

INVITED PAPER *Special Section on Electronic Displays*

# Control of Morphology and Alignment of Liquid Crystal Droplets in Molecular-Aligned Polymer for Substrate-Free Displays

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**SUMMARY** We have proposed composite films composed of a molecular-aligned polymer and liquid crystal (LC) for substrate-free liquid crystal displays with high-contrast images. We successfully controlled the molecular alignment of the LC and formed molecular-aligned LC droplets in the polymer by controlling the fluidity of the LC/monomer mixture and the curing rate of the monomer.

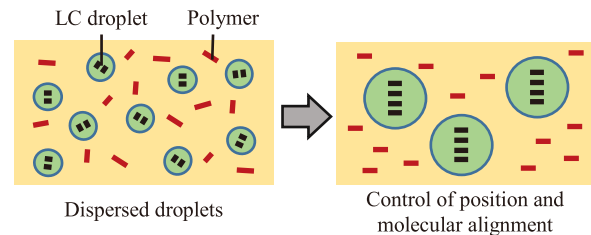
**key words:** *substrate-free display, liquid crystal, polymer, composite film*

## 1. Introduction

Recently, flexible displays have attracted attention because of their advantages of thin thickness, light weight, and bendability. Flexible displays can be carried easily and set up on curved surfaces. Therefore, they can realize ubiquitous society in which information can be easily accessed and are expected to make life more convenient. Current liquid crystal displays (LCDs) have the drawbacks that they are damaged easily and can be set up in a limited range of locations owing to their insufficient flexibility because they are composed of a liquid crystal (LC) material sandwiched between two glass substrates. Currently, flexible LCDs use plastic substrates in many reports instead of the conventionally used glass substrates. To realize the flexible LCDs using plastic substrates, we must solve the following two problems. First, such devices cannot maintain a constant cell gap in a curved state and provide high-quality images because compression and expansion forces are applied from the plastic substrates to the LC layer. Second, the flexibility of the device is restricted by stacking two plastic substrates.

To solve these problems, studies on the single-substrate LCDs and the substrate-free LCDs have been reported [1]–[5]. These devices are composed of LC droplets included in a polymer. In these devices, the thickness of the LC layer in the composite films is maintained in a curved state so that the compression and expansion forces do not affect to the image quality of the LCDs. In addition, it is thought that these devices can achieve high flexibility and elasticity due to the reduced number of substrates.

Conventional substrate-free LCDs have a structure comprising cholesteric LC droplets encapsulated in a poly-



**Fig. 1** Molecular-aligned LC/polymer composite film.

mer. However, these devices have the problem of a low-contrast ratio [5] owing to the scattering of light by the cholesteric LC droplets, because these displays utilize the selective reflection of cholesteric LC. Therefore, it has been difficult to realize high-contrast images in substrate-free LCDs. To achieve substrate-free LCDs similar contrast to that of conventional LCDs, a polarizer and the birefringence effect of the LC must be used and it is necessary to control the molecular alignment of the LC droplets uniformly.

For this reason, we proposed a novel LC/polymer composite film in which the molecular alignment of both the LC and the polymer can be controlled accurately for substrate-free LCDs with high-contrast images (see Fig. 1). By controlling the molecular alignment of the LC and the polymer, optical modulation by birefringence becomes possible, and it is expected to realize substrate-free LCDs with high-contrast images.

In this study, we investigate the conditions required to fabricate a molecular-aligned LC/polymer composite film in an LC cell, which is necessary for the realization of high-contrast substrate-free LCDs. We clarified that LC droplets, which were formed in accordance with the photomask pattern, were precipitated by UV exposure. We also showed that the phase-separated structure of the LC droplets was controlled by controlling the fluidity of the LC/monomer mixture and the curing rate of the polymer. Moreover, we evaluated the electrooptical characteristics of the fabricated device and confirmed the optical modulation based on the birefringence effect of LC.

## 2. Fabrication Principle of the Composite Film

Figure 2 shows the fabrication process of the molecular-aligned LC/polymer composite film schematically shown in Fig. 1. First, we prepared a mixed solution, which consists of a dissolved liquid crystalline monomer in an LC material

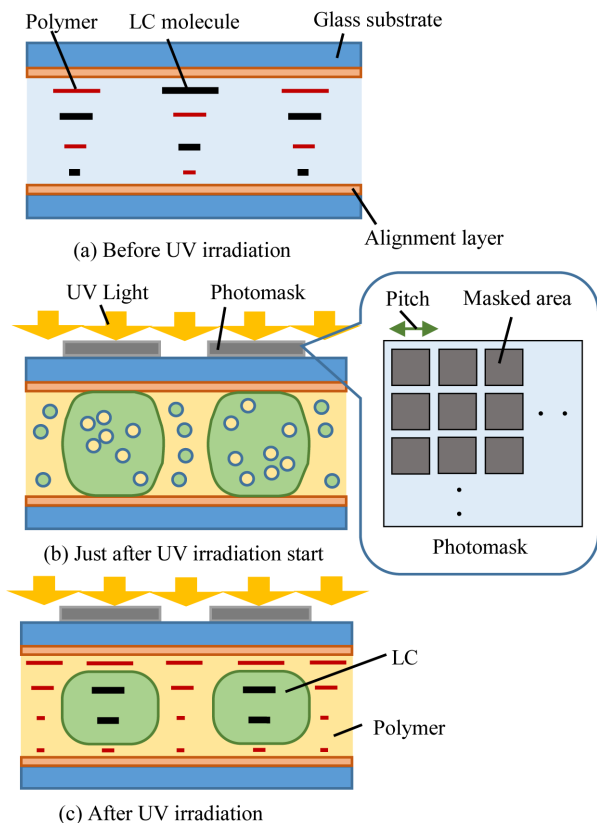
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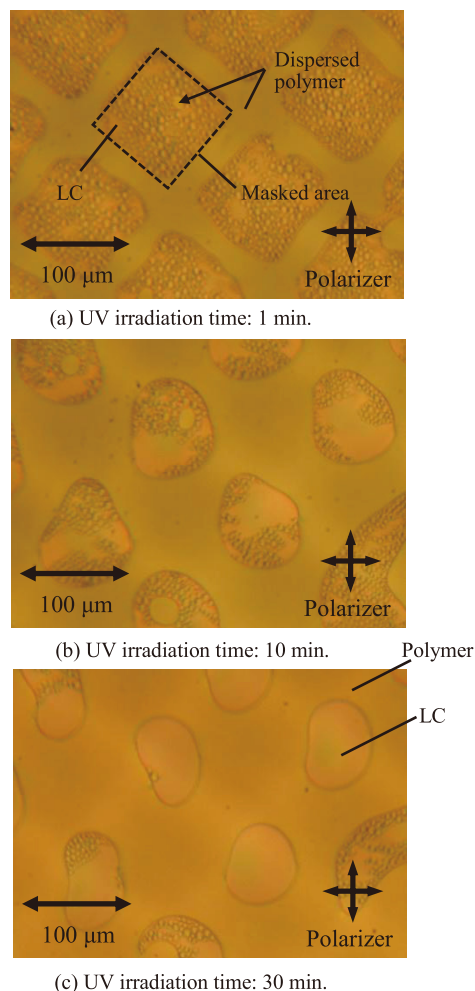
**Fig. 2** Phase separation induced by UV exposure with a patterned photomask.

and injected it in the LC cell, which was treated by rubbing process (Fig. 2 shows an example of a twisted alignment) [6]. We used an alignment layer with a pretilt angle of about  $2\text{--}3^\circ$  (AL-1254, supplied by JSR). Afterwards, the LC cell was irradiated by UV light through a patterned photomask [7]. We consider that the polymer was precipitated on the UV-irradiated area and LC droplets were precipitated at any position as a result of the UV light exposure of the LC cell through a patterned photomask [7]. In addition, it is expected that the molecular alignment of the LC will be maintained by the anchoring force of the polymer surface [8].

We examined the effects of the UV light intensity and polymerization temperature on the morphology of the LC/polymer composite film [9], [10], because these parameters control the fluidity of the LC/monomer mixture and the curing rate of the monomer.

### 3. Observation of Formation Process of the Composite Film

We used an LC material (TD-1013LA, supplied by JNC), a monofunctional liquid crystalline monomer (monomer type-C, supplied by DIC), and a photoinitiator (2,2-dimethoxy-2-phenyl acetophenone, supplied by DIC). The ratios of the LC material, monomer, and photoinitiator in the mixture were 50wt%, 49wt%, and 1wt%, respectively. The mixture was injected into an LC cell in the isotropic phase state.



**Fig. 3** Polarizing micrographs of the LC cell during the fabrication of LC droplets.

The LC cell was treated with twisted-alignment process. We controlled the cell gap of the LC layer using bead spacers with a diameter of  $10\ \mu\text{m}$  (Micropearl SP-210  $10\ \mu\text{m}$ , SEKISUI CHEMICAL). To change the fluidity of the mixture, the temperature during the UV irradiation process was controlled from  $25$  to  $50^\circ\text{C}$  using a hot stage (TS102W, Instec) and a temperature controller (mk1000, Instec). Moreover, to change the curing rate of the polymer, the UV light intensity was controlled from  $3$  to  $100\ \text{mW}/\text{cm}^2$  at a wavelength of  $365\ \text{nm}$ . The UV irradiation time was  $30\ \text{min}$ . We used a lattice-patterned photomask with the pitch of  $120\ \mu\text{m}$  in the UV exposure.

Figure 3 shows polarizing micrographs of the LC cell. The UV intensity was  $3\ \text{mW}/\text{cm}^2$  and the temperature of the LC cell was  $50^\circ\text{C}$ .

First, the polymerization of the monomer began in the UV-irradiated area. We also confirmed that the polymer was dispersed in the masked area (see Fig. 3 (a)). Then, the dispersed polymer moved to the UV-irradiated area and aggregated (see Figs. 3 (b) and (c)). On the basis of these results, we investigated the effect of the fabrication conditions on phase-separated structure.

#### 4. Experiments on Morphological Control of the Composite Film

To control the fluidity of the LC, we examined the effect of the temperature on the phase-separated structure during the UV irradiation process while fixing the UV intensity at  $3 \text{ mW/cm}^2$ . The temperature of the LC cell was controlled from 25 to  $50^\circ\text{C}$ . Figures 4(a) to (c) shows polarizing micrographs of the fabricated LC cells. From these figures, we confirmed that the LC droplets aggregated in a masked area when we increased the temperature from 25 to  $50^\circ\text{C}$  during the UV irradiation process. This is because a mixture with higher fluidity was obtained at a higher temperature and the aggregation of the separated LC was promoted.

Then, to examine the effect of the curing rate of the monomer, we changed the UV intensity from 3 to  $30 \text{ mW/cm}^2$  while fixing the temperature at  $50^\circ\text{C}$ . Figure 4(d) shows the polarizing micrograph obtained as a result. From Fig. 4(d), we confirmed that, compared with a UV intensity of  $3 \text{ mW/cm}^2$  (Fig. 4(c)), the separated LC droplets were more dispersed when the UV intensity was  $30 \text{ mW/cm}^2$ . We considered that the phase-separated structure cannot be controlled because the curing rate of the polymer is increased at a high UV intensity, which restricts of the flow of the LC droplets. From the above, we clarified that the LC droplets, which were formed in accordance with the photomask pattern, precipitated in the molecular-aligned polymer at a temperature of  $50^\circ\text{C}$  and UV intensity of  $3 \text{ mW/cm}^2$ .

On the basis of the two experiments, we attempted to miniaturize the LC droplets by using a lattice-patterned photomask with a pitch of  $60 \mu\text{m}$ . Figure 5(a) shows a polarizing micrographs of the LC cells fabricated with using the narrow photomask with the same temperature and UV in-

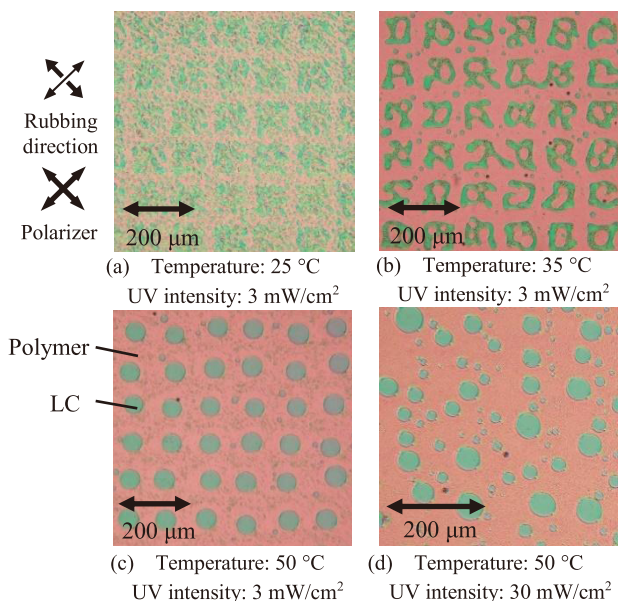


Fig. 4 Polarizing micrographs of the LC cells. (Mask pitch:  $120 \mu\text{m}$ )

tensity as those in Fig. 4(c). We confirmed that the shapes of the LC droplets cannot be controlled adequately because of excessive aggregation of the LC and the polymer. Therefore, we controlled the temperature to  $40^\circ\text{C}$  to reduce the fluidity of the mixture, and the UV intensity and irradiation time were set to  $100 \text{ mW/cm}^2$  and 10 min, respectively, to increase the curing rate of the polymer and prevent excessive aggregation. Figure 5(b) shows a polarizing micrograph of the LC cell fabricated under these optimized conditions. By controlling the fluidity and the curing rate of the monomer, we confirmed that it is possible to precipitate minute and regular LC droplets in the molecular-aligned polymer.

Moreover, we attempted to precipitate LC droplets linearly using a stripe-patterned photomask with a pitch of  $100 \mu\text{m}$ . This experiment was conducted with the same temperature and UV intensity as these in Fig. 4(c). Figure 6 shows the result of this experiment. From these experiments, we clarified that it is possible to precipitate LC droplets, which are formed in accordance with the photomask pattern, by controlling the temperature and UV intensity.

However, it is necessary to debond the composite film from the glass substrates to realize substrate-free LCDs. In the debonding process, the deformation of the composite film by the bending and tensile force is expected. We consider that increasing the strength of the polymer will lead to reduced the physical damage and reduced degradation of the optical characteristics of the composite film. To reduce the damage to the composite film during the debonding process, we plan to use a multifunctional monomer to increase the strength of the polymer structure.

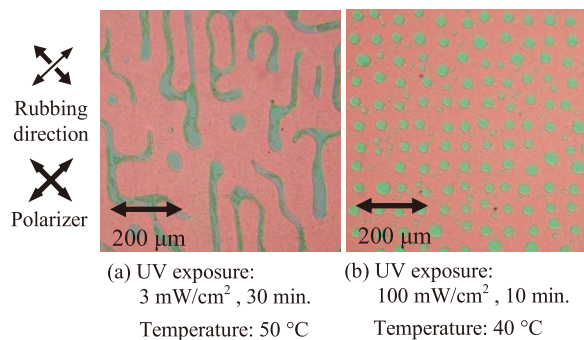


Fig. 5 Polarizing micrographs of the LC cells. (Mask pitch:  $60 \mu\text{m}$ )

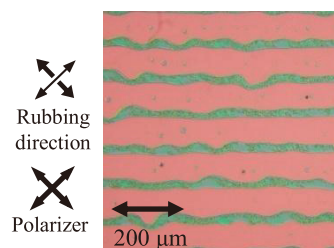


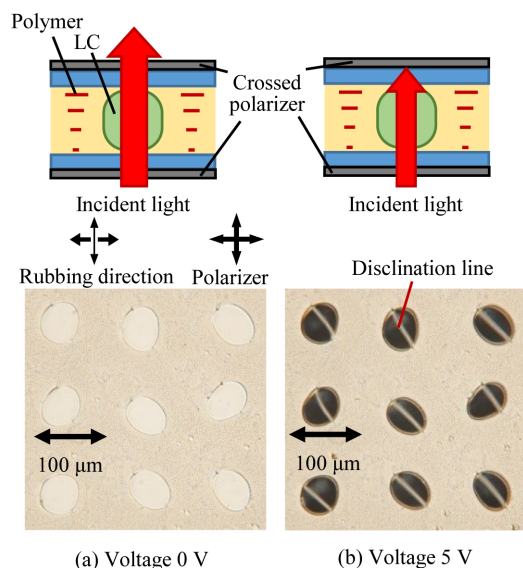
Fig. 6 Polarizing micrographs of the LC cell. (Using stripe-patterned photo mask)

## 5. Electrooptical Characteristics

In this section, we discuss the electrooptical characteristics of the LC droplets contained in the polymer. Figure 7 shows polarizing micrographs of the fabricated device between a crossed polarizer in the voltage-on and -off states. We observed that the LC droplets became bright in the voltage-off state and dark in the voltage-on state.

We measured the optical characteristics of the fabricated LC cell. From Fig. 7(b), we found that a disclination line appears in the LC droplets in the voltage-on state. Therefore, we measured the light intensity in a minute domain away from the disclination line that appeared in the center of the LC droplet using a microscope and monochromatic light of 550 nm. Figure 8 shows the voltage dependence of the transmittance of the device. The measured transmittance of an LC droplet of the fabricated device without the disclination line is depicted by the red line. As a reference device, we also fabricated an LC cell which was injected with only the LC material used in this study, and its measured transmittance is depicted by the blue line. The transmittance of the fabricated device is higher than that of the reference device during the voltage-on state. These results indicate that the polymer precipitating in the upper and lower LC droplets polarize part of the incident light. It is likely that this is caused by the desired ceiling and floor structure of polymer.

However, the birefringence of the polymer precipitated at the surface of the top and bottom substrates does not change in the voltage-on state, which affects the contrast ratio. To solve this problem, we considered the vertical-alignment (VA) mode as the operating mode of the LC. This method does not decrease the contrast ratio, because the phase retardation of the vertically aligned polymer precipi-



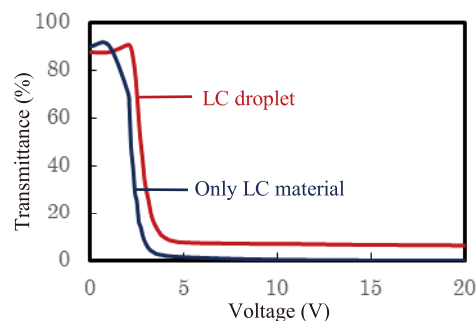
**Fig. 7** Polarizing micrographs of fabricated device in voltage-on and -off states.

tated at the top and bottom substrates is zero. In addition, we expect that the contrast ratio will be improved by laminating phase retardation films to compensate for the birefringence of the polymer precipitated at the top and bottom substrates. Using these techniques, we anticipate the realization of a higher contrast ratio than that achieved in this experiment.

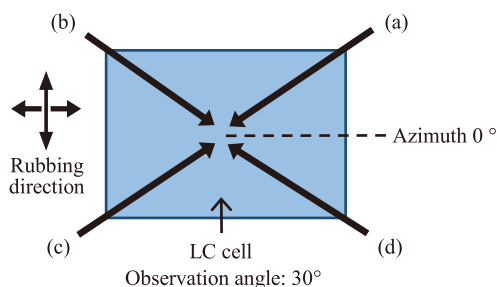
When physical damage for the composite film does not occur in the debonding process, the molecular alignment of the LC and the polymer does not change. Therefore, it will be possible to anticipate identical optical characteristics to those experimentally observed in glass substrates described in this paper.

We also examined the cause of the disclination line. When we observed the LC droplets from the diagonal direction under crossed nicols in the voltage-on state, we found that the viewing angle dependence of the transmittance of each domain is different. Figure 9 shows the definition of the observation angle and Fig. 10 shows polarizing micrographs of LC droplets. The observation angle was  $30^\circ$ .

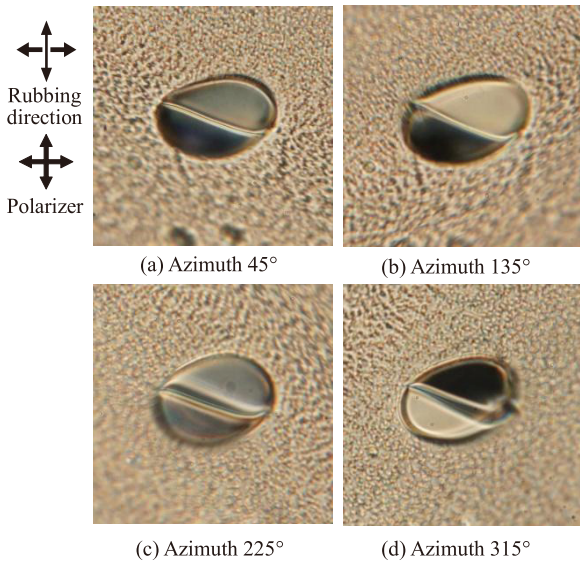
We examined the alignment of LC having such viewing angle characteristics by simulation. We focused on the direction of the pretilt angle at the top and bottom substrates and the twisting direction of the LC molecules. As a result, we clarified that the direction of the pretilt angle reverses at the boundary of the disclination line in each substrate. Figure 11 shows the alignment of the LC and the transmittance when the direction of the pretilt angle reverses at the boundary of the disclination line in each substrate. From Fig. 11, we confirmed that the disclination line appears between domains A and B when the direction of the pretilt angle reverses at domain B in each substrate. Figure 12 shows



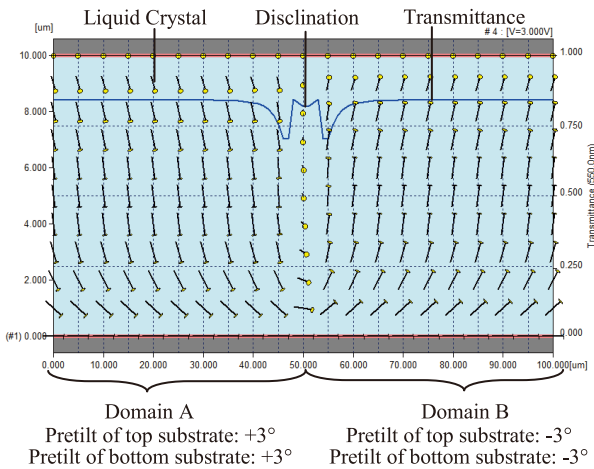
**Fig. 8** Voltage dependence of the transmittance.



**Fig. 9** Definition of observation angle.



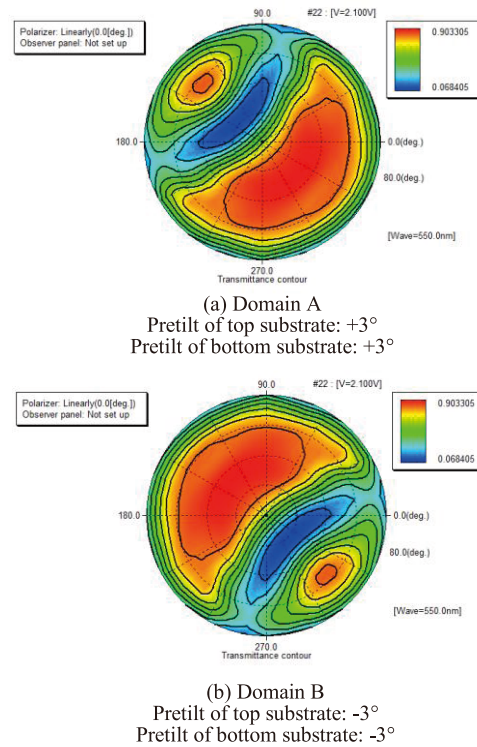
**Fig. 10** Polarizing micrographs of the same LC droplet. (Observation angle: 30°)



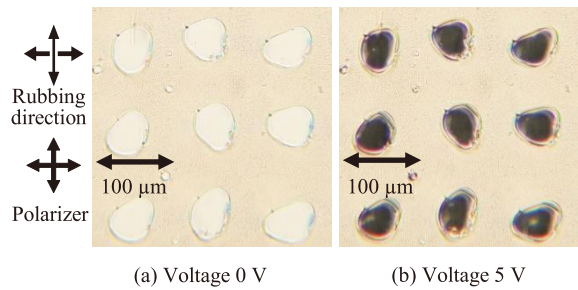
**Fig. 11** Simulation of transmittance and alignment of LC.

the viewing angle characteristics at domains A and B in the voltage-on state. The result of simulation is in agreement with the observation result in Fig. 10. From this result, we consider that the disclination line appears when the direction of the pretilt angle reverses at the boundary of the disclination line in each substrate.

In addition, we consider that the pretilt angle of the substrate can change easily when the polymer precipitates in the substrate surface. On the basis of this consideration, we changed the material of the alignment layer to prevent the reverse of the pretilt angle by the precipitation of the polymer. We used an alignment layer whose pretilt angle is more than 5° (SE-9696, supplied by Nissan Chemical Industries). Figure 13 shows polarizing micrographs of the result using different alignment layer. From this result, we confirmed that the disclination line is suppressed in the case of a high pretilt angle.



**Fig. 12** Simulation of viewing angle in the voltage-on state.



**Fig. 13** Polarizing micrographs of the LC cell.

## 6. Conclusion

To achieve substrate-free LCDs with high-contrast images, we proposed a novel LC/polymer composite film in which the molecular alignment of both the LC and the polymer can be controlled, and we investigated the conditions to fabricate a molecular-aligned LC/polymer composite film in an LC cell. As a result, we clarified that it is possible to aggregate LC droplets that are formed in accordance with the photomask pattern by controlling the viscosity of the mixture, which can be controlled by the temperature during the UV irradiation process, and the curing rate of the polymer, which can be controlled by the UV intensity.

We confirmed that the LC droplets and the polymer maintained their molecular alignment, and the LC droplets exhibited optical modulation based on their twisted alignment. These results will be useful for the realization of

substrate-free LCDs with high-contrast images. In future work, we will investigate the strengthening of the polymer structure and the debonding process of the composite film from glass substrates.

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