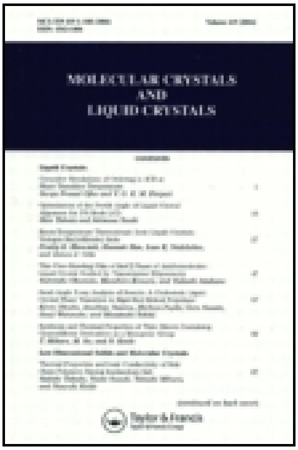

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Effects of Perfluoration of Epoxy-Amine Polymer Matrices on the Electro-Optical Performance of Polymer Dispersed Liquid Crystal Films

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Polymer dispersed liquid crystal (PDLC) films were obtained by combined thermally and polymerization induced phase separation processes initiated by the temperature controlled polycondensation reaction of monomers carrying either epoxy or amine groups. The epoxy diglycidyl ether of bisphenol A (DGEBA) and two different amines very used: an aliphatic amine and an aromatic fluorinated amine. The nematic liquid crystal mixture E7 was employed. The electro-optical performance of the obtained PDLC films was analyzed as a function of reaction cure in the absence and presence of the fluorinated amine. It was found that the addition of the fluorinated amine has a strong influence on the transmission vs voltage curves. A remarkable decrease of threshold- and saturation voltages as well as an increase of the transmission values in the on-state was observed.

Keywords: polymer; epoxy; amine; liquid crystal; perfluorination

INTRODUCTION

Polymer Dispersed Liquid Crystal (PDLC) materials are a special class of polymer/liquid crystal (LC) composites based on a dispersion of micron-sized low molecular weight LC droplets in a polymer environment[1-2]. These polymer/LC systems are particularly interesting because of their potential use in electro-optical applications. PDLC films are currently obtained by a phase separation process of an initially homogeneous mixture of the LC in monomers that undergo polymerization.

The electro-optical properties depend on the morphology (i. e. the size, distribution, and number density of droplets), the strength of the polymer/LC interactions, the LC director configuration in the droplets, and the characteristics of the polymer/LC interface. The presence of strong anchoring effects at the LC boundaries leads generally to increasing switching voltages. Several investigations have been reported on the variation of the polymer/LC interface by chemical modification of the polymer matrix[1]. The perfluoration of the polymer matrix results commonly to a decrease of the LC anchoring and therefore to a better electro-optical reponse. These chemical modifications of the polymer matrix often not only provoke changes in the electro-optical response but also in the sample morphology. As a result, polymer/LC miscibility and therefore the swelling behavior of LC in the polymer host are modified as well. These and other important parameters are interdependent and do not allow easily to investigate them independently.

In this paper an attempt was made to modify the composition of the reactive polymer precursor blend by adding an aromatic fluorinated amine to a mixture of an aliphatic amine and an epoxy monomer. The two last compounds were not fluorinated. As LC the nematic mixture known as E7 was used. The process of polymerization induced phase separation by the thermal epoxy-amine reaction leads to PDLC samples exhibiting controlled properties like the sample morphology, polymer glass transition, surface tension[3-8].

The electro-optical properties of the obtained PDLC films were analyzed in the absence and presence of the fluorinated amine. The optical transmission properties of the obtained PDLC films were studied as a function of film thickness and electrical field. Threshold and saturation voltages (V_{10}, V_{90}, voltages required to reach 10%, 90% of the maximum transmission value, respectively) were also taken into account.

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 used. The aromatic fluorinated amine was prepared in the laboratory and its molecular structure will be given elsewhere[8]. The nematic LC mixture E7 (Merck) was employed. The chemical structures of DGEBA, Jeffamine D-400, and E7 are described in a previous paper[4]. Three different reactive mixtures were prepared keeping the quantities of epoxy and amine groups in a stoichiometric ratio in all cases. The first blend (called blend 1) was composed of 50 weight-% (wt-%) DGEBA/ Jeffamine D-400 and 50 wt-% E7. In the second mixture (called blend 2) a part of the DGEBA was replaced by the aromatic amine in a 3/2 (D-400/fluorinated amine) ratio of reactive groups. The amount of E7 was kept constant at 50 wt-%. The third blend (called blend 3) exhibited the same epoxy-amine composition as blend 2 except that the quantity of LC was adjusted to 70 wt-%.

The homogeneous blends composed of amine(s), epoxy, and E7 were sandwiched between two glass plates (Balzers, Liechtenstein), both coated with indium-tin-oxide. Samples exhibiting film thicknesses between 5 and 40 μm were prepared under isothermal conditions using appropriate spacers. For each blend, 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).

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

The conditions of thermal cure determine to a large extent chemical and physical properties of PDLC materials obtained from the epoxy-amine-E7 mixtures. Starting from homogeneous blends, temperature and reaction time can be varied to control the kinetics of polymerization and the phase separation process between the polymer formed and the LC. This procedure allows to obtain the generally desired so called swiss-cheese sample morphology. Following these lines, blend 1 was kept at T=100°C for three hours followed by cooling to room temperature and storage for 30 days. It has been shown in a previous paper[3] that these thermal conditions are particularly adapted to obtain PDLC films that scatter visible light efficiently. These samples were characterized by a large number of micron-sized LC-droplets in the epoxy-amine polymer matrix. The electro-optical properties of the PDLC films exhibited low transmission values in the initial off-state even at small film thicknesses but on the other hand relatively high switching voltages were found[7]. If the fluorinated amine is added to the initial aliphatic amine/epoxy mixture, the conversion of epoxy groups as a function of reaction time at T=100°C is slowed down compared to the preceeding case. Furthermore the aromatic amine will not react with the epoxy at room temperature. This is the reason why the reaction time at T=100°C for blend 2 was chosen at 15 hours. On the other hand the kinetics of the epoxy-amine reaction in the case of blend 3 are furthermore reduced due to a dilution effect by increasing the E7 content from 50 wt-% to 70 wt-%. A reaction time of 50 hours was applied for these samples. The choice of the reaction conditions used for blends 2 and 3 was strongly influenced by the obtained electro-optical results. Indeed it was found previously[7] that epoxy-amine samples which are not completely cured exhibit an unusual electro-optical behavior. Fully cured films show the expected normal mode.

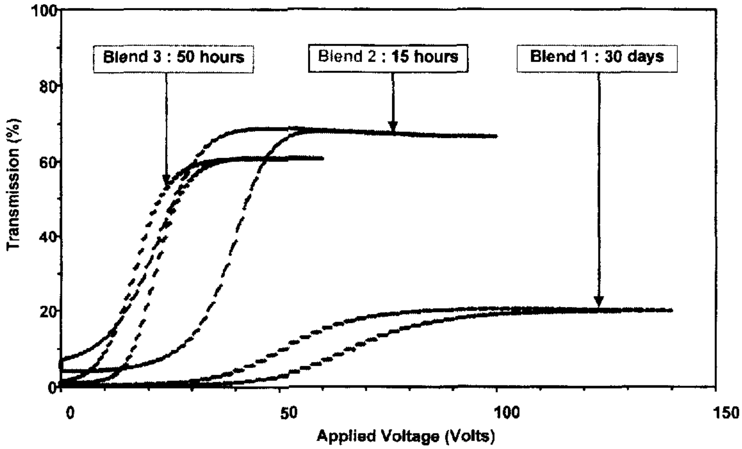

FIGURE 1 Transmission vs voltage curves of 31 μm thick PDLC films prepared from blends 1-3 (λ =632.8 nm, measurements at room temperature, application of sinusoidal voltage ramps of frequency 145 Hz).

Electro-optical measurements

Figure 1 displays electro-optical curves of representative 31 μm thick PDLC films for the three blends considered. Striking differences were found between the results obtained for blend 1 and those for blends 2 and 3. The addition of the aromatic amine to the initial mixture results in a remarkable decrease of threshold and saturation voltages accompagnied by an increase of the transmission values in the on-state. On the other hand transmission values in the inital off-state are slightly higher in the case of samples from blend 2 compared to blend 1. In order to obtain a more enhanced phase separation the composition of E7 was increased which results in lower off-state transmission values and again more reduced switching voltages. Figure 2 shows clearly the

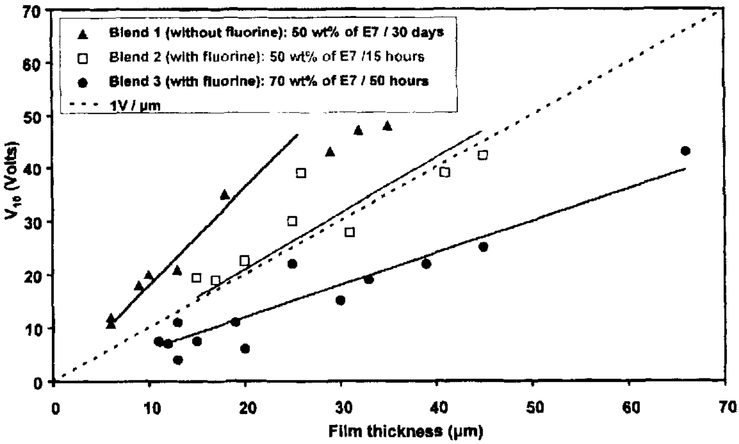

FIGURE 2 Threshold voltages vs film thickness of PDLC films obtained from blends 1-3 (λ =632.8 nm, measurements at room temperature, application of sinusoidal voltage ramps of frequency 145 Hz).

differences obtained in terms of threshold voltages. The dotted line represents an electric field of 1V/µm. The threshold voltages obtained from blend 2 shows a considerable decrease compared to those obtained from blend 1. Electric fields below 1V/µm were found for samples from blend 3. Figure 3 shows the transmission values in the on-state of PDLC films for the three blends together. Samples from blends 2 and 3 exhibit similar behavior indicating a good agreement between the refractive indices of the polymer matrix and the aligned LC droplets. This condition of refractive index matching is less fullfilled in the case of films obtained from blend 1. Increasing film thickness leads to a considerable decrease of the on-state transmission values.

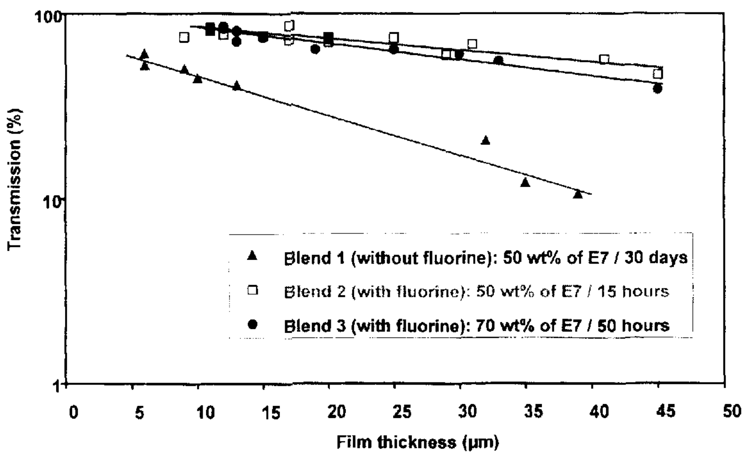

FIGURE 3 Transmission in the on-state of PDLC films obtained from blends 1-3 as a function of film thickness (λ = 632.8 nm, measurements at room temperature, application of sinusoidal voltage ramps of frequency 145 Hz).

All the results presented in Figures 1-3 can indeed be explained by the presence of the fluorinated amine which strongly influences the electro-optical properties of the obtained PDLC films. As a consequence the anchoring effects at the LC droplet/polymer interface are reduced for samples from blends 2 and 3 compared to blend 1. These findings already can explain the different electro-optical behavior observed but the different chemical nature of both amines has also to be taken into account. Indeed the fluorinated amine presents aromatic groups while the other amine is aliphatic. The presence of aromatic groups might also be favorable for the enhanced electro-optical response.

CONCLUSIONS

An attempt has been made to characterize the electro-optical properties of thermally cured epoxy-amine-E7 mixtures. The electro-optical curves show large differences depending essentially on the choice of the compounds of the initial mixtures. Adding an aromatic fluorinated amine by keeping the LC composition constant leads to a strongly enhanced electro-optical performance. The best electro-optical results characterized by low transmission values in the off-state, high transmission values in the on-state, and low threshold and saturation voltages were found for samples of blend 3. First microscopical investigations on these systems exhibit the same sample morphology for all systems considered. Further studies are currently under progress[7].

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References

[1] P.S. Drzaic, *Liquid Crystal Dispersions* (World Scientific, Singapore, 1995).
[2] J.W. Doane, in *Liquid Crystals – Applications and Uses*, edited by B. Bahadur (World Scientific, Singapore, 1990).
[3] H. Masood Siddiqi, M. Dumon, J.P. Eloundou, J.P. Pascault, *Polymer* 37, 4795 (1996).
[4] H. Masood Siddiqi, M. Dumon, J.P. Pascault, *Mol. Cryst. Liq. Cryst.* 312, 137 (1998).
[5] J. Borrajo, C.C. Riccardi, R.J.J. Williams, H. Masood Siddiqi, M. Dumon, J.P. Pascault, *Polymer* 39, 845 (1998).
[6] H. Masood Siddiqi, M. Dumon, J.P. Pascault, *J. Mater. Chem.* 8, 1691 (1998).
[7] L. Sannier, H. Masood Siddiqi, M. Dumon, F. Gyselinck, U. Maschke, to be published.
[8] M. Dumon et al., patent in preparation.