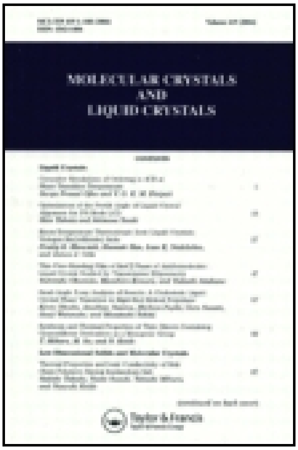

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Electro-Optical Properties of Electron Beam Cured Polymer Dispersed Liquid Crystal Films based on Polysiloxanes and Liquid Crystals

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ELECTRO-OPTICAL PROPERTIES OF ELECTRON BEAM CURED POLYMER DISPERSED LIQUID CRYSTAL FILMS BASED ON POLYSILOXANES AND LIQUID CRYSTALS

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Polymerization and cross-linking induced phase separation initiated by electron beam radiation is used to elaborate Polymer Dispersed Liquid Crystal (PDLC) films made of polydimethylsiloxane and 5CB. Electro-optical properties of the obtained films are investigated in terms of the composition of the initial mixture and amplitude of the applied AC voltage. A particular attention is given to transmission levels and operating voltages.

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INTRODUCTION

Polymer dispersed liquid crystals (PDLCs) consist generally of micron sized droplets of a low molecular liquid crystal (LC) dispersed in a solid polymer matrix [1,2]. PDLC films are elaborated following various routes most of them based on phase separation processes induced either thermally, via solvent evaporation or by chemical reactions. Polymerization induced phase separation (PIPS) initiated by electron beam (EB) radiation is among the prominent techniques used in our laboratory [3–7]. The reason for the choice of this original technique is the possibility to obtain well defined PDLC film, high conversion ratios of monomers with controlled reaction, fast cure rate and no thermal activation. Compared to the ultraviolet technique [8], EB radiation produces efficient polymerization and crosslinking without requiring an initiating agent. When LC molecules in the droplets are submitted to an external electric field, they align with the field inducing switching of the PDLC film from cloudy light scattered to highly transparent films. As such, they are of considerable interest for display devices and light shutters.

Electro-optical properties of these devices can be monitored by a good control of the composition, temperature, film thickness and the conditions of preparation. Here, we focus on electro-optical properties of PDLC films made of polydimethylsiloxane and 5CB prepared via PIPS process under EB curing. To our knowledge, no similar studies of systems were reported so far in the literature. Effects of LC concentration on electro-optical properties of PDLC films were investigated mainly on polyacrylates and thiol-ene systems [3–5,9–11]. In this work, characteristic transmissions and voltages are investigated as function of sample composition. The results are presented in terms of light transmission versus applied voltage and film thickness, and LC concentration dependence of the threshold- and saturation voltages.

EXPERIMENTAL PART

Materials

The liquid crystal 4-cyano-4′-n-pentyl-biphenyl (5CB) (Merck Eurolab, Germany) was used during this work; it exhibits the following transition temperatures $T_{\mathrm{KN}} = 23^{\circ}\mathrm{C}$, $T_{\mathrm{NI}} = 35.3^{\circ}\mathrm{C}$ [12]. The prepolymer consists of a poly(dimethylsiloxane-diacrylate) (PDMS) with a molar mass of 800 g/mol. The chemical structures of the compounds are given in Figure 1.

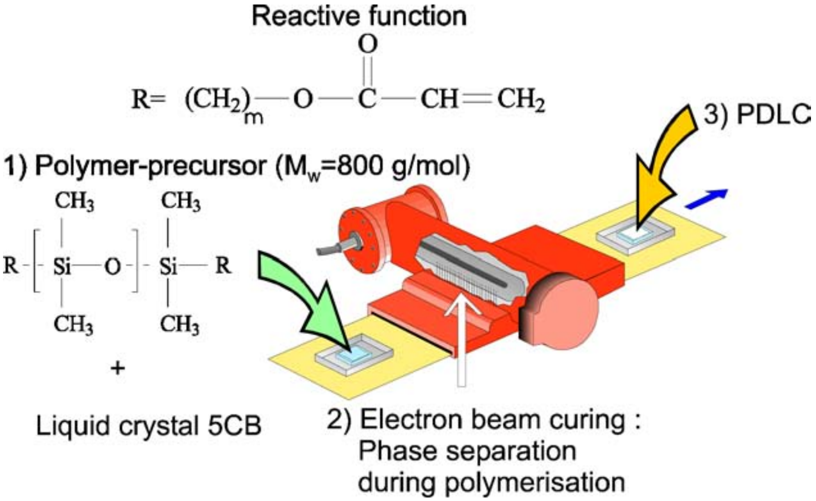

FIGURE 1 Identification of the molecular species in the precursor system (poly (dimethylsiloxane-diacrylate), 5CB) and a scheme of the Electron Beam Machine. (See COLOR PLATE VII)

Preparation of PDLC Films

Several compositions were prepared by mixing the appropriate amount of poly(dimethylsiloxane-diacrylate) prepolymer and the LC 5CB together at room temperature for several hours. To perform electro-optical measurements, the films were elaborated by sandwiching the initial reactive mixture between a glass plate (Balzers, Liechtenstein) and a 50 μm thick Polyethylene-terephthalate (PET) sheet (Renker, Germany), both coated with a thin transparent layer of conducting indium/tin oxide. For each composition, several samples were prepared and exposed to the EB radiation to cure the film.

Electron Beam Curing

The EB generator is an Electrocurtian Model CB 150 (Energy Sciences Inc.) with an operating high voltage of 175 kV. A scheme of the apparatus is given in Figure 1. 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 105 kGy is achieved by using a beam current of 7 mA and a conveyor speed of 0.19 m/s. These values were not changed during the experiments to maintain the same curing conditions. The applied dose was delivered uniformly in the depth of the sample [5–7]. The film thickness is measured by a micrometer calliper

(Mitutoyo; uncertainty: ±1 μm). No temperature control during the irradiation processes has been performed.

Electro-optical Measurements

Electro-optical measurements were made at room temperature using an unpolarized HeNe laser light at a wavelength of $\lambda = 632.8\,\text{nm}$. The glass plates 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 $\pm 2°$, 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 resulting from reversible darkening of the glass plates upon EB exposure.

The optical transmission of the cured films find in the initial off-state were measured at different places on each glass plate. For electro-optical measurements, 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. Typically, the whole scan up and down of the voltage was performed during 120 s, an additional measuring time of 60 s allows to follow the relaxation behavior of the transmission in the off-state. The same procedure was repeated twice to check for the validity of the results.

RESULTS AND DISCUSSION

In the LC concentration range from 0 to 20 wt.-%, the polymer/LC film remains essentially transparent with a very low scattering level at $\lambda = 632.8\,\text{nm}$. This is expected since in this case, the LC molecules form a homogeneous dispersion in the polymer and micro-droplets have not been formed yet. Light transmission drops suddenly from 20 to 80 wt.-% LC where fluctuations induced by phase separation produce a strong scattering of light. These features are valid for poly(acrylate) and poly(siloxane) systems with a modulation depending on the miscibility of polymers and LCs. The present paper deals with EB-cured PDMS/5CB films with an attempt to determine the effect of LC concentration on electro-optical properties. The first example is given in Figure 2 where two electro-optical curves corresponding to different LC concentrations but constant film thickness (18 μm) are shown. A curve shift towards higher threshold and saturation voltages is found when the LC concentration decreases from

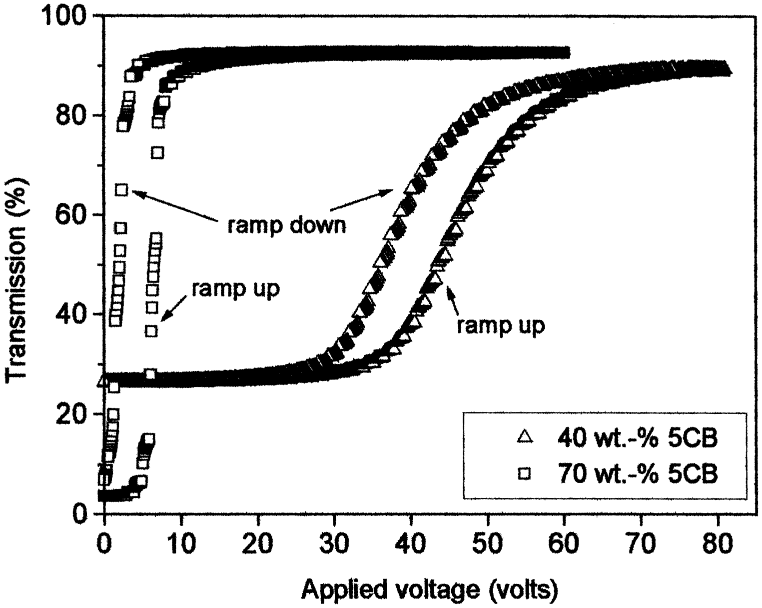

FIGURE 2 Electro-optical response curves for PDLC films with LC concentration 40 wt.-% 5CB (right hand side) and 70 wt.-% 5CB (left hand side) (film thickness 18–19 μm).

70 to 40 wt.-%. Moreover, the off-state transmission drops substantially when the LC concentration increases from 40 to 70 wt.-% consistent with the above remark. At 40 wt.-% LC, upon application of a voltage ramp with a maximum of 80 V, the transmission goes from nearly 30% to 90% and the threshold voltage V_{10} is about 45 V. Increasing the LC concentration to 70 wt.-% leads to a considerable decrease in the off-state transmission while the threshold and saturation voltages are remarkably reduced.

Data show that the on-sate transmission remains practically unchanged in the whole concentration domain covered by the experiments while the off-state transmission decreases sharply in the range from 40 to 60 wt.-% 5CB. These findings are illustrated in Figure 3 where T_{on} and T_{off} are plotted versus film thickness in the semi-log representation for 40 to 60 wt.-% 5CB samples. One observes that T_{on} remains practically constant when film thickness and LC concentration are changed. The off state transmission changes remarkably both with film thickness and LC concentration. The semi-log representation is choosen to highlight these changes since log T_{off} is expected to decrease linearly with the thickness. In terms of the LC concentration, it is found that below 30 wt.-% LC, T_{off} does not vary a lot

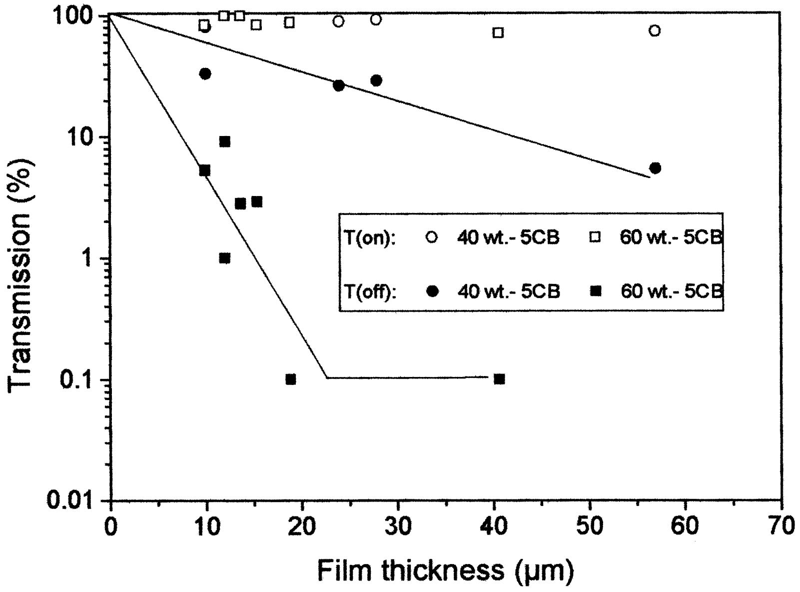

FIGURE 3 Transmission in the on- and off-state versus film thickness of EB-cured PDMS/5CB systems for 40 and 60 wt.-% 5CB.

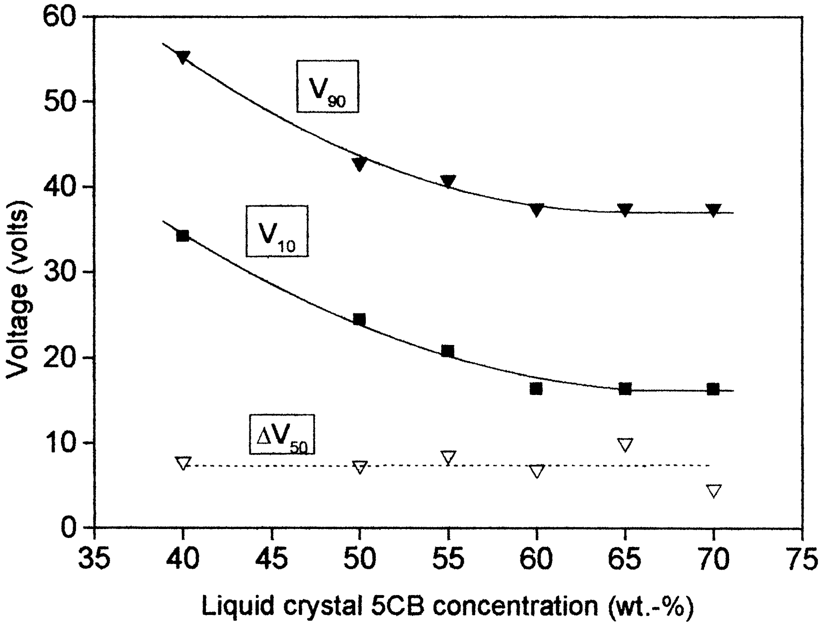

FIGURE 4 Threshold voltage V_{10}, saturation voltage V_{90} and hysteresis width ΔV_{50} (dotted line: estimated curvature) versus LC concentration ($\lambda = 632.8\,\text{nm}$, $\nu = 145\,\text{Hz}$).

but between 30 and 60 wt.-% 5CB, there is a remarkable drop as mentioned earlier in this paper. Interestingly, for the 40 wt.-% sample, the decay of Log T_{off} is linear with a single slope over the entire range of film thickness while in the case of 60 wt.-% LC, a change of slope emerges at a certain thickness. The initial slope of Log T_{off} for the 60 wt.-% LC sample is much higher than that corresponding to 40 wt.-%. However, for films with thicknesses exceeding 20 μm, there is a change of slope whereby T_{off} decreases only slightly with the thickness.

The effects of LC content on V_{10}, V_{90}, and ΔV_{50} are represented in Figure 4. Recall that ΔV_{50} is the voltage difference between ramp up and down at 50% transmission, it is a direct measure of the hysteresis in electro-optical curves. An increase of LC concentration yields a drop of the characteristic voltages V_{10} and V_{90} while ΔV_{50} remains constant. V_{10} and V_{90} show a plateau above 60 wt.-% LC.

A detailed analysis of these results and possible correlations with the film morphology is under progress and will be the subject of a future communication.

CONCLUSIONS

PDLC films made of EB-cured PDMS/5CB systems via polymerization induced phase separation are investigated. Electro-optical properties of these compounds depend strongly on the LC concentration. High off-state scattering was observed above 60 wt.-% LC while the on-state transmission remains essentially constant in the investigated LC concentration domain. Increasing the LC content from 40 to 70 wt.-% leads to large drops in the threshold and saturation voltages while the width of the hysteresis remains constant. Further analysis of these compounds is in progress combining morphology, thermophysical properties and their correlations with electro-optical response functions.

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