Molecular Crystals and Liquid Crystals Science and Technology. Section A. Molecular Crystals and Liquid Crystals

Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/gmcl19

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Version of record first published: 24 Sep 2006

Mol. Cryst. and Liq. Cryst., 2001, Vol. 368, pp. 69-76
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Electro-Optical, Spectroscopical, and Calorimetric Investigations of Electron Beam- and Ultraviolet- Cured Polymer Dispersed Liquid Crystal Materials

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The most convenient method used for the preparation of polymer dispersed liquid crystal (PDLC) films is the polymerization induced phase separation (PIPS) of mixtures composed of polymer precursors and low molecular weight liquid crystals (LMWLC). Ultraviolet (UV) and electron beam (EB) radiation was employed to initiate the PIPS process. A mixture of the nematic LMWLC material E7, an aromatic polyester acrylate, and additional monomeric acrylates was exposed to the EB radiation. Lucirin TPO as a photoinitiator has been included in the initial mixture in the case of UV exposure. The electro-optical properties of the obtained PDLC films strongly depend on the curing conditions, and are highly reproducible. In general it was found that the EB-cured PDLC films show a better electro-optical performance as compared to the UV-cured samples. The extent of cure has been determined by infrared spectroscopy measurements of the carbon-carbon double bond of the acrylate groups. Differential scanning calorimetry was employed to obtain the glass transition temperature of the polymer and the LMWLC solubility limit in the polymer matrix.

Keywords: Polymer Dispersed Liquid Crystal; polymer; liquid crystal; electron beam; ultraviolet

INTRODUCTION

Polymer Dispersed Liquid Crystal (PDLC) materials can be prepared by a polymerization induced phase separation (PIPS) technique of mixtures composed of polymer precursors and low molecular weight liquid crystals (LMWLC)[1-4]. PIPS initiated by ultraviolet (UV) and electron beam (EB) radiation has been frequently used to obtain well defined PDLC films. Compared to the PIPS-UV process, EB-curing does not require the addition of a photoinitiator.

The curing kinetics and the phase separation process control the electro-optical characteristics of PDLC films. The influence of the dose and dose rate on the sample morphology and on the electro-optical properties of PIPS-UV samples has been investigated in recent years[1]. Only a few results on the effect of the dose on electro-optical properties have been reported for PIPS-EB systems[3,4]. All these investigations show the need to control the curing parameters to improve the electro-optical performance for a given polymer/LC system.

In the present paper properties of PDLC films prepared by PIPS-UV and PIPS-EB will be discussed. A selected representative mixture of the nematic LMWLC material E7, an aromatic polyester acrylate, and additional monomeric acrylates was exposed to the EB radiation. A photoinitiator has been included in the same initial mixture in the case of UV exposure. The electro-optical behavior of the obtained PDLC films was investigated depending on curing conditions. Infrared spectroscopy measurements were carried out to determine the extent of cure. Furthermore, several thermodynamic quantities have been deduced from calorimetric measurements.

EXPERIMENTAL PART

Materials and sample preparation

The nematic LMWLC used in this work was the eutectic mixture E7 from Merck, containing essentially cyanoparaphenylene derivatives. The prepolymer chosen consists of an aromatic polyester acrylate (Rahn AG, Switzerland) diluted in additional monomers including Tripropyleneglycoldiacrylate (UCB, Belgium). A blend of 30 weight-percent (wt-%) of the prepolymer mixture and 70wt-% of LMWLC was used for EB-cured samples. UV-cured samples were prepared from the same mixture containing 2wt-% (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 sheet (Renker, Germany), both coated with a thin transparent layer of conducting indium-tin-oxide. The glass support has been replaced by a NaCl plate for infrared measurements. DSC samples were prepared using aluminium sheets as supports.

Samples employed for DSC measurements could be realized by uniform application of the reactive mixtures on aluminium sheets as supports, using a bar-coater of 75μm. For each composition, several samples have been prepared and exposed to the electron beam radiation to cure the polymerizable mixture.

The EB generator was an Electrocurtain Model CB 150 (Energy Sciences Inc.). In the case of UV-curing, a Minicure Model MC4-300 (Primarc UV technology) equipped with a medium pressure mercury arc lamp rated 80W per cm was used. For EB- and UV-curing the samples

prepared as mentioned above were placed in a tray which was passed under the irradiation source on a conveyor belt.

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. A more detailed description of the experimental conditions is given in reference[3].

Infrared spectroscopy

Infrared spectra of thin films (less than 10μm) were recorded in the transmission mode with a Perkin Elmer 2000 model. The spectra have been taken before and after the curing process and the various doses were applied only once and at room temperature.

DSC

DSC measurements were performed on an apparatus of the type SEIKO DSC 220C equipped with a liquid nitrogen system. The DSC cell was purged with nitrogen at a rate of 50ml/min. Rates of 10°C/min (heating) and 30°C/min (cooling) were used in the temperature range from

-100°C to +100°C. The program consists first in cooling the sample followed by several heating and cooling cycles. Data were recorded systematically on the second heating ramp.

RESULTS AND DISCUSSION

Figure 1 illustrates the electro-optical behavior of 30μm thick PDLC films prepared by PIPS-UV and PIPS-EB. The UV-cured films have been exposed to 45mJ/cm^2 whereas a dose of 104kGy was used for the EB-cured samples. All films obtained appeared opaque in the initial off-

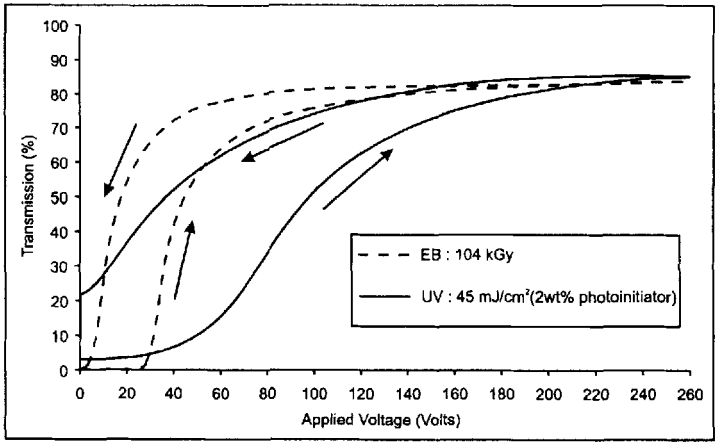

FIGURE 1 Electro-optical response of 30μm thick EB- and UV-cured PDLC films (λ=632.8nm, sinusoidal voltage ramps of frequency 145Hz at room temperature).

state and became transparent if an appropriate electrical field was applied. Both UV- and EB-cured samples show low transmission values in the initial off-state ($T_{off\ init}$) and values higher than 80% in the on-state. It was also found that the UV-cured films did not recover their $T_{off\ init}$ values after application of voltage cycles. This memory effect has not

been observed for the EB-cured samples. In particular, Figure 1 exhibits significantly higher threshold and saturation voltages for the UV-cured sample as compared to the EB-cured film. In order to understand

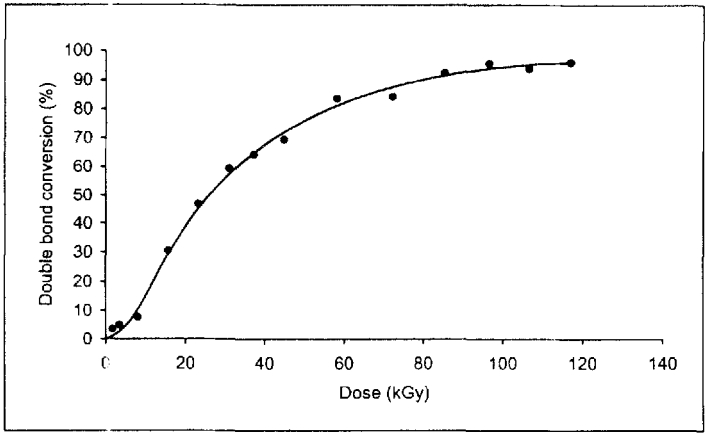

FIGURE 2 Conversion of acrylic double bonds vs dose for the EB-cured system. The continuous line represents a guide for the eye.

these findings, the conversion of the carbon-carbon double bond of the acrylate groups was monitored by infrared spectroscopy. Figure 2 represents the conversion vs dose for the EB-cured prepolymer/E7 mixture while Figure 3 shows the results for UV-cured samples. Constant conversion values of 90-95% were obtained at dose values exceeding 35mJ/cm^2 for the UV system and 90kGy for the EB sample. These results show clearly that although approximately the same high conversion values were found for the systems considered here, the electro-optical properties are substantially different.

Thermophysical results obtained so far indicate similar values for the glass transition temperature of the polymer matrices around T=0°C

in both cases considered here. The fractional amount of LC entrapped in phase separated domains was evaluated to 0.7 for the UV-cured system.

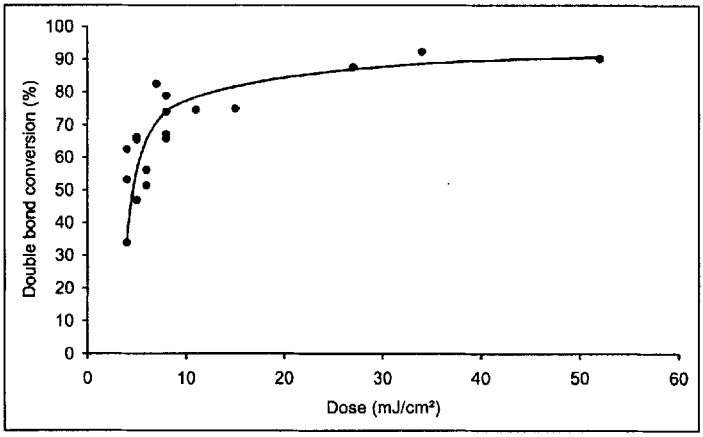

FIGURE 3 Conversion of double bonds as a function of dose for the UV-cured system. The continuous line represents a guide for the eye.

Only slighly increased values of 0.75 have been found for PDLC samples prepared by EB. Significant higher nematic+isotropic/isotropic transition temperatures ($T_{N+I/I}$) were observed in the case of the UV system as compared to EB-cured samples. Assuming similar network architectures and sample morphologies for the two series of heterogeneous materials, these variations of $T_{N+I/I}$ could be explained by a more densified polymer network in the case of UV-cured samples[5]. A more densified network might lead to smaller LC domains which in turn require higher electrical fields to align the LC molecules.

CONCLUSIONS

A comparative study of PDLC samples prepared by UV- and EB-radiation using a PIPS process has been performed. The electro-optical

behavior strongly depends on the curing conditions. Significant higher threshold and saturation voltages were found for UV-cured films compared to EB-cured samples. In addition, a memory effect has been observed for UV-cured films. The extent of cure has been determined by infrared spectroscopy measurements. The conversion vs dose curves exhibit only slight differences of the plateau values obtained in the case of UV- and EB-cured samples. The analysis of DSC thermograms allowed to reveal remarkable differences of the nematic+isotropic/ isotropic transition temperature of the composite materials, which may be attributed to a more densified network in the case of UV-cured films.

Acknowledgement
The authors gratefully acknowledge the financial support of the C.N.R.S, the Région Nord-Pas de Calais, the Ministère de l'Enseignement Supérieur et de la Recherche, the EU programme FEDER, and the Max-Planck-Institut für Polymerforschung in Mainz, Germany.

References

[1] P.S. Drzaic. *Liquid Crystal Dispersions*, World Scientific, Singapore (1995).
[2] U. Maschke, A. Traisnel, J.-D. Turgis, X. Coqueret, *Mol. Cryst. Liq. Cryst.* 299, 371 (1997).
[3] F. Gyselinck, U. Maschke, A. Traisnel, X. Coqueret, *Mol. Cryst. Liq. Cryst.* 329, 569 (1999).
[4] F. Gyselinck, U. Maschke, A. Traisnel, X. Coqueret, *Liq. Cryst.* 27, 421 (2000).
[5] F. Benmouna, L. Bedjaoui, U. Maschke, X. Coqueret, M. Benmouna, *Macromol. Theory Simul.* 7, 599 (1998).