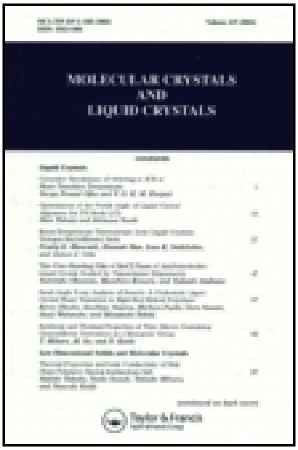

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PROPERTIES OF ELECTRON BEAM CURED REVERSE MODE PDLC FILMS

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In this paper, we present recent electro-optical data of Polymer Dispersed Liquid Crystal (PDLC) films operating under reverse mode conditions. We consider systems prepared by Polymerization Induced Phase Separation (PIPS) using Electron Beam (EB) curing of acrylate monomers mixed with a low molecular weight liquid crystal (LC). In the present investigation, a low molecular weight LC exhibiting a negative dielectric anisotropy is used yielding electro-optical curves characterized by a transparent initial off-state and an opaque on-state film under the influence of an external field. The results enable us to characterize the sensitivity of electro-optical responses to the functionality of monomers in the precursor mixtures as well as the conditions of film preparation. Data showing the phase behavior of a monomer/LC system are also presented to rationalize the electro-optical results of these interesting but relatively less known materials.

Keywords: electro-optical properties; liquid crystal; phase diagram; polymer; solubility

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INTRODUCTION

Unlike mixtures of polymers and liquid crystals (LCs) operating under normal conditions [1–5], reverse mode polymer dispersed liquid crystal (PDLC) materials have received less attention in the literature [6–8]. It has been shown that small amounts of mesogenic monomer polymerised in LC environment could form polymer networks stabilizing certain LC states and modifying the properties of LCs. Such in situ formed anisotropic polymeric networks mixed with low molecular weight liquid crystals showing the reverse mode effect have been intensively studied by Hikmet *et al.* [9–11].

The main difference between normal and reverse systems is essentially due to the sign of the dielectric anisoptropy which is negative in the reverse mode case while positive under normal operating conditions. This has a direct impact on the light transmission since such films are transparent in the reverse mode option and become translucid when they are submitted to an external electric field. Standard films exhibit a low transmission of light in the absence of electric fields (off state) and an increased transmission as a voltage with sufficient amplitude is applied to them. Their dielectric anisotropy $\Delta\varepsilon = \varepsilon_{\parallel} - \varepsilon_{\perp}$ is positive and the LC molecules align parallel to the applied electric field. In reverse mode systems, $\Delta\varepsilon$ is negative and the LC molecules align perpendicular to the electric field. The purpose of this paper is to report recent results of reverse mode films made of Polymer Dispersed Liquid Crystal (PDLC) composite materials prepared according to the Polymerization Induced Phase Separation (PIPS) method using Electron Beam (EB) radiation [4,5].

We investigate both thermal behaviour of monomeric and electro-optical response of EB-cured systems but to keep this communication short, only a selection of the results can be shown.

EXPERIMENTAL PART

Materials and Sample Preparation

The commercial LC MLC-6885 (Merck) was used in this work. It is an AMD-ECB/VA mixture with an unknown formulation having a dielectric anisotropy $\Delta\varepsilon = -3{,}8$ (see Table 1). Tripropyleneglycoldiacrylate (TPGDA) and a 1:1 mixture of TPGDA and 2-phenoxy-ethylacrylate (PEA) were used as polymer precursors. Monomer/LC systems with the composition 60 wt.-% LC were considered. For each blend, a large number of samples have been prepared to check the extent of reproducibility of the results.

TABLE 1 Optic and Dielectric Anisotropy of the Liquid Crystal MLC-6885 (Merck)

Optic anisotropy, $T = 20°C$, $\lambda = 589\,nm$	
Δn	0.0999
n_e	1.5820
n_0	1.4821
Dielectric anisotropy, $T = 20°C$, $\nu = 1.0\,kHz$	
$\Delta\varepsilon$	-3.8
$\varepsilon_\perp$	7.6
$\varepsilon_\parallel$	3.8

Electron Beam Curing

The EB generator is an Electrocurtain Model CB 150 (Energy Sciences Inc.) with an operating high voltage of 175 kV. 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 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 with no damage caused to the molecular species even at the highest beam dose used here. The film thickness is measured by a micrometer calliper (Mitutoyo; uncertainty: ±1 µm) but no temperature control was performed during the irradiation process.

Electro-optical Measurements

Electro-optical measurements were made at room temperature using an unpolarized HeNe laser light at a wavelength of $\lambda = 632.8\,nm$. 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 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 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 allowed to follow the relaxation behavior of the transmission in the off-state. The same procedure was repeated twice to check for the validity and reproducibility of the results.

Polarized Optical Microscopy (POM)

The thermo-optical studies were performed on a POM ZEISS equipped with a Linkham heating/cooling stage and a Linkam temperature control unit. Samples were heated from room temperature to approximately 15 degrees above the transition temperature leading to the isotropic phase. The samples were left for about 15 min in the isotropic state. The subsequent thermal processes applied to the samples depend on the kinetics of reaching the thermodynamic equilibrium state. Data were collected on the second heating and cooling ramps.

RESULTS AND DISCUSSION

Thermal Behaviour of the Precursor System

Figure 1 exhibits the phase diagram of the uncured TPGDA/MLC-6885 system as obtained by POM technique. Two series of measurements were

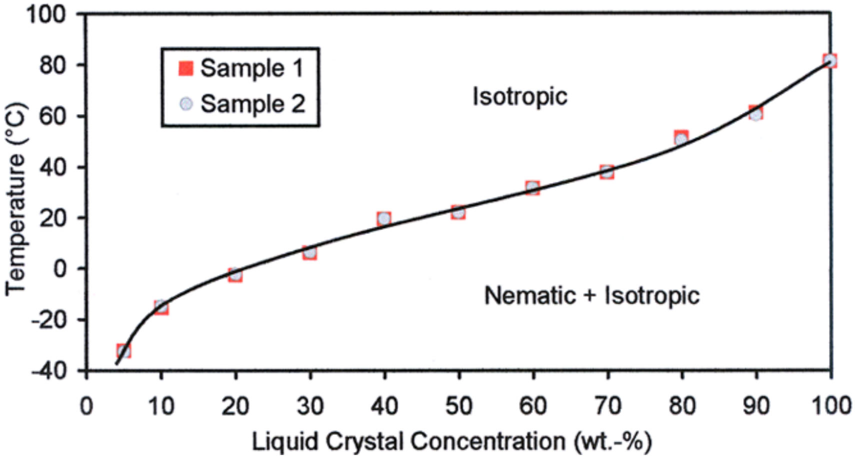

FIGURE 1 Phase diagram of the uncured MLC-6885/TPGDA system obtained by POM. (See COLOR PLATE I)

performed on systems with equal composition prepared independently. A miscibility gap is found at low temperatures whereby a TPGDA rich phase in the isotropic state is in equilibrium with a nematic pure LC phase. In the upper part of the diagram, a single isotropic phase region is found. Figure 1 shows a typical phase diagram for uncured monomer/LC systems. Those reported previously with other acrylate monomers or oligomers and standard LCs such as E7 and 5CB exhibited similar forms [12,13]. The miscibility of the MLC-6885/TPGDA system is found to be slightly lower compared to that of the E7/TPGDA system reported in reference 13.

Electro-optical Responses of EB-Cured Systems

The electro-optic properties of TPGDA/MLC-6885 and TPGDA-PEA/MLC-6885 systems are studied in terms of the film thickness. This allows the assessment of the thickness and the monomer functionality on the electro-optical response functions of the film under consideration. As the monomer functionality increases, the network density also increases inducing strong changes of the morphology, the size of LC domains and consequently the electro-optical properties of the film.

In the present paper, we consider the following systems (i) TPGDA (40 wt%)/MLC-6885 (60 wt.-%) refered to simply as the TPGDA system (ii) PEA (20 wt.-%) TPGDA (20 wt.-%)/MLC-6885 (60 wt.-%) referred to as the PEA system. Figure 2 gives the electro-optic responses of TPGDA

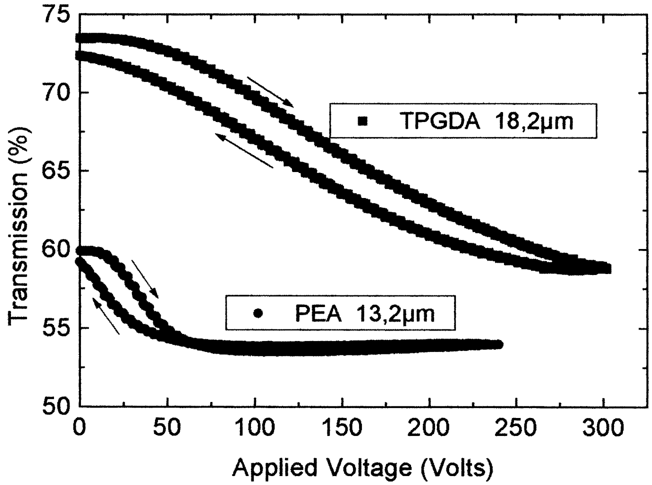

FIGURE 2 Electro-optic responses of TPGDA and PEA films with thicknesses 18,2 µm and 13,2 µm, respectively. ($\lambda = 632.8$ nm, measurements at room temperature, application of sinusoidal voltage ramps of frequency 145 Hz).

and PEA films with thicknesses 18,2 μm and 13,2 μm, respectively. Figure 3 gives similar results for thicker films.

In all cases, one observes the hysteresis phenomena with $T_{\text{off}} > T_{\text{on}}$ indicating that the material becomes translucid when the voltage is applied. After a complete voltage cycle, one recovers the initial level of transmission indicating no residual memory, a reversible process and reproducible results. For thin films, the transmission levels are high as shown in Figure 2 (between 55 and 75%) while for thicker films as in Figure 3, these levels are quite low (15 to 30%). It becomes clear from these results that films made of TPGDA with not too high thicknesses are more suitable for electro-optical applications in the reverse mode conditions. Nevertheless, more effects are necessary to improve the electro-optical response parameters for high performance applications. In particular, in the case of the TPGDA/LC system under consideration, one needs to work along the lines of reducing further the transmission when the film is activated by an electric field. It is clear that the levels reported here remain too high to be efficient in practical applications.

Comparing the results of TPGDA and PEA films, one sees that T_{off} is higher for the former system. However, this system does not show a plateau transmission even at 300 V. The T_{on} value is quickly reached in the PEA system (near 60 V). In this case, one has $\Delta T = 6\%$ for a voltage of 70 V.

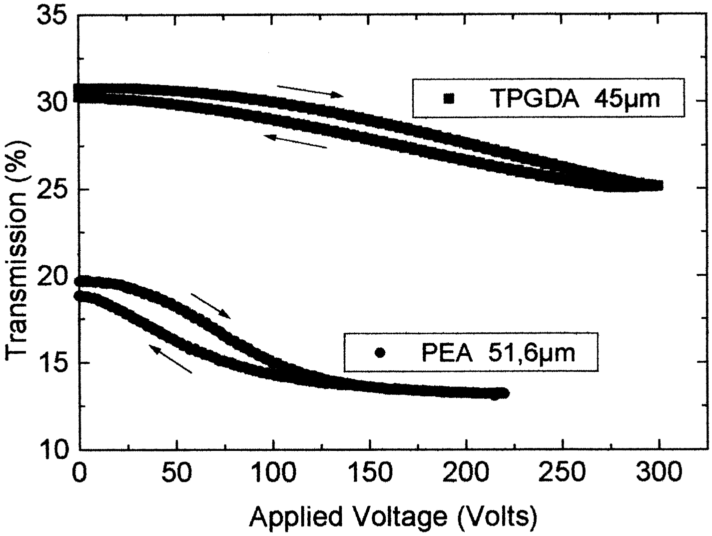

FIGURE 3 Electro-optic responses of TPGDA and PEA films with thicknesses nearly 45 μm and 51 μm respectively. ($\lambda = 632.8$ nm, measurements at room temperature, application of sinusoidal voltage ramps of frequency 145 Hz).

In order to reach the same ΔT for TPGDA, one needs to apply 120 V. In thin TPGDA films, even 300 V the maximum voltage used in our experiments is not sufficient to obtain a stable transmission in the on state. The shape of the curve T vs. V indicates that the transmission should continue to decrease above 300 V. PEA films commute to a transparent state in the range of 60 to 80 V. Increasing the voltage further leads to a horizontal plateau while decreasing it would lead to a curve that return to the off state following the same path within a weak hysteresis phenomenon. There is no plateau for TPGDA/LC films. The difference $T_{\mathrm{off}} - T_{\mathrm{on}}$ is higher for TPGDA films.

CONCLUSIONS

This investigation shows that it is possible to have polymer dispersed LC systems operating under reverse mode conditions. The electro-optic curves are quite reproducible when the films are prepared under similar conditions but the performance of films considered here need to be improved before a reasonable application could be attempted. Such improvements can be realised quite easily by using for example alignment layers, or polymerisation under electric or magnetic fields. The off-state transmission depends on the gap between the refractive index of the polymer matrix and the mean refractive index of the LC which can be controlled by changing the parameters of the radiation exposure. A more detailed analysis is under consideration using other complementary techniques such as light scattering and microscopy.

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