Effects Of Di And Tetra Functional Epoxy Monomers Structure On The Morphology And The Electro-Optical Properties Of Polymer-Dispersed Liquid Crystal Films

Mujtaba Ellahi, Yangzi Gao, Huai Yang

Abstract:- Polymer dispersed liquid crystal (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 properties were carefully investigated. To accomplish this, epoxy curable monomers structure with different composition ratio of two mixtures was examined in PDLC films. The electro-optical properties and morphologies of the PDLC films were strongly influenced by the chemical structure of curable monomers di functional ethylene glycol diglycidyl ether (EGDE) and tetra functional Pentaerythritol tetraglycidyl ether (PTTGE). Higher driven voltage and contrast ratio were achieved when the PDLC films showed a reducing morphology with suitably distributed small holes of LC domain 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 structure and composition ratio of curable epoxy monomers, then the electro-optical of PDLC films could be optimized; which is beneficial to decrease the total LC content in PDLC devices.

Key words: - Polymer dispersed liquid crystal, electro-optical, epoxy monomers, morphology, polymer network, composition ratio.

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1. INTRODUCTION

Polymer-dispersed liquid crystal (PDLC) is comparatively new technologies of materials that consist of micron sized droplets dispersed in a solid polymer matrix are a kind of composite materials [1-3]. Optical and electro-optical (E-O) properties of PDLC films make them perfect for many applications in different fields, such as flexible displays, optical shutter, switchable windows, botanical garden and other technological display devices[4,5]. The instant transition of the PDLC film is helpful for controlling shade and privacy to completely block the view or adjust degree of its opaque based film. When the power turns off, coming visible light scatters through the PDLC film and it turns opacity medium due to the mismatching of refractive index between the LC droplets and polymer networks. On the other hand when the power turns on, coming visible light transmits the PDLC film and it turns transparent because configuration of the LC molecules are parallel to the applied electric field and the ordinary refractive index of the LC match the refractive index of the polymer [6-8].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 [9]. 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 [10-12].

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. In addition, the PIPS methods also allows better control over the E-O behaviors of the PDLC films and enable to produce the large stretchable panels [13]. Epoxy resins are widely utilized for coatings and structural applications, adhesives and composites for microelectronic encapsulates. Epoxies have a large number of advantages including: low thermal expansivity, low dielectric constant, low density, good resistance to environment and heat, ease of process ability, and good dimensional stability. Epoxy resins constitute a group of thermo set polymers with a high crosslink density of covalent polymer networks. 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. Ping Song et al studied a UV polymerization temperature dependence of PDLCs based on epoxies/acrylates hybrid polymer matrix components by the PIPS method [14]. In the present experiments, we have used PIPS method of heat curing processes with curable epoxy monomers, to investigate briefly the combine effects of heat content multiple curable monomers structure on the reducing morphology, composition and weight ratio, the refractive index of polymer network and the E-O properties of the PDLC films. The aim of the present contribution is to describe the fabricating smaller LC droplet size by using different heat curable epoxy monomers which reinforce the stability and strength of the PDLC films. Furthermore, this paper also addresses the combine effects of short flexible chain length, and tetra-functional curable monomers with increasing the cross linking density on the polymer network of PDLC films.

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2 EXPERIMENTAL DETAIL

2.1 Material

The nematic Liquid crystal used in this study was SLC-1717 (T_{NI}=365.2 K, n_o=1.519, n_e=1.720, Shijiazhuang Yongsheng Huatsing Liquid Crystal Co. Ltd.)., di fuctional ethylene glycol diglycidyl ether (EGDE) resin (XY 669, Anhui Hengyuan Chemical Co. Ltd.), tetra functional Pentaerythritol tetraglycidyl ether (PTTGE, Synasia (SuZhou) Co., Ltd.) 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. 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.

Figure 1: Chemical structures, names and abbreviations of the materials used.
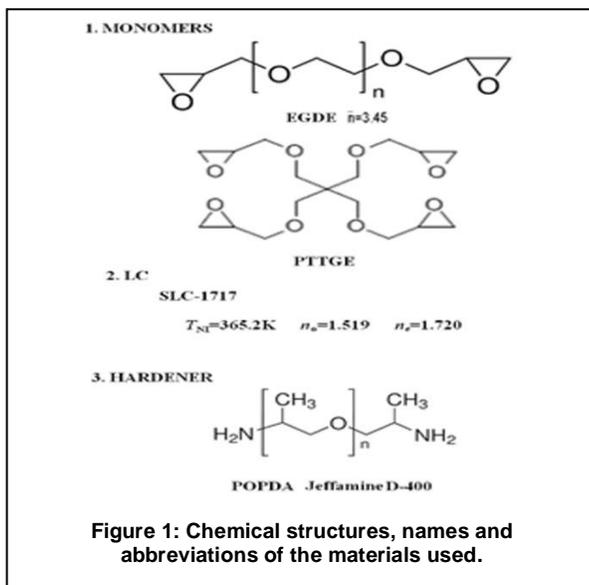
2.2 PDLC Preparation

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 15.0 ± 1.0 μm thick polyester spacers and then cured in an oven at 363.15 K for 7 h. The composition ratios of the samples are listed in Table 1. It is calculated by $Fav=\sum \Phi i\, fi$, where Fav is the average functionality of composite monomer, Φi and fi stand for the relative percentage and functionality respectively [15].The theoretical reaction molar ratios of PTTGE/POPDA and EGDE/POPDA are 1/1 and 2/1, respectively.

Table 1: The compositions of samples A1-A5.

Sample	Monomers (Total 60 wt%)	
	MM1ᵃ/MM2ᵇ	SLC1717/ (wt %)
A1	10 / 50	40.0
A2	20 / 40	40.0
A3	30/ 30	40.0
A4	40/ 20	40.0
A5	50 / 10	40.0

Monomer mixture ᵃ (MM1) PTTGE/POPDA=1/1
Monomer mixture ᵇ (MM2) EGDE/POPDA=2/1

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.

2.4 Electro-optical 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%.

3. RESULTS AND DISCUSSIONS

3.1 Morphology of Polymer Networks in PDLC Films

Figure 2 shows the morphology of the polymer networks of sample A1-A5 where a subtle structural difference gives significantly different film morphology. It can be observed that the domain size of the LC is greatly affected due to the presence of the short flexible chain length (EGDE) and tetra functional monomer (PTTGE); in resulting LCs domain size of the sample A1-A5 decreased in sequence. As shown in Figure 2 the polymer networks of all samples have suitably distributed small holes in the PDLC films. The morphology of PDLC film reduces regularly with increasing the cross linking density and rapid rate of polymerization. The LCs droplet size and morphology of PDLC films were formed during the LC droplet nucleation and the polymer gelatins. When polymerization is initiated, the molecular weight and cross linking density of the polymer network increases and hence the solubility of the LCs domain size decreases leading to the formation of droplets. The LC droplet size is mainly controlled by the rate of polymerization, the relative ratios of materials composition and types of LCs as well as physical parameters such as viscosity, rate of diffusion and solubility of LCs in the polymer [16,17].

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Thus the aim of this study is to explore the effect of the composition ratio of di and tetra functional curable epoxy monomers structure on the morphology of PDLC films.
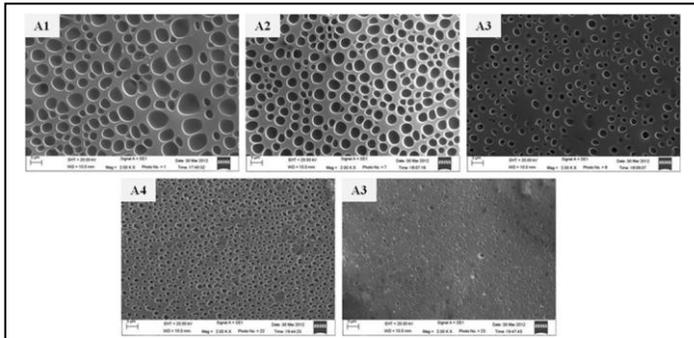

Figure 2: SEM micrographs of the polymer networks of the samples A1-A5.

Figure 2 shows the LC domain size obviously decreases due to the increasing of PTTGE monomers because higher functionality monomer, which has more active centers, has faster reaction rate than lower functionalized monomer; this also resulted in a more rapid rate of polymerization. Therefore, the LC domain size of sample A5 was smaller than that of the sample A1.Usually, the decrease of the length of molecular chain result in the decrease of the distance between two neighboring cross linking points in the polymer network of the PDLC films, though it can induce the decrease of the mesh size (LC domain size) of the polymer network. As a result, the sizes of LC droplet of samples A1-A5 decreased in the sequence.

3.2 Electro-optical properties of PDLC films

The E-O properties are very elemental and significant in the evaluation of PDLC films. In addition, the influences of epoxy monomer structures on PDLC films can be obtained by analyzing the E-O properties of samples A1-A5. The voltage transmittance curves of samples A1-A5 are shown in Figure 3. Comparing Figure 3 with Figure 2; the morphology of the polymer network in the PDLC films had a vital effect on the E-O properties of the PDLC films. Good E-O properties of the PDLC films can be obtained when the microstructure of the PDLC film is appropriate. Although, for a definite system where the LCs content is fixed, the transmittance increases with the increasing size of the LC droplet size because the lager LCs droplet size results in an insufficient number of scattering centers[18,19]. Hence, the transmittal of all the samples decreased with the decreasing size of the LC droplet which was also shown in Figure 3. We can clearly report that threshold voltage (V_{th}) and saturation voltage (V_{sat}) increases with increasing the composition of PTTGE monomer essentially. The V_{th} and V_{sat} are defined as the electric fields required for the transmittance to reach 10% and 90% respectively. It is generally admitted that the size of the LC droplets has a strong relationship with E-O performance in a PDLC system.
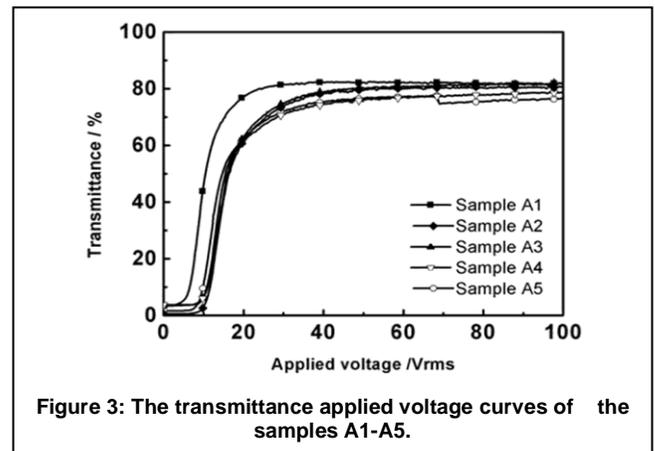

Figure 3: The transmittance applied voltage curves of   the samples A1-A5.

As per our knowledge the V_{th} is a linear function of a reciprocal size of the droplets R according to

$$V_{th} \cong \frac{d}{R}\left[\frac{K(\omega^2-1)}{\varepsilon_0\Delta\varepsilon}\right]^{\frac{1}{2}} \qquad (1)$$

Where d, K, ω and Δε represent film thickness, elastic constant, aspect ratio and dielectric anisotropy of the LC, respectively. Generally, the threshold voltage V_{th} increases with decreasing the LC droplet size; in resulting saturation voltage V_{sat} changes simultaneously.
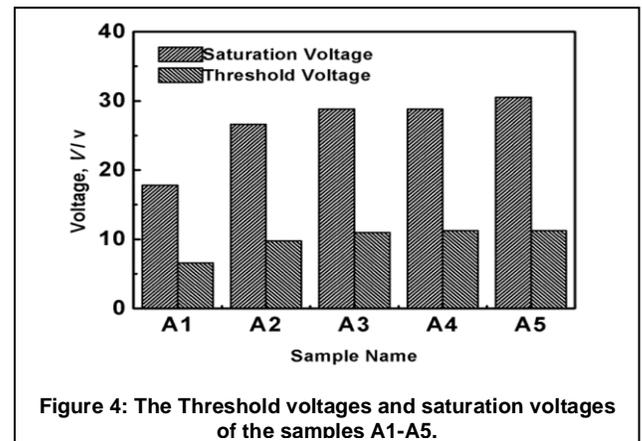

Figure 4: The Threshold voltages and saturation voltages of the samples A1-A5.

The voltage-transmittance values of samples A1-A5 are shown in Figure 4. Conventionally, as we examined Figure 4, the V_{th} and V_{sat} increased with increasing the weight% of PTTGE and decreasing the EGDE monomers. It must be mentioned that the operating voltage of the PDLC films is significantly influenced by the heat content epoxy monomers and the LC content. Equation (1) indicates that the E-O properties of PDLC system can be controlled by LC droplet size and other factors, such as film thickness, the resistivity and the dielectric anisotropy of LC. Hence, V_{th} and V_{sat} increase with the decreasing of the LC droplet sizes. Moreover, with the decreasing of the LC domain size, the interface between LC molecules and polymer matrix increases as shown the Figure 2 resulted, increasing the anchoring effects on LC molecules

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from polymer matrix. Therefore, the LC molecules are more difficult to orientate along the direction of the electric field in the smaller LC droplets, and consequently, V_{th} and V_{sat} increase. In result, by adjusting the composition of heat content epoxy monomers it is possible to optimize the E-O properties of PDLC film with a fix LC content.
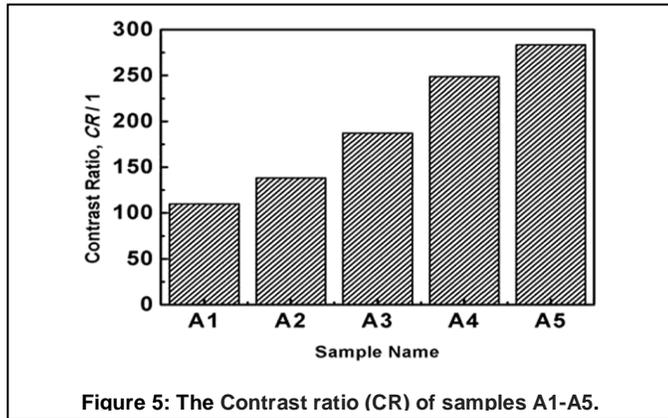

Figure 5: The Contrast ratio (CR) of samples A1-A5.

Contrast ratio (CR) is a key measure of the E-O properties in a PDLC system. CR of PDLC films are used to characterize the difference between a transparent and an opaque state is defined as

$$CR = \tau_R/\tau_D \qquad (2)$$

Where τ_R and τ_D are the ultimate rise time transmittance and the initial decay time transmittance respectively. As shown in Figure 5 that the off-state light transmittance (T_{off}) in fixing wavelength (632.8 nm) and the contrast ratio of all samples A1-A5. It can be seen that in all samples the CR is continuously increasing with decreases the LC domain size. Comparing Figures 2 with Figure 5, the morphology of the PDLC system has an essential effect on the CR of the PDLC system. Despite the fact that CR is inversely proportional to the decreasing the short flexible chain length (EGDE) monomer and it greatly influence to the formation of PDLC films .A high value of CR can be obtained when the microstructure of the PDLC system is appropriate.
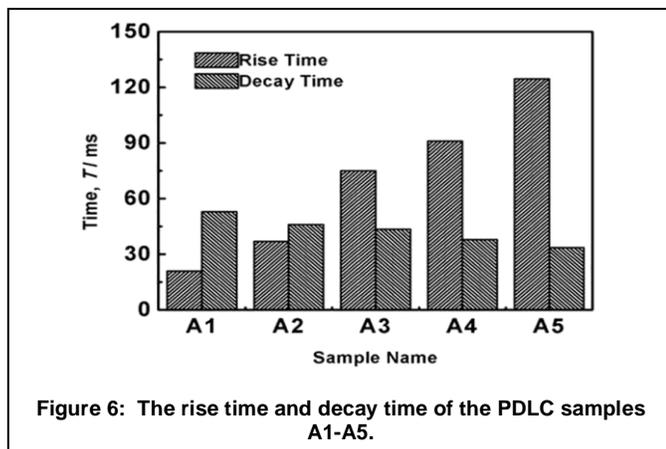

Figure 6: The rise time and decay time of the PDLC samples A1-A5.

As evident from Figure 6, 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-A5. These are two most important factors when evaluating the performance of PDLC films. *The rise time (τ_R) and decay time (τ_D)* are calculated from the time dependence of the transmission coefficient. Rise time is explain 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 [20].The smaller the LC domain size, the stronger the interface elastic forces of the polymer network to the LC molecules. Therefore, smaller LC domain size needs a longer time to overcome more interface anchoring energy. Moreover, many studies have indicated that smaller the LC domain size is, longer the τ_R and shorter the τ_D. The results are associated to the boundary interaction between the polymer matrix and LC droplet, which manage the re-orientation and orientation of LC droplet under electrical field force. It means that if the size of the LC droplet smaller then it contains larger τ_R, in result; the orientation of LC droplet needs longer time to contain on higher anchoring energy. The tetra functional PTTGE DGEBA monomer is inversely proportional to *the decay time (τ_D)* and directly proportional to *the rise time (τ_R)* in all samples A1-A5 respectively; in resulting enhance the surface anchoring energy. Therefore, the τ_R of sample 4 is smaller than that of sample 5 and the τ_D of sample 4 is larger than that of sample 5.It can be seen that in Figure 6 τ_D decreases ceaselessly with increasing the τ_R .

4. **CONCLUSION**

The composition ratio, weight% and combine effects of curable epoxy monomers have significant influenced on the morphology and electro-optical properties of thermal-cured PDLC films. On the morphology tetra functional monomer increases the cross linking density on the polymer network of PDLC films regularly. In resulting reduced the LC domain size of PDLC films, which decreases τ_D and increases CR, τ_R, V_{th} and V_{sat} .The study also shows a special association between the composition of heat content curable epoxy monomers structure and the electro-optical properties of PDLC films with decreasing morphology. Moreover, 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 ratio and structure of di and tetra functional curable epoxy monomers to obtain PDLC films which possess good electro-optical properties. The result in this paper brings significant advantages for manufacturing PDLC films and developing the PDLC market.

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