

## Liquid crystal alignment with a molecular template of imprinted polymer layer during phase separation

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We developed a liquid crystal (LC) alignment method using a molecular template of an imprinted polymer layer during polymerization-induced phase separation. Our results showed that the nematic ordering of LC is transferred to the polymer chain ordering during an anisotropic phase separation, which produces an anisotropic azimuthal surface anchoring. Using in-plane field treatment during phase separation, a twisted nematic cell is demonstrated. © 2006 American Institute of Physics. [DOI: 10.1063/1.2184891]

In the performance of a liquid crystal (LC) device, the initial orientation of the LC plays an important role because its electro-optic (EO) effect is highly dependent on the optic axis distribution of the LCs. Several LC alignment techniques have been reported and they vary depending on the purpose of the LC device. An alignment method prepared by a pair of surface-treated polymer layers is the most common method. The LCs are aligned by anisotropic intermolecular interactions with well-oriented polymer chains,<sup>1</sup> which are produced by a mechanical rubbing or UV exposure process.

Recently, another cell preparation method requiring only one alignment layer was reported, which is referred to as the phase-separated composite film (PSCOF) method.<sup>2,3</sup> In this PSCOF system, LCs are aligned between a pretreated alignment layer and a thin polymer layer, which is fabricated by low rate phase separation of LC from its solution in a prepolymer. It has been reported that properties such as mechanical ruggedness, ease of fabrication, and superior EO effect of the PSCOF structure are very useful for flexible display application with LCs.<sup>4,5</sup> By localizing the phase separation process, the polymer layer can be made into complex geometry and we have demonstrated a flexible LCD with a single substrate using these features.<sup>4</sup> However, in the conventional PSCOF method, the available LC geometry was limited to a uniform homogeneous structure because phase separation should be carried out above the nematic-isotropic transition point of the LC to achieve complete anisotropic phase separation. The resulting orientation of the bulk LC was determined only by the anisotropy of the single alignment layer.<sup>3</sup>

In this letter, LC-aligning effects from a molecular template of an imprinted polymer layer during polymerization-induced phase separation were investigated. In the proposed method, our PSCOF cell was fabricated by two steps of phase separation with different temperature conditions: phase separation in temperature of isotropic LC and phase separation in temperature of nematic LC. During the second phase separation process, the nematic ordering of the bulk LC was transferred to the polymer chain order, which produced an anisotropic azimuthal surface anchoring. To confirm the azimuthal anchoring effect by the imprinted polymer layer, a twisted nematic (TN) structure was fabricated and demon-

strated by applying an in-plane electric field during phase separation in the nematic phase.

Figure 1(a) shows the schematic of a PSCOF cell structure. To achieve a complete separation of the LC and polymer, several fabrication conditions including a LC/prepolymer mixing ratio, an optimum intensity of UV exposure, a sufficient diffusion of LC and polymer, and a distinctive wetting difference between the LC and the polymer to the surface should be satisfied.<sup>3,6</sup> To facilitate diffusion of the LC and the polymer in opposite directions, a homogeneous alignment layer of polyimide (PI), RN1196 (Nissan Chemical Industries) was spin-coated on only one substrate between two indium–tin–oxide (ITO)-coated glass substrates and then rubbed. The other substrate was the bare ITO surface. The cell gap was maintained using 5  $\mu\text{m}$  glass spacers. A solution of a nematic LC (NLC), E48 (Merck) and a UV curable prepolymer, NOA-65 (Norland) with a weight ratio of 70:30 was introduced into the cell by capillary action at a temperature higher than the clearing point of the NLC. The phase transition sequence of E48 is crystal  $\rightarrow$  ( $-19^\circ\text{C}$ )  $\rightarrow$  nematic  $\rightarrow$  ( $87^\circ\text{C}$ )  $\rightarrow$  isotropic phase. To initiate polymerization-induced phase separation, UV light (about  $780\ \mu\text{W}/\text{cm}^2$ ) was irradiated incident normally on the un-

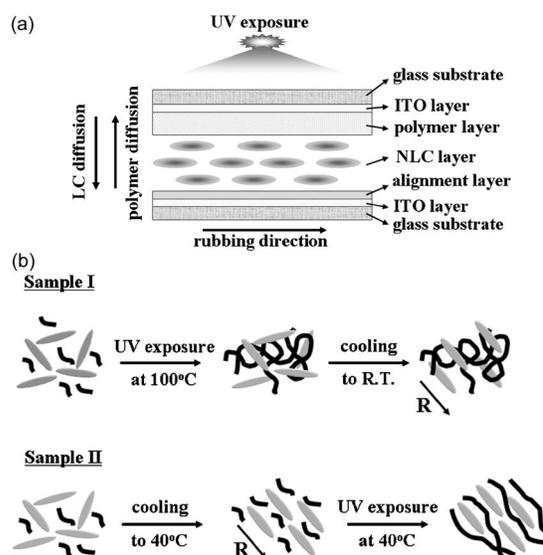


FIG. 1. Schematic diagrams of (a) PSCOF cell structure and (b) orientations of polymer chain and LC molecules depending on phase separation process.

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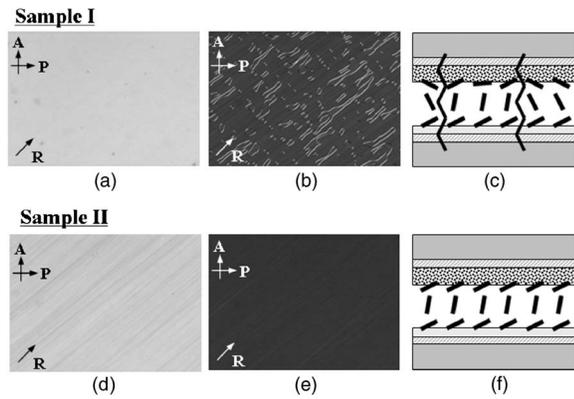


FIG. 2. Polarizing microscopic images of Samples I and II; (a) and (d) were obtained in the absence of an applied voltage and (b) and (e) were obtained in the presence of an applied voltage, 4 V. (c) and (f) Schematic pictures showing LC orientation of Samples I and II in the presence of an applied voltage, respectively.

treated substrate. The UV intensity was so weak and the UV absorption by the NLC molecules was so strong that a sufficient UV intensity gradient existed within the cell and polymerization gradually took place from the substrate closest to the UV source, as shown in Fig. 1(a).

Two types of PSCOF cells were prepared by different phase separation procedures. One cell (Sample I) was fabricated by single step UV exposure at 100 °C for 30 min, representing the conventional PSCOF method. At this phase separation temperature, the NLC was in the isotropic phase. In this case, the polymer chains at the interface of the phase-separated system have random distribution, as shown in Fig. 1(b) and their surface anchoring is azimuthally isotropic. The other cell (Sample II) was fabricated by two steps of UV exposure at a controlled temperature. Sample II was prepared with a first UV exposure of 100 °C for 10 min and a second UV exposure of 40 °C for 30 min. The first UV exposure in the isotropic phase is very important to achieve complete phase separation in our fabrication method. Without this first step, a completely separated bilayer system could not be obtained since the mixture is too viscous for the LC molecules and the polymers to diffuse in the manner depicted in Fig. 1(a). Notice that the LCs in Sample II form a nematic phase during the second phase separation. Contrary to the case of Sample I, the final interface between the NLC and the polymer layers is highly anisotropic in an azimuthal anchoring, since the bulk NLC order promoted by the alignment layer affects the polymer chain order during the second phase separation, as depicted in Fig. 1(b).

The effect of the bulk LC order on the polymer chain formation during phase separation can be observed by polarizing microscopic quantities of LCs by varying an applied voltage. At an initial condition without an applied voltage, the LCs were uniformly aligned along the rubbing direction of the PI in both Samples I and II since the NLC order induced by the surface alignment layer was propagated into the bulk by elastic forces, as shown in Figs. 2(a) and 2(d). When the LC molecules were reoriented by the electric field, the LC texture of Sample II [Fig. 2(e)] was uniform without any defect structure. However, in Sample I, several disclination lines were generated along the rubbing direction, as shown in Fig. 2(b). These different LC textures in the presence of the applied voltage between Samples I and II originate in the different polymer morphologies after phase separation.

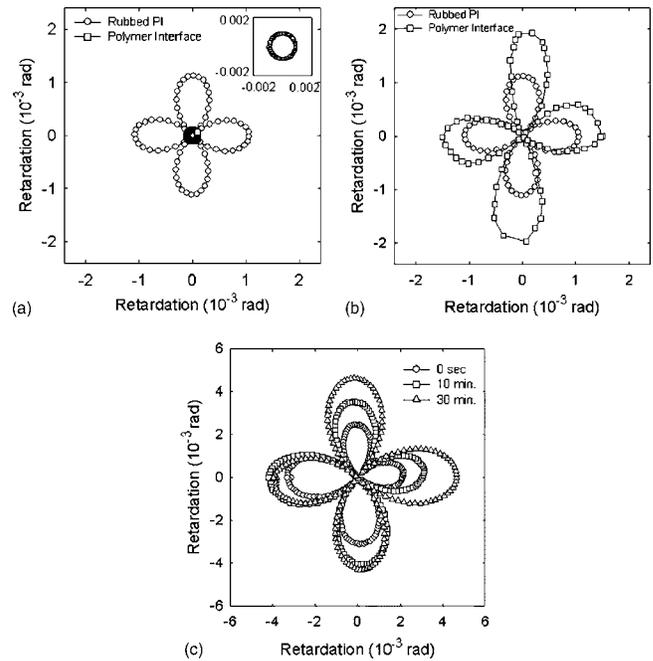


FIG. 3. Angular dependence of birefringence: (a) and (b) experimental results obtained with Samples I and II, respectively, where the open circle and the open rectangle represent birefringence of the rubbed PI layer and the phase-separated polymer layer in each sample, respectively. (c) Optical retardations of polymer chains produced by homogeneously treated alignment layers as polymerization progresses.

ration. In Sample I, the polymer chains at the interface were made with a random distribution by the isotropic LC molecules during phase separation. After phase separation, adsorption of the homogeneously oriented LC molecules may produce anisotropic LC anchoring on the isotropic polymer surface, which is called by the surface memory effect (SME). However, it is reported that the anchoring energy by the SME is much weaker than that by highly oriented polymer chains.<sup>7</sup> Moreover, on this isotropic surface, the tilting direction of the LC molecules in response to the applied field can not be determined, as shown in Fig. 2(c). Therefore, several Néel walls and reverse tilt domains were produced in Sample I, whereas the nematic ordering of Sample II was sustained when the interface was formed by phase separation. Thus, the polymer chains near the interface are highly oriented along the LC molecules. On the imprinted polymer layer, the LC alignment was stable, as shown in Fig. 2(e).

In order to find the mechanism responsible for the LC alignment on the phase-separated polymer layer, we measured optical retardation of the top and bottom substrates after opening the cells and washing the LCs out. The laser beam was incident normal to the substrate. The retardation was monitored while rotating the sample substrate with respect to the surface normal. Figures 3(a) and 3(b) show the optical retardation measured from Samples I and II, respectively, where the open circle and the open rectangle represent birefringence of the rubbed PI layer and the phase-separated polymer layer in each sample, respectively. From the optical retardation measurements with the PI layers of Samples I and II, the existence of the polymer chain ordering could be observed, which was caused by mechanical rubbing treatment. However, in the case of the phase-separated polymer layer, there was no significant birefringence for Sample I, but a large retardation was induced in Sample II. The optical re-

tardation of the polymer layer in Sample II was even larger than that of the rubbed PI layer. It is expected that there might be some trapped NLCs within the polymer during photopolymerization. But the above results obviously showed that the NLC order at the interface affected the polymer chain order during phase separation and polymerization.

To determine the effect of an interfacial material state on the polymer chain order, we prepared an empty cell with unidirectionally rubbed PI layers at both internal surfaces. After filling the cavity with prepolymer only, variations in optical retardation with time were measured as polymerization progressed. Figure 3(c) shows that the optical anisotropy gradually increased as the photopolymerization continued and the direction of the polymer chains was determined by ordering the interfacial material, which meant that polymer chains were chemically or morphologically affected by the anisotropy of the interfacial material.<sup>8</sup> In the case of Sample II, the aligned NLC molecules induced the anisotropy of the polymer layer during polymerization. Notice that the anisotropic polymer surface acts as an alignment layer after the polymerization process is completed, that is a LC alignment by the LC via imprinting of molecular ordering.

Using the above imprinting method, we fabricated a PSCOF cell with a TN structure. After the first step of UV exposure was executed as described previously, an in-plane electric field of about  $1 \text{ V}/\mu\text{m}$  was applied with a patterned chrome electrode to generate an easy axis at the phase-separated NLC/polymer interface along the direction orthogonal to the rubbing direction of the PI layer during the second phase separation process. The rubbing direction of the alignment layer was along with the electrodes. After the phase separation process, the final cell structure in the absence of an applied voltage is depicted in Fig. 4(a). The microscopic images in Fig. 4(b) and the  $V$ - $T$  curves of Fig. 4(c) show that the transmittance monotonically increases or decreases with increasing in-plane electric field under either the parallel polarizers or the crossed polarizers, respectively. This means that the initial LC configuration without an applied voltage is the TN structure. For comparison, the  $V$ - $T$  curve of a PSCOF cell fabricated by a conventional single step phase separation is given in Fig. 4(d). Under the crossed polarizers, the transmittance of the cell initially increased due to increased off-axis birefringence with increasing in-plane electric field. However, at higher voltages, the state of the cell returned to the dark state since the LC molecules were further reoriented to the direction orthogonal to the initial rubbing direction, which was quite different from the results of Fig. 4(c). Notice that no chiral dopant or no rubbing process on the polymer surface is required to get a stable TN structure. The above results show that the field-induced nematic ordering in the bulk is imprinted to the NLC/polymer interface and the azimuthal anchoring strength of the phase-separated polymer layer is strong enough to compete with the elastic energy of the NLC. The twisting angle can be controlled by varying the strength of a bias field, the LC/prepolymer mixing ratio, and the temperature at the second phase separation.

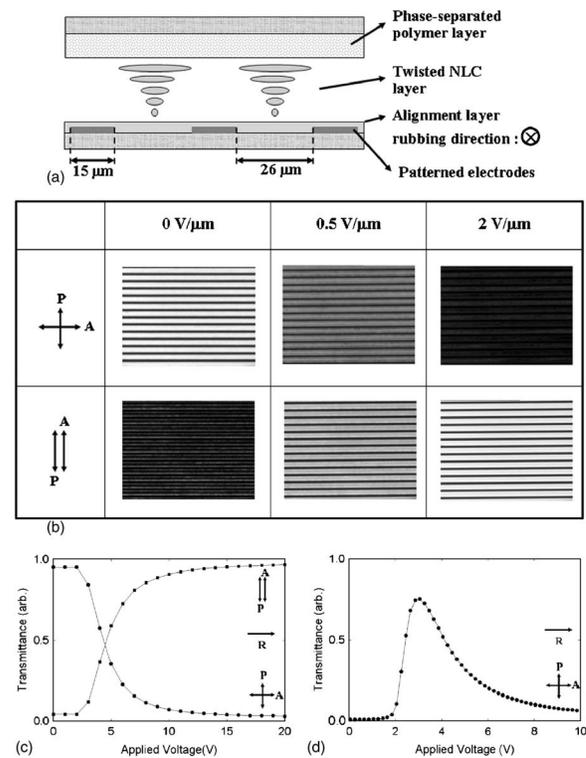


FIG. 4. (a) Schematic diagram of the TN structure in the absence of an applied voltage after phase separation when the cell is fabricated by a two-step phase separation in the presence of an in-plane electric field. (b) and (c) Polarizing microscopic images and the EO results of the TN cell, respectively. (d) EO result of the homogeneously aligned LC cell fabricated by the conventional PSCOF method.

In summary, we propose an LC alignment method that involves imprinting the LC order on the polymer surface during phase separation. Using two steps of phase separation with varying temperature, it was demonstrated that PSCOF cells with any type of LC configuration could be fabricated because the amount and the direction of anisotropy at the phase-separated polymer layer can be controlled by the imprinting method. It is expected that this LC alignment method using the LC itself can be applied to several types of LC devices for enhancing EO performance, especially in flexible display applications using a LC/polymer mixture.

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