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ELECTRO-OPTICAL AND MORPHOLOGICAL PROPERTIES OF ULTRAVIOLET- AND ELECTRON BEAM – CURED MONOMER/LIQUID CRYSTAL MIXTURES

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Polymer Dispersed Liquid Crystal (PDLC) films are obtained by phase separation induced by Ultraviolet (UV) and Electron Beam (EB) curing techniques. A binary system composed of a monomeric diacrylate and the nematic liquid crystal E7 was employed as initial reactive blend prior to the polymerization/cross-linking processes. The analysis of the electro-optical responses of the obtained PDLC films show certain advantages of EB-cured systems, for

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example lower threshold and saturation voltages. Sample morphologies obtained from scanning electron microscopy observations showed a narrow size distribution of ellipsoidal-type LC droplets for EB-cured samples thus explaining the sharp increase of transmission values as a function of voltage. The slow increase of the transmission with voltage for UV-cured samples can be understood by the large size distribution of irregularly shaped droplets.

Keywords: electron beam curing; liquid crystal; polymer dispersed liquid crystal; polymer network; ultraviolet curing

1. INTRODUCTION

Polymer Dispersed Liquid Crystals (PDLCs), discovered some twenty years ago by Fergason [1,2] and extensively studied world wide by a large number of laboratories [3–14], represent great potential for a variety of electro-optical applications such as smart windows and information displays [15]. In their most common form, PDLC films are made of micron-sized liquid crystalline (LC) droplets dispersed in a solid polymer matrix. The orientation of the LC molecules inside the droplets change upon application of an electrical field and under certain conditions, the intensity of the transmitted light can be varied between an opaque off-state to a transparent on-state.

In this work, PDLC films were prepared by radiation induced polymerization/cross-linking processes from a selected monomer/LC blend. A homogeneous solution of Tripropyleneglycoldiacrylate and the nematic LC mixture E7 was prepared. Two different radiation methods involving UV-[16] and EB-[17] techniques were employed in order to initiate free radical polymerization reactions of the monomer. In the case of UV- curing it was necessary to add a photoinitiator to the initial mixture. During the polymerization/cross-linking reactions, the LC becomes less miscible with the growing polymer, and finally the mixture will separate into two phases, an isotropic polymer network and LC domains exhibiting specific sizes and shapes depending on the curing conditions.

It has already been demonstrated that EB-cured PDLC films show better electro-optical performances than their UV analogues [18,19]. The conditions of preparation were chosen to reach complete conversion of the monomer to a chemically crosslinked polymer network. In this paper the electro-optical response functions of EB- and UV-cured films were analyzed and compared to observations of the sample morphology obtained by scanning electron microscopy (SEM).

2. EXPERIMENTAL PART

A. Materials and Sample Preparation

The nematic LC used in this work is the eutectic mixture E7 (Merck KGaA, Darmstadt, Germany) containing four cyanoparaphenylene derivatives. It exhibits a nematic-isotropic transition temperature at $T_{NI} = 61^{\circ}\text{C}$ and a positive dielectric anisotropy. The monomer is Tripropyleneglycoldiacrylate (TPGDA) (UCB, Belgium). A blend of 30 weight-percent (wt-%) of TPGDA and 70 wt-% of E7 was used for EB-cured samples. UV-cured samples were prepared from the same mixture containing 2 wt-% (of the acrylate mixture) of a conventional photoinitiator (LucirinTPO, BASF). These blends were mixed together at room temperature for several hours until they became homogeneous.

Samples for electro-optical studies were prepared by sandwiching the initial reactive mixture between a glass plate (Balzers, Liechtenstein) and a Polyethyleneterephthalate (PET) sheet (Renker, Germany), both coated with a thin transparent layer of conducting indium/tin oxide (ITO). A 100 μm thick PET-sheet has been used for the UV curing process. Our EB generator requires a thinner PET substrate of 50 μm to allow a uniform penetration of the applied dose in the depth of the sample. In that way, the monomer/E7 mixtures are in contact with both transparent conducting ITO-layers.

The film thickness was measured by a micrometer calliper (Mitutoyo; uncertainty: $\pm 1\mu\text{m}$). No temperature control during the irradiation processes has been performed.

B. Electron Beam Curing

The generator used in our experiments was an Electrocurtain Model CB 150 (Energy Sciences Inc.) with an operating high voltage of 175 kV. The samples prepared as mentioned above were placed in a tray which was passed under the electron-curtain on a conveyor belt. The results presented here correspond to a dose of 105 kGy.

C. Ultraviolet Curing

The UV light source used was a Minicure Model MC4-300 (Primarc UV Technology) equipped with a medium pressure mercury arc lamp rated 80 W per cm. The samples were placed on a conveyor belt and irradiated by a dose of 150 mJ/cm^2 .

D. Electro-optical Measurements

The electro-optical experiments were performed at room temperature by measuring the transmission of unpolarized HeNe laser light ($\lambda = 632.8 \text{ nm}$) passing perpendicular through the PDLC film. An external electric field is applied across the PDLC film. The output of a frequency generator is amplified and used to drive the shutter device. Starting from the electrical off-state, the applied sinusoidal voltage of frequency 145 Hz was increased continuously up to a desired maximum value V_{max} . It is subsequently decreased in the same way. The whole scan up and down ramp takes 120 s with an additional measuring time of 60 s allowing to follow the relaxation behavior of the transmittance in the off-state. The same procedure is repeated several times using the appropriate maximum voltage.

E. Scanning Electron Microscopy

Samples for Scanning Electron Microscope (SEM) studies were elaborated in the same way as described above for electro-optical measurements. After irradiation exposure was finished, the sample cells were opened and immersed in tetrahydrofuran in order to extract the LC. The samples were then coated by a thin platinum layer and characterized by a SEM (Philips XL-30 field emission gun). This sample preparation technique leads to the appearance of dark holes that were once filled with LC. The magnification used in our experiments was about 5000x using an acceleration voltage of 10 kV. The obtained images have been analyzed and the results were collected as histograms.

RESULTS AND DISCUSSION

Figure 1 displays the electro-optical response curves of two $29 \mu\text{m}$ thick EB- and UV-cured PDLC films in terms of the transmission as a function of the applied electrical field. Significant changes in the electro-optical response curves can be observed between UV- and EB-cured films. Indeed, EB-samples can be characterized by lower threshold and saturation voltages compared to the UV-films. These findings are in good agreement with results already found in the literature [18,19]. Furthermore, the hysteresis width is much broader for the UV-sample. The EB-cured sample switches from the opaque off- to the transparent on-state at a distinct value of the electrical field whereas the UV-sample needs a relatively large electrical field range to become transparent. Low off-state- and high on-state transmission values were obtained for both EB- and UV-cured films. A plateau value was easily reached in the case of the EB-sample while constant transmission values were not obtained for UV-cured films.

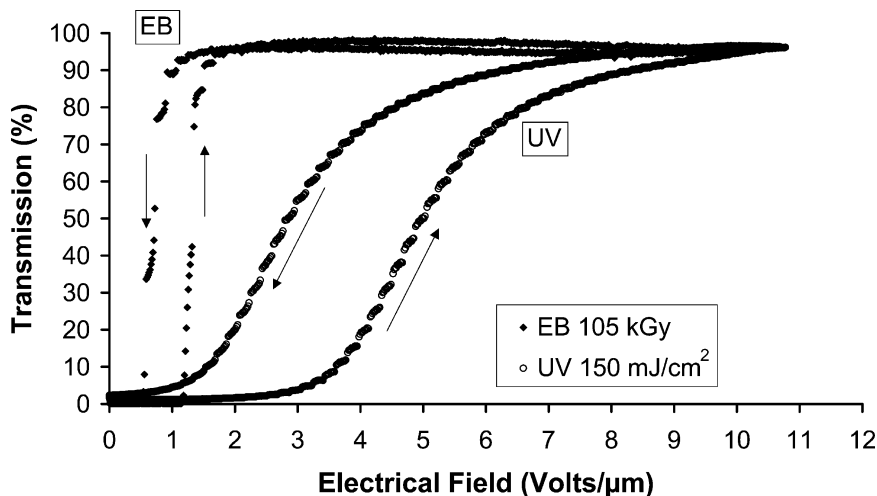


FIGURE 1 Electro-optical response of UV- and EB-cured 30wt-% TPGDA/70wt-% E7 PDLC films ($\lambda = 632.8$ nm, sinusoidal voltage ramps of frequency 145 Hz at room temperature).

Figure 2 gathers the results for threshold (V_{10}) and saturation (V_{90}) voltages of UV- and EB-cured samples collected for a large number of independent samples, characterized by film thicknesses in the range from 4 to 40 μm . As expected from the literature [20], a linear increase of V_{10} and V_{90} with film thickness was found in all experiments. The difference between V_{90} and V_{10} remains nearly constant for EB- films on the scaling of Figure 2 while it increases slightly for UV-cured samples with film thickness. One clearly observes that the UV-cured samples show higher values for both V_{10} and V_{90} , especially for thick films. For example, a UV-cured 30 μm thick PDLC film exhibits threshold and saturation voltages of 100 V and 220 V, respectively, whereas a EB-cured film with the same thickness yields 28 V and 33 V for V_{10} and V_{90} .

The observed electro-optical behavior can be qualitatively explained by analyzing the morphology of UV- and EB- films prepared under the same conditions as those used for the electro-optical experiments. Figures 3a and 3b displays representative SEM pictures of EB- and UV-cured samples, respectively, using the same magnification. These micrographs show a large number of dark domains embedded in a brighter continuous surrounding. The dark domains correspond to the empty cavities after removal of the LC while the surrounding represents the polymer matrix. It can be assumed that no preferential orientation of the droplets takes place during both UV- and EB-curing and that the LC domains are randomly distributed over the

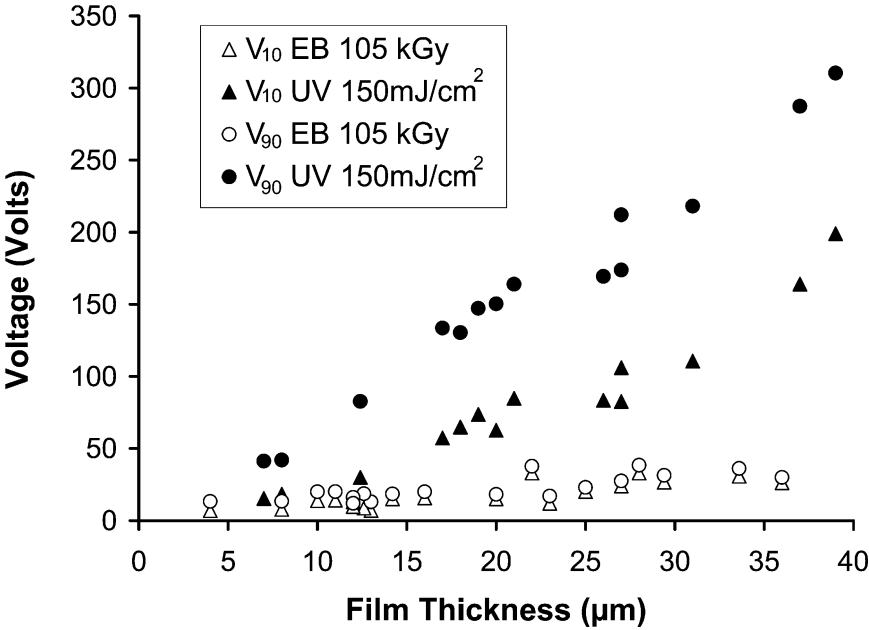
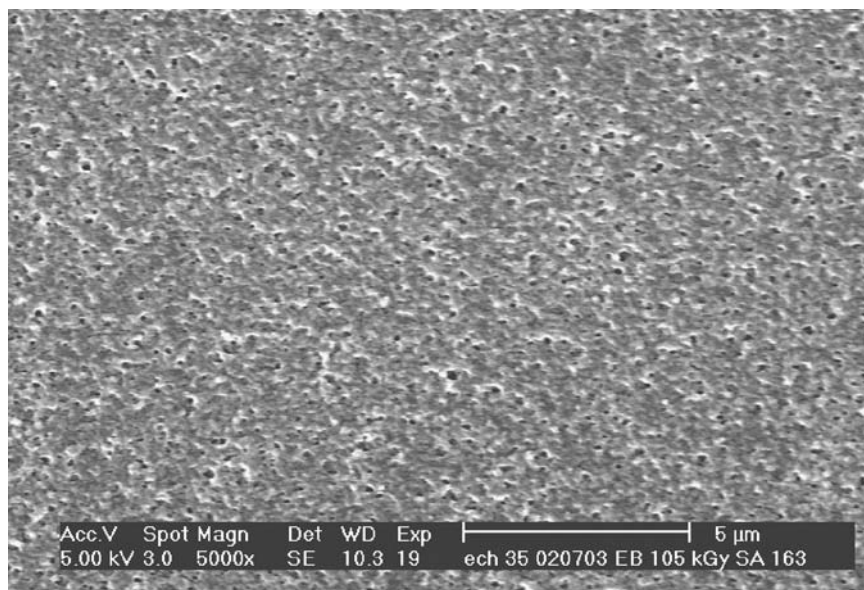


FIGURE 2 Threshold (V_{10}) and saturation (V_{90}) voltages as a function of film thickness for EB- and UV-cured samples.

sample. In the case of UV-curing (Fig. 3b), several additional remarks can be made: The droplets differ strongly in their diameters ranging from few nanometers up to 1 μm. Moreover, a large variety of different droplet shapes can be observed and droplets are often interconnected. On the contrary, the EB sample (Fig. 3a) reveals more regular droplet shapes with nearly ellipsoidal domains, which are smaller than in the UV- sample.

The micrographs were analyzed by a mathematical software obtained from SCION assuming that droplets possess ellipsoidal forms. This model was applied because it corresponds quite well to the EB-case. Application of the mathematical model via Scion Software was compared to a standard method by taking the dimensions manually from tracing paper. Figure 4 displays histograms giving the dependence of the number of objects as a function of the major axis of the ellipsoids. The results of the EB sample are presented in Figure 4a showing a large number of droplets below 150 nm accompanied by a maximum around 50 nm and a sharp decrease from the maximum to a major axis size of 200 nm. The maximum of the droplet size distribution of the UV sample can be found around 80 nm as shown in Figure 4b. Furthermore, a relatively long tailing to higher size

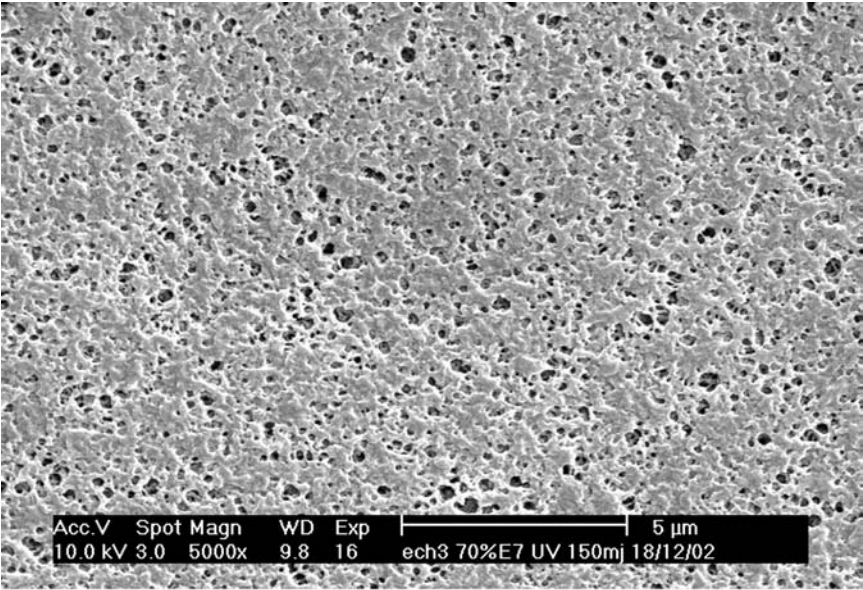


(a)

FIGURE 3 Micrographs obtained by SEM showing the morphology of a) EB and b) UV-cured samples. In both cases, the same experimental conditions were used for the observations of the sample morphology.

values was observed i.e., droplets with a major axis up to 700 nm were found.

The results obtained from the analysis of the morphology can be compared with the electro-optical responses shown in Figures 1 and 2. Indeed, the large droplet size distribution in the case of UV-curing might be responsible for the slow increase of the transmission as a function of the applied electrical field and the relatively high switching voltages compared to EB-cured samples. The sharp response found for the EB- samples can be related to the narrow droplet size distribution. Generally, smaller droplet sizes lead to higher threshold and saturation voltages due to the enhanced curvature of the small droplets. In our case, however, the EB-cured films possessing smaller droplet sizes than the UV analogues, exhibit lower V_{10} and V_{90} values. This behavior can be explained by the presence of a large number of irregularly shaped and often interconnected droplets in the UV case. Moreover, the droplet director configurations might vary between EB and UV and network heterogeneities might lead to locally highly crosslinked areas as well as to regions which are loosely



(b)

FIGURE 3 Continued.

cross-linked. It is assumed that such heterogenities are present particularly in our UV-cured systems.

CONCLUSIONS

The electro-optical responses of EB- and UV-cured TPGDA/E7 films was investigated as a function of the applied voltage. The curves giving the transmission in terms of the applied electrical field show considerable differences between UV- and EB-cured films. In particular, threshold and saturation voltages as well as the hysteresis are considerably lower for EB-cured films, and the shape of the curves are quite different. EB-cured films exhibit a sharp increase of the transmission at an electrical field around 1 Volt/μm whereas the UV-cured film responds roughly between 3 and 8 Volt/μm.

Observations of the morphology of EB- and UV-cured samples were made in order to understand the different electro-optical properties. A detailed analysis of the morphology revealed irregularly shaped droplets with a large size distribution in the UV-case and nearly ellipsoidal shaped objects with a more uniform size distribution for EB-cured samples.

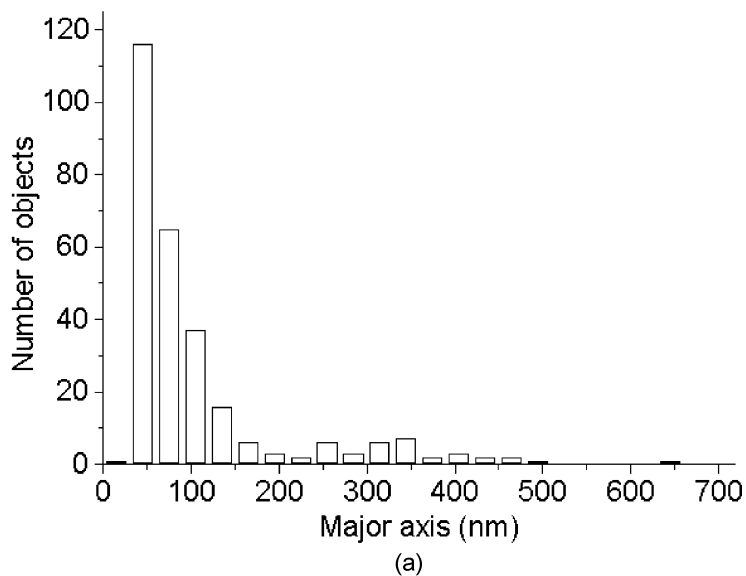


FIGURE 4 Droplet size distributions assuming an ellipsoidal shape of the droplets. Figures 4a and 4b correspond to the EB- and UV-cured sample, respectively.

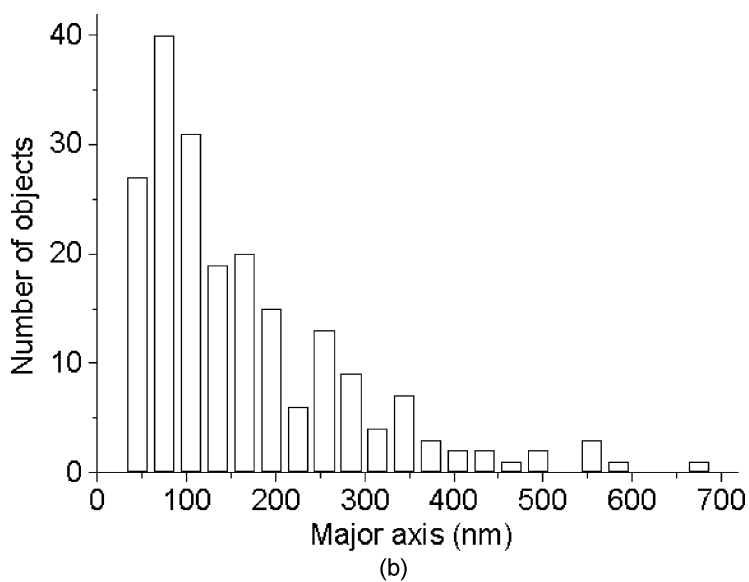


FIGURE 4 Continued.

The high switching voltages of UV-cured samples and the slow increase of the transmission as a function of the applied voltage can be explained by the large droplet size distribution of a large number of irregularly shaped objects. On the other hand, the narrow droplet size distribution of nearly ellipsoidally shaped LC domains are responsible for the sharp response found for the EB- samples.

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