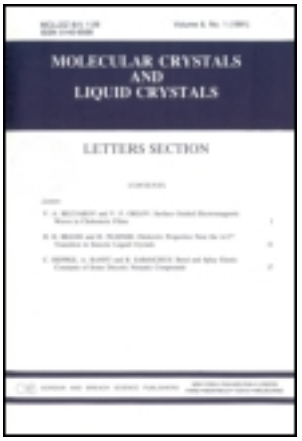

Molecular Crystals and Liquid Crystals
Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/gmcl20

Influence of Curing Frequency on the Morphology and the Electro-Optical Property of Polymer-Stabilized Cholesteric Textures

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Published online: 30 Dec 2013.

To cite this article: Hongbo Lu , Jun Zhang , Minghui Wang , Zhigang Song , Xianfeng Xiong , Guangqing Lin , Guobing Zhang , Xianghua Wang & Longzhen Qiu (2014) Influence of Curing Frequency on the Morphology and the Electro-Optical Property of Polymer-Stabilized Cholesteric Textures, Molecular Crystals and Liquid Crystals, 588:1, 9-16, DOI: 10.1080/15421406.2013.822298

To link to this article: http://dx.doi.org/10.1080/15421406.2013.822298

Mol. Cryst. Liq. Cryst., Vol. 588: pp. 9–16, 2014

ISSN: 1542-1406 print/1563-5287 online
DOI: 10.1080/15421406.2013.822298

Influence of Curing Frequency on the Morphology and the Electro-Optical Property of Polymer-Stabilized Cholesteric Textures

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The effect of curing frequency on the morphology of polymer networks and the electro-optical property of normal-mode polymer-stabilized cholesteric textures (PSCTs) has been investigated. The scanning electron microscopy indicates that the shape of polymer networks transforms from honeycomb-like to fiber-like due to the increased solubility of the monomer at higher curing frequencies. The PSCTs cured at lower frequencies with sufficiently large network voids show a two-stage reorientation process that correlates with two kinds of cholesteric liquid crystal (LC) under different environments. The threshold voltage decreases as the curing frequency increases from 1 Hz to 10,000 Hz, while the field-off response time increases.

Keywords Curing frequency; electro-optical property; morphology of polymer network; polymer-stabilized cholesteric textures; two-stage reorientation process

Introduction

Optical devices, combining the merits of liquid crystals (LCs) and polymers, have been the subject of extensive research and widely employed in advanced display technologies in recent years. For example, polymer-dispersed LCs (PDLCs), with a high monomer content [1–2] and polymer-stabilized cholesteric textures (PSCTs), with a low monomer content, are the mostly widely used light shutters that require no polarizer [3–12]. They can be electrically switched between the strongly scattering state and the highly transparent

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state. PSCTs have several advantages, such as low driving voltage, fast response time, high contrast ratio, bistability for creating a image at zero field, and high brightness of the reflected image, and have been widely applied in optical switches, optical attenuators, and three-dimensional displays [13–15]. According to the textures of the field-on and the field-off, PSCTs can be sorted into a normal-mode and a reverse-mode device [3,11]. In a normal-mode PSCT, the monomer is photopolymerized while the cholesteric LC is in the homeotropic state, the resulting polymer network should thus reflect homeotropic state. In the absence of an applied electric field, this homeotropic state converts into the focal-conic state, which is strongly scattering. In this system, the polymer network provides two important functions. First, it influences the structure of the focal-conic state and thereby strongly influences the scattering properties of the system. Second, upon the removal of the electric field, elastic forces between the polymer network and the LC cause a rapid reorientation back to the focal-conic state [6].

The interest in PSCT systems has considerably stimulated fundamental research especially after the pioneering work of Ingo Dierking et al. [7–9]. Generally, the electro-optical properties of PSCT cells depend on the LC concentration, the cell thickness, the size and the shape of the LC domain, the anchoring energy of polymer networks and the physical properties of both components, such as the elasticity, viscosity, and dielectric anisotropy. Consequently, the morphology of the polymer networks could seriously affect their electro-optical properties including the contrast ratio, switching voltage, switching speed, and hysteresis of the PSCT cells. The influence of polymerization condition on the microstructure of polymer networks as well as the electro-optical properties of the reverse-mode PSCT have been systematically investigated by Ingo Dierking. Higher curing temperatures, higher curing intensities and shorter curing times result in polymer networks with larger voids, which lead to a lower operating voltage, and narrower hysteresis except for the slower response time [7–8]. A two-stage reorientation process was observed only from PSCTs with sufficiently large network voids. This behavior is corresponding to the cholesteric LC being divided between two distinct environments [6]. The influence of monomer structure on the morphology of polymer networks and the electro-optical property of the reverse-mode PSCT have been investigated by Huai Yang. The acrylate monomer without flexible spacers between the acrylate functional groups and the rigid core formed rice-grain-like polymer network with poor orientation. The acrylate monomer with flexible spacers formed fiber-like polymer network with better orientation, which has higher threshold voltage and faster field-off response time [11].

In this study, normal-mode PSCT cells were prepared by photo-polymerization of the mixture of a cholesteric LC and a nematic diacrylate monomer. The influence of the curing frequency on the morphology of polymer networks and the electro-optical property of the PSCT cells was investigated.

Experimental

Materials

The cholesteric LC was a mixture of nematic LC P0616A (Chengzhi Yonghua Display Materials Co., Ltd.) and chiral dopant R6N (Hecheng Chemical Materials Co., Ltd.). The monomer used was lab-synthesized 1,4-di-[4-(3-acryloyloxyhexyloxy) benzoyloxy]-2-methyl benzene (LCM). The photoinitiator was benzoin methyl ether (BME). The material used in this study consisted of P0616A (94%), R6N (1%), LCM (4.7%) and BME (0.3%). The chemical structure of LCM is shown in Fig. 1.

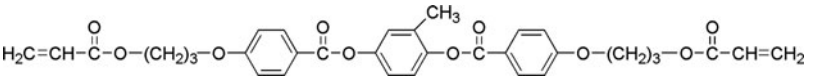

Figure 1. Chemical structure of monomer LCM.

Preparation of the Cells

The cells were fabricated with the indium tin oxide (ITO) glass substrates, which the resistance/square is 90 Ω/□. The inner surfaces of the substrates were coated with unrubbed polyimide layer. The mixture was vacuum filled into 7-μm -thick cells, which was controlled by a dispersion of spacer beads. The cells were sealed and irradiated with UV light at the wavelength of 365 nm and an intensity of 0.2 mW cm^{-2} at about 303 K for about 1 h with sine wave of 140 V of curing frequencies from 1 Hz to 10,000 Hz.

Measurements

The morphology of the polymer networks was characterized using a scanning electron microscope (SEM, JSM-6490LV). Samples for SEM study were prepared as follows. The PSCT cells were separated by using a razor blade with caution, and then put into n-hexane for 24 h at room temperature, and the ITO substrate with the polymer network was subsequently dried in vacuum. As the LC was extracted from the sample, and there was only a polymer network left. Before SEM observation, the polymer network was capped with a thin layer of gold.

The electro-optical properties of the cells were measured by LC device tester (LCT-5046E) (Changchun Lianchen Instrument Co., Ltd.).

Results and Discussion

Figure 2 shows the SEM microscopy of the polymer networks fabricated under curing frequencies of 1 Hz, 10 Hz, 100 Hz, 1000 Hz, and 10000 Hz. As shown in Figs. 2(a) and 2(b), the polymer network cured at lower frequencies is honeycomb-like, and the size of

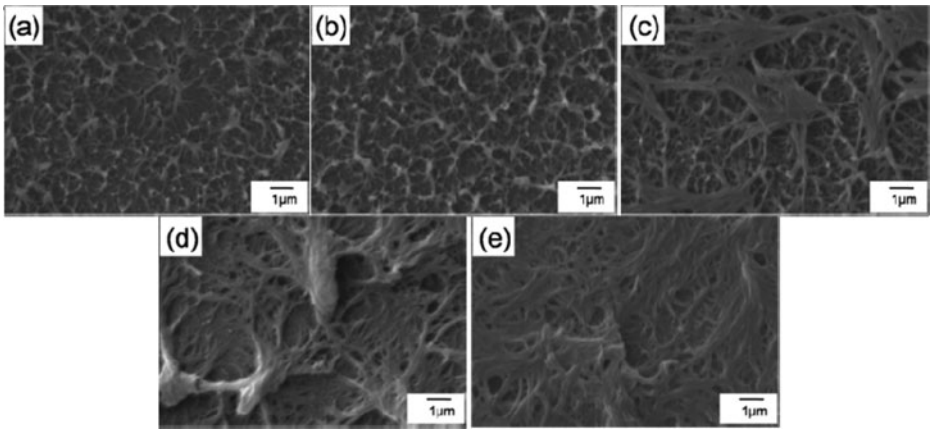

Figure 2. SEM of samples prepared under different curing frequencies: (a) 1 Hz, (b) 10 Hz, (c) 100 Hz, (d) 1000 Hz, and (e) 10,000 Hz.

the voids cured at 10 Hz is smaller than that cured at 1 Hz. On the contrary, the polymer network cured at higher frequencies, as shown in Figs. 2(d) and Fig. 2(e), is fiber-like, and the density of polymer network cured at 1000 Hz is lower than that cured at 10,000 Hz. The SEM results reveals that the transition of the polymer network from honeycomb-like to fiber-like takes place at curing frequencies around 100 Hz.

It is generally understood that monomer solubility played a crucial role in the formation of network morphology. Driven by the applied sinusoidal electric field, the LC molecules flip, thereby improving the ability to dissolve the monomer in the LC. As the curing frequency increases, the movement of molecules is enhanced, and results in a smaller average void size within the polymer network.

Figure 3 shows the electro-optical properties of the cells cured at 10 Hz and 100 Hz. As shown in Fig. 3(a), the transmittance of the cells changes with the voltage. As the voltage applied across the cell increases, for the cell cured at 100 Hz, there is initially very little change in the transmittance of the cell (∼4.5% transmission) until the voltage reaches 25 V when the cell begins to switch to the homeotropic state reaching a steady transparency state (∼87.5% transmission) at about 28 V. However, when the cell was cured at 10 Hz, the plot of transmittance versus the voltage can be divided into three regions. In the first region (0∼10 V), the transmittance decreases from 12.1% to 8%. In the second region (10∼28 V), a slow rise followed by a rapid increase of the transmittance can be observed. In the third region (above 28V), the transmittance stabilizes at about 85.5%. The two reorientation processes in the sample cured at 10 Hz can be observed clearly in the dynamic response

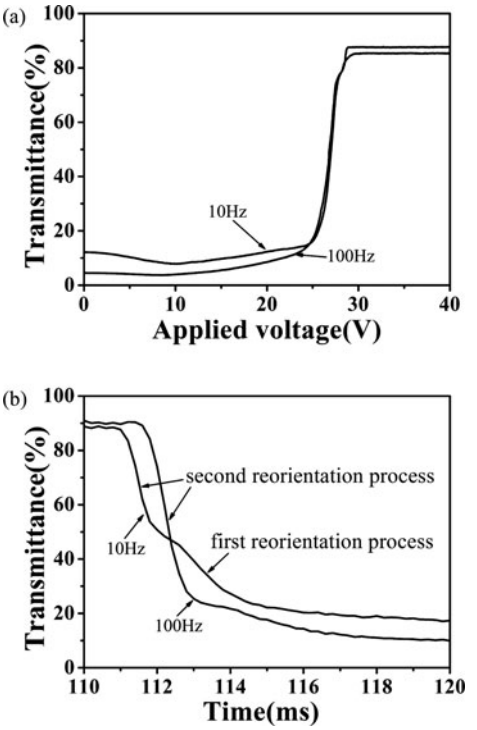

Figure 3. Electro-optical property curves of the cells cured at 10 Hz and 100 Hz. (a) electric transmittance curves of the cells; (b) dynamic response curves of the cells.

Table 1. Electric transmittance parameters of cells under various curing frequencies

Frequency(Hz)	T_0	V_{th}(V)
1	0.161	26.1
10	0.121	25.6
100	0.045	23.9
1000	0.040	19.7
10000	0.035	18.6

measurement (Fig. 3(b)). When the electric field is removed at $t = 110$ ms, the transmittance reveals the dynamics of the transition from the homeotropic to the focal-conic state. For the sample cured at 10 Hz, a fast reorientation process is followed by a second, much slower process, whereas for the sample prepared under curing frequency of 100 Hz, only a single, fast reorientation process can be observed [6].

The two-stage reorientation process can be observed only from PSCTs with sufficiently large network voids. This behavior corresponds to two kinds of cholesteric LC with different environments—the bulk-like cholesteric liquid crystal and the cholesteric LC dominated by the polymer networks [8]. For the sample cured at 10 Hz, the two-stage reorientation process is observed with a large average void size as the result (Fig. 2(b)). With increasing voltage, the LC transforms from the planar to the focal-conic state in the bulk-like region and correspondingly induces a transmittance drop in the first region. In the second region, the transition from the focal-conic to the homeotropic state can be observed. In the third region, all of the LC exhibit homeotropic state. For the sample cured at 100 Hz, a closely packed polymer network structure with a small average void size is observed (Fig. 2(c)). In this case, almost all of the LC is strongly dominated by the polymer network, which results in the transition from the focal-conic to the homeotropic state directly with increasing voltage.

The voltage-transmittance curves of the cells cured at 1 Hz, 10 Hz, 100 Hz, 1000 Hz, and 10,000 Hz are shown in Fig. 4. The electro-optical parameters, the transmittances at zero-field (T_0), and the threshold voltages (V_{th}) of cells under various curing frequencies are listed in Table 1. The T_0 of the cells decreases rapidly from 1 Hz to 100 Hz, and changes

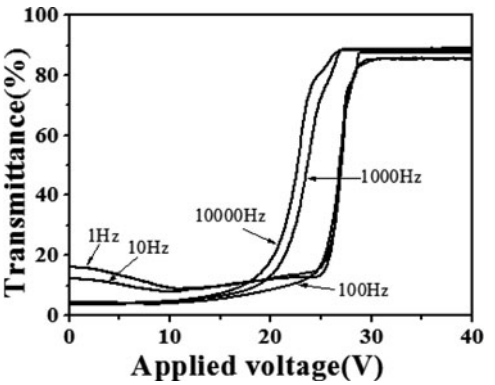

Figure 4. Electric transmittance curves of the cells under curing frequencies of 1 Hz, 10 Hz, 100 Hz, 1000 Hz, and 10,000 Hz.

little from 100 Hz to 10,000 Hz. The V_{th} of the cells decreases all the way from 1 Hz to 10,000 Hz.

Since the cells cured at 1 Hz and 10 Hz have large average void sizes (Figs. 2(a) and 2(b)). The mixed state composed of the planar state from the bulk-like region and the focal-conic state from the polymer network dominated region, is observed at zero-field. And the average size of voids cured at 1 Hz is larger than that cured at 10 Hz. Thus, the T_0 of the cells decreases from 1 Hz to 100 Hz. For the cells cured at 100 Hz, 1000 Hz, and 10,000 Hz, almost all LC exhibits the focal-conic state at zero-field. Therefore, the T_0 of the cells almost remains constant with increasing curing frequency from 100 Hz to 10,000 Hz.

As the curing frequency increases from 1 Hz to 10,000 Hz, the polymer strand density increases, resulting in the formation of a more closely packed polymer structure with smaller average void sizes (Figs. 2(a)–2(e)). Since the strength of the aligning effects of the polymer network was proportional to the polymer network density [3], and the stronger aligning effects of polymer network will lead to a lower V_{th}. Therefore, the V_{th} of the cells decrease as the curing frequency increases from 1 Hz to 10,000 Hz.

The dynamic response curves of the cells cured at various curing frequencies are shown in Fig. 5. The dynamic response parameters of the cells under various curing frequencies, the field-on times (t_{on}), and the field-off response times (t_{off}) are listed in Table 2. The testing voltage was 80 V at the frequency of 120 Hz.

It is stated that the field-on response is the LC response to the electric field, and the network morphology has little influence on the process [9]. Therefore, it is easily to understood that the t_{on} changes little from 1 Hz to 10,000 Hz.

The two-stage reorientation process can be observed, as illustrated in Fig. 5 for the cells cured at 1 Hz and 10 Hz. With the curing frequency increases from 1 Hz to 100 Hz, the bulk-like region reduces until it disappears, and the polymer network dominated region increases until all of the LC molecules are dominated by the polymer network. So, the first reorientation process decreases until it disappears. With increasing the curing frequency from 100 Hz to 10,000 Hz, the dynamic response curve becomes slower and smoother, which is ascribed to the increasing elastic force between the polymer network and the LC molecules. For the cells cured at frequencies ranging from 1 Hz to 10,000 Hz, the elastic force between the polymer network and the LC, which inhibits the transition from

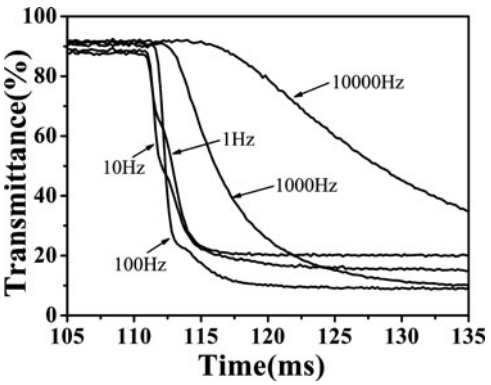

Figure 5. Dynamic response curves of the cells cured at 1 Hz, 10 Hz, 100 Hz, 1000 Hz, and 10,000 Hz.

Table 2. Dynamic response parameters of cells under various curing frequencies

Frequency (Hz)	t_{on} (ms)	t_{off} (ms)
1	1.9	3.1
10	2.1	3.4
100	3.1	3.8
1000	2.2	11.4
10,000	2.7	30.9

homeotropic to focal-conic state, increases with the increases of the curing frequency. So, the decay time of the cells is increased from 1 Hz to 10,000 Hz.

Conclusions

In this study, the influence of the curing frequency on the morphology of the polymer network and the electric-optical property of the normal-mode PSCT cells was investigated. In general, lower curing frequencies result in honeycomb-like polymer network and a larger mesh size. As the curing frequency increases, a smaller average mesh size is achieved. The shape of polymer networks is transformed from honeycomb-like to fiber-like. The switching process was studied with respect to the electric field dependence of the transmittance, and the dynamics of the reorientation processes. For the samples cured at lower frequencies, the two-stage reorientation process with a large average void size can be observed. The threshold voltage of the PSCT cells decreases as the shape of the polymer network changes from honeycomb-like to fiber-like, while the field-off response time increases.

Acknowledgments

This research was supported by National Natural Science Foundation of China (Grant No. 61107014, 51203039, 2120417), Program for New Century Excellent Talents in University (Grant No. NCET-12-0839), National Basic Research Program of China (Grant No. 2012CB723406), National High Technology Research and Development Program of China (Grant No. 2012AA011901).

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