mixtures were investigated : TPGDA/E7, GPTA/E7, and TPGDA/GPTA(1:1)/E7. A chemically crosslinked polymer network will be obtained after EB-curing of the two types of monomers present in the three systems. Only mixtures including monofunctional monomers are expected to be transformed into linear polymers which have been considered elsewhere[9]. In this study the composition of LC was kept constant allowing to compare the obtained results. A particular attention was paid to the relationship between nature and functionality of the monomers on the one hand side and on the transmission properties of

the obtained films with and without application of an electrical field on the other hand.

Transmission in the initial off- and in the on-state

For the three systems involved in this study, Figure 1 illustrates the influence of sample thickness on the maximum transmission in the on-state T_{on} and on the transmission in the initial off-state $T_{off\ init}$. These quantities are represented in Figure 1 on a logarithmic scale. The symbols displayed in the upper part correspond to the values of T_{on}. Interestingly Figure 1 exhibits high transmission values in the on-state reaching nearly 100% for all systems considered here. In particular, the T_{on} values only show a very slight decrease with film thickness, even at values exceeding more than 20μm. This behavior clearly shows that the refractive index matching condition is fullfilled in all cases considered here.

The transmission values in the initial off-states are represented in the lower part of Figure 1. In general the optical transmission of PDLC films at least in the initial off-state can be expressed by writing

$$\log T = \log (I_T/I_0) = - N_v \sigma d \qquad (1)$$

where T represents the optical transmission, I_T is the transmitted intensity, I_0 is the incident intensity, N_v is the number density of LMWLC domains, σ is the scattering cross section of a single domain, and d is the optical path which is in our case identical to the film thickness. The logarithm of the transmission should therefore decrease linearly with film thickness if the product of N_v and σ will be constant. This behavior was indeed found for all systems indicating that the transmission behavior of these polymer/LC materials can be

approximated by considering single particles independently. Multiple scattering effects often found in PDLC systems were not observed for sample thicknesses up to 25µm. For TPGDA/E7, Figure 1 shows a slow decrease of the $T_{off\ init}$ values as a function of thickness compared to the

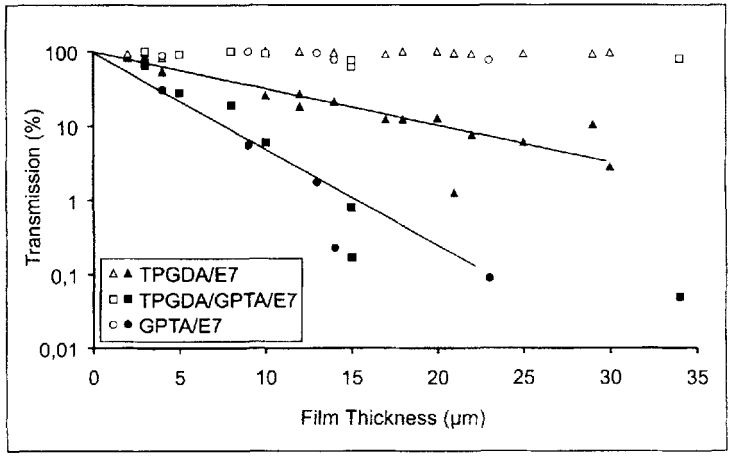

FIGURE 1 Transmission values in the on-state (open symbols) and in the initial off-state of EB-cured PDLC films (closed symbols) (λ=632.8nm, measurements at room temperature).

other systems. Furthermore TPGDA/GPTA/E7 and GPTA/E7 systems exhibit similar $T_{off\ init}$ values at a given sample thickness. As an example, $T_{off\ init}$ values of less than 5% will be obtained for a TPGDA/E7 film exhibiting a thickness of approximately 30µm whereas the same value can already be obtained for a TPGDA/GPTA/E7 or GPTA/E7 sample at a thickness of 10µm. This behavior can be explained by a decrease of the size of LC domains and an increase of their number density in the case of TPGDA/GPTA/E7 and GPTA/E7 systems. Indeed, adding 25% of GPTA to the TPGDA/E7 mixture leads

to a considerable increase in the crosslinking density whereas a complete exchange of TPGDA by GPTA does not furthermore influence the transmission behavior. It should be interesting to evaluate the corresponding electro-optical curves.

Electro-optical curves

Figure 2 exhibits the transmission properties of EB-cured TPGDA/E7 and GPTA/E7 films upon application of an electrical field. A sample thickness of 15μm was selected for this representation making comparison of the results more easier. High transmission values in the on-state in both cases and different values in the initial off-state were observed as already discussed before. In particular, Figure 2 shows

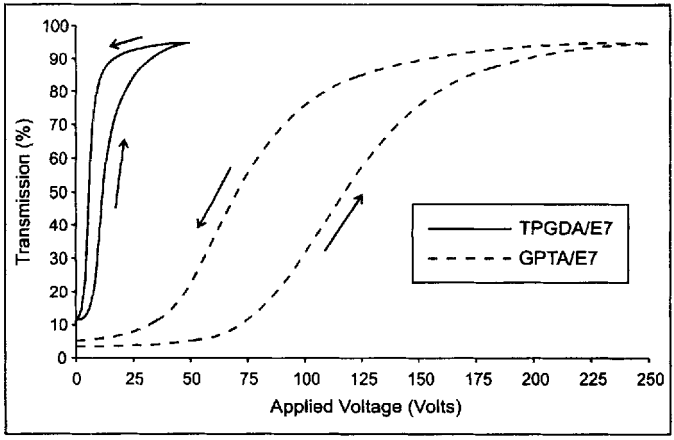

FIGURE 2 Transmission as a function of the applied voltage of 15μm thick EB-cured TPGDA/E7 and GPTA/E7 films (λ=632.8nm, sinusoidal voltage ramps of frequency 145Hz at room temperature).

significantly lower threshold and saturation voltages for the TPGDA/E7 film than for the GPTA/E7 sample. This behavior can be explained by a

decrease of the LC droplet size. Smaller droplets require higher fields for orientation due to their higher degree of curvature[1-2]. Such findings have already been reported on several systems by changing the amount of irradiation dose of a given monomer/LC system : It was found that higher dose values lead to a decrease of the droplet size which in turn requires higher threshold and saturation voltages. In the present case the dose value was kept constant but the additional acrylate function present in the GPTA monomer helps to increase the crosslinking density. The use of GPTA provokes, therefore, a similar electro-optical behavior as if the dose value would have been increased on the TPGDA/E7 system. In all cases discussed here, the values of the transmission in the initial off-state were roughly the same as compared to the following off-states after application of voltage cycles.

CONCLUSIONS

PDLC films based on selected monomer/E7 blends have been successfully prepared by a PIPS-EB process. Two monomers have been considered : TPGDA and GPTA. A 1:1 mixture of these compounds was also taken into account. High transmission values in the on-state have been obtained for all systems considered here. In the case of GPTA/E7, significantly lower transmission values were obtained. However, replacing TPGDA by GPTA as monomer leads to strongly increasing threshold and saturation voltages. A good compromise can be found by considering a 30μm thick PDLC film based on TPGDA/E7 which combines relatively low transmission values in the initial off-state with reduced threshold- and saturation voltages.

Acknowledgement

The authors gratefully acknowledge the financial support of the C.N.R.S, the Région Nord-Pas de Calais, the Ministère de l'Enseignement Supérieur et de la Recherche, and the EU programme FEDER. Part of this work has been accomplished within the scientific agreement CNRS/DRS. We thank these organisations for their kind support.

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