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The influence of the structure of curable epoxy monomers on the electro-optical properties of polymer dispersed liquid crystal devices prepared by UV-initiated cationic polymerisation

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Electro-optical properties are important characteristics of polymer dispersed liquid crystal (PDLC) devices. In this paper, PDLC films based on liquid crystal (LC)/curable epoxy monomers/cationic photoinitiator composites were prepared by ultraviolet-initiated (UV-initiated) cationic polymerisation using triphenylsulfonium hexafluoroantimonate (Ar₃S⁺SbF₆⁻) as the photoinitiator. The effects of the structures of curable epoxy monomers on PDLC films were investigated. The microstructures of the PDLC films were strongly influenced by the curable epoxy monomers, which in turn influenced the electro-optical properties of PDLC films. It was found that the LC domain size of the polymer network could be regulated by adjusting the structure of curable epoxy monomers, and then the electro-optical properties of PDLC films could be optimised.

Keywords: polymer dispersed liquid crystal; cationic polymerisation; epoxy monomers; structure; morphology; electro-optical properties

1. Introduction

Polymer dispersed liquid crystal (PDLC) films can be used as an important class of electro-optical materials for making large and flexible displays, optical shutters and switchable windows [1–4]. Unlike conventional liquid crystal (LC) displays, a PDLC film is flexible and easy to prepare, as well as removing the necessity for polarisers, alignment layers, and precise control of the spacer between two substrates [4–6]. In the PDLC films, the droplets of nematic LC with positive dielectric anisotropy disperse in an isotropic continuous polymer matrix [7, 8]. The molecular organisation within the encapsulated LC droplets depends on the elastic constants of the LC and the interfacial anchoring conditions [9, 10]. The PDLC films can be switched from a scattering state to a transparent state by applying an electric field. It has been found that the electro-optical properties of PDLC films are dependent on the properties of the polymer matrix (structure, molecular weight, electrical and optical properties, etc.), the characteristics of LC (dielectric anisotropy, elastic constant, the morphology of droplets, etc.), the anchoring energy on the boundary surface, the size and morphology of LC domains in the polymer and other parameters [11–13].

The randomly orientated LC droplets separated from an isotropic continuous polymer matrix are induced by either polymerisation induced phase separation (PIPS), thermal induced phase separation (TIPS), or solvent induced phase separation (SIPS). The most convenient technique used in the preparation of PDLC films is PIPS, as the fabrication process is relatively simple, clean and solvent free. The phase separation of PIPS is usually induced by photo-initiated polymerisation or thermal-initiated polymerisation of monomers mixed with the LC. The cure of the former can be finished in a few minutes at room temperature, whereas that of the latter is usually done for few hours at a higher temperature. PDLC films prepared by photo-initiated polymerisation have been attracting much attention. Under intense UV illumination, reactive species such as free radicals or cations can be generated in high concentration by photolysis of initiator, and thus promote the polymerisation of multifunctional monomers. Until now, most researches into PDLC preparation by UV-initiated polymerisation have focused on free-radical systems based primarily upon acrylates and methacrylates, but few detailed investigations have been carried out on preparing PDLC films by UV-initiated cationic polymerisation. It was therefore interesting to use epoxy monomers to form PDLC films to improve their electro-optical properties.

Epoxies can be polymerised and crosslinked via the UV radiation process in the presence of cationic photoinitiators [14, 15]. Among the different families of crosslinking resins, epoxies are widely used due to their outstanding performance, coupled with a very
easy processability and a limited cost. Epoxy resins are well known for their outstanding adhesion, flexibility and chemical resistance. They are convenient to use for this reason: it is easy to mix epoxy resins with the proper refractive index to produce a matrix with superior optical properties [16].

In our previous study, we showed that UV-initiated cationic polymerisation of epoxy monomers can be a means of preparing PDLC films [17]. Furthermore, the effects of the composition of the mixtures and the curing temperature on the microstructure and the electro-optical properties of PDLC films were investigated. Therefore, the objective of this research was to show the effects of the structure and the ratio of curable epoxy monomers on the microstructure of the polymer network and the electro-optical properties of PDLC films.

2. Experimental

2.1 Materials

The nematic LC used in the study was SLC 1717 ($T_{NI} = 365.2$K, $n_o = 1.519$, $n_e = 1.720$, Shijiazhuang Yongsheng Huatsing Liquid Crystal Co. Ltd.). Ethyleneglycol diglycidyl ether (EGDE) resin (XY 669, Anhui Hengyuan Chemical Co. Ltd.), diglycidyl ether of bisphenol F (DGEFB) resin (EPON 862, Zhaochang Int’l Trade (Shanghai) Co. Ltd.), polyethyleneglycol diglycidyl ether (PEGDE) resin (Shanghai Rufa Chemical Technology Co. Ltd.), trimethylolpropane triglycidyl ether (TMPTGE) resin (Nanjing Chemlin Chemical Industry Co. Ltd.) and pentaerythritol tetraglycidyl ether (PTTGE) resin (Synasia (Suzhou) Co. Ltd.) and were used as UV-initiated cationic curable monomers. UV-initiated cationic polymerisation was initiated using the cationic photoinitiator UVI-6976 (Synasia (Suzhou) Co. Ltd.). The chemical structures of the materials are shown in Figure 1. All of the above materials were used as received without further purification.

2.2 Sample preparation

In this study, the PDLC films were obtained by the UV-initiated cationic polymerisation induced phase separation process.

At first, the nematic LC/UV-initiated cationic curable monomers/cationic photoinitiator mixture was prepared and vigorously stirred until a homogeneous mixture formed. Then, 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. The mixture was then irradiated for polymerisation by a UV lamp (365 nm 35-W Hg lamp, PS135, UV Flood, Stockholm, Sweden) for 30.0 min at temperature 318.2K. Thus, the films based on epoxy resins were prepared. The compositions of the PDLC films in the study are listed in Table 1.

2.3 Morphology analysis

The morphology of the PDLC films was observed by scanning electron microscopy (SEM) (ZEISS, EVO18, Germany). The films were first separated and dipped

<table>
<thead>
<tr>
<th>Sample</th>
<th>Monomers used</th>
<th>Weight ratio (wt%)</th>
<th>LC (wt%)</th>
<th>Photoinitiator (wt%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>EGDE</td>
<td>35.0</td>
<td>60.0</td>
<td>5.0</td>
</tr>
<tr>
<td>2</td>
<td>EGDE/PEGDE</td>
<td>30.0/5.0</td>
<td>60.0</td>
<td>5.0</td>
</tr>
<tr>
<td>3</td>
<td>EGDE/PEGDE</td>
<td>29.2/5.8</td>
<td>60.0</td>
<td>5.0</td>
</tr>
<tr>
<td>4</td>
<td>EGDE/PEGDE</td>
<td>28.0/7.0</td>
<td>60.0</td>
<td>5.0</td>
</tr>
<tr>
<td>5</td>
<td>EGDE/PEGDE</td>
<td>26.2/8.8</td>
<td>60.0</td>
<td>5.0</td>
</tr>
<tr>
<td>6</td>
<td>EGDE/PEGDE</td>
<td>23.3/11.7</td>
<td>60.0</td>
<td>5.0</td>
</tr>
<tr>
<td>7</td>
<td>EGDE/PEGDE</td>
<td>17.5/17.5</td>
<td>60.0</td>
<td>5.0</td>
</tr>
<tr>
<td>8</td>
<td>EGDE/DGEBF</td>
<td>28.0/7.0</td>
<td>60.0</td>
<td>5.0</td>
</tr>
<tr>
<td>9</td>
<td>EGDE/TMPTGE</td>
<td>28.0/7.0</td>
<td>60.0</td>
<td>5.0</td>
</tr>
<tr>
<td>10</td>
<td>EGDE/PTTGE</td>
<td>28.0/7.0</td>
<td>60.0</td>
<td>5.0</td>
</tr>
</tbody>
</table>
into cyclohexane for four days at room temperature to extract the LC molecules, and then were dried for 12 hours 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 of the PDLC films were studied using an LCD parameters tester (LCT-5016C, Changchun Liancheng Instrument Co. Ltd.). A halogen tungsten lamp was used as an incident light source and the incident wavelength through the samples was fixed with a wavelength filter (632.8 nm). The transmittance of the PDLC films was recorded by a photodiode, and the response of the photodiode was monitored by a digital storage oscilloscope. A square-wave-modulated electric field was used and the distance between the PDLC film and photodiode was 300 mm. The transmittance of air was normalised as 100%, and the results were recorded with an incident angle, $\delta = 0^\circ$.

3. Results and discussion

3.1 Cationic polymerisation analysis

With the selected polymerisation system, photoinitiators play a key role in UV-induced polymerisation. Onium salts ($\text{On}^+$) containing aromatic groups such as diaryliodonium ($\text{Ar}_2\text{I}^+\text{X}^-$) and triarylsulfonium salts ($\text{Ar}_3\text{S}^+\text{X}^-$), represent a large class of compounds that can be used as cationic photoinitiators. These salts effectively act as sources of cation radicals and Lewis acids upon light exposure, as shown in Scheme 1 [18–25].

Upon irradiation, onium salts decompose to yield a variety of reactive radical, radical-cation and cation intermediates. The cationic species can interact with a proton donor molecule (RH, i.e. monomer or impurity like water) giving rise to the strong Brønsted acid, $\text{H}^+\text{X}^-$ (Equations 1(a) and (b)), which can initiate ring-opening cationic polymerisation of epoxies. Initiation proceeds by protonation of the monomer (Equation (2)) and is followed by polymerisation (Equation (3)).

\[
\begin{align*}
\text{Ar}_2\text{I}^+\text{X}^- & \xrightarrow{\text{hv}} \text{Ar}^+ + \text{ArI}^+\text{X}^- \xrightarrow{\text{RH}} \text{ArI} + \text{R}^+ + \text{H}^+\text{X}^- + \text{Ar}^+ \quad (1-\text{a}) \\
\text{Ar}_3\text{S}^+\text{X}^- & \xrightarrow{\text{hv}} \text{Ar}^+ + \text{Ar}_3\text{S}^+\text{X}^- \xrightarrow{\text{RH}} \text{Ar}_3\text{S} + \text{R}^+ + \text{H}^+\text{X}^- + \text{Ar}^+ \quad (1-\text{b}) \\
\text{H}^+\text{X}^- + M_{\text{EP}} & \rightarrow \text{HM}_{\text{EP}}^\text{X}^- \\
\text{HM}_{\text{EP}}^\text{X}^- + nM_{\text{EP}} & \rightarrow H(M_{\text{EP}})_nM_{\text{EP}}^\text{X}^- 
\end{align*}
\]

Scheme 1. Proposed mechanisms of the photodecomposition of onium salt initiator systems in epoxy monomer polymerisation ($M_{\text{EP}} =$ epoxy monomer).

It is apparent that, with the selected epoxy system, the polymers could be generated as shown in Figure 2. The main interest of the polymerisation of epoxy systems is that the epoxies cured via cationic polymerisation are negligibly toxic and insensitive to oxygen, and have low shrinkage and good adhesion. In contrast to free-radical polymerisation which stops immediately when the radiation source is removed, UV-initiated cationic polymerisation of epoxies continues to proceed in the ‘dark’, which is called dark-curing behaviour [14, 15, 26, 27].

3.2 Morphology of the polymer network of the samples

Figure 3 shows the SEM micrographs of the polymer networks of the PDLC films with different ratios of EGDE/PEGDE at a UV irradiation temperature of 318.2 K. It can be seen that in samples 1–7 the LC domain size of the polymer network increased and the crosslinking density of the polymer network decreased in sequence. The morphology of the PDLC films was gradually formed during the LC droplet nucleation and the polymer gelatins. Droplet size is controlled by the relative amounts of the photopolymerisable monomers and LC, the rate of polymerisation, and some physical parameters such as the viscosity, rate of diffusion, and solubility of the LC in the polymer [28, 29]. In this study, the LC domain size was influenced by the relative ratio of the short flexible chain curable monomers, EGDE, and the long flexible chain curable polymers, PEGDE. In samples 1–7, the content of PEGDE gradually increased in sequence. It is well known that increasing the chain length of curable monomers increases their molecular weight. Thus,
Figure 3. SEM micrographs of the polymer network in samples 1–7 with different ratios of EGDE/PEGDE: (a) sample 1 (35.0/0); (b) sample 2 (30.0/5.0); (c) sample 3 (29.2/5.8); (d) sample 4 (28.0/7.0); (e) sample 5 (26.2/8.8); (f) sample 6 (23.3/11.7); (g) sample 7 (17.5/17.5).

when the content of the curable monomers was constant, with increased content of PEGDE the amount of molecules in the samples decreased. In addition, the introduction of PEGDE resulted in the insertion of the relatively long, flexible branch comprising (10 ethylene oxide repeat units) in the polymer network, so it could result in the increase of the distance between two neighbouring crosslinking points in the polymer network. Finally, the decrease of the amount of molecules and the increase of the distance between two neighbouring crosslinking points induced the decrease in the crosslinking density and the increase of the LC domain size. As a result, the sizes of LC domains in samples 1–7 increased in sequence. This showed that the chain length of curable monomers played an important role in the morphology of the polymer network.

Figure 4 shows the SEM micrographs of the polymer networks of the PDLC films from samples 4 and 8–10 where structural difference gives significantly different morphology. As shown in Figure 4, the LC domain size of the polymer network in sample 4 was larger than samples 8–10. It is well known that aromatic rings are much more rigid than the C–C and

Figure 4. SEM micrographs of the polymer network in samples 4, 8, 9 and 10: (a) sample 4 EGDE/PEGDE (28.0/7.0); (b) sample 8 EGDE/DGEBF (28.0/7.0); (c) sample 9 EGDE/TMPTGE (28.0/7.0); (d) sample 10 EGDE/PTTGE (28.0/7.0).
C–O bonds. For sample 8, the LC domain size obviously decreased due to the introduction of the more rigid molecule, DGEBF. Generally, the viscosity of the rigid chain curable monomers was larger than the flexible chain curable monomers. Due to the introduction of the rigid monomers, the curable monomers became more difficult to diffuse, and the congregation of LC molecules became difficult during UV curing. In addition, the rigid curable monomers had greater chemical affinity with LC molecules due to their similar rigid molecular structure, which promoted the formation of smaller LC domains. In samples 9 and 10, the multifunctional curable epoxy monomers were introduced in the polymer network. Generally, the introduction of multifunctional curable monomers resulted in an increased amount of crosslinking points in the polymer network; this also resulted in a more rapid rate of polymerisation. Therefore the LC domain size of sample 9 was smaller than that of the sample 4. There were more epoxy groups in the single monomer for sample 10 than in sample 9. The rate of polymerisation of the curable monomers in sample 10 was quicker than in sample 9 at the initial moment of polymerisation. However, when polymerisation proceeded, unreactive epoxy curable monomers were more easily fixed and became more difficult to cure in sample 10, causing the rate of polymerisation subsequently to decrease. This resulted in the smaller density of crosslinking and the larger LC domain size than in the polymer network of sample 9.

3.3 Electro-optical properties of the samples

As mentioned above, the structure and the ratio of the curable monomers played important roles in the fabrication of the polymer network. These results suggest that it is possible to regulate the LC domain size by adjusting the structure and the ratio of curable monomers. Figure 5 shows the applied voltage dependence of the transmittance of samples 1–10. As can be seen in Figure 5, the transmittance of the samples reached the saturation level $T_{on}$ when the applied voltage increased. Comparing Figure 5 with Figures 3 and 4, the morphology of the polymer network in the PDLC films had a crucial effect on the electro-optical properties of the PDLC films. Good electro-optical properties of the PDLC films can be obtained when the microstructure of the PDLC film is appropriate.

Contrast ratio (CR) is an important measure of the electro-optical properties in PDLC films. Contrast ratio (CR, $T_{on}/T_{off}$) is commonly known as the switching contrast ratio, where $T_{on}$ and $T_{off}$ are the ultimate on-state transmittance and the initial off-state transmittance respectively. Figure 6 shows the off-state light transmittance ($T_{off}$) in fixed wavelength (632.8 nm) and the contrast ratio of all samples. The optimal LC domain size of PDLC films for scattered light is about a few microns. The off-state transmittance of samples 1–7 increased dramatically from 2.5% to 25.0%. The off-state transmittance of samples 4 and 8–10 was 8.3%, 3.8%, 4.8% and 8.9% respectively. It is well known that the LC domain size has significant influence on $T_{off}$ of the PDLC films. For a definite system where the LC content is fixed, the larger LC domain size resulted in an insufficient number of scattering centres, and the $T_{off}$ of the samples increased with the increasing size of the LC domain. Meanwhile, the decrease in the $T_{off}$ resulted in a rise in the CR due to the CR being strongly influenced by the $T_{off}$. As $T_{off}$ is the denominator of the fraction $CR = T_{on}/T_{off}$, the change of CR was opposite to the change of $T_{off}$. As a result, the CR and $T_{off}$ of PDLC films can be optimised by adjusting the structure and the ratio of curable epoxy monomers. The CR of sample 1 was up to 24, the CR of samples 1-7 decreased from 24 to 3 with the increase of the $T_{off}$ of the samples. The $T_{off}$ of the samples 4 and 8-10 was 11, 11.5, 12 and 7 respectively.

![Figure 5. Applied voltage dependence of the transmittance of: (a) samples 1-7 and (b) samples 4, 8, 9 and 10.](image-url)
Driving voltage is also an important measure of the electro-optical properties in PDLC films. Figure 7 shows the threshold voltage ($V_{th}$) and the saturation voltage ($V_{sat}$) of samples 1–10. Here, the threshold voltage ($V_{th}$) and the saturation voltage ($V_{sat}$) are defined as the voltage required for transmittance to reach 10% and 90% of $T_{on}$ respectively. It is known that the size of LC droplets plays a fundamental role in determining the electro-optical properties of PDLC films. $V_{th}$ is inversely proportional to the LC domain size as shown below [28, 30]:

$$V_{th} = \frac{d}{2a} \times \left( \frac{\rho_p}{\rho_{LC}} + 2 \right) \times \left( \frac{K (l^2 - 1)}{\Delta \varepsilon} \right)^{\frac{1}{2}} \tag{4}$$

where $d$, $\rho_p$, $\rho_{LC}$, $a$, $l$, $K$ and $\Delta \varepsilon$ are the cell thickness, the resistivities of polymer and LC, the major axis and the aspect ratio (major dimension/ minor dimension) of LC droplet (with the assumption that it is an ellipsoid), the elastic constant, and the dielectric anisotropy of the LC. As shown in Figure 7(a), $V_{th}$ of samples 1–7 decreased dramatically from 6.1 V to 1.5 V and $V_{sat}$ from 20.0 V to 6.6 V. Figure 7(b) shows that $V_{th}$ of samples 4, 8, 9 and 10 was 3.9 V, 5.1 V, 4.4 V and 2.4 V, and $V_{sat}$ was 18.4 V, 19.0 V, 16.1 V and 10.0 V, respectively. It is possible to observe a change in $V_{th}$ and $V_{sat}$ which decreases in order of the increasing LC domain size. In addition, the polymer–LC specific surface area and interface anchoring effect of the polymer matrix for the LC molecules increased with the decrease of LC domain size, making the LC molecules more difficult to orientate along the direction of the electric field. Therefore, $V_{th}$ and $V_{sat}$ of the PDLC films increased with the decreasing LC domain size. The polymers containing rigid chain segments, for example DGEBF, also have stronger interaction with the LC molecules due to their similar structure; sample 8 showed higher $V_{th}$ and $V_{sat}$. These changes implied that the electro-optical properties of PDLC films are largely governed by the LC domain size which can be controlled by the structure and the ratio of curable monomers. Therefore, it is possible to optimise the electro-optical properties of PDLC films by adjusting the structure and ratio of curable monomers.

A response time is necessary for the LC molecules to align along the electric field or to relax to their initial orientation when the electric field is removed. Figure 8 shows the electro-optical response time of the samples 1–10 at an applied electric field. The turn-on response time ($t_{on}$) and the turn-off response time...
of the curable monomers significantly affected the morphology of the PDLC films and the LC domain size. The monomers containing flexible chain segments were prone to form large LC domain sizes – the higher the content of the long and flexible chain monomers, the larger the LC domain size. However, the monomers containing rigid chain segments and the multifunctional curable monomers had the opposite effects and were prone to form small LC domain sizes. Meanwhile, the electro-optical properties of the PDLC films depended strongly on the LC domain size. The results presented in this study suggest that it is possible to regulate the LC domain size and optimise the electro-optical properties of PDLC films by adjusting the structure and the ratio of curable monomers.

4. Conclusions
In this study, the influence of the structure of curable epoxy monomers on the microstructure of the polymer network and the electro-optical properties of PDLC films prepared by UV-initiated cationic polymerisation was studied. As mentioned above, the structure

\( t_{\text{off}} \) 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. Generally, a competition among the applied electric field and the interface elastic forces anchoring the LC molecules governed the response time. The smaller the LC domain size, the stronger the interface elastic forces of the polymer network to the LC molecules. Thus, smaller LC domains need a longer time to overcome more interface anchoring energy. When the applied electric field was removed, the LC molecules could revert quickly to the initial off-state due to the higher interface elastic forces. As shown in Figure 8, \( t_{\text{on}} \) decreased with the increase of LC domain size, whereas \( t_{\text{off}} \) increased simultaneously from samples 1–7; the change for samples 8–10 was similar.

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References