Molecular Crystals and Liquid Crystals
Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/gmcl20

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Version of record first published: 18 Oct 2010

To cite this article: L. Benkhaled, L. Mechernene, A. Traisnel, M. Benmouna, J.-M. Gloaguen, X. Coqueret & U. Maschke (2002): Electro-optical Properties of EB-cured PDLC Systems, Molecular Crystals and Liquid Crystals, 375:1, 651-658

To link to this article: http://dx.doi.org/10.1080/10587250210598

Mol. Cryst. Liq. Cryst., Vol. 375, pp. 651-658

1058-725X/02 $12.00 + .00

Electro-optical Properties of EB-cured PDLC Systems

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Electro-optical properties of Tripropyleneglycoldiacrylate/E7 composite materials are investigated. Films of these materials are prepared according to the Polymerization Induced Phase Separation method under Electron-Beam curing. The electro-optical responses depend strongly upon radiation dose. Shortly after film preparation, the transmission in the absence of electric field evolves with the time. Initially, the film is clear and become increasingly opaque as time evolves. This is especially the case for films prepared under low EB dose and gives evidence of the long process of phase separation in late stages. The decrease of transmission with the film thickness is also investigated. The results indicate that such a decrease is exponential but depend on the EB dose used to cure the precursor mixtures.

Keywords Electro-optics; PDLC; Electron Beam

INTRODUCTION

Polymer Dispersed Liquid Crystal (PDLC) films are made of micron sized dispersions rich of liquid crystal (LC) in a solid polymer matrix.

Under normal operating conditions, these systems are opaque due to strong scattering of incident light while by applying an electric field, they become transparent at normal incidence[1,2]. There are several ways of preparing these films but the most familiar methods use the phase separation processes. A particular method is called PIPS for Polymerisation Induced Phase Separation[3-5]. Here the initial mixture contains the LC, the monomer or oligomer and a photoinitiator if UV light is used to cure the system. As polymerisation eventually with cross-linking (for networks) proceeds, phase separation takes place and the composite film is formed. The phase separation proceeds in different steps and could take quite a long time to be completed. Many studies were devoted to this problem which remains still unsolved raising many fundamental questions[6-9].

Here we do not want to embark into a laborious discussion of kinetics of phase separation. An example demonstrating that such time dependent processes have a tremendous impact on the electro-optical (EO) properties is given. In particular it is found that those processes can take several days (or weeks) to be completed.

We consider the EO properties of PDLC films obtained by the PIPS process using electron beam (EB) curing. Significant differences exist between this method and the UV exposure starting from the fact that the latter requires the presence of a photoinitiator. Extensive work has been dedicated to the comparison between these two techniques in our laboratory[10-13].

The EB curing is found to be more effective and yields films with better mechanical, thermal, EO and aging properties. Here we will limit ourselves to some indications related with the influence of EB dose on

EO response functions. Effects of the film thickness and the time lasting between preparation of the film and EO measurements are discussed.

EXPERIMENTAL PART

Materials and sample preparation

The eutectic nematic LC E7 (Merck) was used in this work, containing essentially cyanoparaphenylene derivatives. Tripropyleneglycoldi-acrylate (TPGDA) monomer was obtained from Cray Valley (France). Mixtures including 30wt-% of the monomer 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 different doses by changing the beam current. 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 145Hz. 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 120s, an additional measuring time of 60s allowed to follow the relaxation behavior of the transmittance in the off-state.

RESULTS AND DISCUSSIONS

Figure1 shows the EO response curves for TPGDA/E7 films prepared according to the PIPS method with different EB curing doses.

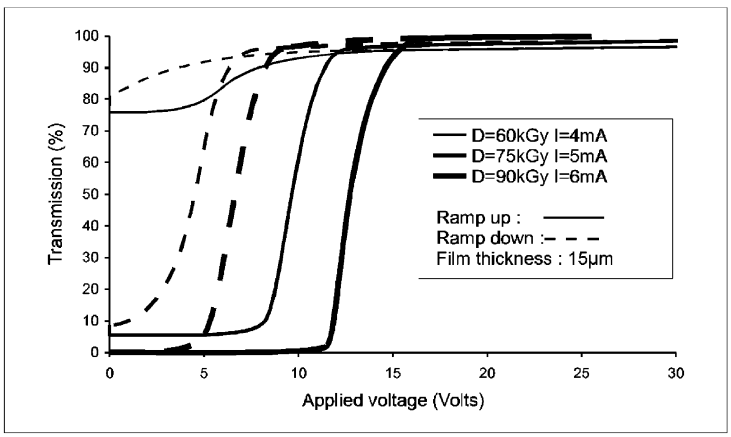

FIGURE 1 Electro-optical curves of TPGDA/E7 films prepared by the PIPS method with different EB doses. Higher doses yield similar results. (1kGy=1J/g=0.1Mrad)

Lower doses would lead to an incomplete polymerization / cross-linking while higher doses do not yield improvement of the EO properties. Outside the range of doses covered in these experiments, no

significant changes are obtained in the PDLC films under consideration. For the lowest EB dose, the film exhibits initially a high level of transmission since the transmission in the off-state T_{off} is practically

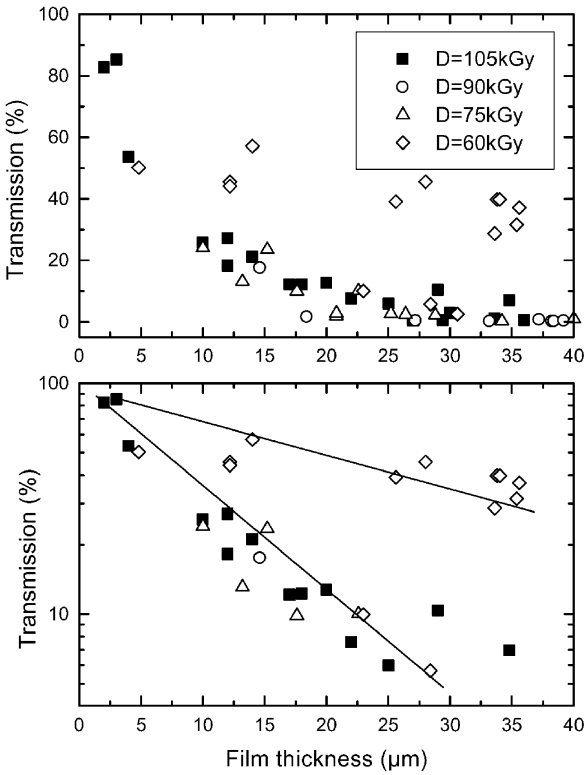

FIGURE 2 The off-state transmission curves versus film thickness for different doses as indicated on the figure. up) Linear plot. down) semi-logarithmic plot.

80%. The transmission rises very smoothly with the applied voltage while threshold voltage V_{10} and saturation voltage V_{90} are quite high and the contrast ratio T_{on}/T_{off} is too low for any reasonable application.

As the EB dose increases, a substantial improvement of the EO response is observed. T_{off} decreases considerably and the contrast ratio is extremely high. Both V_{10} and V_{90} increase with the dose but remain relatively small since V_{90} does not exceed 20V for the highest dose. Increasing the dose does not improve the EO response curve. Data shown in Figure 1 are taken on films with the same thickness of 15μm and substantial changes are expected with different thicknesses keeping the other conditions the same (beam dose, composition etc.).

Figure 2a shows the transmission curves in the off state as a function of the film thickness for several EB doses. Except the lowest dose (i.e. 60kGy), the other results are scattered around the same nonlinear curve. To check if the decrease of transmission is exponential, we plotted the data in the semi-log scale in Figure 2b. Clearly, the transmission obeys the expected form $T = I/I_0 = \exp(-N\sigma d)$ where σ is the scattering cross-section; N the number of scattering centers and d the thickness. The slope of the upper line corresponding to the smallest dose is more than 3 times smaller than that of the line below. This means that the scattering is stronger for films cured with a dose exceeding 75kGy.

Figure 3 shows the EO response functions for films having a thickness comprised between 25.6 and 28.4μm cured with a relatively small EB dose (i.e 60kGy). Data represented by squares are taken in the time range between 1 and 2 days after preparation while data corresponding to circles were taken nearly 2 weeks after preparation. These plots illustrate the effect of the late stage spinodal decomposition process of films prepared according to the PIPS method under EB curing. The EO curves have changed significantly in the time range

between 1 day and a couple of weeks demonstrating that late stage phase separation processes can take days to be completed. The off state

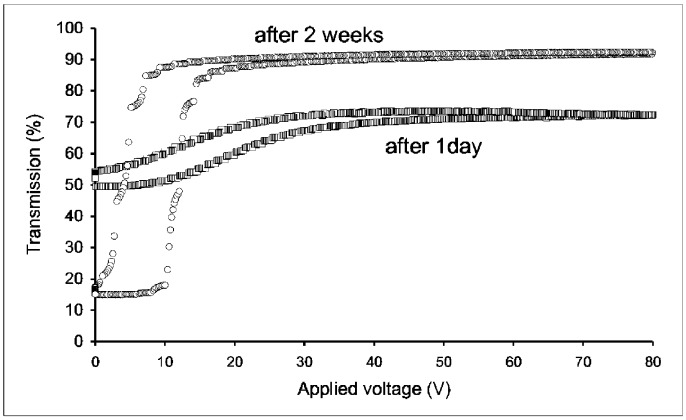

FIGURE 3 Electro-optical curves of TPGDA/E7 films with the same EB dose (60kGy) recorded at different times after film preparation. (circles : data recorded 2 weeks after film elaboration; squares : data recorded 1-2 days after film elaboration.

transmission decreases by more than 30% and the characteristic voltages V_{10} and V_{90} are strongly reduced. After 2 weeks measurement V_{90} is near 25V while after 2 days, it was more than 50V.

CONCLUSIONS

The EO properties of EB cured TPGDA / GPTA / E7 films have been investigated as a function of radiation dose and film thickness. At a small dose (i.e. 60kGy), the film shows a poor EO response. T_{off}, V_{10} and V_{90} are too high while, increasing slightly the dose (i.e. 75kGy) permits to improve significantly the EO responses. T_{off} decreases to less then 10% although V_{10} and V_{90} increase but remain less than 5 and 15V, respectively. The transmission decreases exponentially with film thickness. This decrease is quite slow for small doses due to the fact

that the phase separation is not complete as one can see from the EO response curves shortly after film preparation and several days after film preparation. EO properties are significantly improved as time evolves. The phase separation may take several days to be completed after film preparation and during this time EO characteristics of the films can vary substantially. At high doses this was not the case since stable systems were obtained immediately after preparation.

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