

Mechanical and Electro-optic Properties of Thiol-ene based Polymer Dispersed Liquid Crystal (PDLC)

*Askim F. Senyurt
Charles E. Hoyle
Joe B. Whitehead
Garfield Warren*

*School of Polymers and High Performance Materials
University of Southern Mississippi
Hattiesburg, MS*

Abstract: *The morphology development in thiol-ene based PDLC/H-PDLC films has been investigated in conjunction with the electro-optical properties of the films. The concentration of LC has been systematically changed in order to correlate electro-optic properties with the morphology of the nanometer sized liquid crystalline droplets.*

Introduction

Holographic-PDLCs are formed by illumination of reactive monomer/LC mixtures with the interference pattern of two laser beams¹⁻⁵. The interference pattern of the split laser beam forms dark and bright regions in the initial monomer/LC mixture. Since the polymerization rate is proportional to the light intensity, the difference in the reaction rate in different regions ensures the periodic phase separation of LC molecules from the emerging polymer matrix. In H-PDLCs, the refractive index modulation is achieved by alternating LC droplet layers in volume gratings that coherently scatter the incident light. Applying an electric field across the H-PDLC films reorients the director of the LC droplets and erases the refractive index modulation between LC and polymer matrix in a reversible process. The electro-optic properties are determined by the phase separated morphology, and the phase separated morphology is determined by the polymerization kinetics and the concentration of LC^{2,4}. Photopolymerizable thiol-ene based resins are alternatives to acrylate systems which comprise the majority of the H-PDLC literature¹⁻⁵. Herein, we present results of a systematic investigation of the material properties of several different thiol-ene based polymer matrices and how structural features of the monomer components affect the properties of the phase separated networks. Different weight percentages of a typical LC mixture, E7, were added to the monomer mixture with the aim of monitoring its effect on the glass transition temperature of the PDLC films, the phase separated morphology and the electro-optic properties of the final H-PDLC transmission gratings.

Experimental

Trimethylolpropane tris(3-mercaptopropionate), pentaerythritol triallyl ether, triallyl triazine trione, and triallyloxytriazine were obtained from Aldrich Chemical Company. The nematic liquid crystal mixture, E7, was obtained from EM industries. 2,2-dimethoxy 2-phenyl acetophenone (DMPA)

was obtained from Ciba Specialty Chemicals. All chemicals were used as received without further purification.

PDLC samples that were analyzed for thermal properties as a function of temperature were cured with a UV Fusion line EPIQ 6000 (D bulb, 394.6 mJoule/cm²) at a line speed of 10 m/min. Thermal transitions of the PDLC films were recorded using a TA Q1000 differential scanning calorimetry (DSC) by heating/cooling 10 mg samples from -50 to 100 °C at a rate of 10 °C/min under a nitrogen purge flow.

Voltage-dependent laser light transmission measurements were used to probe the electro-optic properties, and thus the spatial and compositional phase separated morphology of the H-PDLCs gratings. The data was analyzed in order to compute the typical electro-optic properties including switching time and the voltage required to reach 90% transmission (V_{90}). The details of the electro-optic measurement set-up are given elsewhere ⁵.

Scanning electron microscopy (SEM) was performed on a Quanta 200 SEM in the high voltage mode. Freeze-fractured samples ⁶ were mounted on the SEM sample holders and sputter coated with gold by using a Polaron E5100 sputter coater to enhance the image quality.

Results and Discussion

The structures of the monomer components used in this study are shown below. The polymerization exotherms obtained with thin-film calorimetry and real-time IR based conversion studies show that all three of the pure (i.e. without added LC) thiol-ene mixtures polymerize efficiently within several seconds to high conversions. The phase separation behavior of liquid crystal (LC) and monomer mixtures were established by optical microscopy. The samples with LC content between 30 wt % and 60 wt % were chosen to work with more extensively due to the presence of a single phase at room temperature.

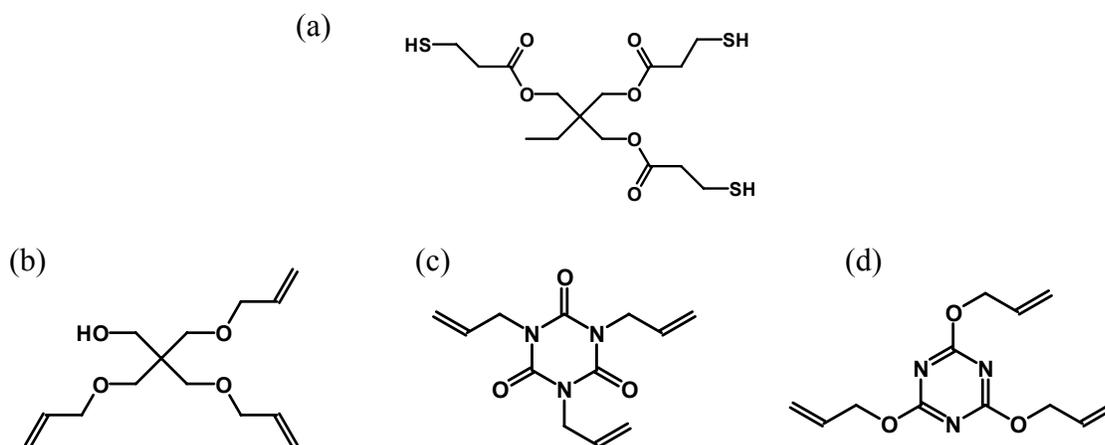


Diagram I: Chemical structures of (a) Trimethylolpropane tris (3-mercaptopropionate), [3T] (b) pentaerythritol triallyl ether, [E1] (c) triallyloxytriazine, [E2] and (d) triallyltriiazine trione, [E3].

Thermal transition plots of the heat capacity of thoroughly photocured films (medium pressure-UV Fusion lamp EPIQ 6000, D bulb 394.6 mJoule/cm² at a line speed of 10 m/min) obtained by DSC

(10 °C/min scan rate) reveal that the trithiol-triallyltriiazinetrione polymer matrix has a glass transition (T_g) of 28 °C. The T_g decreases from 28 to 3 °C as the LC (E7) weight percentage increases from 0 to 30 (Figure 1A). Unreactive LC small molecules suppress the T_g of the polymer matrix due to a plasticizing effect. The T_g of the LC/polymer matrix reaches a lower limit at 30 wt % LC concentration. A summary plot of thermal transition temperatures for all cured trithiol/triene/LC mixtures obtained by DSC analysis (Figures 1B) indicates the same tendency, i.e., a decrease in T_g with LC content up to a certain critical LC concentration, for all three thiol-ene crosslinked systems. The LC/polymer films exhibit a variation in T_g due to the different molecular architecture of the ene monomers.

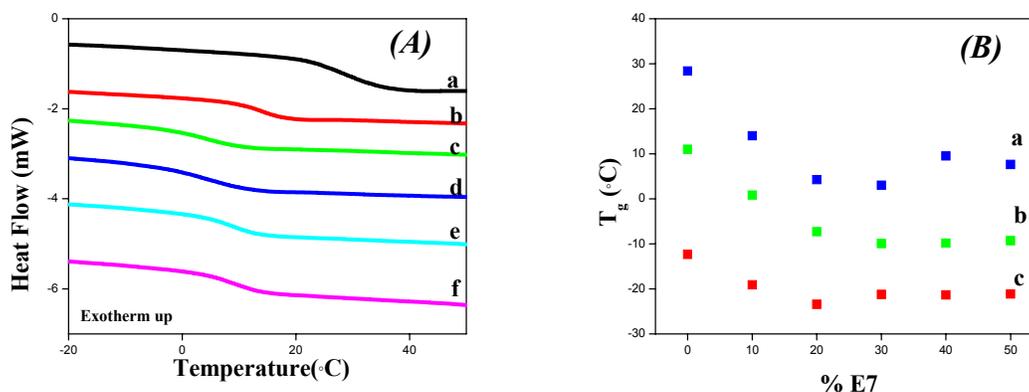


Figure 1: (A) Thermal transitions of trithiol-triallyltriiazinetrione films cured with (a) 0% E7, (b) 10% E7, (c) 20% E7, (d) 30% E7, (e) 40% E7, and (f) 50% E7 and (B) the summary of glass transition temperatures (T_g) of (a) [3T/E3] (b) [3T/E2] and (c) [3T/E1] obtained with DSC (10 °C/min scanning rate).

Transmission hologram gratings were recorded in the Bragg regime (spacing less than 1.5 μm) by illuminating thiol-ene/LC mixtures with the interference pattern created by the splitting and recombination of the output beam from an argon ion laser ($\lambda = 364 \text{ nm}$).

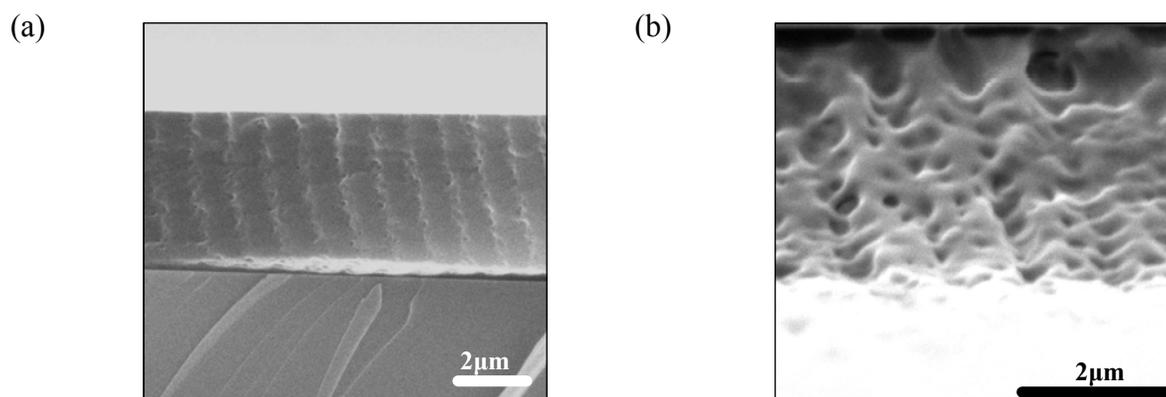


Figure 2: SEM images of trithiol-pentaerythritol triallylether H-PDLC films with a) 35 % and b) 50% E7. The scale bar in each image is 2 μm .

As an example of the type of morphology that can be achieved with the trithiol-ene systems, Figure 2 shows SEM images of a H-PDLC formed from trithiol-pentaerythritol triallylether. The SEM images of sample with 35 wt% and 50 wt% E7 depict the effect of LC concentration on the droplet size and the numbers of droplets per unit volume for each thiol-ene combination. The droplet planes were more uniform and well-defined for the sample with the lower E7 percentage. The grating spacing of the sample in Figure 2a is approximately 1.1 μm with droplet sizes between 0.05 and 0.2 μm in diameter. At the higher LC concentration, the LC droplet planes are less well defined and the droplets larger (see Figure 2b). A similar general trend is observed for the other trithiol-ene/LC systems with increasing LC concentration.

Analysis of the electro-optic parameters of the H-PDLCs reveals that the switching times are on the order of a millisecond, with the switching voltages showing a LC concentration dependence for all thiol/triene/LC films.

%LC	t_{switch} (msec)	V_{90} (volts/ μm)
30	1.70	6.2
40	1.40	6.79
50	1.20	5.39
60	3.10	3.8

Table 1: Summary of electro-optic responses of trithiol-pentaerythritol triallylether H-PDLC films with 30% to 60 wt % E7.

The results for the H-PDLCs obtained from the trithiol-pentaerythritol triallylether/E7 mixtures are shown in Table 1. The voltage required to achieve 90% response, V_{90} , ranges from 6.2 to 3.8 volts/ μm as the LC percentage in the initial mixture increases from 30% to 60 %. The decrease in the switching voltage with LC concentration reflects the larger size of the droplets as shown in Figure 2b. The longer switching time for 60% LC concentration is in accordance with the larger droplet sizes.

Conclusions

The effect of LC concentration on the morphology and the electro-optic properties of H-PDLC films has been investigated by fabricating transmission gratings with thiol-ene monomers. Increasing LC concentrations increase the switching times with lower switching voltages for all thiol/triene/LC films. This result was interpreted in view of SEM images which reveal the larger droplet sizes for high LC contents. Also, thermal properties of the films studied with DSC showed LC concentration dependence.

Acknowledgements

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