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THERMOPHYSICAL AND ELECTRO-OPTICAL CHARACTERIZATION OF NEMATIC LIQUID CRYSTAL / ACRYLATE SYSTEMS

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Abstract : New Polymer Dispersed Liquid Crystal (PDLC) materials were prepared by a Polymerization Induced Phase Separation (PIPS) mechanism using U.V. radiation. The samples are obtained from the liquid crystalline mixture E7 and a blend of monofunctional (2-Ethyl Hexyl Acrylate) and difunctional (1,6-Hexane Diol DiAcrylate) monomers as precursors of the matrix. The thermodynamic properties of both cured and uncured samples were studied by Differential Scanning Calorimetry and Optical Microscopy. The optical transmission of selected PDLC films has been measured as a function of frequency and amplitude of the applied voltage for several film thicknesses.

INTRODUCTION

Polymer Dispersed Liquid Crystal (PDLC) films consisting commonly of discrete micron-sized liquid crystalline droplets dispersed in a solid polymer matrix, have considerable potential for electro-optical applications[1,2]. In the general frame of the preparation of PDLC materials by a Polymerization Induced Phase Separation (PIPS) - UV process[3-5], we have undertaken a study of polymer - liquid crystalline composite materials prepared from precursors of simple chemical structure. The reactive starting mixtures include a monofunctional monomer (2-Ethyl Hexyl Acrylate (EHA)), a difunctional monomer (1,6-Hexane Diol DiAcrylate (HDDA)), and a nematic liquid crystal component (E7).

The thermodynamic properties of both cured and uncured samples were studied by Differential Scanning Calorimetry and optical microscopy. The fractional amount of Liquid Crystal (LC) contained in PDLC microdroplets has been determined from calorimetric measurements. The optical transmission of selected PDLC films has been investigated as a function of frequency and amplitude of the applied voltage for several film thicknesses.

The goal of the present experiments dealing with the particular mixture of composition EHA:HDDA:E7 (10:30:60) is to demonstrate the electro-optical functionality of such materials exhibiting efficient phase separation after U.V. polymerization.

BACKGROUND

One of the major parameters that govern the formation of PDLC films is the phase separation process. Therefore, the quantification of each of the segregated phases (polymer / LC) is an important goal. Smith and Vaz[6] proposed a model based on experimental data allowing to evaluate α, the fractional amount of LC contained in the microdroplets. α can be determined from calorimetric determinations of either ΔH_{NI}, the nematic - isotropic transition enthalpy (unit of mass), or from ΔCp, the increase in heat capacity (unit of mass) at Tg_{LC} (liquid crystal glass transition temperature in the PDLC). This calculation is based on the assumption that the liquid crystals dispersed in the polymer matrix exhibit the same thermophysical behavior as in the bulk state. Smith et al. provided a simple equation for α[6] :

$$\alpha = \frac{m_{LC}^{D}}{m_{LC}} = \left(1 + \frac{m_P}{m_{LC}}\right) P(x),$$

where m_{LC}^{D} is the mass of LC which has phase separated from the polymer, m_{LC} and m_P are the masses of LC and polymer in the PDLC, x is the LC concentration, and for :

$$P(x) = \frac{\Delta H_{NI}(x)}{\Delta H_{NI}(LC)} \text{ or } P(x) = \frac{\Delta Cp_{LC}(x)}{\Delta Cp_{LC}(LC)},$$

representing the ratios of nematic - isotropic transition enthalpy or the heat capacity increment for the PDLC to the equivalent value for the starting liquid crystal mixture. Both ΔH_{NI} and ΔCp values are determined from DSC curves.

EXPERIMENTAL

Materials

The liquid crystalline mixture E7 (Merck Ltd, UK) was used during this work ; it exhibits a nematic phase at room temperature, which easily forms a glassy nematic upon

cooling, and crystallization does not readily occur upon rewarming. The glass gradually becomes a fluid nematic at Tg = - 62°C with ΔCp = 0.479 mJ/(mg.°C). The nematic - isotropic transition of E7 occurs at T_{NI} = 59°C with ΔH_{NI} = 4.5 J/g. The precursors of the matrix consist of a mixture of EHA and HDDA in the ratio EHA:HDDA = 1:3. EHA exhibits an isotropic phase on the temperature range -100 to +100°C. HDDA presents a melting transition at T_{KI} = 0.2°C with ΔH_{KI} = 139.2 J/g. The UV polymerization was induced by 2wt.% per gram of monomer of Darocur 1173 (Merck Darmstad, G).

Preparation of PDLC samples

The monomers and the liquid crystals were mixed together at room temperature in the ratio (40:60) by weight until the mixture became homogeneous. Samples for calorimetry were prepared by introducing 2.9 ± 0.1 mg of PDLC precursors into aluminium DSC pan. The low viscosity of the compounds led rapidly to the formation of a thin film in close contact to the pan bottom allowing to perform reproducible measurements. The DSC pans containing the uncured and cured samples have been sealed to avoid evaporation effects during the temperature treatment. Samples for optical microscopic observations were prepared between standart glass slides. Samples for electro-optical measurements could be realized by placing a small amount of the reactive mixture between two glass plates coated with a thin transparent layer of conducting Indium Tin Oxyde ITO (Balzers, Liechenstein). In order to obtain a uniform film thickness, a 23 μm PET spacer (Goodfellow) was placed between the plates. Accurate PDLC film thicknesses were determined using a micrometer calliper (Mitutoyo ; uncertainty : ± 1μm) after UV exposure.

UV curing was carried out for all our samples in the DSC furnace under isothermal conditions (T = 30°C) and nitrogen atmosphere. The wavelengh of the UV lamp was fixed at λ = 365 nm with a beam intensity of 94 mW/cm^2. The UV exposure time was set at three minutes.

Characterization methods

The DSC measurements were performed on a SEIKO DSC 220C. A liquid nitrogen system allows cooling experiments. The DSC cell was purged with 50 ml/min of nitrogen. Rates of 10°C/min (heating) and 30°C/min (cooling) were used in the temperature range -120 to +100°C. The program consist first in cooling the sample followed by several heating and cooling cycles. Data analysis have been carried out on second heating ramp.

The thermo-microscopical studies were performed on an optical polarizing microscope LEICA DMRXP, equipped with an heating / cooling stage Chaixmeca (-160

to +600°C). The same temperature program as used by DSC experiments was applied. Photomicrographs were picked up at different given temperatures with magnifications from 50 to 320.

The electro-optical experiments were carried out at room temperature using a Cary 219 spectrophotometer (Varian Associates) at a wavelengh of $\lambda = 625$ nm with a bandwidth of 3 nm using a driving AC voltage. The transmission properties of the PDLC cells were measured by passing the light through the cells normal to the film surface. Starting from the electrical OFF-state, the applied voltage was increased in steps of ten volts, with a step time of one minute until a further increase of voltage did not vary the transmission values. After the first scan up cycle, the voltage was decreased in the same way before the whole procedure was twice repeated. Between two complete cycles, the cells were kept for a period of five minutes in the field OFF-state.

RESULTS AND DISCUSSION

Thermophysical studies

The thermal spectra of the uncured mixture EHA:HDDA:E7 (10:30:60) exhibits two glass transitions at Tg = -99°C and Tg = -76°C (Figure 1.a)). Both transformations are due to the presence of phase separated liquid crystals and monomers after cooling at -120°C ; at low temperature, glassy states of each of the phases (LC / monomers) are obtained. The glass transition at Tg = -76°C is fourteen degrees below the glass transition of crude E7. This allows to associate this transformation to a Ng - N transition of a phase principally constitued of liquid crystals and significant amounts of monomers. The lower transition temperature Tg = -99°C results from the glass transition of the most part of the monomers mixed with some liquid crystals from E7. Three weak thermal events are also observed in the temperature range -35 to 0°C. Optical observations allow to characterize those transitions as : first the nematic - isotropic transition at T ~ -35°C, second the crystallisation of the difunctional monomer HDDA (crystalline state at temperature below 0°C) and then the melting at T ~ 0°C. Therefore, it can be assumed that the uncured mixture is in the isotropic and homogeneous state at T > 0°C.

The DSC curve of the cured composite material (Figure 1, curve b)) shows only two transitions : a glass transition at Tg = -60°C and an endothermic peak at T = +52°C. Both thermal events are very similar to those of pure E7. These transitions can be assigned as the transformations of the segregated liquid crystalline phase.

Electro-optical response

Figure 2 shows representative results of the transmission properties of a 17 μm thick PDLC film as a function of the applied voltage. The frequency of the sinusoidal voltage was 140 Hz. The films investigated exhibited a low transmission in the initial OFF-state. The electro-optical response of the PDLC film revealed a threshold voltage of V_{10} = 100V. High transmission values could be achieved using voltages up to 240V. This behavior can be explained by the UV intensity and exposure time used. In our experiments, the UV irradiation exposure was in the range of 100 mW/cm^2. Investigations have been carried out studying the influence of the dose rate on the electro-optical response curves. It was shown[8,9], that the threshold voltage increases by increasing the dose and the dose rate. This behavior has been attributed to the formation of smaller droplets at higher dose rates (from ref. 8, Figure 1 and 3 : Droplet radius 4.7 μm (UV dose : 1.7 mW/cm^2, exposure time : 23 min), droplet radius 1.5 μm (UV dose : 12.9 mW/cm^2, exposure time : 3 min)). Surface interactions occuring at the polymer / inclusion boundary are increased so that a higher electric field is needed to obtain a significant electro-optical response[5,9]. It can be assumed, therefore, that our PDLC films require high voltages to obtain high transmission in the ON-state. The memory effect[10] observed in some cases was almost non existent with our PDLC films. A hystereris effect[11-13] commonly associated with PDLC displays was found in all transmission vs voltage curves of our samples. Scanning electron microscopy investigations are currently in progress to correlate the morphology of the samples with the observed electro-optical behavior.

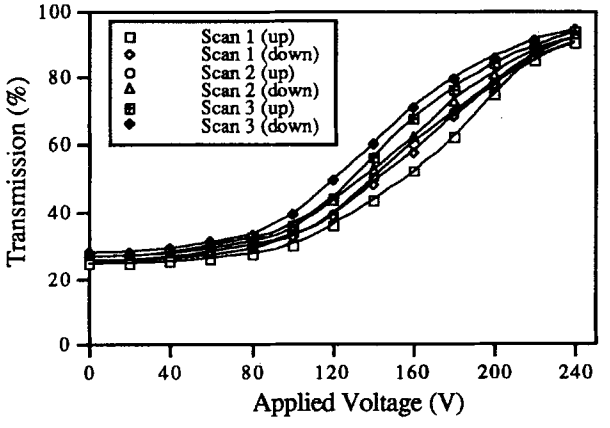


FIGURE 2 Electro-optical response of a 17 μm thick PDLC film taken in repeated increasing and decreasing voltage scans (ν = 140 Hz).

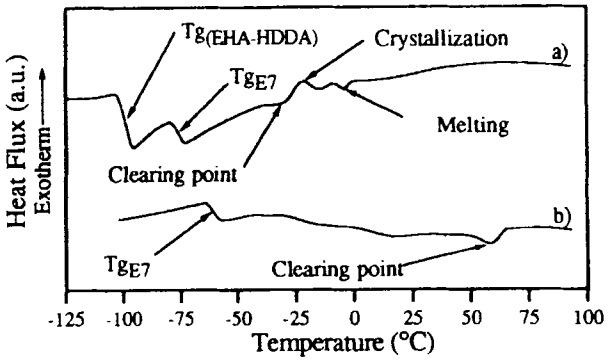
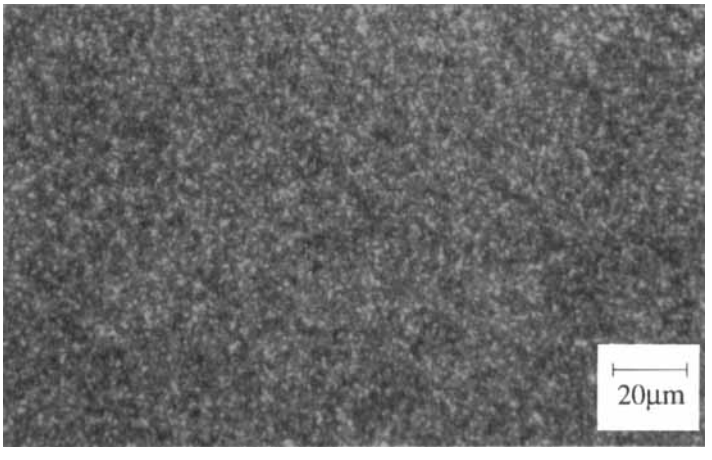


FIGURE 1 DSC thermal spectra for the mixture EHA:HDDA:E7 (10:30:60) : a) uncured, b) cured.

The fractional amount α of liquid crystal contained in the PDLC microdroplets has been determined using two different methods. From the increase of the heat capacity at Tg, a value of α = 80% was found. The second method includes the enthalpy change at the nematic isotropic transition and yields α = 50%. The difference between those two results can be explained by the lower solubility of the liquid crystal in the matrix at low temperature (Tg = -60°C) than at the nematic - isotropic transition temperature (T_{NI} = +52°C)[7]. Microscopical analysis of the texture of the PDLC sample (optical micrograph) revealed a great number of very small birefringent microdomains, which are thought to represent the liquid crystal microdroplets. Although the magnification was as high as possible (x320), the droplet size could not be accurately determined.



OPTICAL MICROGRAPH Morphology of a EHA:HDDA:E7 (10:30:60) UV-cured blend (Transmitted polarized illumination).

The electro-optical transmission curves of three prepared PDLC cells with film thicknesses in the range of 15 to 30 μm are presented in Figure 3. It can be seen that an increase in the film thickness results in an increase in the applied voltage necessary for its electro-optical activation. The transmittance $Tr = I_{Tr}/I_0$ can be expressed as a function of thickness of the films by[14-16] :

$$\log(Tr) = \log\left(\frac{I_{Tr}}{I_0}\right) = -\alpha d$$

where I_{Tr} is the transmitted intensity, I_0 the incident intensity, α the scattering coefficient, and d the thickness of the scattering film. The logarithm of the transmission in the OFF-state of our samples varies linearly with d (inserted Figure in Figure 3). Because the droplet distributions and droplet densities are unknown, it is not possible to analyse more deeply the scattering properties of the film deduced from the slope -log(Tr) as a function of d.

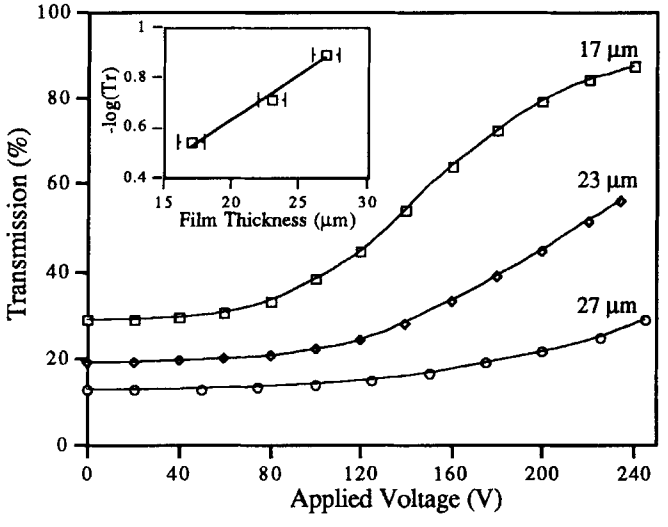


FIGURE 3 Effect of PDLC film thickness on transmission curves (ν = 140 Hz) ; Insert : Logarithm of the transmission (OFF-state) as a function of PDLC film thickness.

CONCLUSION

The reactive composition including a mixture of simple acrylate monomers and nematic liquid crystal exhibits phase separation evidenced by optical microscopy and quantified by DSC analysis. The opaque cured materials can be switched to a highly transparent ON-state under application of an AC field of ca. 10 V/μm. This work is part of an extensive study[17] of the phase behavior of mixtures EHA:HDDA:E7 (x:y:z) which affords additional information for understanding the morphological modifications observed upon changing the mixture composition and the curing conditions.

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