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Dependence of Cure Parameters on Pdlc Films Prepared by Electron Beam and Ultraviolet Curing

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One basic method for the preparation of Polymer Dispersed Liquid Crystal (PDLC) films is the formation of microdroplets of liquid crystals (LCs) in a polymer matrix by a phase separation process. This can be achieved by radiation-initiated polymerization of a mixture including polymer precursors and LCs. The PDLC films used in this study were prepared by two different methods: Electron Beam (EB) or Ultraviolet (UV) curing. The electro-optical properties of the obtained PDLC-films based on a selected representative composition were investigated as a function of the chosen radiation. The transmission versus voltage curves exhibit a good reproducibility and a strong dependence on the curing conditions for samples prepared in the same experimental conditions. The evaluation of the electro-optical behavior indicates remarkable differences between EB- and UV-cured samples. The results are discussed in terms of off-/on-state transmission values and threshold voltage.

Keywords: Polymer Dispersed Liquid Crystal; Electron Beam; Ultraviolet curing; phase separation; nematic liquid crystals

INTRODUCTION

Polymer dispersed liquid crystal (PDLC) films consist commonly of micron sized dispersions of nematic liquid crystalline (LC) droplets within a solid polymer matrix[1-3]. These films can be electrically switched from a cloudy light scattering off-state to an activated transparent on-state. Applications of PDLC

materials include a variety of light control applications such as optical shutters and information displays.

A basic method for the preparation of PDLC films is the radiation initiated-polymerization induced phase separation (PIPS) of a mixture of reactive polymer precursors and LCs. Photoinitiated PIPS systems have been frequently used to obtain PDLC films[1,2]. PIPS initiated by electron beam (EB) radiation has been used as a powerful method to obtain well defined PDLC films[4-7]. Compared with the PIPS process by UV light, EB curing of acrylate compositions has the unique advantage of not requiring the presence of a photoinitiator which may be detrimental to the PDLC film performances and to long term ageing.

The electro-optical characteristics of PDLC films are determined primarily by the curing kinetics and the phase separation process depending on the initial reactive mixture. Several authors have investigated the electro-optical properties of PDLC films as a function of the initial UV curing conditions[8-11]. Relationships between parameters of preparation and morphology for some particular PDLC systems were also discussed[12]. It was generally found that the droplet size decreases with increasing UV intensity[8,9]. Smaller droplets require higher fields for orientation due to their higher degree of curvature[2]. Optimum UV dose and curing temperature are necessary to improve electro-optical performance for a given system.

In this paper, PDLC films were prepared via a PIPS process using UV or EB radiation. The electro-optical properties of the obtained PDLC films based on a selected representative composition were investigated as function of curing conditions. The evaluation of the electro-optical behavior indicates remarkable differences between UV- and EB-cured samples. The results are discussed in terms of off-/on-state transmission values and threshold voltages.

EXPERIMENTAL

Materials

The nematic LC used in this work was a commercial mixture (E7 from Merck Ltd, Poole, GB) containing essentially cyanoparaphenylene derivatives. It exhibits a positive dielectric anisotropy at T=20°C and a nematic-isotropic transition temperature T_{NI} = 61°C[13]. The refractive indices of E7 at T=20°C are given as: n_o=1.5183, n_e=1.7378 (λ=632.8 nm)[13]. 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=632.8 nm)[14].

Preparation of PDLC films

30 weight-percent (wt-%) of the prepolymer and 70 wt-% of the LCs were mixed together at room temperature for several hours, and used as initial reactive mixture 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).

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. 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. Film thickness was measured by a micrometer calliper (Mitutoyo; uncertainty: ±1 μm). For samples prepared by UV curing, a constant film thickness of 30±3 μm was found. Due to the higher deformation of the 50 μm PET sheet covering the liquid mixture as compared to the 100

μm substrate, film thicknesses in the range of 9-32 μm were found for EB-cured samples. No temperature control during the irradiation processes has been performed.

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. In our experiments the applied dose range was 60–120 kGy. This was achieved by using a beam current of 4, 5, 6, 7 and 8 mA and a constant conveyor speed of 0.19 $m \cdot s^{-1}$.

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 prepared as mentioned above were placed on a conveyor belt. The dose received by the sample was varied between 11 and 52 mJ/cm^2. This was achieved by using a constant light intensity and changing the conveyor speed in the range 0.43-1.25 $m \cdot s^{-1}$.

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 =632.8 nm. The PDLC films were oriented normal to the laser beam. The distance between the sample cell and the detector (silicon photodiode) was approximately 30 cm. The collection angle of the transmitted intensity was about ±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 measurements were corrected using appropriate calibration standards.

For electro-optical measurements, 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 145 Hz was increased continuously up to a desired maximum value V_{max}. Subsequently it was decreased in the same way. The whole scan up and down ramp was usually performed during 120 s, an additional measuring time of 60 s allowed to follow the relaxation behavior of the transmittance in the off-state. The same procedure was repeated several times using appropriate voltage maximum values.

RESULTS AND DISCUSSIONS

The obtained electro-optical curves are characterized by low transmission values in the initial off-state (< 1%) for both UV- and EB-cured PDLC films, whereas the corresponding values in the activated state were always higher than 80%. The transmission values in the off- and on-state are apparently not influenced by the nature of the PIPS process and are independent of the dose in the range applied in our experiments.

Figure 1 illustrates the electro-optical response of UV- (Dose 45 mJ/cm^2) and EB- (Dose 89 kGy) cured PDLC films. In this figure, transmission vs. voltage curves of representative samples prepared with high dose values are presented. Striking differences can be found : Although the transmission values in the off- and on-state remain roughly the same as already discussed above, the threshold (V_{10}) and saturation voltages (V_{90}) (V_{10}, V_{90}: Voltages required for obtaining 10 and 90 % of the maximum transmission value, respectively)

are considerably increased in the UV-cured sample as compared to the EB-cured film. Moreover, the UV-cured film did not recover its scattering

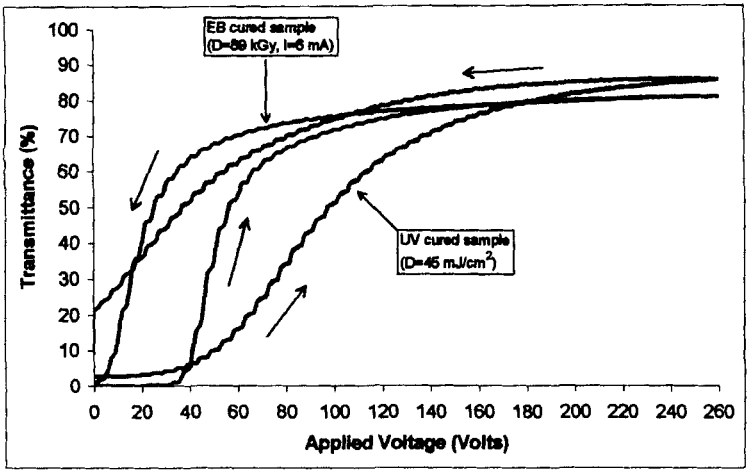

FIGURE 1 Electro-optical response (λ=632.8 nm, ν=145 Hz) of 30 μm thick PDLC films prepared by UV and EB curing.

properties after the voltage scan cycle was completed. The transmission in the initial off-state was substantially lower as compared to the following off-state.

The effect of dose on the threshold voltage for UV-cured PDLC films is presented in Figure 2. An increase in the UV-dose results in an increase of the threshold voltage. Several authors have attributed this behavior to a decrease of the droplet size with higher dose[8,9]. Under the curing conditions chosen for this work, V_{10} has not reached a constant maximum value at high doses. This behavior indicates that the UV-cured system can still be modified by applying higher dose values, thus the obtained composite is not in a chemically stable state.

Figure 3 illustrates V_{10} for EB-cured PDLC samples, when the dose and the film thickness were varied. The threshold voltages of samples cured with

60 and 74 kGy remain nearly constant at the same value of approximately 20 volts independent of film thickness. V_{10} changes drastically as a function of

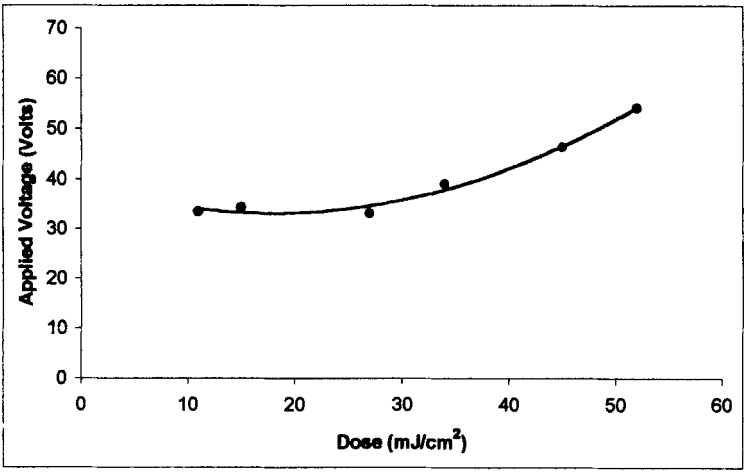

FIGURE 2 Threshold voltage V_{10} of PDLC films as a function of UV-dose.

thickness if the dose is changed from 74 to 119 kGy : V_{10} increases with increasing film thickness. The curves corresponding to 104 kGy and 119 kGy are superimposed whereas the threshold vs. thickness curve for 89 kGy shows the same slope but shifted to higher voltage values. The same general behavior has been also found for V_{90}.

The effects of UV-dose and curing temperature on V_{90} have been investigated by Nolan et al.[10] for the TL213/PN393 (80:20) system : At a given temperature, V_{90} first slowly then strongly increases with increasing UV-dose before reaching a plateau value, where further increase of dose did not change the V_{90} value. Qualitatively, the behavior found in our EB-cured samples is roughly the same at a given film thickness (take for example 28 μm in Figure 3). The EB-cured systems might have reached chemical stability for dose values higher than 90 kGy. Further analysis of the PDLC materials is in

progress to correlate the morphology of the samples with the observed electro-optical behavior.

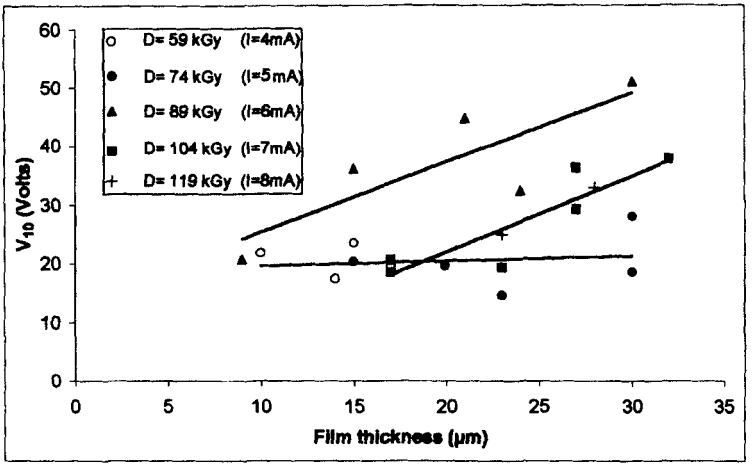

FIGURE 3 Effect of thickness and dose of EB-cured PDLC films on the threshold voltage.

CONCLUSIONS

PDLC samples based on the same initial mixture were cured by UV or EB radiation using a PIPS process. The obtained electro-optical curves are characterized by low transmission values in the initial off-state and by transmission values higher than 80% in the on-state. The radiation curing conditions differ in two major aspects : Initiation rates and thermal conditions. One expects that these external factors control the competition between network formation and phase separation during the PIPS process. This is not revealed by comparing the off- or on-state transmission values of the two series of radiation cured samples. However, the threshold voltages exhibit a strong dependence on the PIPS process. Under the curing conditions choosen in this work, EB curing leads to PDLC films characterized by reduced

threshold and saturation voltages as compared to UV-cured films thus to a better electro-optical performance. Moreover, chemical stability can be more easily achieved for EB-cured films.

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