

## Control of the Anisotropic Phase Separation and the Electro-Optical Stability of Ferroelectric Liquid Crystal-Photopolymer Composites

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The criteria for controlling the anisotropic phase separation process in ferroelectric liquid crystal (FLC)-photopolymer mixtures are presented. Depending on the FLC composition and the irradiated intensity of the ultraviolet light, one of the polymer-dispersed, anisotropic phase separated (PS), and polymer-network structures is found to be energetically favored to form it from the FLC-photopolymer mixture. In contrast to a surface-stabilized FLC cell, no broken layers and defects are observed under an external mechanical or a thermal shock exerted on the PSFLC cell and thus the electro-optical stability is obtained.

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Ferroelectric liquid crystals (FLCs) have important features such as fast response and wide viewing characteristics for display applications. However, they show intrinsically limited gray scales and the weak mechanical stability because of the presence of fragile smectic layers. For instance, a surface-stabilized (SS) FLC possesses bistable states<sup>1)</sup> and thus no analog gray scales are available unless a time- or a space-averaging process is employed. Moreover, it is very sensitive to external perturbations such as a mechanical or a thermal shock.

Recently, a phase separation of the FLC from its solution in a prepolymer has been studied for electro-optical applications.<sup>2–4)</sup> Unlike conventional polymer dispersed (PD) FLC devices operated in light scattering by FLC droplets,<sup>5,6)</sup> such FLC devices utilize the smectic layers bounded at the polymer layer which is formed parallel to the cell surface.<sup>3)</sup> They are expected to have several advantages over the SSFLC devices such as the simplicity of fabrication and the mechanical stability. One of the most significant features of the phase separated (PS) FLC film is to exhibit analog gray scales with preserving the nature of the fast response to an external electric field. However, the physical mechanism and the criteria for producing the PSFLC have not been explored so far.

In this Letter, we report on the criteria for controlling the anisotropic phase separation process in the PSFLC film in terms of the composition of the FLC-photopolymer mixture and the irradiated intensity of the ultraviolet (UV) light. Depending on the FLC composition and the UV intensity, it was found that the phase separation of the FLC-photopolymer mixture occurs to select one of three composite structures, namely, a three-dimensional PDFLC structure, or a two-dimensional PSFLC planar interface, or a three-dimensional polymer network-stabilized (PN) FLC structure. This tells us that a subtle change in the surface interaction at the FLC-photopolymer interface together with the anisotropic diffusion properties of the FLC and the photopolymer play a critical role in selecting one of the above three structures during UV irradiation. The electro-optic (EO) characteristics and the mechanical stability of the PSFLC devices are discussed in view of the nature of the planar interface formed through the anisotropic phase separation

process.

The FLC material used in this study was CS1024 of Chisso Petrochemical Co. The FLC has the phase sequence of the cholesteric-smectic A-smectic C\* transition and the natural pitch of about 20  $\mu\text{m}$  long in the smectic C\* phase. The photopolymer material was NOA 65 of Norland Products, Inc. The FLC composition was varied in the range from 10% to 90% in volume. The FLC composite cells were made with patterned indium-tin-oxide coated glasses. The cell gap was maintained using glass spacers of 3  $\mu\text{m}$  thick. One of the substrates was coated with Nylon 6 and unidirectionally rubbed to promote homogeneous alignment. Each FLC-photopolymer mixture was filled into the sample cell in the isotropic state of the FLC at 110°C. The cell was maintained in the isotropic state for 10 minutes to diminish any spatial irregularity of the FLC-photopolymer composition involved during the filling process. The UV irradiation was carried out for 10 minutes through the glass substrate with no alignment layer. The UV intensity with the wavelength of 350 nm was varied in the range from 10 mW/cm<sup>2</sup> to 100 mW/cm<sup>2</sup>. The EO measurements of each cell, mounted in a motorized rotary stage, were performed with a digitizing oscilloscope, an arbitrary waveform generator, and a laser source of 632.8 nm at room temperature.

The scanning electron microscopic textures of the PDFLC and the PSFLC formed in two different FLC-photopolymer mixtures were shown in Figs. 1(a) and 1(b), respectively.

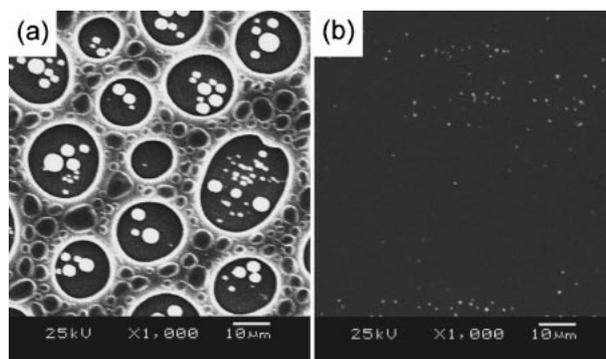


Fig. 1. The scanning electron microscopic textures of the FLC-photopolymer composites after extracting them with methanol: (a) the PDFLC and (b) the PSFLC.

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Note that the UV intensity was fixed at  $40 \text{ mW/cm}^2$  for both cases. For the FLC-photopolymer composition of 3:7, relatively large spherical FLC droplets (on the order of  $10 \mu\text{m}$  in diameter) were formed and uniformly distributed in the polymer matrix as shown in Fig. 1(a). In this PDFLC, the EO switching from an opaque to a transparent state occurs by the application of an external electric field.<sup>5,6</sup> For the nematic LC case, the nucleation and growth of LC droplets from the polymeric matrix were described previously<sup>7,8</sup> but no quantitative description including smectic layers has been made so far. Figure 1(b) shows the PSFLC with a planar interface formed from the FLC-photopolymer composition of 5:5. In contrast to the PDFLC, most of the polymer molecules were solidified near the substrate so that a planar interfacial structure was produced. The remaining polymer molecules were locally solidified around nucleation sites to form microdomains whose average size is much smaller than the wavelength of the visible light. As a consequence, the FLC molecules were considered to be homogeneously aligned on the planar interface along the rubbing direction. This is consistent with the previous results.<sup>3,5</sup> Such PSFLC film will optically resemble the SSFLC but it will possess the alignment stability of the smectic layers since any mechanical stress stored at the FLC-polymer interface will be easily relaxed into the FLC bulk.

We first examine the structural phase diagram to determine the criteria for controlling the anisotropic phase separation process in terms of the FLC composition and the UV intensity during solidifying the photopolymer. As shown in Fig. 2, there exists three structural types of the FLC-photopolymer composites depending on the FLC composition and the UV intensity. When the FLC volume is relatively high ( $>60\%$ ), the mixture forms the PNFLC which would have the mechanical stability to some extent because of the elastic nature of the elongated polymer network.<sup>9</sup> When the FLC volume is less than  $30\%$ , the PDFLC is produced since surface interactions between the FLC and the photopolymer favors to form the FLC droplet structure. In the intermediate range of the FLC volume between  $30\%$  and  $60\%$ , the PSFLC planar interface was formed only in a certain range of the UV intensity from  $30 \text{ mW/cm}^2$  to  $80 \text{ mW/cm}^2$ . In the low intensity regime ( $<30 \text{ mW/cm}^2$ ), no considerable diffusion of the photopolymer occurs and thus a slow phase separation

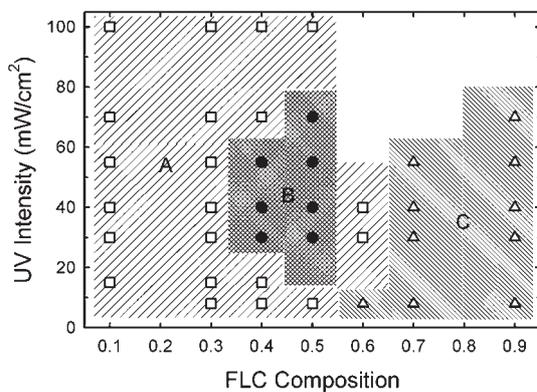


Fig. 2. The structural phase diagram of three types in the plane of the FLC composition and the UV intensity. The PDFLC, the PSFLC, and the PNFLC were represented by open squares (A), filled circles (B), and open triangles (C), respectively.

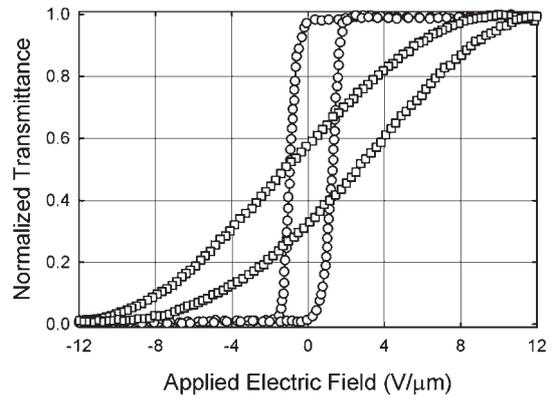


Fig. 3. The normalized transmittance of the SSFLC and that of the PSFLC as a function of the applied electric field were represented by open circles and open squares, respectively.

process is involved to form the PDFLC structure. In the regime of the strong intensity ( $>80 \text{ mW/cm}^2$ ), the solidifying process of the photopolymer is so fast that most photopolymer can not be moved onto the substrate toward the UV source. This prevents the photopolymer from forming a planar interface separated from the FLC-photopolymer mixture.<sup>4</sup> It should be noted that the formation of the PSFLC structure is not favorable below the isotropic temperature since the growth of micro droplet of the FLC will develop.

Figure 3 shows the normalized transmittance of the SSFLC and PSFLC cells as a function of the applied electric field. Note that the SSFLC cell clearly shows the well-known bistability<sup>1</sup> while the PSFLC cell exhibits gray scale capability with some degree of hysteresis. For PDFLC, however, there exists essentially no hysteresis and no threshold.<sup>5</sup> In general, optical transmission through the PSFLC cell is much higher than through the PDFLC because the PSFLC experiences sufficient molecular rotation due to the presence of the planar interface separating the photopolymer and the FLC. In our PSFLC case, the optical switching angle is comparable to the SSFLC case and it is about  $10$  degrees larger than the PDLC case. Another point is that the EO stability of the PSFLC cell is better than that of the SSFLC cell due to the polymer/FLC bonds at the interface.

We now describe the alignment stability of smectic layers against an external mechanical shock and a thermal shock exerted on the PSFLC. Such stability has been one of the main problems to commercialize the FLC devices.<sup>1,3</sup> Figure 4 shows the variations of the transmitted intensities through the SSFLC cell and the PSFLC cell under an external mechanical shock and a thermal shock. For the mechanical shock, each cell was dropped onto a rigid plate from the height of  $1 \text{ m}$ . For the thermal shock, each cell was thermally quenched from the isotropic temperature ( $110^\circ\text{C}$ ) to the room temperature at the rate of  $30^\circ\text{C/min}$ . The EO stabilities associated with smectic layers of the SSFLC and the PSFLC are shown in Figs. 4(a) and 4(b), respectively. Clearly, the PSFLC exhibits negligible change in the transmitted intensity but the SSFLC shows more than  $75\%$  change in the transmitted intensity after the mechanical or the thermal shock. This is mainly due to broken smectic layers present in the SSFLC shown in Fig. 5(a) after the thermal shock. It can

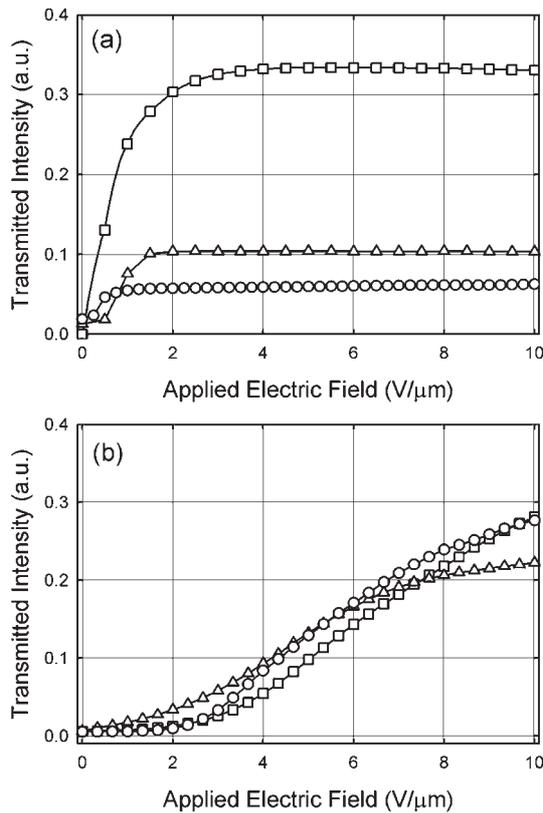


Fig. 4. The variations of the transmitted intensities after a thermal shock and an external mechanical shock: (a) the SSFLC and (b) the PSFLC. The initially aligned cell, the thermally shocked cell, and the mechanically shocked cell were represented by open squares, open circles, and open triangles, respectively.

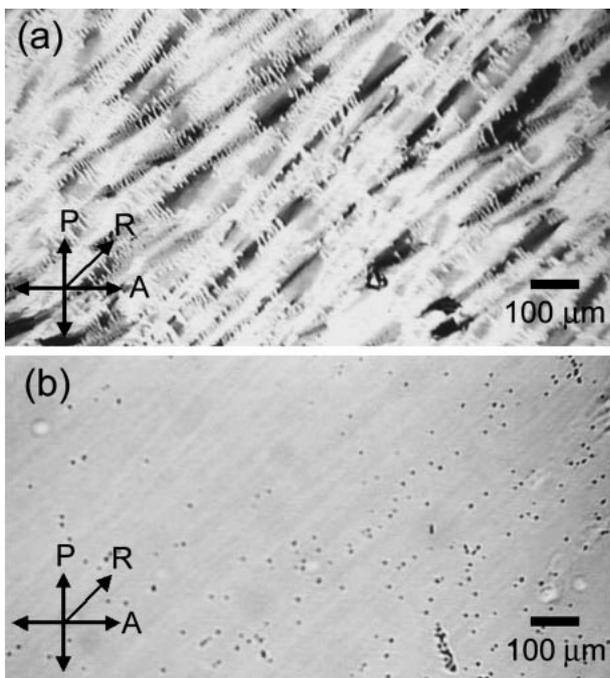


Fig. 5. Microscopic textures after a thermal shock: (a) the SSFLC and (b) the PSFLC. Each cell was placed under crossed polarizers whose axes made an angle of 45° to the optic axis of the sample.

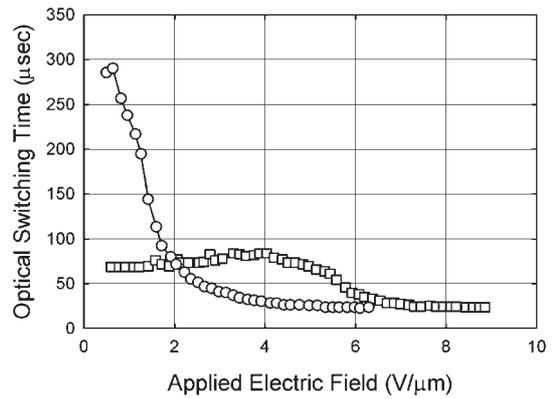


Fig. 6. The optical switching times of the SSFLC and the PSFLC as a function of the applied electric field were represented by open circles and open squares, respectively.

be seen from Fig. 5(b) that no appreciable structural change in the PSFLC was present. Therefore, the precise control of anisotropic phase separation process in the FLC-polymer composite will be crucial for obtaining the mechanical stability as well as the EO characteristics of the PSFLC-based devices.

Figure 6 shows the optical switching times as a function of the applied electric field. The switching times of the SSFLC were strongly field-dependent due to the presence of the intrinsic threshold while those of the PSFLC weakly dependent on the field. In both cases, the optical switching times were less than 100 μs.

In summary, we presented the criteria for obtaining the PSFLC having a planar interface and the alignment stability of smectic layers in the PSFLC film under an external mechanical shock and/or a thermal shock. The criteria were primarily described in terms of two key parameters of the FLC composition in volume and the UV intensity. It may be interesting to see the effect of other physical quantities such as temperature and viscosity on the formation of the PSFLC structure. The work presented here would be useful for devising fast EO devices based on the PSFLC films. Further studies on other FLC-photopolymer composites will provide a deep understanding of anisotropic phase separation process and the dynamical features of the associated diffusion process.

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