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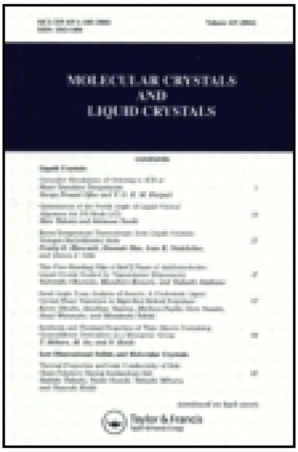

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Effects of Mesogenic Compound with High Birefringence on Electro-Optical Properties of Heat-Cured Polymer-Dispersed Liquid Crystal Films

Zongcheng Miao [a] , Dong Wang [b] , Yongming Zhang [a b] , Ping Song [b] , Jingjing Wang [b] & Xiaojuan Wu [b]

[a] Xijing University , Xi'an , Shaanxi Province , PR China

[b] Department of Materials Physics and Chemistry, School of Materials Science and Engineering , University of Science and Technology , Beijing , PR China

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Effects of Mesogenic Compound with High Birefringence on Electro-Optical Properties of Heat-Cured Polymer-Dispersed Liquid Crystal Films

ZONGCHENG MIAO,[1] DONG WANG,[2,*] YONGMING ZHANG,[1,2] PING SONG,[2] JINGJING WANG,[2]
AND XIAOJUAN WU[2]

[1]Xijing University, Xi'an, Shaanxi Province, PR China
[2]Department of Materials Physics and Chemistry, School of Materials Science and Engineering, University of Science and Technology, Beijing, PR China

Addition of mesogenic compound with high birefringence in nematic liquid crystal resulted change in the electro-optical properties of polymer-dispersed liquid crystal (PDLC) films considerably. The PDLC films were prepared from thermally polymerization-induced phase separation in heat curable monomers/nematic liquid crystal mixtures, and the effect of mesogenic compound with high birefringence on the electro-optical properties of PDLC films was studied. Therefore, when the mesogenic compound was doped in different concentrations, their quality fraction played considerable role in deciding the electro-optical parameters of the PDLC films.

Keywords Electro-optical properties; high birefringence; liquid crystal; PDLC; thermally polymerization

1. Introduction

Polymer-dispersed liquid crystal (PDLC) films consist of micron-sized liquid crystal (LC) droplets embedded in a continuous polymer matrix [1], then the isotropic polymers have a refractive index near that of the ordinary refractive index of the LC [2–4]. PDLC films are important materials due to their unique optical and electro-optical properties and can be applied universally to various electro-optical devices such as flexible large-scale displays, smart windows, and other devices [5–8]. They can be electrically switched between the opaque off-state and the transparent on-state. The phenomenon occurs due to refractive index mismatching or matching between the LC and the polymer matrix [9–12].

Generally, the electro-optic properties of PDLC films depend on the LC concentration, film thickness, the size and shape of the LC domain, anchoring energy on the boundary surface, and physical properties of both components, such as the elasticity, viscosity, and dielectric anisotropy of the LC and the polymer [13, 14]. Depending on the chemical nature of polymer and LC, the interface of LC and polymer will experience different constraints

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[*] Address correspondence to Dong Wang, University of Science and Technology, Beijing 100871, PR China. Tel.: 86-10-62333969; Fax: 86-10-62333969. E-mail: ustbwangd@163.com

with different effects on the molecular orientation of the LCs inside the droplet [15–17]. It is well known that higher values of Δn is favorable to increase the contrast ratio and decrease driving voltage of PDLC films [18]. But, with the increasing of Δn, the viscosity and dielectric anisotropy of LC in PDLC films will increased, viscosity and dielectric anisotropy of the LC are the important influencing factors of electro-optical properties of the PDLC films [19].

In this study, we chose nematic LC of SLC1717 to combine a kind of phenyl-diacetylenes mesogenic compound **1** (Figure 1) with high birefringence into one composite, then the PDLC films were prepared with thermally polymerization-induced phase separation (PIPS) method [20, 21]. The effect of mesogenic compound **1** on the morphology of polymer network and the electro-optic properties of films were investigated in details.

2. Experimental

2.1. Materials

Mesogenic compound **1** was synthesized according to reference [22]. A nematic LC (SLC1717, $T_{NI} = 365.2$ K, $\Delta n = 0.201$) was purchased from Slichem Liquid Crystal Material Co., Ltd. (Shijiazhuang, China) and used without any purification. The heat curable monomers used were a mixture of ethylene glycoldiglycidyl ether (EGDE) resin (Anhui Hengyuan Chemical Co., Ltd., Anhui, China) and 2, 2′-(ethylenedioxy) bis (ethylamine) (EDBEA, Alfa Aesar, A Johnson Matthey Company, Beijing, China). EDBEA is a polyamine hardener for epoxy resins EGDE. Fig. 1 shows the chemical structures of all the materials.

2.2. Preparation of PDLC Films

The PDLC samples were fabricated by heat curing procedure. In forming these materials, a suitable oligomer was prepared by mixing EGDE and hardener EDBEA in the molar ratio according to $n_a = 0.5 \times n_b$, where n_a and n_b were the mole number of epoxy resin EGDE and hardener EDBEA, respectively. And then the oligomer was mixed with equal weight of LC and stirred for 2 hours. After that the homogenous solution was sandwiched between two pieces of indium–tin–oxide (ITO) coated glass substrates. A group of samples with different content of compound **1** in the mixture were prepared, and the compositions of

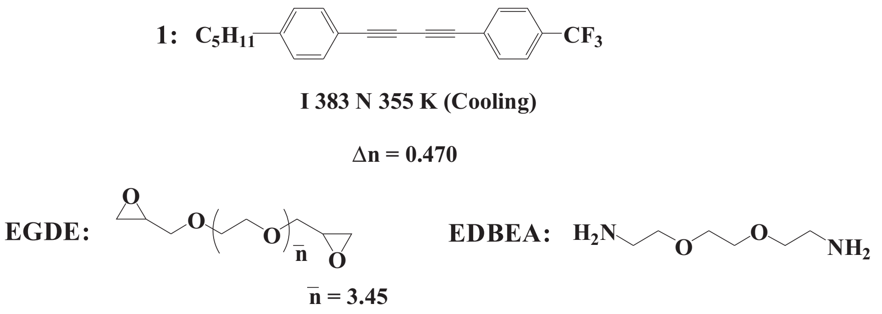

Figure 1. Chemical structure and properties of mesogenic compound **1** and the heat curable monomers.

Table 1. The compositions of samples **A–F**

	LC (%)		
Sample	Total	SLC1717/**1**	Monomer (%)[a]
A	50	100/0	50
B	50	99/1	50
C	50	98/2	50
D	50	95/5	50
E	50	90/10	50
F	50	85/15	50

[a]The monomer was EGDE/EDBEA with the weight of 4/1.

samples **A**–**F** were listed in Table 1. All samples utilized 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 cyclohexane for 5 days at room temperature to extract the LC molecules, and then the polymer network was dried for 12 hours under vacuum. After polymer matrix was sputtered with carbon, the microstructures of the polymer matrix were observed under SEM.

The electro-optic properties were studied using an LCD parameters tester (LCT-5016C, Changchun Liancheng Instrument Co., Ltd., Changchun, China). A halogen tungsten lamp (12 V, 75 W; OSRAM, Beijing, China) was used as an incident light source and the incident wavelength through the sample was fixed with the 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 photodiode was 300 mm. The transmittance of air was normalized as 100%.

3. Results and Discussion

3.1. *Morphology of Polymer Network in PDLC Films*

Figure 2 shows the droplet morphology of PDLC samples **A**–**F**. It could be seen that the mesh size (the LC domain size) of the polymer network in sample **A** was about 1.0 μm. Whereas in samples **B–F**, the mesh size further increased and the cross-linking density of polymer network decreased in the sequence. It was clearly seen that the LC domain increased in size with increasing the content of compound **1**. For a definite system, the LC domain size was controlled by the relative content of the polymerizable monomers and LC, the rate of polymerization, and some physical parameters such as viscosity, rate of diffusion, and solubility of the LC in the polymer [22, 23]. Therefore, the relative content of compound **1** in SLC1717 had a great effect on the microstructure of the polymer matrix. One generally approved explanation was that the increase of compound **1** content decreased the

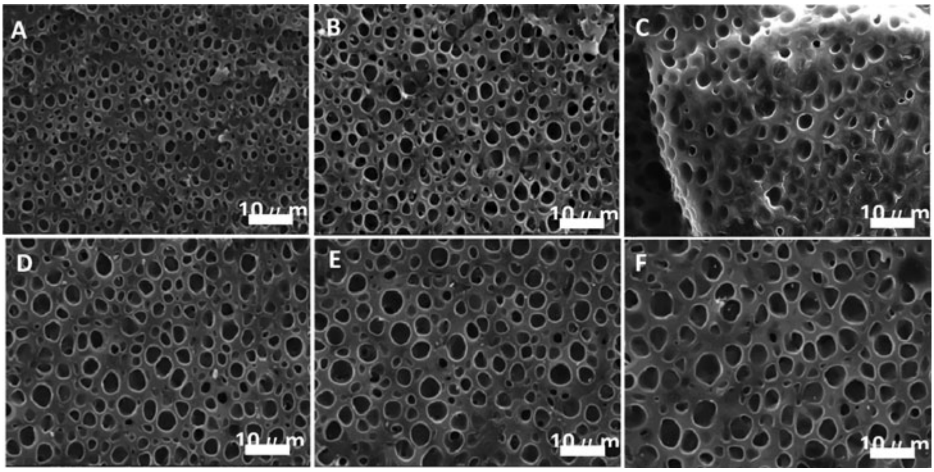

Figure 2. SEM micrographs of the polymer networks of samples **A–F**.

miscibility of the polymerizable monomers and the mixed LC, consequently decreased the cross-linking density between molecules of the polymerizable monomers [24]. Thus, the diffusion of LC molecules became difficult with the increase of **1** content, and vice versa. As a result, the size of the LC domain increased with increasing the content of **1** as shown in Fig. 2.

Generally, it was convenient to fix the contents of two components and investigate the electro-optical properties of the system by only changing the content of the third component. In our subsequent consideration of LC/polymerizable monomers/**1** composites, the contents of the LC and polymerizable monomers were fixed, and the modification of the LC/polymerizable monomers composites by compound **1** was taken into account. When the applied voltage increased, the transmittance of the samples reached the saturation level T_s, and CR $= T_s/T_o$ was commonly known as the switching contrast, where T_o was the initial off-state transmittance. The threshold voltage (V_{th}) and the saturation voltage (V_{sat}) were defined as the electric fields required for the transmittance to reach 10% and 90% of T_s, respectively.

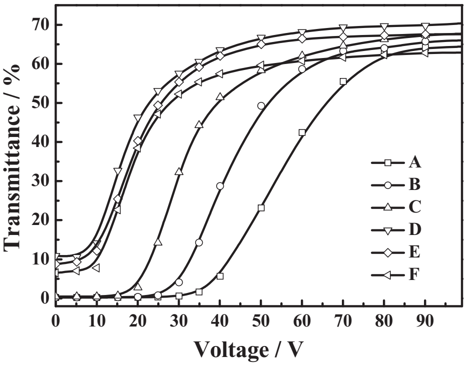

Figure 3. The applied electric field (1 kHz) dependence of the transmittance of samples **A–F**.

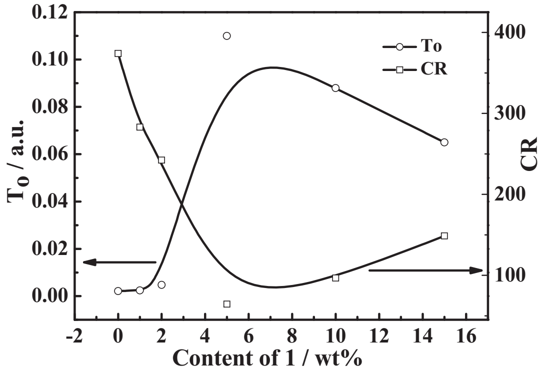

Figure 4. **1** concentration dependence of CR and T_o, respectively.

Figure 3 shows the voltage dependence of the transmittance of samples **A**–**F**. As the mesogenic compound **1** content increased, the gradient of curves **A–F** were increased slightly, because **1**, which possessed higher dielectric anisotropy [25], would been rapid orientated under electric field to increase the samples respond speed [26, 27]. In addition, T_s increased obviously when the content of **1** was less than 5 wt%; however, T_s decreased significantly for **1** contents increasing from 5 wt% to 15 wt%. Meanwhile, T_o had the same change to T_s. These behaviors of T_o were more evident in Fig. 4, which shows the content of **1** dependence of T_o and CR. CR decreased at first for **1** content up to 5 wt%, and then CR increased when **1** content increased from 5 wt% to 15 wt%, because CR was strongly influenced by T_o, which was the denominator of the fraction, and then decreased dramatically as T_o increased fast [28].

The explanation was that the changes of the refractive index (n_{mp}) of mixed LC are formed with doping **1** in LC/polymerizable monomers composites. The refractive index of the LC doped with **1** (n_{np}) was a linear function of the content of **1** [29]:

$$n_{mp} = n_p \varphi_p + n_{np} \varphi_{np} \tag{1}$$

where φ_p and φ_{np} are the volume fractions of the LC and **1**, n_p was the refractive index of the LC doped without **1**. For PDLC composites, the modification of n_p might result in

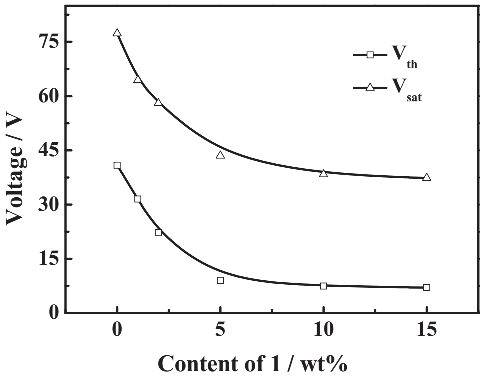

Figure 5. Compound **1** concentration dependence of V_{th} and V_{sat}.

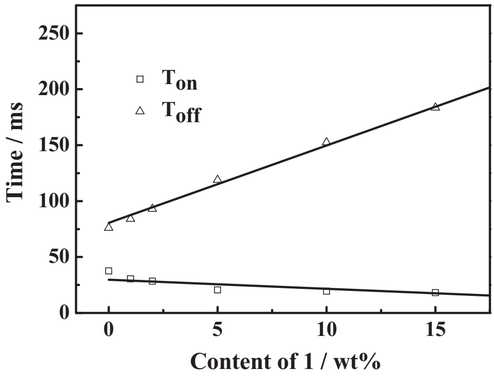

Figure 6. **1** concentration dependence of T_{on} and T_{off}.

significant changes of light scattering characteristics caused by the refractive index match of the coexisting phases. As a result, the matching degree of the refractive index of the LC and the polymer matrix increased continuously with the increasing of **1** content until the maximum matching degree was reached. But then the content of **1** further increased, the matching degree decreased slightly to cause the T_s decrease [28]. When an electric field was applied to the samples, the light scattering caused by the refractive index mismatch of coexisting LC and polymer could be reasonably considered as a major factor for the samples in the transparent state.

Figure 5 shows the content of **1** dependence of V_{th} and V_{sat}. V_{th} and V_{sat} both decreased obviously with increasing the **1** content. It was well known that there was an inverse relationship between the variety of V_{th} (or V_{sat}) and the change in LC domain size, because the polymer–LC interface anchoring energy of polymer network increased with the decrease in LC domain size, and the LC molecules were in a more difficult orientation along the direction of the electric field [17]. According to Fig. 2, with the increasing of LC domain size from **A** to **F**, V_{th} and V_{sat} decreased with increasing the content of **1**.

It is shown in Fig. 6 that turn-off time (T_{off}) increased dramatically, whereas turn-on time (T_{on}) decreased simultaneously with increasing the **1** content. It was well known that the relationship between T_{off} and T_{on} was inverse [14], and the increase of T_{off} leaded the decrease of T_{on}. The polymer–LC interface anchoring energy of polymer network is an important factor to T_{off}. T_{off} increased with the decrease of the interface anchoring energy, which was decided by the LC domain size [17].

4. Conclusions

Obviously, compound **1** played a key role in the variation of the parameters of electro-optical properties as mentioned earlier. Generally, a mesogenic compound with high birefringence had higher dielectric anisotropy and higher viscosity. However, dielectric anisotropy and viscosity of LC were all important factors to electro-optical properties of PDLC films, and higher dielectric anisotropy and lower viscosity were benefit to improve the electro-optical properties. In our experiment, with the increasing of **1** content in SLC1717, the dielectric anisotropy and viscosity of the mixed LC were increased obviously. When **1** content was less than 5 wt%, dielectric anisotropy of the mixed LC increased rapidly, the electro-optical properties was improved expectatively. However, when **1** content was more than 5 wt%, the viscosity of the mixed LC was enough to affect the electro-optical properties.

Acknowledgments

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References

[1] Ding, X., Cao, M., Liu, H., Cao, H., Li, W., & Yang, H. (2008). *Liq. Cryst.*, *35*, 587.
[2] Doane, J. W., Vaz, N. A., Wu, B. G., & Zumer, S. (1986). *Appl. Phys. Lett.*, *48*, 269.
[3] Zhang, T., Kashima, M., Zhang, M., Liu, F., Song, P., Zhao, X., Zhang, C., Cao, H., & Yang, H. (2012). *RSC Adv.*, *2*, 2144.
[4] Zou, J., & Fang, J. (2011). *J. Mater. Chem.*, *21*, 9149.
[5] Li, W., Yu, L., He, W., Yuan, X., Zhao, D., Huang, W., Cao, H., Yang, Z., & Yang, H. (2008). *J. Phys. Chem. C*, *112*, 13739.
[6] Kashima, M., Cao, H., Liu, H., Meng, Q., Wang, D., Li, F., & Yang, H. (2010). *Liq. Cryst.*, *37*, 339.
[7] Li, W., Cheng, Z., Pan, G., Liu, H., Cao, H., Yang, Z., & Yang, H. (2008). *Opt. Mater.*, *31*, 434.
[8] Song, P., Yu, L., Cao, H., Wang, F., Liu, F., Zhang, C., Yang, H., & Yang, H. (2012). *Liq. Cryst.*, *39*, 313.
[9] Vaz, N. A., & Montgomery, G. P., Jr. (1987). *J. Appl. Phys.*, *62*, 3161.
[10] Olivares-Perez, A., Perez-Cortez, M., Juarez-Perez, J. L., & Trevino-Palacios, C. G. (2002). *Opt. Lett.*, *27*, 1022.
[11] Perju, E., Marin, L., Grigoras, V. C., & Bruma, M. (2011). *Liq. Cryst.*, *38*, 893.
[12] Senyurt, A. F., Warren, G., Whitehead, J. B., Jr, & Hoyle, C. E. (2006). *Polymer*, *47*, 2741.
[13] Nastał, E., Zuranska, E., & Mucha, M. (1999). *J Appl. Poly. Sci.*, *71*, 455.
[14] Meng, Q., Cao, H., Kashima, M., Liu, H., & Yang, H. (2010). *Liq. Cryst.*, *37*, 189.
[15] Drzaic, P. S., & Gonzales, A. M. (1993). *Appl. Phys. Lett.*, *62*, 1332.
[16] Patnaik, S. S., & Pachter, R. (1999). *Polymer*, *40*, 6507.
[17] Li, W. B., Cao, Y. B., Cao, H., Kashima, M., Kong, L. J., & Yang, H. (2008). *J. Polym. Sci., Part B: Polym. Phys.*, *46*, 1369.
[18] Kooa, J. J., Noa, Y. S., Jeona, C. W., & Kima, J. H. (2008). *Mol. Cryst. Liq. Cryst.*, *491*, 58.
[19] Eloualiabc, M., Eloualiab, F. Z., Beyensa, C., Yaroshchukd, O., & Abba, B. (2012). *Mol. Cryst. Liq. Cryst.*, *38*, 136.
[20] Bhargava, R., Wang, S. Q., & Koenig, J. L. (1999). *Macromolecules*, *32*, 2748.
[21] Jin, J. M., Parbhakar, K., & Dao, L. H. (1995). *Liq. Cryst.*, *19*, 791.
[22] Miao, Z., Wang, D., Zhang, Y., Jin, Z., Liu, F., Wang, F., & Yang, H. (2012). *Liq. Cryst.*, *39*, 1291.
[23] Kalkar, A. K., Kunte, V. V., & Deshpande, A. A. (1999). *J. Appl. Polym. Sci.*, *74*, 3485.
[24] Mucha, M. (2003). *Prog. Polym. Sci.*, *28*, 837.
[25] Fay, J. J., Murphy, C. J., Thomas, D. A., & Sperling, L. H. (1991). *Polym. Eng. Sci.*, *31*, 1731.
[26] Okano, K., Tsutsumi, O., Shishido, A., & Ikeda, T. (2006). *J. Am. Chem. Soc.*, *128*, 15368.
[27] Hudson, C. M., Shenoy, R. A., Neubert, M. E., & Peischek, R. G. (1999). *Liq. Cryst.*, *26*, 241.
[28] Hird, M., Toyne, K. J., Goodby, J. W., Gray, G. W., Minter, V., Tuffin, R. P., & McDonnell, D. G. (2004). *J. Mater. Chem.*, *14*, 1731.
[29] Li, W., Zhu, M., Ding, X., Li, B., Huang, W., Cao, H., Yang, Z., & Yang, H. (2009). *J. Appl. Polym. Sci.*, *111*, 1449.
[30] Yaroshchuk, O. V., Dolgov, L. O., & Kiselev, A. D. (2005). *Phys. Rev. E*, *72*, 051715.