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Influence of enhanced curing temperature of epoxy monomers structure on the electro-optical properties and morphology of polymer-dispersed liquid crystal films

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Abstract: The effect of enhanced curing temperature of epoxy monomers structure on the electro-optical properties and morphology of Polymer dispersed liquid crystal (PDLC) films has been studied. PDLC films were prepared by polymerization induced separation (PIPS) method with nematic liquid crystal (LC) content as low as 40 wt% and the electro-optical (E-O) properties were carefully investigated. To accomplish this, epoxy curable monomers structure with different molar ratio of two mixtures was examined in PDLC films. The LC domain size in the PDLC films decreased at first and then increased with the gradual raise of the curing temperature with lower LC content. Meanwhile, the E-O properties of the PDLC film depended strongly on the LC droplet size. The detailed characteristics and morphology of polymer network of PDLC films were analyzed by employing liquid crystal device (LCD) parameters tester and scanning electron microscopy (SEM).It was found that the LC domain size of the polymer network could be regulated by adjusting the curing temperature, structure and composition ratio of curable epoxy monomers, then the electro-optical of PDLC films could be optimized; which is beneficial to a novel generation of materials with sophisticated properties and new effects ready for use in various areas of modern technologies.
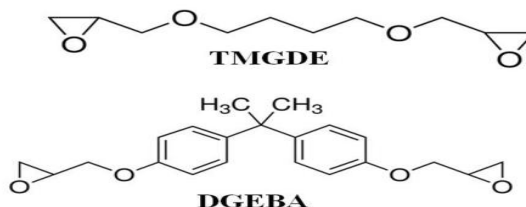
I.   INTRODUCTION

Polymer-dispersed liquid crystal (PDLC) films have been studied for many years. PDLC films constitute a high active research area in polymer science comparatively new technology of materials that consist of micron-sized LC droplets dispersed in a solid polymer matrix [1-3].Usually, the E-O properties of PDLC films can be affected by the LC concentration, film thickness, separation degree and dimension, composition ratio of monomers and morphology of the LC domain size [4]. Four general methods have been developed for the formation of PDLC films, including encapsulation, PIPS (polymerization-induced phase separation), TIPS (thermal-induced phase separation) and SIPS (solvent-induced phase separation) methods [5-7]. However, the PIPS method with heat curing technique is more reliable to provide homogeneity and forms a uniform morphology of polymer networks that renders it insensitive to temperature changes. Epoxy resins are widely utilized for coatings and structural applications, adhesives and composites for microelectronic encapsulants.Among the various families of cross linking resins, epoxies are widely used due to their exceptional performance, coupled with very easy usage methods and limited cost. The effect of curing temperature on the electro-optic behavior and polymer network morphology has been studied by Dierking I et al [8]. In our group, Ping Song et al studied a UV polymerization temperature dependence of PDLCs based on epoxies/acrylates hybrid polymer matrix components by the PIPS method [9]. In the present experiments, PDLC films with LC content as low as 40 wt% were prepared by curable epoxy monomers with different temperatures, molecular structures and same weight%, to investigate briefly the combine effects of two mixtures on the altering morphology of polymer networks and the E-O properties of the PDLC films.

II.   EXPERIMENTAL DETAILS

2.1 Materials

The heat curable epoxy monomers used were a mixture of bisphenol a diglycidyl ether (DGEBA, Alfa Aesar, A Johnson Matthey Company), Tetra methylene glycol diglycidyl ether (TMGDE, Sigma Aldrich Company) and Poly oxy propylene di amine (POPDA, Jeffamine D-400, Heowns Biochem Technologies Tianjin). POPDA is also used as a polyamine hardener for epoxy resins in this study. Figure 1 shows the chemical structures of these materials.
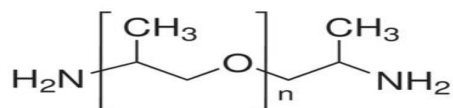

Figure 1. Chemical structures, names and abbreviations of materials used.

All of the above materials were used as received without further purification. The compositions of curable epoxy monomers/hardener/LC mixtures are listed in Table 1.

1.2 PDLC Preparation

In this study, the PDLC films were obtained by the PIPS process. The samples we prepared consisting of heat curable epoxy monomers/hardener and the less amount of nematic LC content (wt: 40%). At the beginning, they were mixed uniformly in a different proportions until they had been homogenized and then treated in different ways to investigate properties. In order to measure the electro-optical properties, the mixture was sandwiched between two pieces of indium-tin-oxide (ITO) coated glass substrates. The film thickness was controlled by 20.0 ± 1.0 μm thick polyester spacers and then cured in an oven at different temperatures for 7 h. The composition ratios of the samples are listed in Table 1. It is calculated by $F_{av}=\sum \Phi_i f_i$, where F_{av} is the average functionality of composite monomer, Φ_i and f_i stand for the relative percentage and functionality respectively [10].The theoretical reaction molar ratios of Monomer mixture[a] (MM1)DGEBA/POPDA and Monomer mixture[b] (MM2)TMGDE /POPDA are 2/1 and 1/1, respectively.

Table 1.   The compositions of the samples A1-A7.

Sample	Monomers (Total 60 wt %) MM1[a]/MM2[b]	SLC-1717 (wt%)	Curing Temperature (K)
A1	30/30	40	344.2
A2	30/30	40	347.2
A3	30/30	40	350.2
A4	30/30	40	353.2
A5	30/30	40	356.2
A6	30/30	40	359.2
A7	30/30	40	362.2

2.3 Observation of the polymer network in the PDLC films

The morphology of the polymer network of the samples was observed by scanning electron microscopy (SEM, ZEISS, EVO18, Germany). The PDLC films were first separated and dipped into cyclohexane (C_6H_{12}) for four days at room temperature to extract the polymer network and then dried for 12 h under vacuum. After the films were sputtered with carbon, the microstructure of the polymer network was observed under SEM.

1.3 Electro-optical properties measurement

The electro-optical properties were measured by a liquid crystal device (LCD) parameters tester (LCT-5016C, Changchun Liancheng Instrument Co. Ltd.). A halogen laser beam (560 nm) was used as the incident light source and the incident wavelength (λ) through the samples were fixed with the help of wavelength (λ) filter (632.8nm).The transmittance of the PDLC systems was recorded by a photodiode, and the response of the photodiode was monitored by a digital storage oscilloscope. The active area of the detector was 0.36 cm^2. An electric field square wave (100 Hz) was applied, and the distance between the PDLC systems and photodiode was 300 mm. The transmittance of air was normalized as 100%.

III.   RESULTS AND DISCUSSION

3.1 Morphology of Polymer Network of the samples

Figure 2 shows the morphology of the polymer networks of the samples A1 to A7 was observed by SEM to ascertain whether phase separation for the samples had taken place at different curing temperatures. It can be observed that the domain size of the LC is greatly affected due to the presence of the short chain length (TMGDE) and rigid chain segment containing curable monomer (DGEBA). As shown in Figure 2, the polymer networks of all samples have suitably distributed small holes in the PDLC films. As can be seen in figure 2, the domain size of the polymer network of samples A1-A7 proved that phase separation in the samples took place, and that with the raise of the curing temperature, the LC domain size of the polymer network decreased rapidly at first for the temperature from 344.2 K to 350.2 K, and then increased dramatically for the temperature from 350.2 K to 362.2 K. This variation was related to the competition between the diffusion of LC molecules and the polymerization rate of the epoxy monomers. In heat curing PIPS method the rate of diffusion of the LC domain size is directly proportional to the curing temperature, and it is given by the Fick's second law [11, 12].
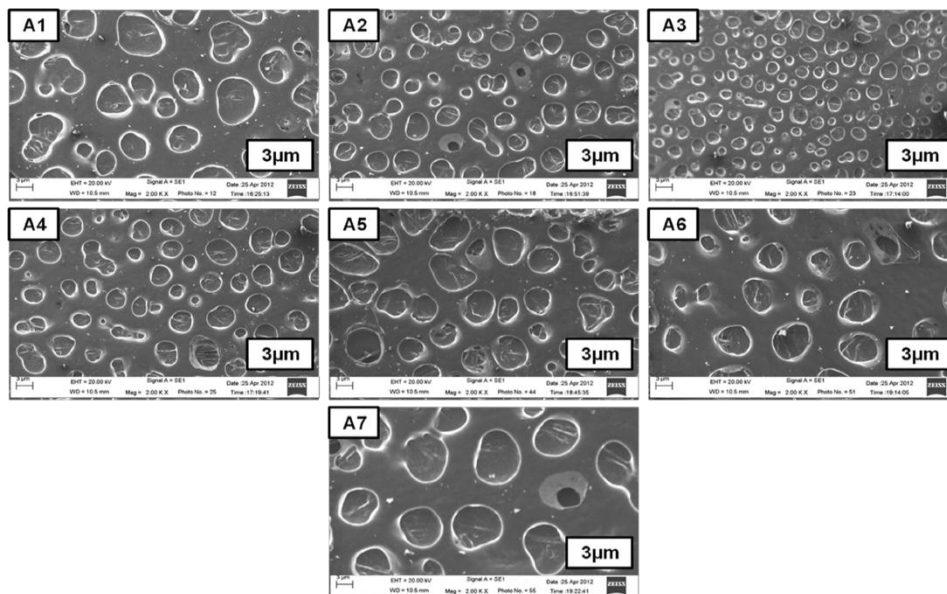

Figure 2. SEM micrographs of the polymer networks of the samples A1-A7.

$$D = D_0 \exp\left(-Q/RT\right)$$

(1)

Where D, D_0, Q, T and R represent diffusion coefficient, diffusion coefficient constant, activation energy, absolute temperature and ideal gas constant of the LC, respectively.

Additionally, the initial increases of the curing temperature could particularly decrease the viscosity of the LC. The decrease of the viscosity of the LC was helpful to the diffusion of the LC, and then developed the accumulation of the LC and the growth of the domain size of LC. Although, the polymerization rate coefficient (k) of the epoxy heat curable monomers depends exponentially on temperature according to Arrhenius equation [13, 14, 15].

$$k = A exp\left(\frac{-E_{act}}{RT}\right)$$

(2)

Where E_{act} is the activation energy, R is the ideal gas constant, A is the frequency (collisions) factor and T is the absolute temperature. Analysis of Equations (1) and (2) indicated the conclusion given below. When the epoxy curable monomers were cured from 344.2 K to 350.2 K, the increase in temperature could have significantly increased the solubility of the LC in the epoxy monomers, and then prevented the diffusion and the accumulation of the LC. For that reason, the LC domain size of the polymer network decreased in sequence in samples A1-A3.Though, when the polymerization the monomer occurred at above 350.2 K, the increase in the solubility of the LC in the epoxy monomers slowed down relatively. In other words, the diffusion rate of the LC molecules and the polymerization rate of the epoxy monomers depend exponentially on the heat curing polymerization at different temperatures and the 40 wt% of nematic LC also. It plays a vital role during the formation of the polymer networks and corresponds to the generation of macro-molecular polymer structures in all samples.

1.4 Electro-optical properties of the samples

The E-O properties are very elemental and significant in the evaluation of PDLC films. The transmittance applied voltage curves of sample A1-A7 are shown in figure 3. It can be seen that the transmittance of the all samples reached the saturation level Ton with the applied voltage increased. We observed that the transmittance curves were gentler for all samples.

Figure 4 shows the threshold voltage (V_{th}) and the saturation voltage (V_{sat}) of all samples A1-A7.The V_{th} and V_{sat} are defined as the electric voltage required for the transmittance to reach 10% and 90% of Ton respectively As we can seen that V_{th} and V_{sat} of samples A1-A7 increased at first and then decreased in sequence.
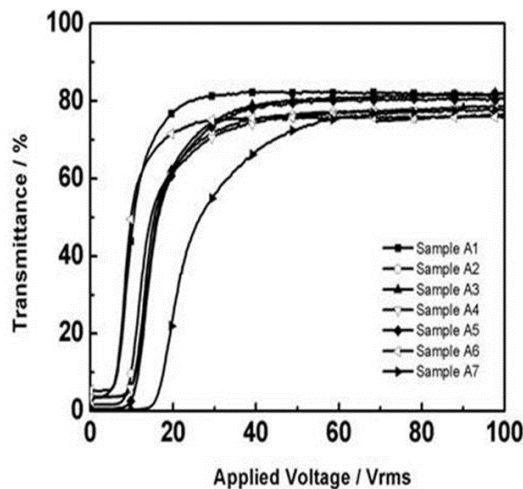

Figure3. The transmittance applied voltage curves of of the samples A1-A7.
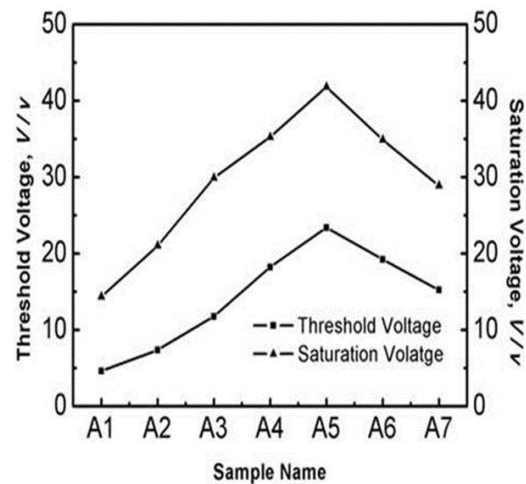
Figure 4.The threshold voltages and saturation voltages of the samples A1-A7.

It must be mentioned that, the size of the LC droplet has a strong association with E-O performance in a PDLC system. Usually, the V_{th} is inversely proportional to the radius of LC droplet(R) as shown below [16].

$$V_{th} = \frac{d}{3a} \times \left(\frac{\rho_p + 2}{\rho_{LC}}\right) \times \left(\frac{K(l^2 - 1)}{\Delta\varepsilon\,\varepsilon_o}\right)^{\frac{1}{2}}$$

(3)

Where d, l, ρp, ρLC, K, $\Delta\varepsilon$ and εo thickness of the PDLC film, the ratio of the length of the semi-major axis, resistivity of the polymer, resistivity of the liquid crystal, elastic constant of liquid crystal, dielectric anisotropy of the liquid crystal and Vacuum permittivity of the LC, respectively.

Contrast ratio (CR) is a key measure of the electro-optical properties in a PDLC films. CR of PDLC films are used to characterize the difference in between a transparent and an opaque state. It is define as,

$$CR = \tau_R / \tau_D$$

(4)

Where τ_R and τ_D are transmittance in the on and off-state of PDLC film. A high value of CR can be

obtained when the microstructure of the PDLC film is appropriate. Figure 5 shows the off-state light transmittance (T_{off}) in fixing wavelength (632.8 nm) and the contrast ratio of all samples A1-A7.It can be seen that in samples A1-A4 the CR is continuously increased at first, then decreased in sequence increasing with altering the LC domain size and T_{off} also.
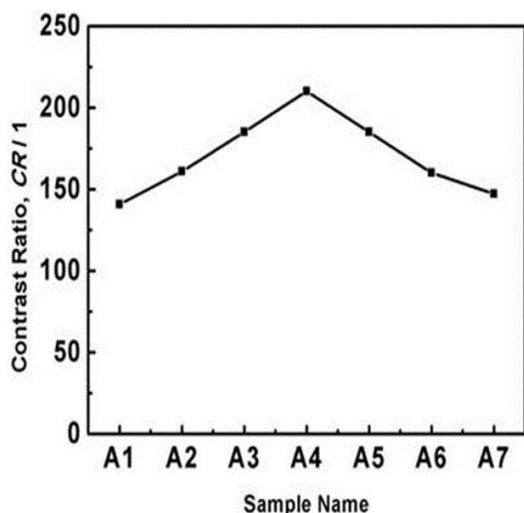

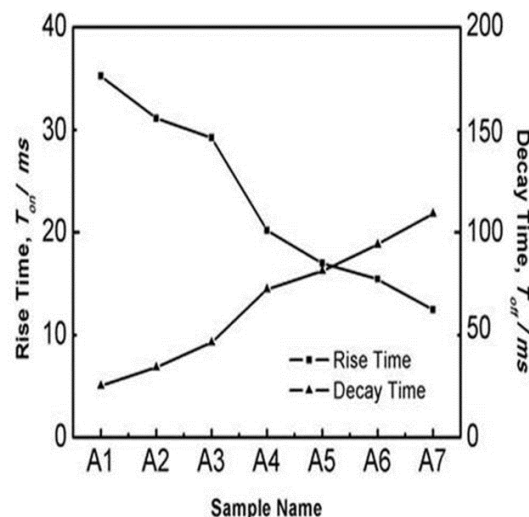Figure5. The contrast ratio (CR) of the samples A1-A7.

Figure 6. The rise time and decay time of the samples A1-A7.

Figure 6 shows about the response time of the PDLC films with applied voltage dependence of the *rise time* (τ_R) *and decay time* (τ_D) of samples A1-A7. *Rise time* is explained as the time which required to go from 10% to 90% of the maximum transmittance of the sample upon turning on and which required to go from 90% to 10% of the maximum transmittance of sample turning off is known as *decay time*. Usually, a competition between the applied electric field and the interface elastic forces anchoring the LC molecules governs the response time [17].The τ_R of samples A1-A3 decreased slightly whereas their τ_D increased slightly at first, then the τ_R and τ_D of samples A4-A7 decreased rapidly and increased rapidly ,respectively. This behavior was related to the competition between the applied field and the interface anchoring forces of the polymer network to the LC molecules of PDLC films. The smaller the LC droplet size, the stronger was the interface anchoring forces of the polymer network to the LC molecules. Thus, smaller LC droplets need more time to overcome more interface anchoring energy. When the applied electric field was detached, the LC molecules could revert quickly to the initial off-state due to the higher interface anchoring forces.

IV.   CONCLUSION

We have investigated PDLC films by curable epoxy monomers structure using heat curing processes with different temperature, molecular structures and same weight%. The effects of short chain length and rigid chain segment containing monomers structure on the morphology and electro-optical properties have been studied. On the morphology, the LC droplet size in the PDLC films decreased at first and then increased with enhanced curing temperature; and existence of TMGDE and DGEBA monomers form suitably distributed small hole. Meanwhile, the variable E-O properties of the PDLC films depended strongly on the LC droplet size. The study also shows a special association between the epoxy curable monomers structure and the electro-optical properties of PDLC films with varying morphology. Furthermore, the results have been presented in this study also suggest that it is possible to regulate the LC domain size and optimize the electro-optic performance by adjusting the composition and weight ratio of heat curable epoxy monomers to obtain PDLC films which possess good electro-optical properties which is beneficial to decrease the total LC content in PDLC devices. The result in this paper brings significant advantages for manufacturing PDLC films and developing the PDLC market.

V.   ACKNOWLEDGEMENTS

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