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Effects of Molar Ratios of Thiol-Ene Monomers on the Morphology and Electro-Optical Properties of Polymer Dispersed Liquid Crystal Films

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ABSTRACT

We synthesized tetrafunctional allyl ether monomer (4-AE) and investigated the effects of the different molar ratios of trimethylolpropane tris-(3-mercaptopropionate) (3-SH) to 4-AE on the photopolymerization behavior, morphology, and electro-optical properties of thiol-ene-based PDLC films. Photo-DSC and DSC analyses revealed that the PDLC sample containing 45 wt% 3-SH and 45 wt% 4-AE gave the highest exotherm, the fastest photocure rate, and the highest T_g due to the matched stoichiometry. Morphological observations and electro-optical measurements showed that the PDLC sample with the matched molar ratio gave the smallest LC droplet size, the highest threshold, driving voltages, and lowest saturation transmittance because the orientation of LC molecules got difficulty in small droplets. The stoichiometric ratios of 3-SH to 4-AE played an important role in controlling the photocure rate, phase separation rate, microstructures of LC droplets, and electro-optical properties of thiol-ene-based PDLC systems.

Keywords: Photopolymerization; PDLC; Thiol-Ene; Stoichiometry; Driving Voltage

1. Introduction

Polymer dispersed liquid crystal (PDLC) is a composite containing low-molecular-weight liquid crystal (LC) domains randomly dispersed within a continuous polymer matrix. A thin (5 - 25 μm) film between transparent conducting substrates can be switched between an intensely scattering state and a transparent state by applying an electric field across the film. In the field-off (OFF) state, the incident light is scattered due to the mismatch in the refractive indices of the randomly oriented liquid crystal molecules and the polymer matrix. Under an electric field, the LC directors are oriented in the direction of the electric field within the LC domains, which matches the refractive index of the polymer matrix to that of the ordinary component of the LC, and thus, the PDLC film appears transparent. These attractive intrinsic electro-optical characteristics mean that the PDLC can be used as a switchable glass, an optical devices, and a display devices [1-6].

A large number of researches have performed since the early 1990s which address the phase separation process, morphology, and electro-optical properties of PDLC systems based on photopolymerization processes. Thiol-ene and acrylate systems have been the major photopolymerization processes used to produce PDLC films. Thiol-ene systems polymerize via the step-growth polymerization mechanism, whereas acrylate systems polymerize via the chain-growth radical polymerization mechanism [7-13].

In the step-growth polymerization, the increase in molecular weight is much slower and the gelation takes place at a higher degree of monomer conversion. These intrinsic properties of thiol-ene systems enable the PDLC films to be produced with a uniform morphology with narrow dispersity in the shape and size of LC droplets and a higher degree of LC phase separation. The thiol-ene system used most widely to construct PDLC films is commercial Norland Optical Adhesive (NOA65). The refractive index of cured NOA65 is 1.50 - 1.52, which corresponds to the normal range of refractive indices of conventional nematic LC mixtures consisting of cyanobiphenyl molecules, which yields PDLC films with good electro-optical performance [7,10,14-16].

One of the most important factors determining the

electro-optical properties of PDLC is its morphology which is strongly affected by the prepolymer composition, solubility between the LC and prepolymer, the polymerization kinetics, and the phase separation mechanism [17-27]. For the PDLC films prepared using thiol-ene systems, the droplet morphology and structural parameters such as droplet size, shape, distribution and density can be varied with the chemical characteristics of the prepolymer and polymerization kinetics. Therefore, it is important to elucidate how the molar ratios of thiol-ene monomers affect their morphology and electro-optical properties.

While the morphology and electro-optical properties of thiol-ene-based PDLC films have been examined extensively, systematic approaches to the prepolymer compositions have been very limited because most studies have used a formulated commercial product (NOA65) as the prepolymer. It is important to consider variations in the kinetics and network structure of thiol-ene systems according to the molar ratio of thiol-ene monomers. In this study, we investigated the effects of the molar ratio of thiol-ene monomers on the photopolymerization-induced phase separation process, morphology, and PDLC performances.

2. Experimental

2.1. Materials and Sample Preparation

Tetrafunctional allyl ether monomer (4-AE) was prepared from trimethylolpropane diallyl ether (2-AE) and isophorone diisocyanate. The synthesis scheme is shown in **Figure 1**. Trimethylolpropane tris-(3-mercaptopropionate) (3-SH) was used as the thiol monomer. The monomers were purchased from Aldrich Chemical and used without further purification. 2,2-Dimethoxy-2-phenylacetophenone (Irgacure 651, Ciba Specialty Chemicals) was used as the photoinitiator. A multicomponent eutectic LC
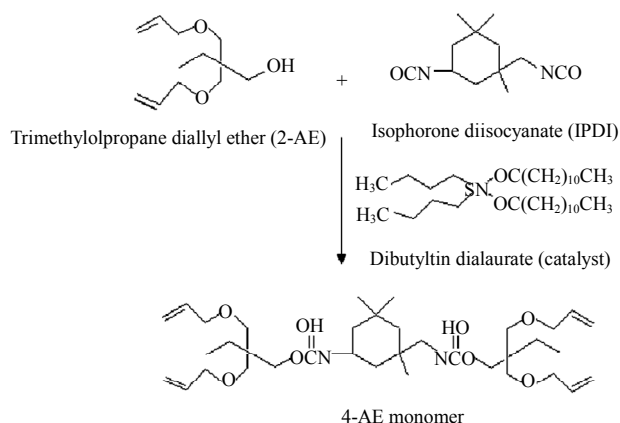

Figure 1. Synthesis of tetrafunctional allyl ether monomer (4-AE) from trimethylolpropane diallyl ether (2-AE) and isophorone diisocyanate.

mixture of cyanobiphenyls (E7, Merck) was used as a nematic LC. The mixtures for the PDLC films were prepared by directly mixing the E7 and the formulated prepolymer at a 1:1 weight ratio over 5 h at room temperature; these were used as the initial reactive mixtures for UV curing. The PDLC films were prepared by sandwiching the initial reactive mixtures between two conductive ITO-coated PET films (10×10 cm^2). The film gap was adjusted to 20 μm by using polymer ball spacers. The PDLC samples were irradiated by a black-light lamp (ENF-240, Spectronics) at a light intensity of 1.6 mW/cm^2 at 365 nm for 3 min.

2.2. Measurements

Photo differential scanning calorimetry (photo-DSC) was used to examine the photopolymerization behavior. Photo-DSC thermograms were obtained using a photocalorimeter (TA5000, Thermal Analysis) under a nitrogen atmosphere. Photopolymerization was initiated using a black light lamp (B-14N, Spectronics) with a light intensity of 1.6 mW/cm^2 at 365 nm. Samples weighing 1.0 ± 0.1 (mean $\pm$ SD) mg were placed in uncovered aluminum pans, and a reference aluminum pan was left empty. All measurements were performed at room temperature. The area of the exothermic peak is proportional to the heat released as the thiol monomer is added across the double bonds to form single bonds during photopolymerization.

The thermal behaviors of the samples cured in photo-DSC measurements were examined using DSC thermograms obtained with a DSC device (N-650, Scinco).

Scanning electron microscopy (SEM) was used to examine the PDLC morphology. The PDLC samples were freeze-fractured, soaked in hexane for 24 h to remove the LCs from the exposed surface, and then placed in a vacuum chamber for 24 h to remove the solvent.

Normal-normal spectral transmittance of PDLC cells was measured using an experimental setup comprising a halogen lamp (AvaLight-HAL, Avantes) and a CCD detector (AvaSpec-2048, Avantes). The transmittance spectra were obtained at a collection angle of $\pm 3°$. The transmittance value at 650 nm was recorded from the transmittance-voltage curve.

3. Results and Discussion

The prepolymer formulations based on thiol-allyl ether chemistry were prepared to examine the effects of stoichiometric ratios of thiol to allyl ether monomer on the polymerization-induced phase separation, morphology, and electro-optical properties of PDLC films. In the polymerization mechanism of the thiol-ene system, the polymerization reaction is terminated by the stoichiometric imbalance, and there is no more thiol available to react with the ene or vice versa [7,10]. This approach was used

to prepare prepolymer formulations with different stoichiometric ratios as listed in **Table 1**. The prepolymer formulations of the samples are expected to result in different degrees of monomer conversion. The numbers suffixed to "TE (the abbreviation of thiol-ene)" denote the molar percentage of the thiol group in the prepolymer formulation.

The photopolymerization behaviors of the prepolymers were investigated using photo-DSC. Photo-DSC experiments can provide kinetics data in which the measured heat flow can be converted directly to the ultimate percentage conversion and polymerization rate for a given formulation, with the data obtained reflecting the overall curing reaction of the sample [28-30]. **Figure 2(a)** shows the photo-DSC thermograms of the prepolymer samples, and **Table 2** collects the parameters obtained from **Figure 2(a)**, in which the ΔH_{cure} is the amount of heat released (the exotherm related to the conversion) and the t_{max} is the peak maximum (the time to attain the exotherm peak maximum related to the cure rate). As expected, the results reveal that as the molar ratio of thiol-ene mono-

Table 1. Prepolymer formulations with various molar ratios of thiol to allyl ether ([SH]:[AE]) monomers.

Sample	3-SH (wt%)	4-AE (wt%)	[SH]:[AE]
TE-35	30	70	35:65
TE-40	35	65	40:60
TE-45	40	60	45:55
TE-50	45	55	50:50
TE-60	55	45	60:40

Table 2. Parameters obtained from the photo-DSC thermograms and thermal analysis of the prepolymer and PDLC samples.

Sample	ΔH_{cure}[a] (J/g)	t_{max}[b] (s)	T_g[c] (°C)
TE-35	158	5.0	1.6
TE-40	190	4.4	4.5
TE-45	207	4.2	6.9
TE-50	237	4.0	7.4
TE-60	203	4.2	−8.4
TE-35 + E7	179	9.6	−24.8
TE-40 + E7	205	8.8	−22.9
TE-45 + E7	215	8.2	−13.4
TE-50 + E7	239	7.6	−12.3
TE-60 + E7	214	8.6	−26.5

a. ΔH_{cure}: the amount of heat released. b. t_{max}: the time to attain the exotherm peak maximum. c. T_g: glass transition temperature of the polymer matrix.
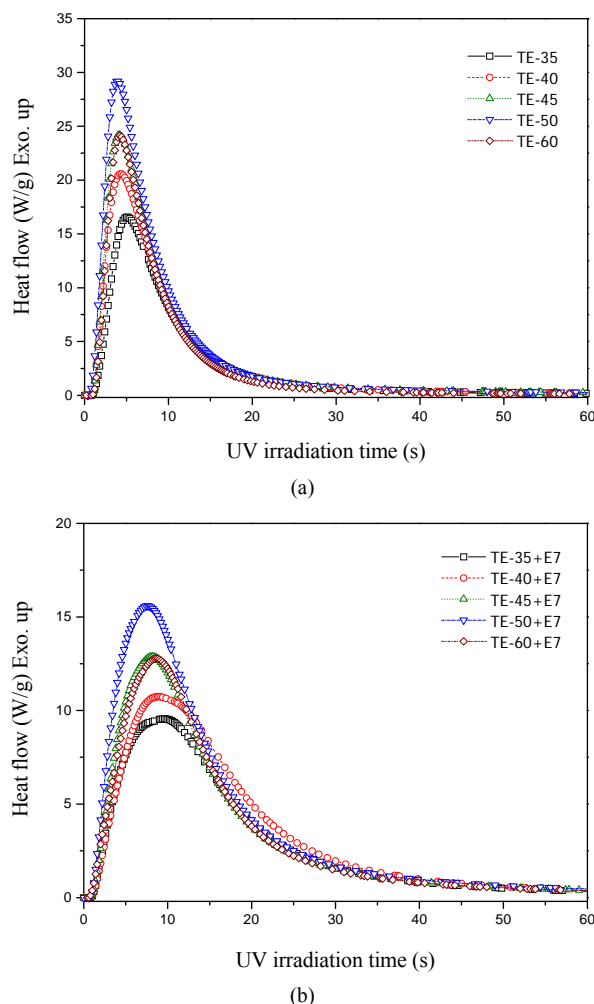

(a)

(b)

Figure 2. Photo-DSC thermograms of (a) the prepolymer samples and (b) the PDLC samples with various [SH]/[AE] values.

mers approaches the stoichiometric balance of [SH]:[AE] = 50:50, both the exotherm and the photopolymerization rate increased to a maximum, and then decreased at the 60:40 molar ratio of [SH]:[AE] due to the stoichiometric imbalance.

The photo-DSC thermograms of the PDLC samples are shown in **Figure 2(b)**, and the ΔH_{cure} and the t_{max} are also listed in **Table 2**. To compare the photopolymerization behaviors of the PDLC samples with those of the prepolymer samples, the photo-DSC thermograms of the PDLC samples were normalized by the weights of the prepolymers. As shown in **Table 2**, the changes of the ΔH_{cure} and the t_{max} for the PDLC samples exhibited similar trend with those of the prepolymer samples. However, the PDLC samples gave higher exotherm than did the prepolymer samples, which is due to the effect of plasticization by the LC molecules. For the photopolymerization rate, the PDLC samples exhibited slower cure rates than those for the prepolymer samples probably due to

the photopolymerization reaction being restricted by the LC molecules (a dilution effect) [1].

DSC experiments were carried out to investigate the thermal properties of the polymer matrix in PDLC network. First, DSC thermograms of the cured prepolymer samples are shown in **Figure 3(a)** and the obtained glass transition temperatures (T_g) of the polymer matrix are listed in **Table 2**. As the molar ratio of thiol-ene monomers approaches the stoichiometric balance of [SH]:[AE] = 50:50, the T_g values of the cured prepolymers increased to a maximum and then sharply decreased at the 60:40 molar ratio of [SH]:[AE]. Interestingly, the TE-60 sample showed relatively lower T_g than those for the other samples, which may be attributed to the chemical structure of 4-AE monomer with urethane groups. Hydrogen bonds could be formed by urethane groups and act as physical cross-links within the polymer matrix, probably contributing to increase the T_g value of the matrix. Therefore, it seems that the TE-60 sample containing less content of 4-AE showed the relatively low T_g. And the

reason that the maximum T_g was obtained for TE-50 sample could be the matched stoichiometry by which the highest exotherm and degree of monomer conversion were achieved.

For the cured PDLC samples, as shown in **Figure 3(b)** and **Table 2**, the T_g values revealed similar behaviors with those of the cured prepolymer samples. However, the cured PDLC samples gave much lower T_g than did the cured prepolymer samples, which is probably due to the plasticizing effect by the LC molecules dissolved within the polymer matrix. Here, the endotherm peaks shown within the range 50°C - 60°C in **Figure 3(b)** are the nematic-isotropic enthalpy of the LC droplets. Eventually, the T_g of thiol-ene-based PDLC systems was affected by the chemical structure of 4-AE monomer, stoichiometry, and the plasticizing effect by the LC molecules.

The relationship between the photopolymerization behaviors and morphology of the thiol-ene-based PDLC systems was examined using SEM. **Figure 4** exhibits SEM photographs of the surface of the polymer matrix of the PDLC samples with different ratios of [SH]:[AE]. The figure clearly shows that the largest LC droplet size was obtained for TE-35 + E7 and the smallest for TE-50 + E7, which is probably related to the photopolymerization rate. The slow photocure rate of TE-35 + E7 would prolong the phase separation between the LC molecules and the prepolymer, leading to the largest LC droplet size. Presumably, the opposite phenomenon occurred in TE-50 + E7.

To investigate the relationship between the morphological and electro-optical properties of thiol-ene-based PDLC samples, the voltage dependencies of the transmittance of PDLC samples are shown in **Figure 5**. When the applied voltage increases, the transmittance of the PDLC samples reaches the saturation level T_s. **Figure 6** plots the threshold voltage (V_{th}) and the driving voltage (V_{dr}) as functions of the thiol concentration. Here, V_{th} and V_{dr} are defined as the electric fields required for the transmittance to reach 10 and 90% of T_s, respectively. As the thiol content increased, both V_{th} and V_{dr} decreased obviously up to the stoichiometric balance of [SH]:[AE] = 50:50, and then increased at the 60:40 molar ratio of [SH]:[AE]. These behaviors are strongly influenced by the morphological properties with different LC droplet size [1,2]. The smaller the LC droplet size, the higher the V_{th} and V_{dr} and the lower the T_s. As a result, TE-50 + E7 sample with the smallest LC droplet size gave the highest threshold, driving voltages and lowest saturation transmittance because the orientation of LC molecules gets difficulty in small droplets.
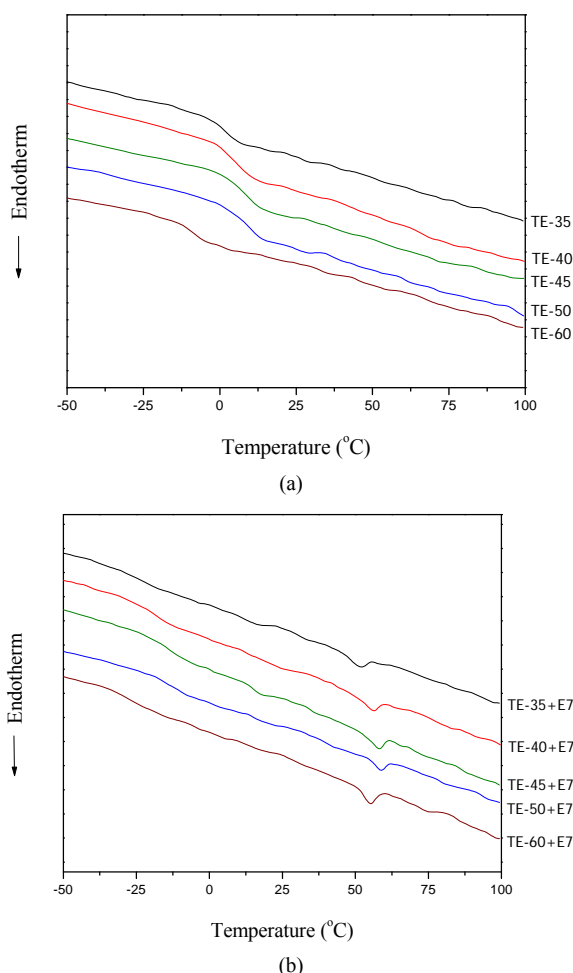

Figure 3. DSC thermograms of (a) the cured prepolymer samples and (b) the cured PDLC samples with various [SH]/[AE] values.

4. Conclusion

Tetrafunctional allyl ether monomer (4-AE) was synthe-
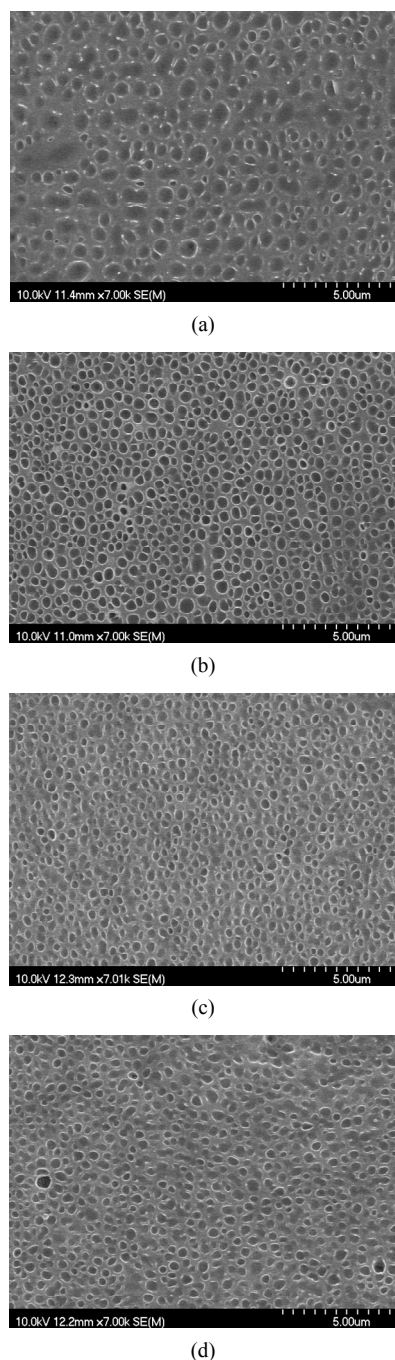
(a)

(b)

(c)

(d)

Figure 4. SEM micrographs of PDLC samples with various [SH]/[AE] values: (a) TE-35+E7, (b) TE-40+E7, (c) TE-50+E7, and (d) TE-60+E7.

sized, and the effects of the different stoichiometric ratios of trimethylolpropane tris-(3-mercaptopropionate) (3-SH) to 4-AE on the photopolymerization behavior, morphology, and electro-optical properties of thiol-ene-based PDLC systems have been elucidated using photo-DSC, DSC, SEM, and electro-optical measurements. Photo-DSC and DSC analyses revealed that the PDLC sample containing 45 wt% 3-SH and 45 wt% 4-AE gave the
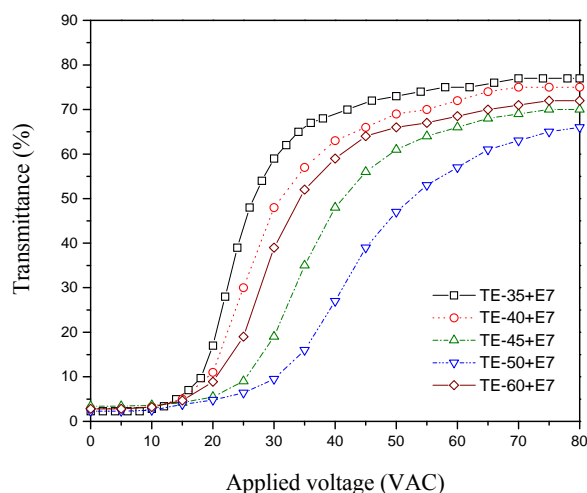

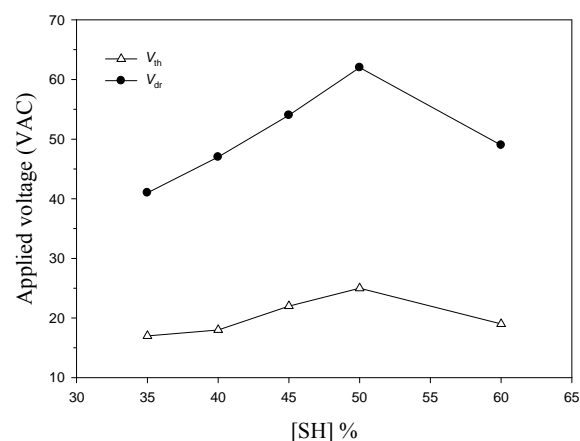**Figure 5. Transmittance of PDLC samples as functions of applied voltage.**

Figure 6. The thiol concentration dependence of V_{th} and V_{dr}.

highest exotherm, the fastest photocure rate, and the highest T_g due to the matched stoichiometry. The morphological observations showed that the maximum LC droplet size was obtained for the PDLC sample with 30 wt% 3-SH and the minimum for the sample with 45 wt% 3-SH due to the different curing rate and phase separation behavior. The electro-optical measurements revealed that the PDLC sample with the matched molar ratio and smallest LC droplet size gave the highest threshold, driving voltages and lowest saturation transmittance because the orientation of LC molecules got difficulty in small droplets. Lastly, it was found that the stoichiometric ratios of 3-SH to 4-AE played a key role in controlling the photocure rate, phase separation rate, microstructures of LC droplets, and electro-optical properties of thiol-ene-based PDLC systems.

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