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Polymer-dispersed liquid crystal (PDLC) films were prepared by photochemical polymerisation from an ultraviolet-curable monomer/crosslinking agent/initiator/liquid crystal (LC) mixture. The influences of the chain length of crosslinking agents on the PDLC system have been studied. The microstructures of the PDLC films were strongly influenced by the chain length of the crosslinker, which in turn influences the electro-optic properties of PDLC films. It is proved that adjusting the chain length of the crosslinking agents and the LC content can produce PDLC films that have good electro-optic properties with a lower LC content.

Keywords: polymer-dispersed liquid crystal; ultraviolet curing; electro-optical properties

1. Introduction

A polymer-dispersed liquid crystal (PDLC) film consists of micron-sized droplets of liquid crystals (LCs) dispersed in a continuous polymer matrix [1]. In an electrical off-condition, PDLC film is opaque because of the light scattering caused by the refractive index mismatch between the LC droplets and the polymer matrix. In an electrical on-condition, PDLC film becomes transparent because the alignment of the LC molecular is parallel to the applied electric field and the ordinary refractive index of the LC matches the refractive index of the polymer [2–4]. It has been found that the electro-optic property of PDLC films is influenced by the size and morphology of LC domains, the compositions ratios, separation degree and other parameters [5].

PDLC films can be fabricated using polymerisation-induced phase separation (PIPS) [6], thermally induced phase separation (TIPS) [7], solvent-induced phase separation (SIPS) [8] or the nematic curvilinear-aligned phase (NCAP) [9]. PIPS has been considered to be the most popular method since the fabrication process is relatively simple, clean and solvent-free. The matrixes used in the PIPS include photo-curable and thermal-curable monomers [2].

The electrically switchable materials based on chromogenic technologies are now widely used in buildings, vehicles, aircrafts and displays [10]. During the last two decades, the PDLC market has been developed to supply the construction and motor vehicle industries, and it has made extensive progress [11]. For further development of the worldwide PDLC market, attention has to be paid to the quality of the product as well as the market price. LCs are usually quite expensive, so the overall ratio of LCs has a large impact on the production cost in PDLC manufacturing. In general, the electro-optic properties of PDLC films with lower LC content are insufficient for use in daily life, so most commercial PDLC films consist of 70.0–85.0 wt% of LCs; this causes the higher price of PDLC materials. So, lowering the LC content of PDLC films is a very important factor for lowering the production cost of PDLC materials, while increasing the monomer content will result in higher tensile strength of the polymer matrix and improve the interfacial adhesion between films, which provide easier handling during PDLC manufacturing. Consequently, PDLC films with a lower LC content that have optimised electro-optic properties are the primary key to success in the PDLC industry.

In this study, PDLC films were prepared with the PIPS method from monomer/initiator/LC composite. The effects of the chain length of crosslinking agents and different LC contents on morphology, and the electro-optical performance of the PDLC films were investigated.

2. Experimental details

2.1 Materials

The nematic LC used in this study was SLC 1717 ($T_{\mathrm{NI}} = 365.2$ K, $n_0 = 1.519$, $n_e = 1.720$, Shijiazhuang Yongsheng Huatsing Liquid Crystal Co. Ltd., China). Diethylene glycol diacrylate (DEGDA), Polyethylene glycol (200) diacrylate (PEGDA 200), Polyethylene glycol (400) diacrylate (PEGDA 400), Polyethylene glycol (600) diacrylate (PEGDA 600) (Sartomer, Exton, PA)

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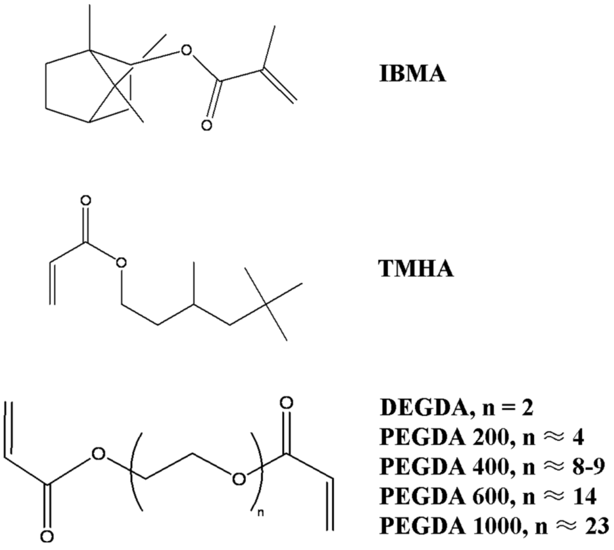

Figure 1. Chemical structures of co-monomers and crosslinking agents.

and Polyethylene glycol (1000) diacrylate (PEGDA 1000) (Shin-Nakamura Chem. Co. Ltd., Japan) were used as crosslinking agents. Isobornyl methacrylate (IBMA) and 3,5,5-trimethelhexyl acrylate (TMHA) (Aldrich, St. Louise, MO) were used as co-monomers. Photo-polymerisations were initiated using Irgacure 651 (Ciba Geigy, Jingjiang Hongtai Chem. Co. Ltd., China). Figure 1 shows the chemical structures of the photo-polymerisable monomers. 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 PIPS process.

The monomer/crosslinking agent/initiator/LC mixture was placed between two glass slides coated with a thin transparent layer of conducting indium/tin oxide. The film thickness was controlled by a 16 ± 1 μm thick polyethyleneterephtalate (PET) spacer. The mixture was then exposed to ultraviolet (UV) irradiation for about 7.0 minutes from a 35.0 W high pressure Hg lamp, yielding intensities at the cell surface of about 6.0 mW cm^{-2} at 365.0 nm. In this study, the ratio between the diacrylate crosslinkers and the acylate co-monomers was maintained at the weight ratio of 1/4. The ratio between the two acrylate co-monomers was fixed.

2.3 *Morphology analysis*

The morphology of the PDLC films was studied with a scanning electron microscope (SEM, Leica S440i, Germany). The film was dipped in hexamethylene at room temperature in order to extract the LC molecules, then the film was sputtered with carbon before viewing under the SEM.

2.4 *Electro-optic measurement*

The electro-optic experiments were measured at room temperature by a liquid crystal device (LCD) parameters tester (LCT-5016C, Changchun Liancheng Instrument Co. Ltd., China). A halogen laser beam (560 nm) was used as the incident light source. The transmittance of the PDLC films was recorded by a photodiode, and the response of the photodiode was monitored by a digital storage oscilloscope. The distance between the sample cell and the detector was approximately 300 mm. The collection angle of the transmitted intensity was about ±2°, so that principally forward scattering was detected. The UV-visible spectra of off-state PDLC films were measured using a UV/visible/near infrared (NIR) spectrophotometer (V-570, Jasco Corp., Tokyo, Japan). The wavelengths of 300.0–800.0 nm were measured and recorded with an incident angle, $\delta = 0°$. The transmittance of air was normalised as 100.0%.

3. Results and discussion

The morphologies of various chain lengths of crosslinking agents with a LC content of 50.0 wt% and various ratios of LC with a PEGDA 400 crosslinker were studied with the SEM. The LC domain size and morphology of the PDLC film are determined during the LC droplet nucleation and the polymer gelation. The LC domain size is influenced by the rate of polymerisation, the relative ratios of the materials, the types of LCs and polymers used and the physical parameters, such as viscosity, rate of diffusion and solubility of the LCs in the polymer. As shown in Figure 2, the LC domain size increased with increasing the chain length of the crosslinking agents. Increasing the chain length of the crosslinking agent caused the molecular weight of the crosslinkers to increase, so the amount of molecules in the same weight ratio of each sample decreased, and this resulted in lowering the crosslinking density and increasing the LC droplet size. As shown in Figure 3, along with decreasing the LC content, the LC droplet size decreased. So the chain length of the crosslinkers and the LC content played important roles in the fabrication of the polymer network. The results suggest that it is possible to regulate the LC domain size by adjusting the chain length and the ratio of the LC content.

The contrast ratio (CR) is an important measure of the electro-optic performance in a PDLC system.

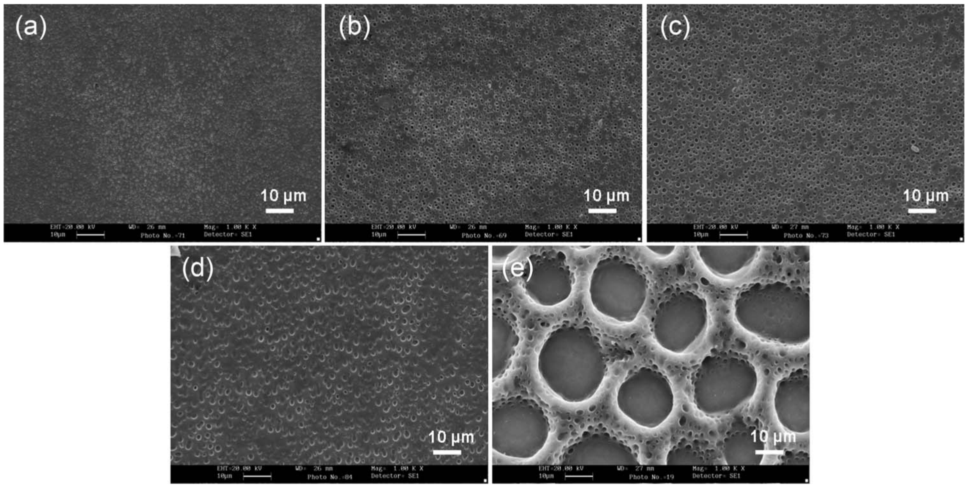

Figure 2. Morphologies of PDLCs for different chain lengths of crosslinking agents with LC content of 50.0 wt%: (a) DEGDA; (b) PEGDA 200; (c) PEGDA 400; (d) PEGDA 600; (e) PEGDA 1000.

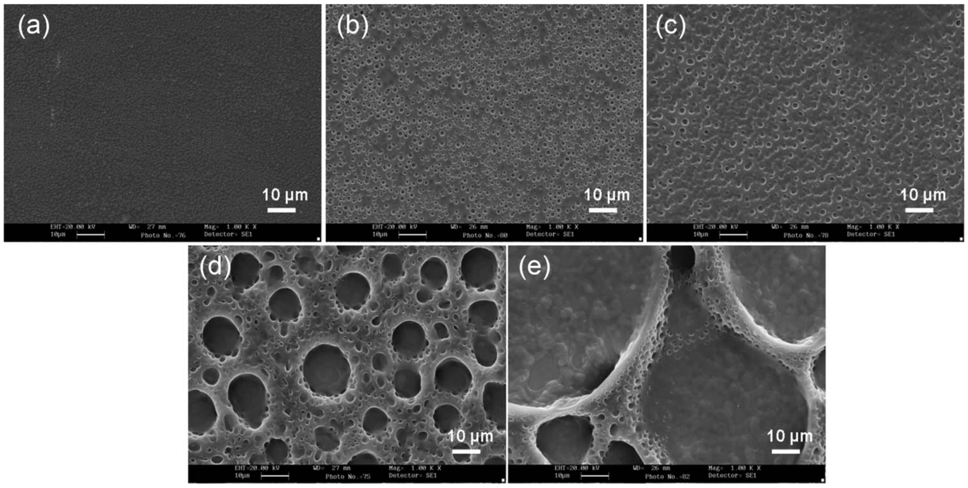

Figure 3. Morphologies of PDLCs for different LC content with the PEGDA 400 crosslinker: (a) 40.0 wt%; (b) 50.0 wt%; (c) 60.0 wt%; (d) 70.0 wt%; (e) 80.0 wt%.

The CR of PDLCs to characterise the difference between a transparent and an opaque state is defined as:

$$CR = T_{\mathrm{on}}/T_{\mathrm{off}}, \tag{1}$$

where T_{on} and T_{off} are transmittance in the on- and off-state of the PDLC film. As shown in Figure 4, the CR increased along with increasing the chain length of the crosslinking agents up to PEGDA 400, and then the CR decreased with further increasing of the chain length of the crosslinker. For the PEGDA 400 samples, the CR was the highest at a LC content of 50.0 wt%. Comparing Figures 2 and 3 with Figure 4, the morphology of the PDLC film has an indispensable effect on the CR of the PDLC film. A high value of CR can be obtained when the microstructure of the PDLC film is appropriate.

It is known that the size of the LC droplets plays a fundamental role in determining the electro-optic performance of a PDLC system. The threshold voltage (V_{th}) and the saturation voltage (V_{sat}) are defined as the electric voltage required for the transmittance to reach 10% or 90%. V_{th} is inversely proportional to the radius of LC droplets (R) as shown below:

$$V_{\mathrm{th}} \simeq \frac{d}{R}\left[\frac{K(\omega^2-1)}{\varepsilon_0 \Delta\varepsilon}\right]^{1/2}, \tag{2}$$

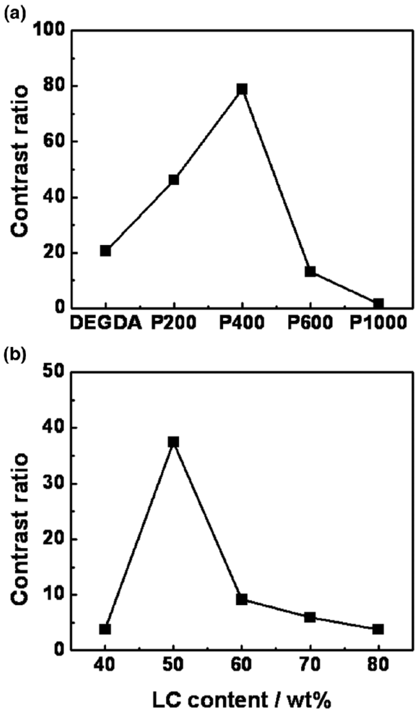

Figure 4. Dependence of the CR: (a) different chain lengths of crosslinking agents with a LC content of 50.0 wt%; (b) different LC content with the PEGDA 400 crosslinker.

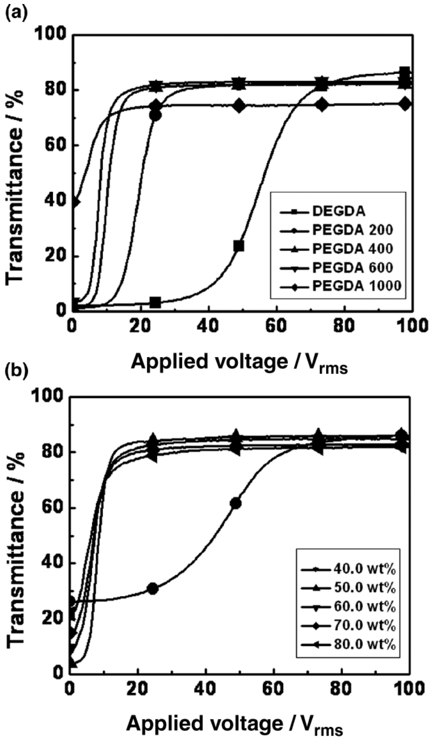

Figure 5. Transmittance dependence on the applied voltage: (a) different chain lengths of crosslinking agents with a LC content of 50.0 wt%; (b) different LC content with the PEGDA 400 crosslinker.

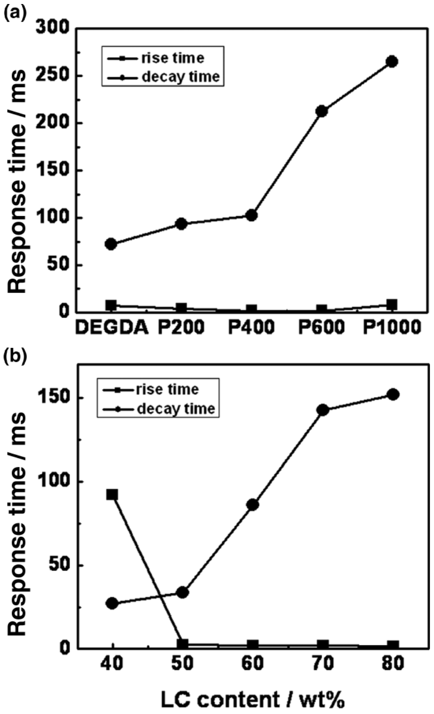

Figure 6. Dependence of response times: (a) different chain lengths of crosslinking agents with a LC content of 50.0 wt%; (b) different LC content with the PEGDA 400 crosslinker. The PDLCs were driven by an applied field of 100 V_{rms}.

where d, K, ω and $\Delta\varepsilon$ represent film thickness, elastic constant, aspect ratio and dielectric anisotropy of the LC, respectively [12–15]. Larger LC droplet size leads to lower V_{th} and V_{sat}. As shown in Figures 2, 3 and 5, the V_{th} and V_{sat} generally decreased with increasing the LC domain sizes. It is shown that the operating voltage of the PDLC film is significantly influenced by the chain length of the crosslinking agents and the LC content. By adjusting the content of the LCs and the chain length of the crosslinking agent, it is possible to optimise the electro-optical properties of PDLC film with a lower LC content.

The time it takes to switch to a transparent state (rise time, τ_R) or to an opaque state (decay time, τ_D) is one of the most important factors for evaluating PDLC performance. These are the times necessary for the LC molecules to align along the electric field, or to relax to an arbitrary orientation where the electric field is suppressed. τ_R and τ_D are defined as the time from 10% to 90% or 90% to 10% of the total change between a transparent and an opaque state. τ_R and τ_D depend on the field strength forcing molecular orientation and the viscoelastic parameters influencing the forces that oppose such orientation [14, 16]. τ_R and τ_D for an elongated droplet of an aspect ratio l are defined as:

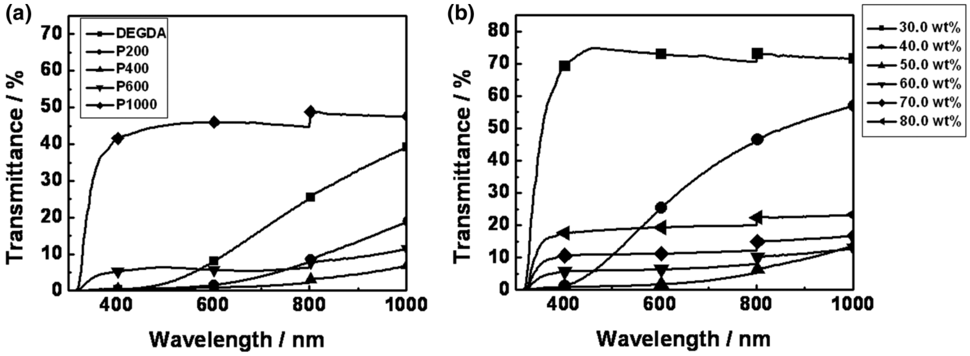

Figure 7. Dependence of UV-visible spectra of off-state PDLCs: (a) different chain lengths of crosslinking agents with a LC content of 50.0 wt%; (b) different LC content with the PEGDA 400 crosslinker.

$$\tau_R = \frac{1}{\gamma_1}\left[\frac{9\varepsilon_0\Delta_\varepsilon V^2}{d^2\left(\frac{\rho_p}{\rho_{LC}}+2\right)^2}+\frac{K\left(l^2-1\right)}{a^2}\right] \tag{3}$$

and

$$\tau_D = \frac{\gamma_1 \times a^2}{K(l^2-1)}, \tag{4}$$

where γ_1, ε_0, V, ρ_p, ρ_{LC} and a represent the rotational viscosity of the LC, vacuum permittivity, applied voltage, resistivity of the polymer, resistivity of the LC and the major axis of the LC droplet, respectively [16]. In general, the smaller the LC domain size, the larger the τ_R and the smaller the τ_D. As shown in Figure 6, along with decreasing the LC domain size, τ_R increased and τ_D decreased.

As shown in Figure 7, the lowest transmittance of off-state PDLC film was the sample with PEGDA 400 with a LC content of 50.0 wt%. Comparing Figures 2 and 3 with Figure 7, it was shown that the transmittance of the off-state was significantly dependent on the morphology of the PDLC films.

4. Conclusion

The influences of the chain length of the crosslinking agents and the LC content on the PDLC system have been studied. The microstructures of the PDLC films were strongly influenced by the chain length of the crosslinker; adding the longer crosslinker along the network bone affected the LC domain size and influenced the electro-optic properties of the PDLC films. So, adjusting the chain length of the crosslinking agents and the LC content can produce PDLC films that have good electro-optic properties with a lower LC content. Consequently, it is possible to lower the LC content with optimised electro-optic performance by adjusting the chain length of the crosslinking agents. The result in this paper brings very important advantages for manufacturing PDLC films and developing the PDLC market.

Acknowledgements

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References

[1] Doane, J.W.; Golemme, A.; West, J.; Whitehead, J.; Wu, B.G. *Mol. Cryst. Liq. Cryst.* **1988**, *165*, 511–532.
[2] Whitehead, J.B.; Gill, N.L. *Proc. SPIE Int. Soc. Opt. Eng.* **2001**, *4463*, 188–197.
[3] Whitehead, J.B.; Zumer, S.; Doane, J.W. *J. Appl. Phys.* **1993**, *73*, 1057–1065.
[4] Zumer, S. *Phys. Rev. A: At. Mol. Opt. Phys.* **1988**, *37*, 4006–4015.
[5] Cheng, S.X.; Bai, R.K.; Zou, Y.F.; Pan, C.Y. *J. Appl. Phys.* **1996**, *80*, 1991–1995.
[6] Petti, L.; Mormile, P.; Blau, W.J. *Opt. Lasers Eng.* **2003**, *39*, 369–377.
[7] Hoppe, C.E.; Galante, M.J.; Oyanguren, P.A.; Williams, R.J.J. *Macromol. Chem. Phys.* **2003**, *204*, 928–935.
[8] Kalkar, A.K.; Kunte, V.V.; Deshpande, A.A. *J. Appl. Polym. Sci.* **1999**, *74*, 3485–3491.
[9] Drzaic, P.S. *J. Appl. Phys.* **1986**, *60*, 2142–2148.
[10] Lampert, C.M. *Mater. Today* **2004**, *7*, 28–35.
[11] Park, S.; Hong, J.W. *Thin Solid Films* **2009**, *517*, 3183–3186.
[12] Amundson, K.; Blaaderen, A.; Wiltzius, P. *Phys. Rev. E: Stat. Nonlinear Soft Matter Phys.* **1997**, *55*, 1646–1654.
[13] Drzaic, P.S. *Liq. Cryst.* **1988**, *3*, 1543–1558.
[14] Maschke, U.; Coquerent, X.; Benmouna, M. *Macromol. Rapid Commun.* **2002**, *23*, 159–170.
[15] Mucha, M. *Prog. Polym. Sci.* **2003**, *28*, 837–873.
[16] Wu, B.G.; Erdmann, J.H.; Doane, J.W. *Liq. Cryst.* **1989**, *5*, 1453–1465.