**Comparative Studies of Polymer Dispersed Liquid Crystal Films via a Thiol-ene Click Reaction**

**Tingjun Zhong1, Richard J Mandle2, John W Goodby2, Lanying Zhang1 and Cuihong Zhang3**

1 Tingjun Zhong, Lanying Zhang; Department of Materials Science and Engineering, College of Engineering, Peking University, Beijing, People’s Republic of China; tingjun.zhong@pku.edu.cn, [zhanglanying@pku.edu.cn](mailto:zhanglanying@pku.edu.cn).

2 Richard J Mandle, John W Goodby; Department of Chemistry, University of York, York YO10 5DD, United Kingdom; richard.mandle@york.ac.uk, john.goodby@york.ac.uk.

3 Cuihong Zhang; Key Laboratory of Organic Polymer Photoelectric Materials, School of Science, Xijing University, Xi’an, Shaanxi Province 710123, People's Republic of China; [cuicui1008@126.com](mailto:cuicui1008@126.com).

Correspondence to: Lanying Zhang (E-mail: [zhanglanying@pku.edu.cn](mailto:zhanglanying@pku.edu.cn)), Cuihong Zhang (E-mail: cuicui1008@126.com).

**ABSTRACT**

In this work, the thiol-ene click reaction is employed to fabricate polymer dispersed liquid crystal (PDLC) films by photoinitiated polymerization. The PDLC films are prepared by systematic variation of key conditions: variety and content of -ene monomer; LC content; curing time; and curing light intensity. We find that both the morphologies and electrooptic properties of these films are adjustable. When increasing the length of alkyl main chain of -ene monomers, the driving voltages reduce but in turn the contrast ratio decreases. Increasing -ene monomer content raises the driving voltages as well as the response time, and the increase of liquid crystal content lowers the driving voltages but has a negative effect on the contrast ratio. The changes to the curing conditions (both curing time and UV light intensity) can be used to modify the driving voltages, response times and contrast ratios of PDLC films. These comparative studies will elucidate new insights in commercial applications of intelligent PDLC films.

**KEYWORDS:** thiol-ene reaction, vinyl ether, polymer dispersed liquid crystal, morphology, electrooptic property

**SHORT TITLE: Thiol-ene Based PDLC**

**INTRODUCTION**

Polymer dispersed liquid crystals (PDLCs) compose of micro-sized liquid crystal (LC) domains embedded in a continuous polymer matrix1. PDLC films are classified as an important class of materials that have promising photoelectrical applications, such as switchable windows2, microlenses3, reflective displays4, multicolor displays5, holographic films6, light shutters7 and bio-sensors8, due to their abilities to switch opaque scattering state to transparent state when applying an electric field.9,10 Additionally, PDLC films doped with nanographites11,12, carbon nanotubes13,14, nonlinear medium15, dyes16 or quantum dots17 have been investigated.

Phase separation method is a traditional way for preparing PDLC films, where the three following methods including polymerization-induced phase separation (PIPS), thermal-induced phase separation (TIPS), and solvent-induced phase separation (SIPS) are widely used. The PIPS method is versatile and usually applied for fabricating PDLC films due to its stability, fast curing speed, uniformity and controllability under photo-initiated polymerization conditions.18 Applied PDLC devices in the present typically have high driving voltages (> 50 V), long response times (> 50 ms) and low contrast ratios (< 100), which can be achieved by varying the morphology of the PDLCs19-24, via changing the LCs and the monomers employed25-30 such as the polymerizable group31, and the polymerization conditions32-37.

The thiol-ene click reaction is the hydrothiolation of a C=C bond, defined by Kolb et al.38, and has often conducted via the dissociation of a photoinitiator into a radical species.39,40 Moreover, the thiol-ene click reaction has simplicity, robustness and fast reaction speed in the field of polymer and materials chemistry.41-56 The reactivity in the radical thiol-ene reaction can vary considerably depending on the chemical structure of the -ene and thiol components, and the   
-ene reactivity with alkyl 3-mercaptopropionates, alkyl thioglycolates, as well as alkyl thiols under radical conditions, following the order: vinyl ether > allyl ether > acrylate.40 Herein, we employed the thiol-ene click reaction between the vinyl ether and thiol to fabricate PDLC films in this work, and we report a systematic investigation into the crosslinking agent, the composition of monomer blends, the LC content as well as the curing time and intensity on the morphologies and electrooptic properties of the fabricated PDLC films.

**EXPERIMENTAL**

**Materials**

The -ene monomer *bis*(2-vinyloxyethyl ether) (**M1**) was obtained from Aladdin Industrial Inc., China. The thiol monomer Pentaerythritol tetrakis(3-mercaptoacetate) (**M2**) and the photo-initiator Irgacure 651 were purchased from Heowns Biochem Technologies. The -ene monomers tri(ethylene glycol) divinyl ether (**M3**), trimethylolpropane diallyl ether (**M4**) and 1,6-hexanediol diacrylate (**M5**) were purchased from Sigma-Aldrich Chemicals. The nematic LC mixture SLC1717 (TNI = 365 K, Δ*n* = 0.201, *no*= 1.519, *ne*= 1.720) was provided by Shijiazhuang Chengzhi Yonghua Display Materials Co. Ltd. All the materials were used as received without any further purification. The chemical structures of **M1**-**M5** and Irgacure 651 are shown in Figure S1.

**Preparation**

All the PDLC films were fabricated by the photo-initiated PIPS method. Mixtures of monomers, LCs and photo-initiator were prepared in defined weight ratios. Then the mixtures were filled into LC cells between two glass slides coated with a thin transparent layer of conducting indium tin oxide (ITO) in the inner surfaces. The cell gap was controlled to 20.0 ± 1.0 µm by polyethylene terephthalate (PET) spacers. After that, the LC cells were irradiated using a UV Lamp (365 nm, 35 W Hg Lamp, PS135, UV Flood, Stockholm, Sweden) at room temperature. The UV curing time and light intensity at the cell surface were set as defined in different series.

**Analysis of Morphologies**

To observe the polymer morphologies of PDLC films, scanning electron microscopy (SEM, S-4800, Hitachi, Tokyo, Japan) was used. All the PDLC films were soaked in cyclohexane solvent to extract the LCs from the polymer matrix at room temperature and dried at 80 °C for 24 h in the oven under vacuum. The surfaces of the pre-treated PDLC films were sputtered with gold and the polymer morphologies were observed by SEM.

**Measurements of Electrooptic Properties**

The electrooptic properties of all the PDLC films were measured at room temperature by a liquid crystal device parameter tester (LCT-5016 C, Changchun Liancheng Instrument Co., Ltd., China), where a halogen laser (λ = 560 nm) was used as the incident light source and an electric field square wave (100 Hz) was applied. The transmittance of the PDLCs was recorded by a photodiode and monitored by an oscilloscope. The distance between the samples and photodiodes was measured to be 300 mm. The collection angle of the transmitted intensity was about ± 1º so that the forward scattering was detected. The transmittance of air was normalized as 100 %.

The major parameters of the electrooptic performance of PDLC films are transmittance, driving voltages (Vth and Vsat), contrast ratio (CR) and response time (Ton and Toff). Vth is defined as the voltage of the electric field required to reach 90 % of the maximum transmittance (Tmax), whereas Vsat isdefined as the voltage of electric field required to reach 10 % of Tmax. CR is the relative ratio of the on-state transmittance and the off-state transmittance. Ton is the time required to switch from 10 % to 90 % of Tmax when the electric field is turned on, whereas Toff is the time required to switch from 90 % to 10 % of Tmax when the electric field is turned off.

**RESULTS AND DISSCUSSION**

**Effects of variety of crosslinking agent on the polymer morphologies and electrooptic properties of PDLCs**

PDLC films I1-I4 with different -ene monomers were prepared under 5.0 mW cm−2 UV light intensity for 800.0 s. Films I1, I2, I3 and I4 contained monomers **M1**, **M3**, **M4** and **M5** respectively, at a fixed composition, 24.75/24.75/49.50/1.00 (wt%), of   
-ene/thiol/LC/photoinitiator.

As shown in Figure 1, the average sizes of the LC domains of films I1-I4 are varied, and the LC domains dispersed in film I1 are somewhat uniform, whereas films I2-I4 are non-uniform. As mentioned before, the polymerization kinetic of monomer **M1** and monomer **M2** was the fastest, moreover, the phase separation of polymer and LC was in total, thus a PDLC film with uniform LC droplets has been formed. The average sizes of the LC domains in films I1-I4 are found to be 1.2 µm, 5.1 µm, 5.9 µm and 1.7 µm, respectively. The LC domains in films I2 and I3 are larger than those in film I4, on the condition that the polymerization kinetic of monomer **M3** and monomer **M4** were faster than that of monomer **M5**, the LCs gathered together due to the less time of phase separation. Additionally, the average size of LC domains in film I2 is larger than that of film I1, for the longer length of the alkyl main chain, which results in a lower crosslinking density and bigger size of LC droplets. Thus, film I1 possesses the smallest and most uniform sized LC domains.

(Insert Figure 1 here.)

Figure 2(A) illustrates the variation of the transmittance of PDLC films I1-I4 as a function of the magnitude of the applied voltage. With an increase in the applied voltage, the highest gradient is found for film I1. The transmittance values for the off-state of films I1-I4 are 0.6 %, 2.7 %, 4.0 % and 0.9 % respectively, whereas at the saturation state the transmittance values are 67.1 %, 55.5 %, 39.8 % and 53.1 %, respectively. As shown, the transmittance of PDLC films without electric field is related to the average size of LC domains dispersed in polymer matrix. With the smallest uniform LC domains in film I1, the transmittance of film I1 at off state is the smallest, accompanying with the increase of the average size of LC domains, the transmittance at off-state increases due to the attenuated light scattering. As to the transmittance of PDLC films at on-state, because of the most uniform LC domains in film I1, light scattering has greatly decreased when applying the electric field as the LC domains align with the direction of the electric field, this gives the contrast ratios shown in Figure 2(C). Increasing the length of the main alkyl chain lowers both the Vth and Vsat values, exemplified by comparing film I1 with I2, the side groups lower both the Vth and Vsat values, see Figure 2(B). Thus, the Vth and Vsat values of film I3 are both the smallest because of the largest LC domains dispersed in the polymer network. While the average size of LC domains in film I4 is smaller than that in film I2 and I3, due to the larger viscosity of polymer in film I4, the free energy needed from the reorientation of LC domains is higher than that in film I2 and I3, thus the Vth and Vsat of film I4 are higher than that in film I2 and I3. For the response time, the Ton and Toff of films I1-I4 are all sub 10 ms.

(Insert Figure 2 here.)

**Effects of the crosslinking agent content on the polymer morphologies and electrooptic properties of PDLCs**

PDLC films H1-H5 with 49.5 wt% LC content and 1 wt% Irgacure 651 but different relative content ratios of **M1** and **M2** (1:1, 9:10, 4:5, 7:10, 3:5) were prepared under 5.0 mW cm−2 UV light intensity for 800.0 s. Generally, the polymer morphologies of the PDLC films (see Figure S2) were determined during the LC droplet nucleation and the polymer gelation. The average sizes of the LC domains are influenced significantly by the relative content ratio of **M1** and **M2**, which are 1.1 µm, 1.2 µm, 1.9 µm, 2.0 µm and 2.2 µm respectively. With the relative increase of monomer **M2**, the polymerization kinetic of ene-thiol click reaction decreased, thus the LC droplets gathered together for forming larger LC domains.

With the decrease of **M1**, the slopes of the light transmittance-voltage curves change markedly as shown in Figure 3(A). For example, the curves of relatively high -ene content have steep slopes between 20 V and 40 V. The transmittance values of films H1-H5 for the scattering state are respectively 0.6 %, 0.4 %, 0.4 %, 3.0 % and 0.6 %, whereas the transmittance values for the transparent state are 67.1 %, 67.9 %, 59.1 %, 60.3 % and 38.4 %, respectively. Herein, the transmittance of PDLC film has no direct relation to the average size of LC domains dispersed in the polymer network due to high refractivity of the added thiol monomer. While for the largest LC domains in film H5, the transmittance at transparent state is the smallest due to the strongest interfacial light scattering between polymer and LC domains. As described in Figure 3(B), the Vth values increase slightly and the Vsat values increase significantly with the decrease content of -ene monomer. Accompanying with the larger LC domains in the films H1-H5, the energy to re-align the LC domains with the direction of electric field is higher when the average size of LC domains is in the scale of 0.1-3.0 µm. The CR values of films H1-H3 are higher than those of films H4-H5, as shown in Figure 3(C). Due to the smaller initial transmittance and the larger transparent state transmittance in film H2, film H2 owns the highest CR. The Ton values of films H1-H5 increase with less addition of **M1**. The Toff for the LC molecules to revert back to the equilibrium distribution decreases in PDLC films H1-H4, but with the exception of film H5. Here, considering both the low driving voltage and high CR, we find a 1:1 ratio of **M1**:**M2** gives the best performance out of the mixtures studied.

(Insert Figure 3 here.)

**Effects of LC content on the polymer morphologies and electrooptic properties of PDLCs**

Generally, LCs are as solvent in the polymerization of monomers, the LC content has a profound influence on the performance of PDLCs. As determined a 1:1 ratio of **M1**:**M2** to be optimal, we next investigated PDLC films with varying the concentration of liquid crystal while keeping the **M1**:**M2** ratio constant. PDLC films L1-L5 were prepared as the listed in Table 1 and with 1 wt% of Irgacure 651 under 5.0 mW cm−2 UV light intensity for 800.0 s.

The SEM photomicrographs of the polymer matrix in PDLC films L1-L5 is presented in Figure S3, where the average sizes of LC domains increase correspondingly with the increase of LC content. The average sizes of the LC domains in films L1-L5 are 0.8 µm, 0.9 µm, 1.2 µm, 1.7 µm and 2.0 µm, respectively. The LC domains in film L1 are relatively sparse compared with that in film L2 even though their calculated average sizes by statistics are close to each other, which might be due to the weaker phase separation between LCs and monomers. When increasing the LC content, the LC domains in films tend to be uniform as shown in films L2 and L3. However, as the sizes of LC domains become larger, they become heterogeneous as the LC content is more than 50 wt%, as seen in Film L4 and L5.

Figure 4 shows the results of the electrooptic performances of films L1-L5. As the LC content increases, the transmittance of the clear state is reduced, due to the light scattering of more nematic LC domains, as depicted in Figure 4(A). The transmittance values of films L1-L5 at off state are 4.5 %, 1.8 %, 0.6 %, 3.3 % and 1.2 %, respectively. Additionally, the transmittance of films L1-L5 will reach the saturation transmittance, for the values of 73.9 %, 74.7 %, 67.1 %, 44.3 % and 51.2 %, respectively. For the transmittance at off state, with numerous LC domains in film L3, multiple scattering takes place, thus film L3 owns the lowest transmittance. Once applied an electric field, films L1 and L2 obtain higher transmittance because of the relative low LC content. Both the Vth and Vsat reduce with the increase in LC content and the increased size of the LC domains, see Figure 4(B). As shown in Figure 4(C), the values of CR increase with the continuing addition of LC content when the weight ratio of LCs to monomers is less than 1, whereas they decrease when the weight ratio of LCs to monomers is over 1. Hence, the CR value of film L3 is the highest. All the Ton values of films L1-L5 are sub millisecond whereas all of the Toff values are longer than 5.0 ms except for that of film L3.

(Insert Figure 4 here.)

**Effects of curing time on the polymer morphologies and electrooptic properties of PDLCs**

Except for the relative content of composite content, the curing conditions such as curing time and curing intensity have a great effect on the properties of PDLCs. PDLC films J1-J5 were prepared with an identical weight ratio of **M1**, **M2**, SLC1717 and Irgacure 651 (24.75/24.75/49.5/1) but the curing time was varied from 400.0 s for film J1 to 1200.0 s for film J5 in 200.0 s increments. A constant UV light intensity of 5.0 mW cm−2 was used. During UV curing, with the sufficient curing time, the polymerizable monomers were separated with LC domains, as depicted in Figure S4. As a result, the average sizes of LC domains of films J1-J5 decrease in the sequence, which are 1.3 µm, 1.3 µm, 1.2 µm, 0.9 µm and 0.7 µm, respectively. The phase separation in film J1 was not sufficient because of the short curing time, resulting in fewer LC domains. The curing time for film J5 was too long, leading to the smallest LC domains dispersed in the polymer network.

As shown in Figure 5, the electrooptic performance of films J1 (400.0 s curing time) and J5 (1200.0 s curing time) are significantly different from those of J2-J4 (600.0 s – 1000.0 s curing time). The transmittance values of films J1-J5 at off state are 0.2 %, 0.5 %, 0.6 %, 0.4 % and 0.6 %, respectively. Because the average sizes of LC domains dispersed in films J1-J5 are all in the range of 0.1-1.5 µm and less difference among them, the transmittance values of films J1-J5 at off state are similar, although the transmittance will reach the saturation transmittance with increasing the applied voltage for the values of 58.8 %, 65.9 %, 67.1 %, 68.1 % and 68.5 % respectively. It demonstrates that short curing times (see film J1) and long curing time (see film J5) both have a great influence on the slope of the light transmittance-voltage curve, as shown in Figure 5(A). The Vth values of films J2-J4 increase slightly maybe due to the decreased sizes of LC domains. As the low number of LC domains in film J1 and the compact polymer network in film J5, the Vth and Vsat values of films J1 and J5 are high. The CR values of films J1-J5 are high and decrease with the increase of curing time except for those of film J4, which are 321.6, 140.5, 131.5, 192.3 and 120.0, respectively. The Ton values of films J2-J4 tend to increase, whereas Toff values tend to decrease with increasing curing time, which is probably due to the decrease in the sizes of LC domains and increasingly dense network.

(Insert Figure 5 here.)

**Effects of curing intensity on the polymer morphologies and electrooptic properties of PDLCs**

In the aforementioned part, we have studied the effect of curing intensity on the performance of PDLCs. Besides, the average size of the LC domains dispersed in polymer matrix is strongly dependent on the curing light intensity as well as the curing time. Films K1-K5 were fabricated to investigate the influence of the curing light intensity varied from 1.0 to 9.0 mW cm−2 in 2.0 mW cm−2 intervals, with an identical weight ratio of **M1**, **M2**, SLC1717 and Irgacure 651 (24.75/24.75/49.5/1). All the films were cured for 800.0 s.

The LC domains dispersed in the polymer matrix turn to be uniform with the increasing curing light intensity (see Figure S5), where the average sizes of the LC domains dispersed in the film K1-K5 are 4.1 µm, 1.4 µm, 1.2 µm, 0.7 µm and 0.7 µm, respectively. With weaker curing light intensity, a longer time is needed for the phase separation, therefore the average size of LC domains is larger. With stronger curing light intensity, the average size of LC domains is smaller owing to the relative time needed for the phase separation.

The results for the measured electrooptic properties of PDLC films K1-K5 are as shown in Figure S6. With increase in light intensity, the slopes of the light transmittance-voltage curves in Figure S6(A) change slightly with the exception of that of film K1. The Vth and Vsat values of films K1-K5 increase with increasing light intensity, see Figure S6(B). This might because with the decreasing sizes of the LC domains, the anchoring effects of polymer matrix on the molecules increase, so that the LC molecules are difficult to reorient along with the direction of the electric field. This regularity also fits with the linear function for the relationship of Vth and a reciprocal size of the domains *R* according to

(1)

Where *d* is the film thickness, *R* is the average size of the LC domains, *K* is the LC effective elastic constant, is the LC aspect ratio of elongated droplet, is the LC dielectric anisotropy, and is the vacuum dielectric constant.53 The CR value of film K3 is the highest as shown in Figure S6(C). The Ton of films K1-K5 is fast and the values vary negligibly when increasing the light intensity, whereas Toff values trend to decrease which might be due to the decrease in the sizes of LC domains, see Figure S6(D). Thus, the optimal UV light intensity is 5.0 mW cm−2.

**CONCLUSIONS**

In conclusion, the effects of the variety and content of -ene monomer, the LC content as well as the curing time and light intensity on the morphologies and electrooptic properties of the thiol-ene based PDLC films have been investigated systematically, and both the polymer morphologies and electrooptic properties of these PDLC films have been shown to be adjustable through material selection. Increasing the length of the alkyl main chain of the -ene monomer reduces the driving voltages at the cost of increased Toff and decreased CR. Increasing the concentration of -ene monomer raises the driving voltages and Ton. Increasing the LC content lowers the driving voltage but has no significant effects on CR. An appropriate curing light intensity and the curing time are required to achieve a superior PDLC film with good electrooptic performance. Future efforts in this area should be focused on optimization of LCs, using the other parameters delineated in this work, to obtain superior performance PDLC films with low driving voltages, high contrast ratio and fast response time. The comparative investigation will be of great interest for the developments in commercial applications of intelligent PDLC films.

**ACKNOWLEDGEMENTS**

This work was supported by the National Natural Science Foundation of China (NSFC) (Grant No. 51573003 and 51602007).

**REFERENCES**

1. Coates D. Polymer-dispersed liquid crystals. J Mater Chem 1995;5:2063-2072.

2. van Boxtel MCW, Janssen RHC, Broer DJ, Wilderbeek HTA, Bastiannsen CWM. Polymer-flled nematics: a new class of light-scattering materials for electro-optical switches. Adv Mater 2000;12:753-756.

3. Xiong G-R, Han G-Z, Sun C, Xu H, Wei H-M, Gu Z-Z. Phototunable microlens array based on polymer dispersed liquid crystals.Adv Funct Mater 2009;19:1082-1086.

4. Su C-W, Liao C-C, Chen M-Y. Color transparent display using polymer-dispersed liquid crystal. Journal of Display Technology 2016;12:31-34.

5. Kumano N, Seki T, Ishii M, Nakamura H, Umermura T, Takeoka Y. Multicolor polymer-dispersed liquid crystals.Adv Mater 2011;23:884-888.

6.White TJ, Natarajan LV, Tondiglia VP, Lloyd PF, Bunning TJ, Guymon CA. Holographic polymer dispersed liquid crystals (HPDLCs) containing triallyl isocyanurate monomer. Polymer 2007;48:5979-5987.

7. Liu YJ, Ding X, Lin S-CS, Shi J, Chiang I-K, Huang TJ. Surface acoustic wave driven light shutters using polymer-dispersed liquid crystals. Adv Mater 2011;23:1656-1659.

8. Ailincai D, Farcau C, Paslaru E, Marin L. PDLC composites based on polyvinyl boric acid matrix - a promising pathway towards biomedical engineering. Liq Cryst 2016;43:1973-1985.

9. Higgins DA. Probing the mesoscopic chemical and physical properties of polymer-dispersed liquid crystals. Adv Mater 2000;12:251-264.

10. Nicoletta FP, Chidichimo G, Cupelli D, Filpo GD, Benedittis MD, Gabriele B, Salerno G, Fazio A. Electrochromic polymer-dispersed liquid-crystal film: a new bifunctional device. Adv Funct Mater 2005;15:995-999.

11. Wang J, Shi S, Han X, Zhou S, Zhang B. The effect of nanographites dispersed in undec-10-enic acid on optical property and morphology of PDLC films. Colloid Polym Sci 2012;290(16):1659-1664.

12. Wang JH, Zhang BY, Qu WZ, Chu HS, Li H. The kinetics of photo-polymerisation in the fabrication of polymer-dispersed liquid crystals doped with nano-graphite. Liq Cryst 2010;37:1-11.

13. Sadovoy AV, Nazvanov VF. Optical transmission of polymer dispersed liquid crystals doped with carbon nanotubes. Technical Physics Letters 2006;32:659-660.

14. Wu Y, Cao H, Duan M, Li E, Wang H, Yang Z, Wang D, He W. Effects of a chemically modified multiwall carbon nanotubes on electro-optical properties of PDLC films.Liq Cryst 2018;45:1023-1031.

15. Zegadlo KB, Ouazzani HE, Cieslik I, Weglowski R, Zmija J, Klosowicz S, Majchrowski A, Mysliwiec J, Sahraoui B, Karpierz MA. Nonlinear optical properties of polymer dispersed liquid crystals doped with La2CaB10019. Optical Materials 2012;34:1704-1707.

16. Kumar P, Sharma V, Jaggi C, Raina KK. Dye-dependent studies on droplet pattern and electro-optic behaviour of polymer dispersed liquid crystal. Liq Cryst 2017;44:757-767.

17. Cao M, Zhang Y, Song X, Che Y, Zhang H, Yan C, Dai H, Liu G, Zhang G, Yao J. Enhanced amplified spontaneous emission in a quantum dot-doped polymer-dispersed liquid crystal. Nanotechnology 2016;27(26):26LT01-05.

18. Bronnikov S, Kostromin S, Zuev V. Polymer-dispersed liquid crystals: progress in preparation, investigation, and application. Journal of Macromolecular Science, Part B 2013;52:1718-1735.

19. White TJ, Natarajan LV, Bunning TJ, Guymon CA. Contribution of monomer functionality and additives to polymerization kinetic and liquid crystal phase separation in acrylate-based polymer-dispersed liquid crystals (PDLCs). Liq Cryst 2007:34:1377-1385.

20. Ahmad F, Jamil M, Jeon YJ, Woo LJ, Jung JE, Jang JE, Lee GH, Park J. Comparative study on the electrooptical properties of polymer-dispersed liquid crystal films with different mixtures of monomers and liquid crystals, Journal of Applied Polymer Science 2011;121:1424-1430.

21. Dzhons MM, Bulgakova SA, Pantyukhina IA, Kazantzeva IA. Effects of chemical structure and composition of the polymer matrix on the morphology and electro-optical performance of polymer-dispersed liquid crystal films. Liq Cryst 2011;38:1263-1268.

22. Kim J, Han JI. Effect of liquid crystal concentration on electro-optical properties of polymer dispersed liquid crystal lens for smart electronic glassed with auto-shading and auto-focusing function. Electron Mater Lett 2014;10:607-610.

23. Henry RM, Sharma SC, Ramsey RA, Cramer ML, Atman JB. Effects of formulation variables on liquid crystal droplet size distributions in ultraviolet-cured polymer-dispersed liquid-crystal cells. Journal of Polymer Science Part B: Polymer Physics 2005;43:1842-1848.

24. Kim J, Han JI. Effect of cell gap on electro-optical properties of polymer dispersed liquid crystal lens for smart electronic glasses. Electron Mater Lett 2014;10:857-861.

25. Li W, Cao Y, Cao H, Kashima M, Kong L, Yang H. Effects of the structures of polymerizable monomers on the electro-optical properties of UV cured polymer dispersed liquid crystal films. J Polym Sci Part B: Polym Phys 2008;46:1369-1375.

26. White TJ, Natarajan LV, Tondiglia VP, Bunning TJ, Guymon CA. Polymerization kinetics and monomer functionality effects in thiol-ene polymer dispersed liquid crystals. Macromolecules 2007;40:1112-1120.

27. White TJ, Natarajan LV, Tondiglia VP, Lloyd PF, Bunning TJ, Guymon CA. Monomer functionality effects in the formation of thiol-ene holographic polymer dispersed liquid crystals, Macromolecules 2007;40:1121-1127.

28. Kashima M, Cao H, Liu H, Meng Q, Wang D, Li F, Yang H. Effects of the chain length of crosslinking agents on the electro-optical properties of polymer-dispersed liquid crystal films. Liq Cryst 2010;37:339-343.

29. Kashima M, Cao H, Meng Q, Liu H, Wang D, Li F, Yang H. The influence of crosslinking agents on the morphology and electro-optical performances of PDLC films. Journal of Applied Polymer Science 2010;117:3434-3440.

30. Ahmad F, Jamil M, Woo LJ, Jeon YJ. The investigation of molecular affinity involved in poly(ethylene glycol)-based polymer-dispersed liquid crystal display. Colloid and Polymer Science 2012;290:599-606.

31. Liu F, Cao H, Mao Q, Song P, Yang H. Effects of monomer structure on the morphology of polymer networks and the electro-optical properties of polymer-dispersed liquid crystal films. Liq Cryst 2012;39:419-424.

32. Ahmad F, Jamil M, Lee JW, Kim SR, Jeon YJ. The effect of UV intensities and curing time on polymer dispersed liquid crystal (PDLC) display: a detailed analysis study. Electron Mater Lett 2016;12:685-692.

33. Abdoune FZ, Benkhaled L, Coqueret X, Maschke U, Mechernene L. Effects of ultraviolet-curing conditions on the electro-optical behavior of polymer dispersed liquid crystal films. Mol Cryst Liq Cryst 2004;422:163-172.

34. Kim Y, Jung D, Jeong S, Kim K, Choi W, Seo Y. Optical properties and optimized conditions for polymer dispersed liquid crystal containing UV curable polymer and nematic liquid crystal. Current Applied Physics 2015;15:292-297.

35. Kim J, Han JI. Effect of UV intensity on the electro-optical properties of polymer dispersed liquid crystal lens for smart electronic glasses. Electron Mater Lett 2014;10:665-669.

36. Ahmad F, Jamil M, Jeon YJ. The effect of voltage controlled orientation order of liquid crystals in non-acrylic polymer dispersed liquid crystal films. Journal of Dispersion Science and Technology 2018;39:1115-1120.

37. Carrasco-Hernandez S, Gutierrez J, Cano L, Tercjak A. Thermal and optical behavior of poly(ethylene-b-ethylene oxide) block copolymer dispersed liquid crystal blends. European Polymer Journal 2016;74:148-157.

38. Kolb HC, Finn MG, Sharpless KB. Click chemistry: diverse chemical function from a few good reactions. Angew Chem, Int Ed 2001;40:2004-2021.

39. Hoyle CE, Lee TY, Roper T. Thiol-Enes: chemistry of the past with promise for the future. J Polym Sci Part A: Polym Chem 2004;42:5301-5338.

40. Morgan CR, Magnotta F, Ketley AD. Thiol/ene photocurable polymers. J Polym Sci, Polym Chem Ed 1977;15:627-645.

41. Lowe AB. Thiol-ene ‘‘click’’ reactions and recent applications in polymer and materials synthesis. Polym Chem 2010;1:17-36.

42. Kumar R, Raina KK. Morphological control and switchable photoluminescence responses of silica nanoparticles-modified polymer-dispersed liquid crystal composite films. Liq Cryst 2015;42:119-126.

43. Lee JW, Kim JK, Ahmad F. Properties of thiol-vinyl PDLC films without additional photoinitiator. Liq Cryst 2014;41:1109-1115.

44. Sun Y, Zhang C, Cao H, Xiao J, Ding H, Li F, Yu H, Yang Z, Yang H. Effects of functionality of thiol monomer on electro-optical properties of polymer-dispersed liquid crystal films. Liq Cryst 2017;44:1086-1092.

45. Sun Y, Zhang C, Zhou L, Fang H, Huang J, Ma H, Zhang Y, Yang J, Zhang L, Song P, Gao Y, Xiao J, Li F, Li K. Effect of a polymercaptan material on the electro-optical properties of polymer-dispersed liquid crystal films. Molecules 2017;22(1):43-55.

46. Sun Y, Gao Y, Zhou L, Huang J, Fang H, Ma H, Zhang Y, Yang J, Song Pi, Zhang C, Zhang L, Li F, Zhao Y, Li K. A study on the electro-optical properties of thiol-ene polymer dispersed cholesteric liquid crystal (PDChLC) films. Molecules 2017;22(2):317-329.

47. Zhang Y, Zhou L, Yang J, Zhang J, Hai M, Zhang L, Li F, Zhang C, Yang Z, Yang H, Zhu S. Effects of crosslinking agent/diluents/thiol on morphology of the polymer matrix and electro-optical properties of polymer-dispersed liquid crystal. Liq Cryst 2018;45:728-735.

48. Shi Z, Shao L, Zhang Y, Guan Y, Wang F, Deng F, Liu Y, Wang Y. Fabrication of polymer-dispersed liquid crystals with low driving voltage based on the thiol-ene click reaction. Polymer International 2017;66:1094-1098.

49. Shi Z, Guan Y, Wang F, Zhang Y, Deng F, Liu Y, Wang Y. Facile fabrication of polymer-dispersed liquid crystal films via nucleophile-initiated thiol-ene click reaction. Liq Cryst 2017; 44:1695-1700.

50. Shi Z, Shao L, Wang F, Deng F, Liu Y, Wang Y. Fabrication of dye-doped polymer-dispersed liquid crystals with low driving voltage based on nucleophile-initiated thiol-ene click reaction. Liq Cryst 2018;45:579-585.

51. Shi Z, Wang Y, Wang Y. Effects of thiol monomers on the electro-optical properties of polymer-dispersed liquid crystal films prepared by nucleophile-initiated thiol-ene click reaction. Liq Cryst 2018;45:1746-1752.

52. Natarajan LV, Tondiglia VP, Sutherland RL, Tomlin D, Bunning TJ. Electro-optical and morphological properties of bragg transmission gratings written in holographic polymer dispersed liquid crystals by thiol-ene photopolymerization. MRS Online Proceedings Library 2003;776:Q11.12. DOI: 10.1557/PROC-776-Q11.12

53. Natarajan LV, Shepherd CK, Brandelik DM, Sutherland RL, Chandra S, Tondiglia VP, Tomlin D, Bunning TJ. Switchable holographic polymer-dispersed liquid crystal reflection gratings based on thiol-ene photopolymerization. Chem Mater 2003;15:2477-2484.

54. Natarajan LV, Brown DP, Wofford JM, Tondiglia VP, Sutherland RL, Lloyd PF, Bunning TJ. Holographic polymer dispersed liquid crystal reflection gratings formed by visible light initiated thiol-ene photopolymerization. Polymer 2006;47:4411-4420.

55. Sutherland RL, Tondiglia VP, Natarajan LV, Lloyd PF, Bunning TJ. Coherent diffraction and random scattering in thiol-ene-based holographic polymer-dispersed liquid crystal reflection gratings. Journal of Applied Physics 2006;99:123104-1-12.

56. Mormile P, Musto P, Petti L, Ragosta G, Villano P. Electro-optical properties of a PDLC based on unsaturated polyester resin. Appl Phys B 2000;70:249-252.

Figure List:

**Figure 1** The morphologies of PDLC films I1-I4 with various amounts of -ene monomers.

**Figure 2** The electrooptic properties of PDLC films I1-I4 with various amounts of -ene monomers. (A) The transmittance-applied voltage curves; (B) The threshold voltages (Vth) and saturation voltages (Vsat); (C) The contrast ratios (CR); (D) The response time Ton and Toff.

**Figure 3** The electrooptic properties of PDLC films H1-H5 with various relative content ratios of monomers. (A) The transmittance-applied voltage curves; (B) The threshold voltages (Vth) and saturation voltages (Vsat); (C) The contrast ratios (CR); (D) The response time Ton and Toff.

**Figure 4** The electrooptic properties of PDLC films L1-L5 with various LC content. (A) The transmittance-applied voltage curves; (B) The threshold voltages (Vth) and saturation voltages (Vsat); (C) The contrast ratios (CR); (D) The response time Ton and Toff.

**Figure 5** The electrooptic properties of PDLC films J1-J5 with different curing time. (A) The transmittance-applied voltage curves; (B) The threshold voltages (Vth) and saturation voltages (Vsat); (C) The contrast ratios (CR); (D) The response time Ton and Toff.

Tables:

**Table 1** The compositions of PDLC films L1-L5.

|  |  |  |  |
| --- | --- | --- | --- |
| Sample ID | Compositions (wt%) | | |
| **M1** | **M2** | SLC1717 |
| L1 | 29.70 | 29.70 | 39.60 |
| L2 | 27.23 | 27.23 | 44.54 |
| L3 | 24.75 | 24.75 | 49.50 |
| L4 | 22.27 | 22.27 | 54.46 |
| L5 | 19.80 | 19.80 | 59.40 |

Figures:

****

**Figure 1** The morphologies of PDLC films I1-I4 with various amounts of -ene monomers.



**Figure 2** The electrooptic properties of PDLC films I1-I4 with various amounts of -ene monomers. (A) The transmittance-applied voltage curves; (B) The threshold voltages (Vth) and saturation voltages (Vsat); (C) The contrast ratios (CR); (D) The response time Ton and Toff.



**Figure 3** The electrooptic properties of PDLC films H1-H5 with various relative content ratios of monomers. (A) The transmittance-applied voltage curves; (B) The threshold voltages (Vth) and saturation voltages (Vsat); (C) The contrast ratios (CR); (D) The response time Ton and Toff.

**Figure 4** The electrooptic properties of PDLC films L1-L5 with various LC content. (A) The transmittance-applied voltage curves; (B) The threshold voltages (Vth) and saturation voltages (Vsat); (C) The contrast ratios (CR); (D) The response time Ton and Toff.

**Figure 5** The electrooptic properties of PDLC films J1-J5 with different curing time. (A) The transmittance-applied voltage curves; (B) The threshold voltages (Vth) and saturation voltages (Vsat); (C) The contrast ratios (CR); (D) The response time Ton and Toff.