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Effects of the structures of epoxy monomers on the electro-optical properties of heat-cured polymer-dispersed liquid crystal films

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Polymer-dispersed liquid crystal (PDLC) films were prepared from thermal polymerisation-induced phase separation in heat-curable monomers/nematic liquid crystal (LC) mixtures. For PDLCs with a certain amount of LCs, the microstructure and the refractive index of polymer networks could be influenced by the relative content of epoxy monomers, owing to their different chemical structures. The effect of these factors on the electro-optic properties of films was also investigated.

Keywords: polymer-dispersed liquid crystal; heat curing; microstructure; refractive index; electro-optic properties

1. Introduction

Polymer-dispersed liquid crystals (PDLCs) are dispersions of micrometre-sized nematic liquid crystal (LC) droplets in a continuous polymer matrix [1]. Their unique optical and electro-optical properties make them suitable for applications in various technological fields, such as light valves, smart windows and other devices [2, 3].

A PDLC film exhibits transparent and light-scattering states in the electric field-on and field-off states, respectively. In the field-off state, the random orientations of the droplets and the mismatch between the refractive index of the droplets and that of the polymer create a scattering condition, making the film opaque. When a sufficiently strong electric field is applied to the material, the symmetry axes of the bipolar droplets align parallel to the electric-field direction for a material with a positive dielectric constant ($\Delta\epsilon > 0$). If the refractive index of the polymer (n_p) approximately matches that of the ordinary refractive index of the LC (n_o), the film becomes transparent. After the voltage is removed, the configurations within the droplets return to their random orientations, restoring the opaque-scattering state [4, 5].

Generally, the electro-optic properties of PDLC films depend on the LC concentration, film thickness, the size and shape of the LC domain, the anchoring energy on the boundary surface and the physical properties of both components, such as the elasticity, viscosity and dielectric anisotropy of the LC and the polymer [6–10]. Depending on the chemical nature of the polymer and the LC, the interface of the LC and polymer will experience different constraints with

different effects on the molecular orientation of the LCs inside the droplet [11–13].

To describe the light-scattering properties and the transparency of a PDLC film, the concept of an effective refractive index n_d was introduced by Wu *et al.* [14]. At normal incidence, n_d is equal to \bar{n}_o , where \bar{n}_o is the average ordinary index of a LC droplet. In the case of $n_e > n_o$, we have $\bar{n}_o > n_o$ and $\bar{n}_e < n_e$.

In this paper, PDLC films were prepared with the thermal polymerisation-induced phase separation (PIPS) method. The influence of the chemical structures of epoxy resins on the morphology of the polymer network and the electro-optic properties of films were investigated in detail. Meanwhile, the effect of the refractive index on the electro-optic properties was also studied.

2. Experimental

2.1 Materials

The heat-curable monomers used were a mixture of diglycidyl ether of bisphenol F (DGEBF) resin (EPON 862, Zhaochang Int'l Trade (Shanghai) Co., Ltd.), ethylene glycol diglycidyl ether (EGDE) resin (XY 669, Anhui Hengyuan Chemical Co., Ltd.) and 2, 2'-(ethylenedioxy) bis (ethylamine) (EDBEA, Alfa Aesar, A Johnson Matthey company). EDBEA is a polyamine hardener for epoxy resins DGEBF and EGDE. Figure 1 shows the chemical structures of these materials.

The nematic LC (SLC-1717, $T_{NI} = 365.2$ K, $n_o = 1.519$, $n_e = 1.720$, Shijiazhuang Yongsheng Huatsing Liquid Crystal Co., Ltd.) was used.

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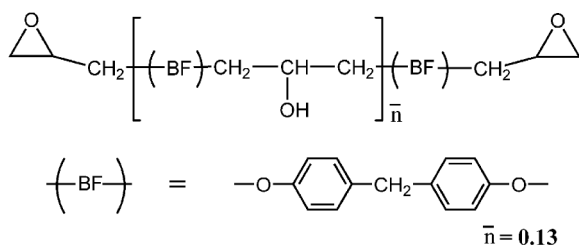
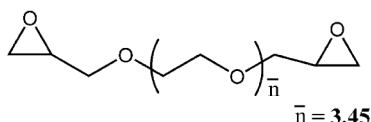
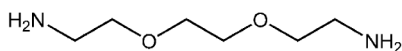
DGEBF**EGDE****EDBEA**

Figure 1. The chemical structures of heat-curable monomers.

2.2 Preparation of PDLC films

PDLC samples were fabricated by the heat-curing procedure. In forming these materials, a suitable oligomer was prepared by mixing DGEBF, EGDE and the hardener EDBEA in the molar ratio according to the equation below.

$$n_c = n_a + 0.5n_b, \quad (1)$$

where n_a , n_b and n_c are the mole numbers of the epoxy resin DGEBF, EGDE and the hardener EDBEA, respectively.

Then, the oligomer was mixed with an equal weight of LCs and stirred for 2 hours. After that the homogenous solution was sandwiched between two pieces of indium tin oxide (ITO)-coated glass substrate. A group of samples, with different molar ratios of DGEBF to EGDE, were prepared as listed in Table 1. All samples

Table 1. The compositions of all samples.

Sample	Monomers (total 50 wt%)	
	DGEBF/EGDE/EDBEA/mol%	SLC1717/wt%
1	8/0/8	50
2	6/2/7	50
3	4/4/6	50
4	2/6/5	50
5	0/8/4	50

utilised 20 μm spacers to obtain uniform film thickness and were heated in an oven at 363.15 K for 7 hours.

2.3 Measurements

The morphology of the polymer network of the PDLC films was studied by scanning electron microscopy (SEM, Cambridge S360). The film was first separated, and then dipped into acetone for 13 days at room temperature so that the LC molecules were extracted, and then the polymer network was dried for 12 hours under vacuum. After the polymer matrix was sputtered with carbon, the microstructure of the polymer matrix was observed under SEM [15].

The refractive index of the matrix was measured using an Abbe Refractometer (WAY-2WAJ, Hangzhou Kebo Instrument Co., Ltd.) at room temperature. The polymer matrices were prepared with the molar ratio according to the samples 1–5, but LCs were absent. The curing conditions were the same as that of PDLCs. It is worth mentioning that the influence of LCs on the refractive index of the polymer network was neglected in this study.

The electro-optic properties were studied using a liquid crystal device (LCD) parameters tester (LCT-5016C, Changchun Liancheng Instrument Co., Ltd.). A halogen tungsten lamp (12 V, 75 W; OSRAM) was used as an incident light source and the incident wavelength through the sample was fixed with a wavelength filter (632.8 nm). The transmittance of the PDLC films was recoded with a photodiode, and the response of the photodiode was monitored with a digital storage oscilloscope. The active area of the detector allowing the estimation of acceptance angle was 0.36 cm^2 . An electric field square wave (1 kHz) was applied and the distance between the PDLC film and the photodiode was 300 mm. The transmittance of air was normalised as 100%.

The transmittance of the PDLC film in the wavelength range from ultraviolet (UV) to near infrared (NIR) region was measured with UV-visible (VIS)-NIR spectrophotometers (V-570, Jasco Corp., Tokyo, Japan). The results were recorded at normal incidence.

3. Results and discussion**3.1 Morphology of polymer network in PDLC films**

Figure 2 shows the droplet morphology of the PDLC samples at room temperature. It can be seen that the mesh size (the LC domain size) of the polymer network in sample 1 is relatively large, whereas in samples 2–5 the mesh size increases and the crosslinking density of the polymer network decreases in the sequence.

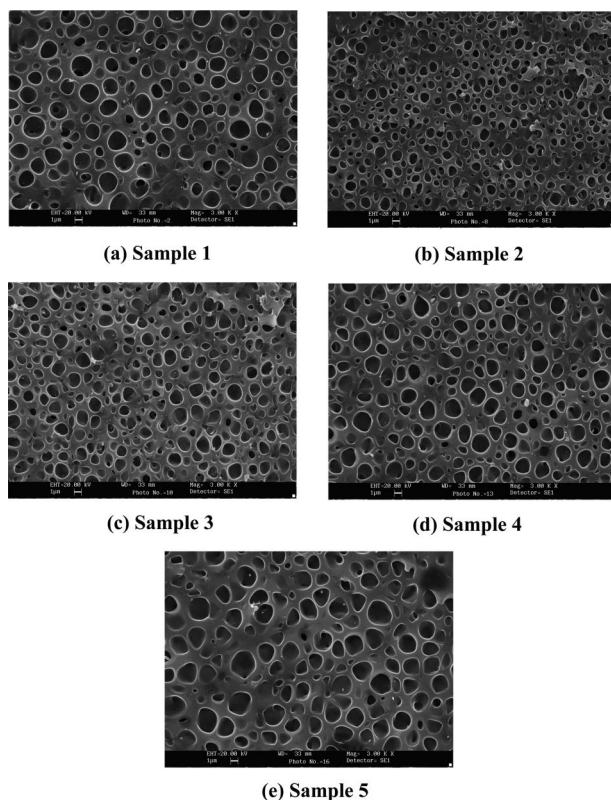


Figure 2. SEM micrographs of the polymer networks of all samples.

This variation is related with the hardener dose and the molecular flexibility. As listed in Table 1, the molar ratio of the hardener to the resins decreases in the sequence. In sample 1, where the molar ratio of EDBEA to DGEBF is 1:1, only half of the amino hydrogens react with epoxy groups, so the crosslinking density is lower and the mesh size of this sample is larger. With the decrease of the hardener dose, the mesh size decreases followed by an obvious increase, which is attributed to the introduction of EGDE. It is well known that the C–C and C–O bonds are much more flexible than the aromatic ring. In other words, the resin EGDE is more flexible and shows a more rapid rate of polymerisation than resin DGEBF. This increasing in the rate of polymerisation may be one of the major factors responsible for a reduction in droplet size. With the further increase of EGDE, the viscosity of the composites decreases greatly and the mesh size of the polymer network increases, which has been demonstrated by Kim *et al.* [16].

3.2 Refractive index of polymer matrix

Table 2 shows the refractive indices of the polymer matrices. In our experiment, the refractive indices of

Table 2. The refractive indices of polymer matrices.

Sample	Refractive index			
	Mixture ^a	n_p^b	n_o^c	$n_p - n_o$
1	1.5466	1.5749	1.5190	0.0559
2	1.5330	1.5596	1.5190	0.0406
3	1.5162	1.5515	1.5190	0.0325
4	1.4983	1.5337	1.5190	0.0147
5	1.4613	1.5047	1.5190	-0.0143

^aThe refractive index of the mixture before curing.

^bThe refractive index of the polymer matrix without the dissolved LC material.

^cThe ordinary refractive index of the SLC-1717 used.

the three kinds of heat-curable monomers are 1.5736 for resin DGEBF, 1.4635 for resin EGDE and 1.4538 for hardener EDBEA. When comparing the refractive indices of cured epoxy matrix materials with those of the resin hardener mixtures prior to the onset of cure, we found that, in all cases, the refractive index increases significantly as a result of the curing process and the refractive index of the polymer matrix decreases in the sequence owing to the composition variation. It is worth noting that the refractive index of sample 5 is closest to the ordinary refractive index of LC material. In an actual PDLC film, the matrix index should also be much closer to the ordinary refractive index of LCs, because LCs are dissolved to some extent in the cured polymer matrix [14].

3.3 Electro-optical properties of PDLC films

Figure 3 shows the applied voltage dependence of the transmittance of samples 1–5. When the applied voltage increases, the transmittance of the samples reaches the saturation level T_{on} . The contrast ratio (CR, T_{on}/T_{off}) is commonly known as the switching

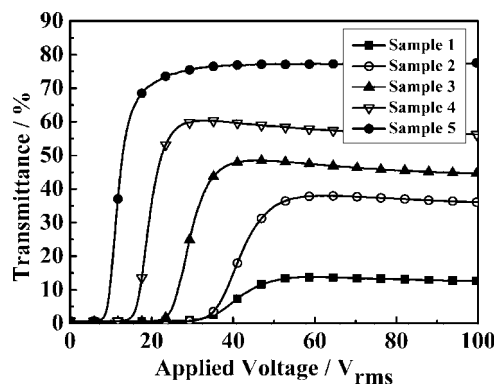


Figure 3. The applied voltage (1 kHz) dependence of the transmittance as a function of the relative content of the epoxy monomers.

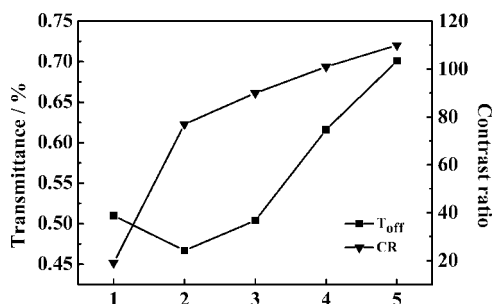


Figure 4. The off-state transmittance (T_{off}) and CR of samples 1–5.

CR, where T_{off} is the initial off-state transmittance in the field-off state.

Figure 4 shows the off-state light transmittance and the CR of all samples. The on-state transmittance (T_{on}) of the samples increases dramatically from 12% to 78%, while the off-state transmittance (T_{off}) initially decreases followed by a slight increase. The CR of films is optimised by adjusting the relative content of the epoxy monomers. The CR of sample 5 is up to 110.

The enhancement of T_{on} is largely caused by the considerable reduction of the mismatch between n_p and n_o , as shown in Table 2. The T_{off} is mainly determined by the LC domain size of the films. As the domain size is increased, the T_{off} increases because of the decrease of the light scattering.

Figure 5 shows the driving voltage of all samples. The threshold voltage (V_{th}) and the saturation voltage (V_{sat}) of samples 1–5 decrease apparently in the sequence. Here, V_{th} and V_{sat} are defined as the electric fields required for the transmittance to reach 10% and 90% of T_{on} , respectively. Generally, the threshold voltage for PDLC displays is given by the following equation [13, 17]:

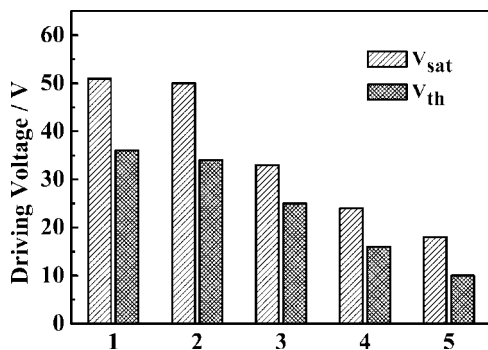


Figure 5. The driving voltage of samples 1–5.

$$V_{\text{th}} = \frac{d}{3a} \times \left(\frac{\rho_P}{\rho_{LC}} + 2 \right) \times \left(\frac{K(l^2 - 1)}{\Delta\epsilon} \right)^{\frac{1}{2}}, \quad (2)$$

where d is the cell thickness, ρ_p and ρ_{LC} are the resistivities of the polymer and the LC, a and l are the major axis and the aspect ratio (major dimension/minor dimension) of the LC droplet (with the assumption that it is an ellipsoid), K is the elastic constant and $\Delta\epsilon$ is the dielectric anisotropy of the LC.

Equation (2) indicates that the threshold voltage (V_{th}) is in inverse proportion to the LC domain size. With increased LC domain size, the specific surface area decreases, weakening the anchoring effect of the polymer matrix on the LC molecules. Thus, the LC molecules are more easily oriented along the direction of the electric field, therefore V_{th} decreases. Generally, V_{sat} changes with V_{th} synchronously. This coincides with the experimental results, except in sample 1.

Although the LC domain size of sample 1 is relatively large, the V_{th} and the V_{sat} of this sample are higher than those of samples 2–5. One conceivable reason for this behaviour may be the different chemical structures of the two resins. In sample 1, the existence of the aromatic ring makes the polymer network have a stronger interaction with the LC molecules due to their similar structure and in samples 2–5, with increased concentration of EGDE, the anchoring energy at the LC/polymer interface decreases. Thus, the required driving voltage is lower.

Figure 6 shows the electro-optical response time of the samples to an applied driving field (100 V, 1 kHz) at normal incidence. The rise time (τ_R) and the decay time (τ_D) are defined as the time required for transmittance change from 10.0% to 90.0% upon turn on, and from 90.0% to 10.0% upon turn off, respectively. All

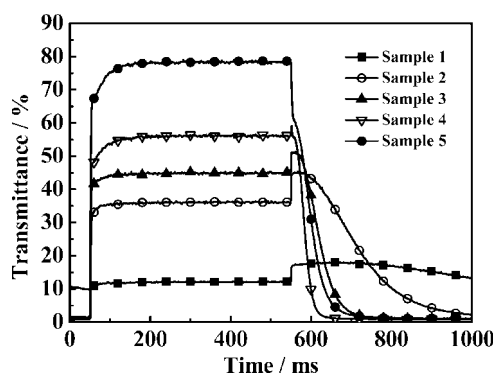


Figure 6. The electro-optical response time of the samples to an applied driving field (100 V, 1 kHz) at normal incidence. An increase in transmittance following removal of the field is present in the refractive index unmatched case, but not in the matched case.

samples show a rapid rise time to their own saturation transmittance. Upon removal of the voltage, in samples 1–4 the transmittance initially increases followed by a slow decay to the scattering off-state, while in sample 5 the transmittance decreases directly.

This behaviour is related to the refractive index mismatch between the polymer network and the LC [14]. Under the condition $n_p > n_o$, e.g. in samples 1–4, upon the removal of the electric field, relaxation of the droplet alignment will initially lead to an increase in n_d to a value above n_o . When n_d reaches maximum, the films exhibit the maximum transmittance due to the minimum difference value between n_d and n_p . Then, the films return to the original scattering state as the value of n_d decreases away from n_p . Under the condition $n_p < n_o$, e.g. in sample 5, the film shows the index-matched condition state of maximum transmittance when the LC molecules align with the electric field.

Under the condition $n_p \approx n_o$, the influence of the refractive index on the response time can be neglected. The τ_R and τ_D are affected by a competition between the applied field and the elastic forces anchoring the LC molecules at the interface. Smaller LC domains result in larger τ_R and smaller τ_D , because of the existence of the stronger surface anchoring energy [18]. Meanwhile the polymer network containing the rigid chain segment can also enhance the surface anchoring energy [13]. Therefore, the rise time of sample 4 is larger than that of sample 5 and the decay time of sample 4 is smaller than that of sample 5.

Figure 7 shows the wavelength (λ) dependence of the off-state transmittances for the samples. The transmittances of all samples tend to increase with increasing wavelength in the range of 300–2500 nm. Furthermore, in the VIS region, the transmittance is very low, which is in good agreement with the results as showed in Figure 4.

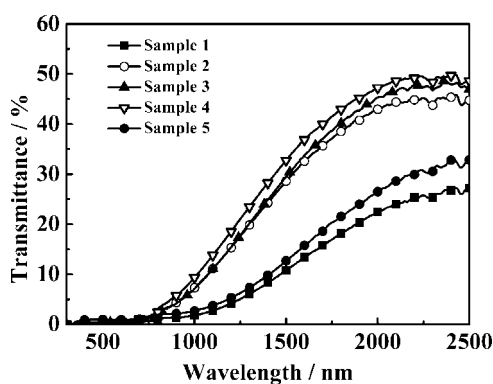


Figure 7. The wavelength (λ) dependence of the off-state transmittance (T_{off}) for the samples.

4. Conclusions

For PDLC films, the composition of heat-curable mixtures affects the microstructure of the polymer network and the LC domain size. The monomers containing flexible chain segments are prone to form large-size polymer networks and thus the anchoring energy at the LC/polymer interface decreases, resulting in the driving voltage decreasing significantly. Meanwhile, the structures of epoxy resins also influence the refractive index of the polymer matrix. With the increase of the flexible segment, the refractive index of the polymer matrix decreases and the mismatch between n_p and n_o is reduced, thus the on-state transmittance is optimised.

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