

Effects of Monomer Structure on the Morphology of Polymer Network and the Electro-Optical Property of Reverse-Mode Polymer-Stabilized Cholesteric Texture

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ABSTRACT: The morphologies of the polymer networks in the polymer network/LC composite of reverse-mode polymer-stabilized cholesteric texture (PSCT) films was observed. The polymer network/LC composite was prepared from photopolymerization of the acrylate monomers, which had rod-like rigid cores in monomer/LC mixture. The effects of the structure of the acrylate monomers on the morphology of polymer network were studied. The acrylate monomer without flexible pacers between the acrylate functional groups and the rigid core

formed rice-grain-like polymer network with poor orientation. The acrylate monomer with flexible pacers formed fiber-like polymer network with better orientation. Meanwhile, the effects of morphology of polymer network on the electro-optical property of reverse-mode PSCT films were also investigated. © 2008 Wiley Periodicals, Inc. *J Appl Polym Sci* 111: 1353–1357, 2009

Key words: monomer structure; morphology; orientation; electro-optical property

INTRODUCTION

The use of polymer networks to stabilize liquid crystal (LC) phases for display-based applications has become widespread in recent years.^{1–3} One of such systems in recent years has attracted wide interest is reverse-mode polymer-stabilized cholesteric textures (PSCTs), which can be prepared from photopolymerization of monomers in monomer/LC mixtures.^{4–7} In reverse-mode PSCT films, when there is no voltage applied, the planar texture (helical axis perpendicular to the substrates) of helical structure of cholesteric liquid crystal (CLC) is stabilized by the polymer network. This planar texture appears transparent for visible light. When applied on a certain voltage, the planar texture changes into the focal-conic texture, in which state there are many domains, and the helical axes of the domains are

randomly oriented. There is an abrupt change of the refractive indices at the domain boundaries. Therefore, the reverse-mode PSCT is light scattering in the focal-conic texture. When the voltage is removed, because of elastic forces from the polymer network, the reverse-mode PSCT returns to the planar texture and becomes transparent again. In this system, the polymer network serves two important functions. First, it influences the structure of the focal-conic texture, and thus greatly influences the scattering properties of the system. Second, following the removal of the electric field, elastic forces between the polymer network and the LC cause a rapid reorientation back to the planar texture.^{8,9}

It is known that to form polymer network stabilizing the phase of LC, the monomers should be rod-like and have rigid cores.^{2,10,11} In this study, two acrylate monomers with different structures were used to fabricate reverse-mode PSCT films. The effects of the structure of the monomers on the morphology of polymer network and the electro-optical property of the reverse-mode PSCT films were studied.

EXPERIMENTAL

Materials

The CLC was obtained by doping the chiral dopant into nematic LC. The nematic LC used in this study

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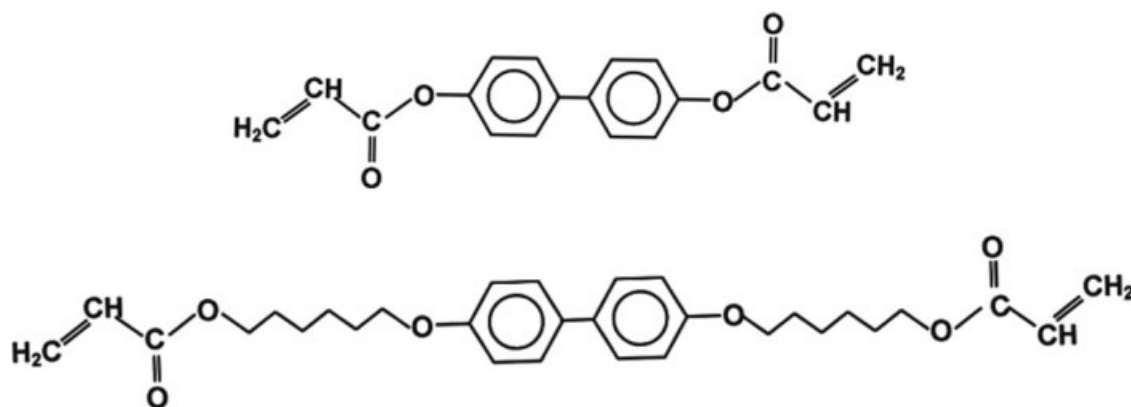


Figure 1 Structures of the monomers.

was SLC-1717 (Yongshenghuaqing Liquid Crystal Co., Ltd.) [Hebei, China] and the chiral dopant was CB-15 (Yongshenghuaqing Liquid Crystal Co., Ltd.) [Hebei, China]. The monomers used were lab-synthesized 4,4'-bisacryloylbiphenyl (BAB), 4,4'-bis[6-(acryloyloxy)hexyloxy]biphenyl (BAHB). The chemical structures of the monomers are shown in Figure 1. The two monomers are all rod-like and with rigid cores. BAB has no flexible spacers between the acrylate functional groups and the rigid core, while BAHB has flexible spacers. The photoinitiator used was IRG-184 (Kyaku Co., Ltd.) [Hiroshima, Japan].

Preparation of the cells

The cells were fabricated with the indium tin oxide (ITO) glass substrates. The inner surfaces of the substrates were coated with antiparallel rubbed polyvinyl alcohol layer to obtain the homogeneous orientation of LC molecules. Sixteen micrometer-thick poly(ethylene terephthalate) films were used as the spacer for the cells.

The monomer/SLC-1717/CB15/IRG-184 mixtures were prepared and filled into the cells by capillarity action. The compositions of the cells are listed in Table I. Then the cells were irradiated with UV light at the wavelength of 365 nm and an intensity of 0.75 mW/cm² at about 293 K for about 5 h.

TABLE I
Composition of the PSCT Cells

Cell	CLC-1717	CB15	BAB/BAHB	IRG-184
A	95	2	2.85 (BAB)	0.15
B	95	2	2.85 (BAB : BAHB=3 : 1)	0.15
C	95	2	2.85 (BAB : BAHB=1 : 1)	0.15
D	95	2	2.85 (BAB : BAHB=1 : 3)	0.15
E	95	2	2.85 (BAHB)	0.15

Numbers to material percentages by weight.

Measurements

The electro-optical properties of cells were measured with LCT-5016C LC display parameters tester (Changchun Lianchen Instrument Co., Ltd.) [Changchun, China]. The UV-cured PSCT films sandwiched between two ITO-coated cells were placed normal to the direction of collimated beam of He/Ne laser (wavelength of 632.8 nm). As the pitch of the LC (about 8000 nm) is well beyond the wavelength of the tasting light, and the transmittance of a blank cell is normalized as 1.0, we ignore the reflection of the light by the LC and the ITO glass.

The morphologies of the polymer networks were observed with ZEISS SUPRA 55 scanning electron microscope (SEM) [Berlin, Germany] operated at 5 kV in secondary electron-imaging mode. Samples for SEM study were prepared as follows. The sealant material on the opposite edge of the cell was removed to allow hexanaphthene to diffuse into the cell to replace the LC. The cell was taken out of the solvent and allowed to dry in a vacuum oven for a few hours. In this way the LC was extracted from the sample, and there is only a polymer network left. Then the polymer network was covered with a coating of carbon for SEM study.

RESULTS AND DISCUSSION

Morphology of polymer network

Figure 2 shows the SEM photos of the morphologies of the polymer networks of cells A–E. The polymer network of cell A made by pure BAB, as shown in Figure 2(a), is not well oriented, and the shape of the polymer network is rice-grain-like. On the contrary, the polymer network of cell E made by pure BAHB, as shown in Figure 2(e), is well oriented and the shape of the polymer network is fiber-like. And the polymer network of cell B made by a mixture of BAB and BAHB (the weight contrast is 3 : 1), as shown in Figure 2(b), is also rice-grain-like and there

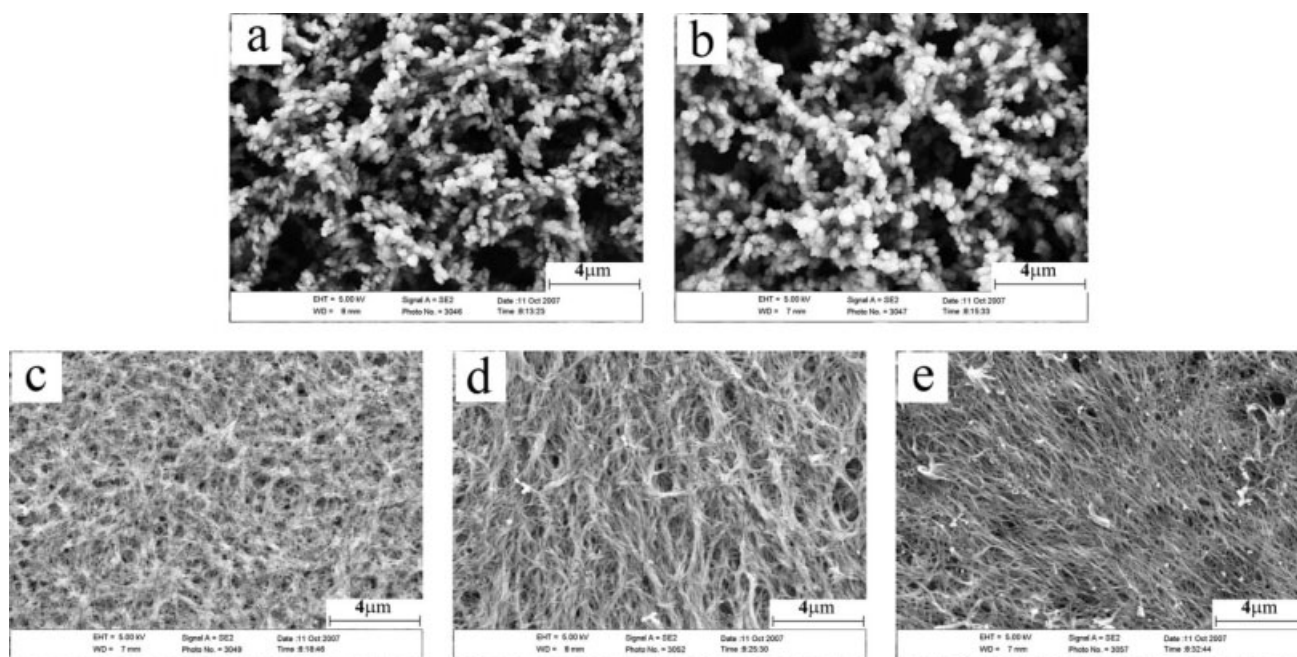


Figure 2 SEM images of the polymer network morphologies of the cells. (a–e) Cells A–E, respectively.

is no orientation shown. The polymer network of cell C made by a mixture of BAB and BAHB (the weight contrast is 1 : 1), as shown in Figure 2(c), is neither rice-grain-like nor fiber-like, and there is no visible orientation shown. However, the polymer network of cell D made by a mixture of BAB and BAHB (the weight contrast is 1 : 3), as shown in Figure 2(d), is fiber-like in some degree, and there is visible orientation shown.

It is well known that monomer solubility plays a crucial role in the formation of network morphology.¹² However, in this experiment both the monomers BAB and BAHB have poor solubility in the LC (about 4.5% and 7.0%, respectively). So we believe that it is not the difference of the solubility that causes the differences of the polymer networks. The change of the morphologies of the polymer network from samples A and E indicates that flexible spacers between the acrylate functional groups and the rigid core have important influence on the morphology of the polymer network. It is known that the rod-like monomers with rigid cores can be oriented by the LC. However, as monomer BAB has no flexible spacers between the acrylate functional groups and the rigid core, its rigid cores need to twist when its bonds linking together in the LC during UV curing to decrease the space hindrance. Therefore, they could not get a well-oriented polymer network. By contrast, monomer BAHB had flexible spacers between the acrylate functional groups and the rigid core, which makes it possible for the rigid cores of the monomer to be organized by the LC during UV curing in the LC.¹ Thus, they could get a polymer

network with good orientation. So we can see the trend of orientation of polymer network from cell A to E as the concentration of BAHB increases. Meanwhile, the change of the shape of the polymer networks from cell A to E indicates that a badly oriented polymer network is often rice-grain-like while well-oriented polymer network is often fiber-like.

Voltage–transmittance property of the cells

The voltage–transmittance curves of cells A–E are shown in Figure 3. The transmittance of a blank cell is normalized as 1.0. The electro-optical parameters, the transmittances at zero-field (T_0), and the threshold

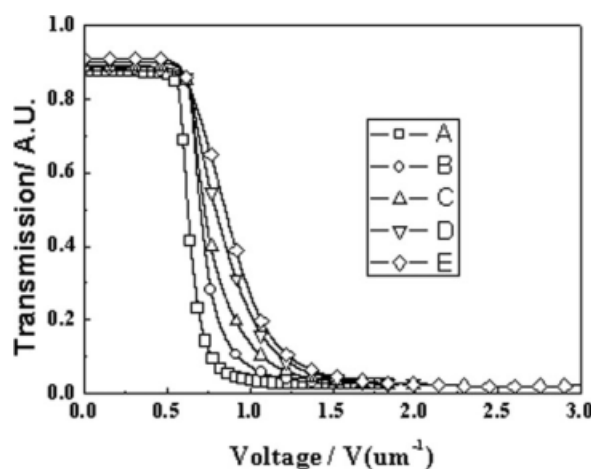


Figure 3 Electric–transmittance curves of the cells.

TABLE II
Electric-Transmittance Parameters of Cells

Cell	T_0	V_{th}/V
A	0.875	9.2
B	0.879	9.7
C	0.889	10.0
D	0.901	10.1
E	0.910	10.5

voltages (V_{th}) of cells A–E are listed in Table II. The T_0 and V_{th} of the cells increase from cell A to cell E.

It is reported that, as the polymer network is very little, the influence of its birefringence is negligible.¹³ Therefore, we consider that the increase of T_0 from the cell A to E is caused by the increase of the orientation order of the LC. It indicates that the increase of the orientation of polymer network enhances stabilization of the orientation of the LC during UV curing.

It is reported that, with the same concentration, the elastic interactions between LC and rice-grain-like polymer networks are weaker than that between LC and rice-grain-like polymer networks,^{7,11,12} and so the cell with rice-grain-like polymer network has lower V_{th} than that with fiber-like polymer network. Thus, it is reasonable that the V_{th} of the cells increase from cell A to cell E as the polymer networks of the cells change gradually from rice-grain-like to fiber-like.

Dynamic response parameters of the cells

The dynamic response curves of the cells A–E are shown in Figure 4. The dynamic response parameters of the cells A–E, the field-on response times (T_{on}), and the field-off response times (T_{off}) are listed

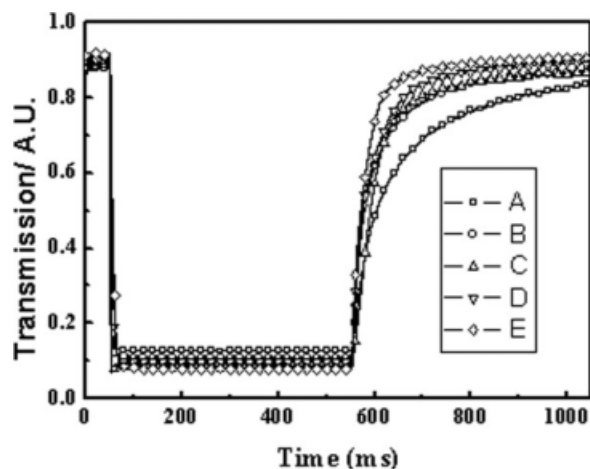


Figure 4 Dynamic response curves of the cells.

TABLE III
Dynamic Response Parameters of Cells

Cell	T_{on} (ms)	T_{off} (ms)
A	10.5	244
B	11.0	186.5
C	12.5	172
D	12.0	118
E	13.5	76

in Table III. The testing voltage was 35.0 V at the frequency of 100.0 Hz.

It is stated that field-on response is the LC's response to the electric field, while the network morphology has little influence on the process.¹¹ Thus, it is easily understood that the increase of T_{on} from cell A to E is very slow, despite the change of polymer networks from rice-grain-like to fiber-like.

It is known that the elastic force between the polymer network and the LC, which is the driving power for the focal-conic texture to rapidly return to the planar texture, increases with the increase of the concentration of polymer network.^{11,14} It is reported that, with the same concentration, the cell with rice-grain-like polymer network has lower elastic force to the LC than that with fiber-like polymer network. So the decay times of the cells decrease from cell A to cell E as the polymer networks of the cells change gradually from rice-grain-like to fiber-like.

CONCLUSIONS

In this study, the effects of the structure of monomer on the morphology of the polymer network and the electro-optical property of the reverse-mode PSCT films were investigated. The monomer BAB without flexible spacers between the acrylate functional groups and the rigid core formed rice-grain-like polymer network with poor orientation. The monomer BAHB with flexible spacers between the acrylate functional groups and the rigid core formed fiber-like polymer network with smaller meshes and better orientation. When BAB and BAHB were mixed together, as the concentration of BAHB increased, the polymer networks change from rice-grain-like to fiber-like and become better oriented. The threshold voltage (V_{th}) and field-off response times (T_{off}) of the reverse-mode PSCT films increase as shape as the polymer network changes from rice-grain-like to fiber-like, while the field-on response times (T_{on}) change little.

References

- Hikmet, R. A. M. *Liq Cryst* 1991, 9, 405.

2. Rajaram, C. V.; Hudson, S. D.; Chien, L. C. *Chem Mater* 1995, 7, 2300.
3. Yang, D. K.; Doane, J. W. *SID Dig Tech* 1992, 23, 759.
4. Yang, D. K.; Chien, L. C.; Doane, J. W. *Appl Phys Lett* 1992, 60, 3102.
5. Dierking, I.; Kosbar, L. L.; Lowe, A. C.; Held, G. A. *Liq Cryst* 1998, 24, 387.
6. Dierking, I.; Kosbar, L. L.; Lowe, A. C.; Held, G. A. *Liq Cryst* 1998, 24, 397.
7. Dierking, I.; Kosbar, L. L.; Afzali-Ardakani, A.; Lowe, A. C.; Held, G. A. *J Appl Phys* 1997, 81, 3007.
8. Dierking, I. *J Phys D: Appl Phys* 2002, 35, 2520.
9. Dierking, I. *Adv Funct Mater* 2004, 14, 883.
10. Liu, J. H.; Hung, H. J.; Wu, D. S.; Hong, S. M.; Fu, Y. G. *J Appl Polym Sci* 2005, 98, 88.
11. Dierking, I. *Adv Mater* 2000, 12, 167.
12. Dierking, I.; Kosbar, L. L.; Afzali-Ardakani, A.; Lowe, A. C.; Held, G. A. *Appl Phys Lett* 1997, 71, 2454.
13. Rajaram, C. V.; Hudson, S. D.; Chien, L. C. *Chem Mater* 1996, 8, 2451.
14. Dierking, I. *Adv Mater* 2003, 15, 152.