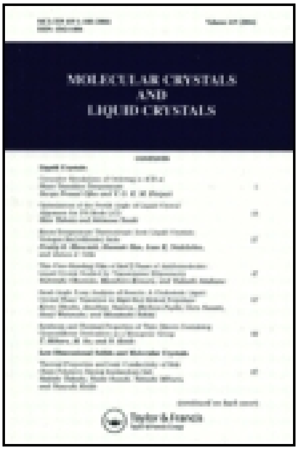

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Evolution of Electro-Optical Properties of Polymer Dispersed Liquid Crystal Materials During Processing

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Evolution of Electro-Optical Properties of Polymer Dispersed Liquid Crystal Materials During Processing

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Polymer dispersed liquid crystal (PDLC) films are interesting materials particulary for optical devices. The initial mixture was composed of diglycidyl ether of bisphenol A (DGEBA), polypropylene oxide diamine (Jeffamine D-400), and the nematic low molecular weight liquid crystal E7. PDLC films were obtained by combined thermally and polymerization induced phase separation processes initiated by the temperature controlled polycondensation reaction of DGEBA and Jeffamine D-400. The electro-optical curves of the obtained films strongly depend on the monomer conversion. It was found that both the transmission in the off-state as well as in the on-state decrease with the extent of cure. In addition, threshold and saturation voltages increase for PDLC films characterized by higher monomer conversion values. The electro-optical curves obtained for a conversion of approximately 80% exhibit an unusual behavior. At monomer conversions approaching 100% the transmission versus voltage curves show the expected normal mode.

Keywords: Polymer Dispersed Liquid Crystal; polymer; epoxy; amine; liquid crystal; phase separation

INTRODUCTION

Polymer Dispersed Liquid Crystal (PDLC) materials consist commonly of micron-sized droplets of low molecular weight liquid crystal (LMWLC) dispersed in a solid polymer matrix[1-3]. The starting materials are chosen so that an external electrical field applied across the PDLC film aligns the LMWLC in the droplets and switches the film from a cloudy light scattering off-state to a highly transparent on-state. These materials are of considerable interest for display applications and light control devices like optical shutters.

In the present paper, PDLC films are prepared by a phase separation process of an initially homogeneous mixture of the LMWLC in monomers that undergo polycondensation[4-9]. The composite material was obtained from a selected blend including an epoxy monomer (diglycidyl ether of bisphenol A - DGEBA), a polypropylene oxide diamine, and the nematic LMWLC E7. A particular attention was paid to the influence of the polymerization conditions on the electro-optical response. The optical transmission properties of the obtained PDLC films were investigated as a function of film thickness and amplitude of the applied AC voltage. Threshold voltages (V_{10}, voltage required to reach 10% of the maximum transmission value) were also considered.

EXPERIMENTAL PART

Materials and sample preparation

As polymer matrix precursors a diglycidyl ether of bisphenol A, DGEBA (DER 332 from Dow Chemicals) and polypropylene oxide diamine (Jeffamine D-400 from Huntsman) were employed. DGEBA and Jeffamine D-400 were mixed together in stoichiometric quantities of epoxy and amine groups. The composition of the nematic LMWLC E7 (Merck) was adjusted to 50 weight%. Figure 1 represents the chemical structures of the monomers. A more detailed description of these compounds are given in a previous paper[4]. The homogeneous blend composed of DGEBA, Jeffamine D-400, and E7 was sandwiched between two glass plates (Balzers, Liechtenstein), both coated with indium-tin-oxide. Samples exhibiting film thicknesses between 5 and 40μm were prepared under isothermal conditions using appropriate spacers. For each reaction time, a large number of samples have been prepared to check for reproducibility. The film thickness was measured by a micrometer calliper (Mitutoyo; uncertainty: ±1 μm).

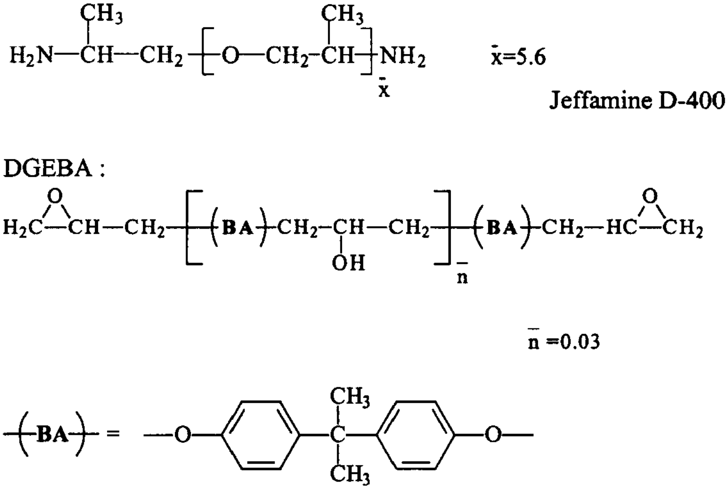

FIGURE 1 Chemical structures of the monomers

Electro-optical measurements

A standard set-up was used to measure the transmission properties of PDLC films at room temperature. The PDLC cells were oriented normal to the beam of an unpolarized HeNe laser (λ =632.8nm). The transmission values were corrected using appropriate calibration standards.

To evaluate the electro-optical properties of the PDLC films, light transmission changes upon application of an AC electrical field of frequency 145Hz were investigated. Starting from the off-state, a linear increasing voltage ramp was applied up to a desired maximum value V_{max}, followed by a similar decrease of the voltage. 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. The same procedure was repeated several times using the same sequence of appropriate voltage maximum values.

RESULTS AND DISCUSSION

Epoxy-amine reaction kinetics

The reaction between DGEBA and Jeffamine D-400 is conducted as an isothermal step copolymerization between the epoxy and amino groups. In particular, the choice of the reaction temperature influences the extent of cure and the phase separation process. The reaction rate can be controlled by the applied temperature, hence affecting the morphology of the obtained PDLC sample. Following these lines, the kinetics of the epoxy-amine reaction of the DGEBA/Jeffamine D400/E7 system has been previously investigated at two isothermal curing temperatures, i.e. at T=100°C and T=30°C[5]. The knowledge of the monomer conversion allows to study PDLC films as a function of the extent of cure. Two different cure cycles have been employed to realize PDLC films for electro-optical analysis. First, all sandwiched prepolymer/LMWLC samples have been kept for 180min at T=100°C to reach a monomer

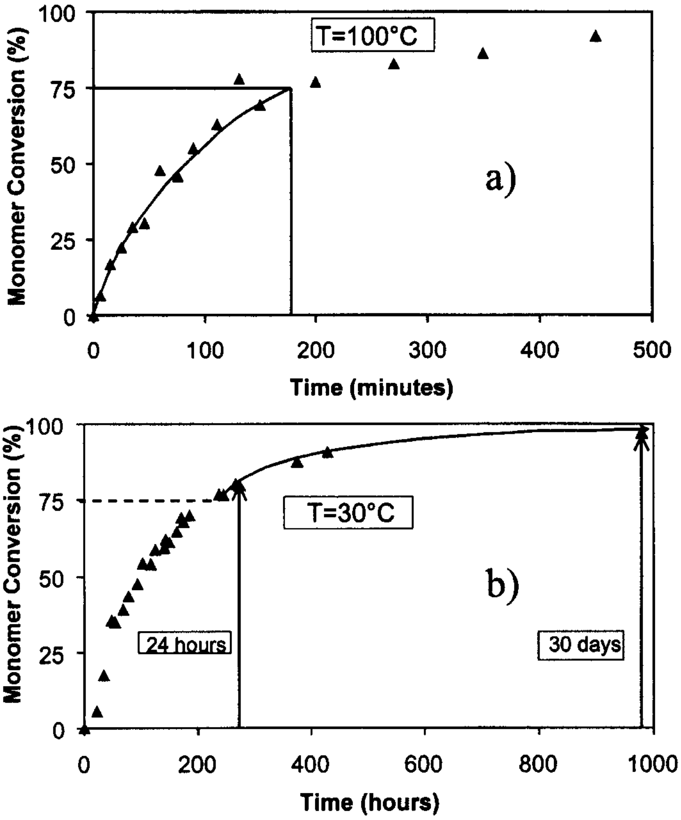

FIGURE 2 Epoxy monomer conversion as a function of reaction time for a 1:1 (DGEBA/Jeffamine D400)/E7 mixture a) at T=100°C; b) at T=30°C.

conversion of 75% as displayed in Figure 2a. In a second step, samples were cooled down and then post-cured at room temperature (RT). The polycondensation reaction still continues at RT because the system does not vitrify following roughly the kinetic evolution at T=30°C shown in Figure 2b. Two series of samples have been characterized by electro-optical measurements. Samples of the first series were left a post-cure time of 24h at RT leading to an epoxy conversion of approximately 80%. A post-cure time of 30 days at RT applied on samples of the second series enables the epoxy-amine reaction to be completed (100% conversion).

Electro-optical measurements

Figure 3 represents transmission vs voltage curves of representative 30µm thick PDLC films after a curing time of 180min at T=100°C followed by 24h and 30 days of post-cure at RT, respectively. This figure clearly shows that both the transmission in the off-state as well as in the on-state decreases with the extent of cure. The electro-optical reponse obtained for the 24h-sample exhibits an unusual behavior : The maximum of transmission has been reached for a voltage lower than the maximum voltage applied on the sample. Further increasing the electrical field leads to a decrease of the transmission and a constant value characterizing the on-state was not observed. The transmission vs voltage curve of the 30 days-sample shows the expected normal mode. This variation of the electro-optical behavior can be explained as follows: i) a change in morphology which occurs between 80 and 100% conversion; ii) a variation in composition of LMWLC domains which might contain monomers at a conversion of 80% for the first series; iii) an evolution of the elasticity of the epoxy-amine network whose crosslinking density increases with the reaction extent and influences the interface between LMWLC domains and polymer matrix. Environmental scanning electron microscopy (ESEM) investigations exhibit only little change in droplet size between samples of the first and second series. The gel point conversion, which defines the appearance of the first tridimensional molecule starting to form the network, was measured at a conversion of 60%[4]. 24h-samples are characterized by a more weakly crosslinked network with a large amount of low molar mass species in the LMWLC droplets[8]. Upon application of an electrical field the absence of a well defined polymer/LMWLC interface could lead to the obtained electro-optical

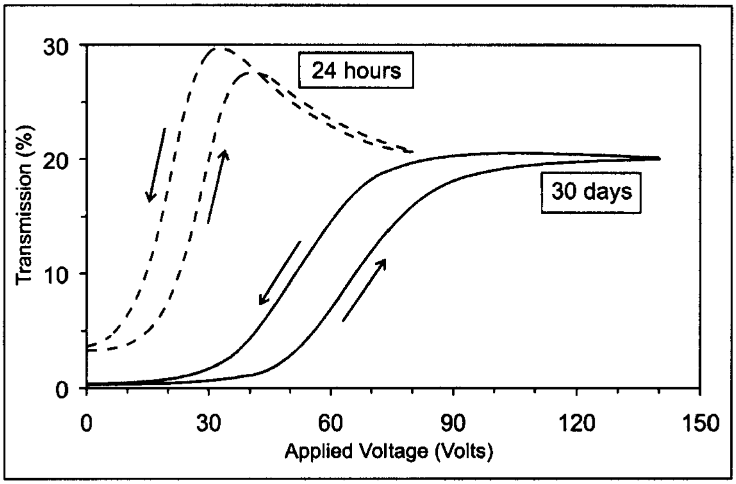

FIGURE 3 Electro-optical curves of 30μm thick PDLC films prepared using a curing time of 180min at T=100°C followed by 24h at RT (upper curves) and 30 days at RT (lower curves), respectively (λ =632.8 nm, measurements at room temperature, application of sinusoidal voltage ramps of frequency 145 Hz).

behavior. In the case of the 30 days-samples the environment of the LMWLC droplets has changed to a fully crosslinked polymer network. As a consequence, threshold (V_{10}) and saturation voltages increase for PDLC films characterized by higher monomer conversion values. Figure 4 illustrates the dependence of film thickness on V_{10} for both 24h- and 30 days-samples. Striking differences can be found: 24h-samples show low V_{10} values but increasing film thickness leads to a non-linear behavior. 30 days-samples exhibit higher V_{10} values. The expected linear relationship between V_{10} and film thickness was observed in this case.

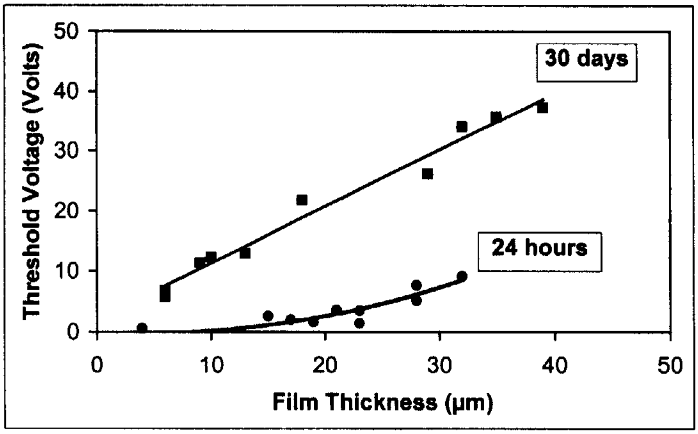

FIGURE 4 Threshold voltages for 24h- and 30days-samples as a function of film thickness (first voltage cycle, ramp up, λ=632.8nm, ν=145Hz).

CONCLUSIONS

The electro-optical behavior of thermally cured epoxy-amine-E7 mixtures has been investigated. The transmission vs voltage curves exhibit a strong dependence on the monomer conversion but are highly reproducible for each reaction conversion. The change in the polymer network density by increasing the extent of conversion induce modifications of electro-optical properties such as the initial off-state transmission, threshold- and saturation voltages. The advantage of our PDLC processing by polymerization and thermally induced phase separation is the great versatility of possible PDLC materials from the same initial system. Indeed, several morphologies can be obtained by varying the conditions of the cure cycle. A more detailed study will appear in a future communication[9].

Acknowledgement

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