Formation of Polymer Walls by Monomer Aggregation Control Utilizing Substrate-Surface Wettability for Flexible LCDs

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SUMMARY   We examined the novel aggregation control of the LC and monomer during formation of the polymer walls from a LC/monomer mixture in order to suppress the presence of the residual monomers and polymer networks in the pixel areas. The method is utilization of the differing wettabilities among LC and monomer molecules on a substrate surface. We patterned a substrate surface with a fluororesin and a polyimide film, and promoted phase separation of the LC and monomer by cooling process. This resulted in the LC and monomer aggregates primarily existing in the pixel areas and non-pixel areas, respectively. Moreover, the polymer-walls structure which was formed in this method partitioned into individual pixels in a lattice region and prevented the LC from flowing. This polymer-walls formation technique will be useful for developing high-quality flexible LCDs.
key words: *polymer wall, wettability, phase separation, fluororesin, polyimide film*

1. Introduction

Flexible liquid crystal displays (LCDs) are manufactured by sandwiching a liquid crystal (LC) between two plastic substrates. The development of such displays has been expected for various applications because they are thin, lightweight, and bendable. In a curved state of flexible LCDs, there are two critical issue for degradation of image quality. One is the flow of LC having fluidity. Another is to maintain the LC cell thickness. These issues are related to the characteristics of optical modulation in LCDs which is controlled by retardation. To overcome these drawbacks, bonding spacer between substrates is necessary for flexible in a curved state. Recently, formation of a bonding-spacer structure inside the LC cell has been proposed [1]. Polymer walls are promising candidates for the spacer structure. Generally, such a polymer structure is fabricated using patterned UV irradiation through a photo mask to photopolymerize monomers [2]–[4]. It has also been reported that the polymer-walls structure can be fabricated by phase separating the LC and melted polymers through utilization of their differing wettabilities on a substrate surface [5]. In the former method, a large number of monomers remain in the pixel areas, which are covered with the photo mask, and form polymer networks, as shown in Fig. 1(a) [6]. Similarly, in the latter method, some polymers remain in the pixel areas because of their

(a) Using patterned UV irradiation
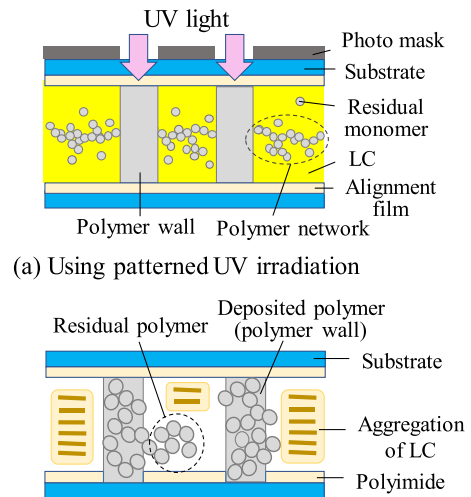
(b) Polymer deposition utilizing the wettability of polyimide

Fig. 1   Conventional polymer-walls formation techniques.

low fluidity, as shown in Fig. 1(b). These residual monomers and polymer networks lead to degradation of the light transmittance and driving voltages of flexible LC devices [6]. Therefore, a novel technique for formation of the polymer-walls structure is required to suppress residual monomers and polymer networks in the pixel areas and develop of high-quality flexible LCDs.

Here, in this study, we proposed and examined a novel technique that controlled the monomer morphology by utilizing its wettability on a substrate surface. To promote separation of the LC and polymer, we investigated the influence of temperature during the UV irradiation process on phase separation between the LC and polymer in the LC cell.

2. Proposal of Monomer Morphology Control

One substrate surface of a LC cell is patterned with highly hydrophobic fluororesin (CYTOP) and hydrophilic polyimide. LC/monomer mixture is heated to dissolve, and injected into the cell as shown in Fig. 2(a). Hence, the LC and monomer exist uniformly in the cell. The injected mixture phase-separates into the LC phase domain and isotropic phase domain by cooling because the LC orientation order increases and its solubility decreases (Fig. 2(b)). Deposited LC aggregates and flows onto the polyimide surface owing
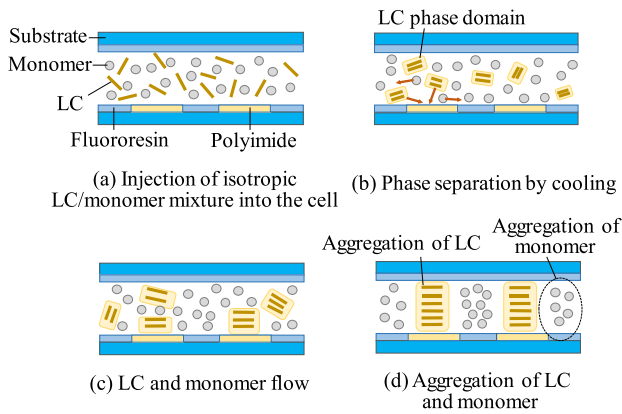
Fig. 2 Monomer aggregation control utilizing the wettability of a fluororesin and polyimide surface.

Fig. 3 Fabrication process of LC-cell.

to its low wettability on CYTOP (Fig. 2(c)). On the other hand, the monomer exhibits excellent fluidity due to its low molecular weight and wets CYTOP surface more easily than the LC. Therefore, the monomer aggregates on CYTOP surface against the LC flow. The droplets of LC on the polyimide surface and monomer on the CYTOP surface become nucleus, and nearby LC or monomer aggregates mainly on the nucleus while they flow slightly in the LC cell. Finally, as shown in Fig. 2(d), the LC and monomer aggregate and are piled up primarily existing on the polyimide and CYTOP surface, respectively.

After control of monomer aggregation morphology, the monomer is photopolymerized by UV irradiation to entire LC-cell surface. Then, although a photo-mask is not used, we expect that polymer-walls structure is formed only on CYTOP surface, which monomer aggregates before monomer photopolymerization. In the novel method, therefore, there are possibilities as follows: the residual monomers or polymers in the pixel areas are suppressed, and phase separation between the LC and polymer is promoted.

3. LC-Cell Fabrication

We fabricated a LC cell using the following procedure. First, as shown in Fig. 3(a), the fluororesin CYTOP (CTL-809A, AGC Co., ltd) was spin-coated at 3000 rpm for 30 s on two ultrasonically cleaned glass substrates with ITO electrodes. The CYTOP was then baked in an oven at 200°C for 1 h. Second, the CYTOP on one substrate was formed into a lattice pattern by selective removal using laser beam (MD-V9600A, KEYENCE Co., Ltd.) as shown in Fig. 3(b). The line width of the lattice was 50 μm, and the distance between the line patterns was 300 μm. A polyimide film (AL1254, JSR Co., Ltd.) was then spin-coated at 4000 rpm for 30 s on the areas of the substrate surface where CYTOP was not coated (Fig. 3(c)). The polyimide film was then baked at 200°C for 1 h. Thereafter, we performed rubbing treatment to both substrates using a rubbing machine (EHC RM-50). The conditions for the rubbing treatment were as follows: the rubbing-roller rotation speed was 500 rpm, the substrate
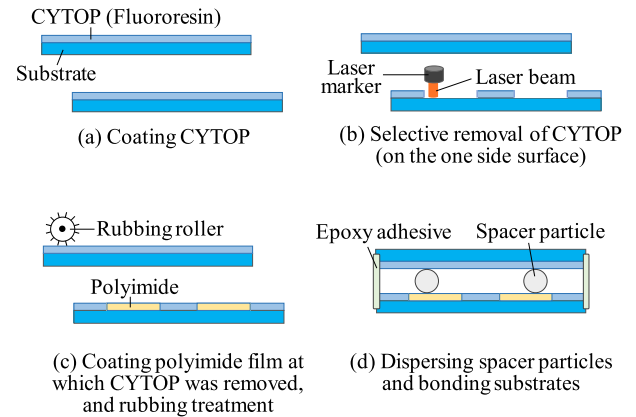
carrier speed was 0.35 cm/s, and the pushing length of velvet cloth to substrate was 0.4 mm. We then dispersed spacer particles and constructed the LC cell of a homogeneous alignment mode using the two substrates (Fig. 3(d)). The cell thickness was 5 μm.

Next, we fabricated a mixture of LC material (TD-1016XX, JNC Co., Ltd.), non-LC fluorinated monomer material (Osaka Organic Chemical Industry Ltd.), and photo-polymerization initiator, 2,2-Dimethoxy-2-phenyleacetophenone. The monomer concentration in the mixture was 29.7wt%, and the concentration of the photo-polymerization initiator was 0.3wt%. Finally, the mixture was injected into the cell at 80°C and then cooled at the phase-transition temperature of the mixture for 15 min. This resulted in separation of the LC and monomer inside of the LC cell and formation of their respective aggregates. Thereafter, the LC cell was exposed to UV light (365 nm wavelength and 1 mW/cm^2 intensity) for 25 min without a photo mask to initiate polymerization while cooling off.

4. Evaluation of Surface Wettability for LC and Monomer

In order to control the LC and monomer aggregation by utilizing differences in their wettability on the substrate surface, we evaluated the LC and monomer wettability. We measured the surface tension and contact angle in both of the LC and monomer materials. Using a pendant-drop method, we dropped the liquid sample from a needle with 0.30 mm diameter, and measured the liquid-droplet mass at which the surface tension matched that calculated using Eq. (1), where m is the droplet mass, R is the droplet outer diameter, and γ is the surface tension. We showed the averaged values of three measurements for both materials

$$mg = \pi R \gamma \qquad (1)$$

The estimated droplet mass and surface tension results are shown in Table 1. The surface tension of fluorinated-monomer was lower than that of the LC and it wetted surfaces more easily than the LC. This is attributed to the lower intermolecular forces among the monomer molecules than

Table 1   Surface tension measurements

Sample	Droplet mass [mg]	Surface tension [mN/m]
LC (TD-1016XX)	3.4	35.4
Non-LC fluorinated monomer	1.9	19.8

Table 2   Contact angle measurements

Liquid sample \ Surface material	Glass	Polyimide	CYTOP
LC (TD-1016XX)	35.8 °	16.5 °	68.8 °
Non-LC fluorinated monomer	7.0 °	2.4 °	16.1 °
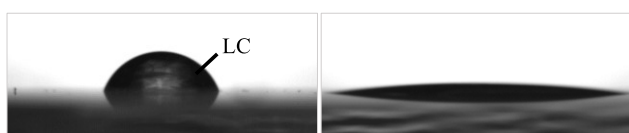
(a) CYTOP surface   (b) Polyimide surface

Fig. 4   LC droplet on substrate surface

that of the LC, because of the presence of fluorine atoms [7].

Moreover, we dropped the LC and monomer onto ultrasonically cleaned glass, CYTOP, and polyimide substrates. The droplet volume was 1 μL. We then measured the droplet contact angle of the droplet 2 s after dropping using contact-angle-measurement equipment (LSE-ME2, NiCK Co., Ltd.). We took the average of three measurements for both materials measurement.

Table 2 shows the LC and monomer contact angles. For both the LC and monomer, the contact angle on the CYTOP surface was higher than that on glass, and the contact angle on the polyimide substrate was lower than that on glass (Fig. 4). The LC contact angle on the CYTOP substrate was particularly high, which indicates that the LC exhibits low wettability toward the CYTOP surface. Furthermore, the monomer contact angle on each substrate was lower than that of the LC and the monomer exhibited high wettability on CYTOP, which is an excellent hydrophobic resin. This is attributed to the low surface tension of the monomer (Table 1) and a high affinity with CYTOP because they both contain fluorine.

5. Evaluation of the Morphologically Controlled LC Cell

5.1 Effect of Compatibility between LC and Monomer on Aggregation Control

We coated CYTOP and the polyimide film, and formed a lattice-shaped pattern on the substrate, as shown in Fig. 5(a). Here, we defined the CYTOP-coated area as the "wall area", and the polyimide-coated area as the "pixel area". We then constructed the LC cell using CYTOP/polyimide-coated substrate and a CYTOP-coated substrate. The LC/monomer
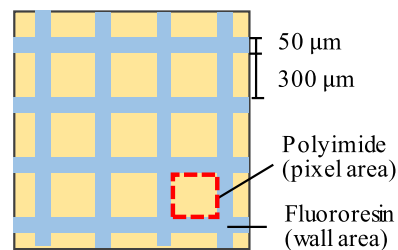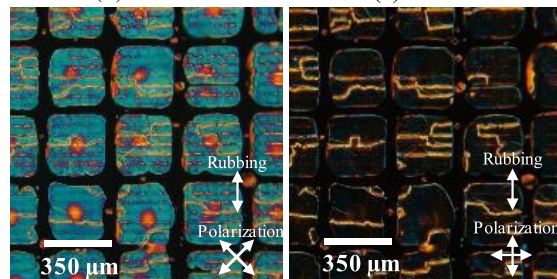

(a) Surface material pattern
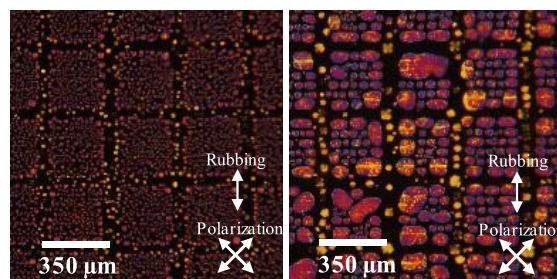
(b) at 60 °C   (c) at 25 °C

(d) at 5 °C   (e) at 5 °C
(Polarization at 45 °)   (Polarization at 0 °)

Fig. 5   Aggregation control of LC and monomer: (a) designed surface pattern and (b-e) polarized micrographs.

mixture was injected into the cell at 80°C and we observed the LC cell with a microscope using crossed-nicols polarizer while the mixture cooled off and a phase transition occurred.

Figure 5(b) shows a state that the LC droplets (observed as white-colored grains) had begun to separate from the isotropic liquid during cooling process. Then, deposited LC flowed from the wall areas to the pixel areas. This is attributed to the low wettability of the LC on CYTOP. Moreover, as the mixture temperature decreased to room temperature (25°C, Fig. 5(c)), the LC appeared much more from an isotropic liquid (black-colored regions). This is caused by the promotion of LC and monomer phase separation because the LC orientation order increases on cooling, similar to the phase separation, as shown in LC-polymer mixture systems [8]. Therefore, we confirmed that the isotropic liquid consisted of the LC and the monomer. On cooling the mixture further to 5°C (Fig. 5(d)), we observed the formation of a large LC droplet in each pixel area. We attribute this behavior to the higher surface tension of the LC than that of the monomer, which causes the LC to aggregate strongly in order to decrease its surface energy in the LC/monomer-mixture system. Moreover, by reconciling the rubbing direction and extinction direction (Fig. 5(e)), we

confirmed that the LC aggregation aligned to the rubbing direction. However, a little LC droplets remained at the wall areas. This is attributed to decreasing of fluidity of the LC by drop of the temperature. It is difficult to gather all LC droplets to pixel areas perfectly, but amount of remained LC can be reduced by cooling and separation of LC while the LC droplets at pixel areas get large and nearby droplets aggregate. Incidentally, the several stripes with about 50 μm widths in the pixel areas are irradiation traces with a laser beam scanning which is irradiated while selective removal of CYTOP on the substrate. In the pixels, we confirmed some disclination lines which were parallel to the irradiation traces. We considered that the alignment or thickness of LC is ununiformity, because of the low flatness at the pixel areas surface.

From these microscopy measurements, we confirmed that the LC aggregates in the pixel areas and the isotropic LC/monomer- mixture aggregates in the wall areas. In the phase separation, the LC mixture separates into the regions of high LC concentration and low LC concentration [8]. Therefore, we consider that separated LC in pixel areas includes some monomer. The phase change diagram is different from the solubility property, and it is difficult to observe and measure the dissolved monomer directly and quantitatively including in the pixel areas. On the other hand, it is easy to observe the separation of LC rich regions from the monomer rich regions, so we focused on the amount of LC dissolved in the monomer. In referring to the phase change diagram of the LC/monomer mixture by the temperature, we estimated approximately the amount of dissolved LC in the monomer. We consider that this discussion shows approximately how much amount the LC and monomer separate.

We investigated phase-transition temperature of the LC/monomer mixture at different monomer concentrations, from 10wt% to 90wt%, and constructed a phase diagram for the LC in the mixture, as shown in Fig. 6. The mixture becomes isotropic with increasing monomer concentration. This is caused by a decreasing the orientation order of LC because of mixing an isotropic material. In other word, the mixture including a lot of LC is easy to separate into nematic phase and isotropic phase, and the separated nematic phase regions include a small amount of monomer. We focused on the phase transition at different temperatures. At 25°C, the mixture showed isotropic phase when the monomer concentration was over 65wt%. The mixture at 25°C indicated isotropic phase as shown in Fig. 5(c). This mixture at wall areas contained a monomer concentration over 65wt%. In other words, up to 35wt% concentration of LC was remained in the wall area at 25°C. Similarly, at 5°C, the mixture was isotropic at monomer concentrations over 90wt%. The isotropic liquid at 5°C (as shown in Fig. 5(d)) contains up to 10wt% concentration of LC.

Moreover, in order to confirm the pretilt angle at the pixel areas, we manufactured another LC cell which is constructed by one polyimide substrate and one CYTOP substrate at same conditions as above. Then, we measured the angle-retardation properties using M-2000 (J.A.Woollam
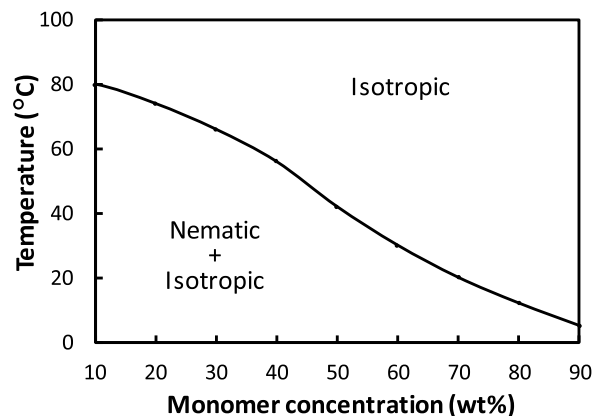

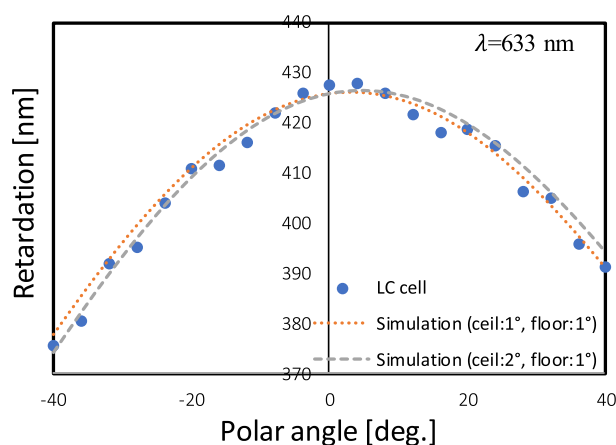**Fig. 6** LC phase diagram for the LC/monomer mixture.

Fig. 7 Angle-retardation properties and fitting results

Table 3 Fitting parameter

Elastic constant	K_{11}=10.47, K_{22}=10.00, K_{33}=22.34
Permittivity	$\varepsilon_{//}$=17.31, $\varepsilon_{\perp}$=4.63
Extraordinary light refractive index	n_e=1.617 (λ=633 nm)
Ordinary light refractive index	n_o=1.494 (λ=633 nm)
LC cell thickness	3.5 μm

Co., Ltd), and performed the fitting by simulation. We show the results in Fig. 7 and the fitting parameter in Table 3. As shown in Fig. 7, we confirmed that both pretilt angle of polyimide surface side and CYTOP surface side was just only 1° or 2°. Though CYTOP surface exhibits low wettability for the LC, the alignment mode of this LC cell was homogeneous type mode, not hybrid mode.

5.2 Formation of Polymer Walls by UV Irradiation

In Sect. 5.1, we showed that the LC and monomer aggregation increased with decreasing mixture temperature through the promotion of phase separation. Polymer molecular weight depends on the monomer concentration in radical polymerization. Hence, we predict that including LC in the monomer affects the polymer-walls formation by UV irradiation and photopolymerization. To confirm this, we exposed
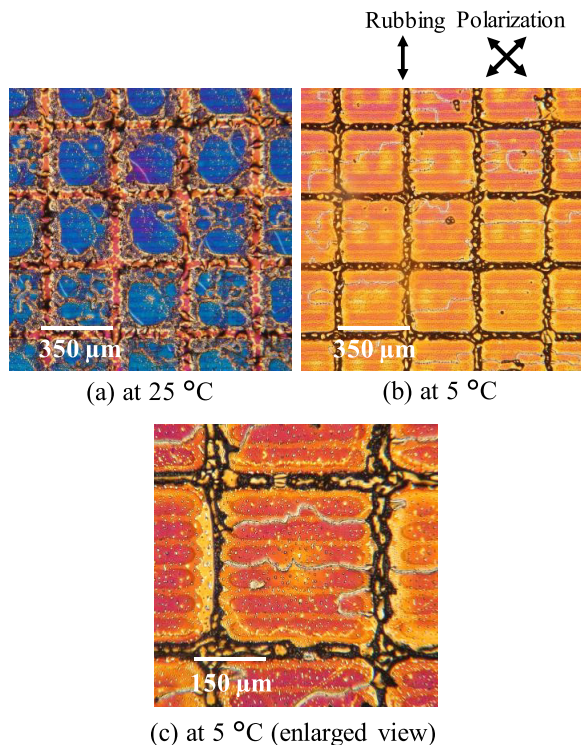
(a) at 25 °C   (b) at 5 °C

(c) at 5 °C (enlarged view)

Fig. 8   Monomer photopolymerization by UV irradiation.

(a) Polarization at 45°   (b) Polarization at 0°

(c) Pressure added from top   (d) 20 V applied voltage

Fig. 9   Properties of the LCD.

the entire LC-cell surface to UV irradiation (365 nm wavelength, 1500 mJ/cm^2 intensity) to initiate photopolymerization; this process was performed while cooling the cell to 25 and 5°C (Fig. 5(c-d)), which lead to different extents of LC and monomer aggregation in the pixel areas and wall areas, respectively.

Microscope image of the LC cell after UV irradiation are shown in Fig. 8. UV irradiated LC cell at 25°C showed colored image on the lattice-patterned wall areas which is derived from birefringence of LC (see Fig. 8(a)). The monomer show no birefringence; consequently, the LC causes this birefringence on the wall areas. Thus, a lot of LC was remained in the polymer walls, which is attributed significant concentrations of LC dissolved in the isotropic-mixture monomer aggregates before UV irradiation, as discussed in Sect. 5.1. After cooling to 5°C and UV irradiation, polymer walls exhibited less birefringence, as shown in Fig. 8(b). We confirms that decreasing the temperature and, consequently, promoting phase separation can be used to decrease the quality of LC in the polymer walls. The structure of the polymer walls, which join the two substrates, must have a high bond strength to sustain the cell thickness; we showed that decreasing the temperature and promoting phase separation of the LC/monomer mixture is effective for producing a strong wall structure by minimizing the LC content in the walls. On the other hand, we confirmed a large number of white particles at the pixel areas (see Fig. 8(c)). We attributed these particles to influence owing to remained monomer, oligomer or polymer. Moreover, some LC were remained in the polymer walls. We consider
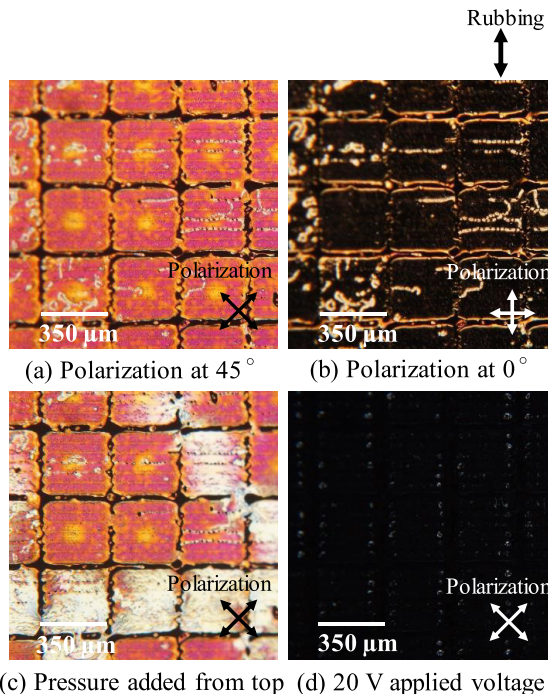
that these LC dissolved slightly in a monomer before photopolymerization of monomer. As for the problems, it can be pointed out to suppress their deposition.

To evaluate the suitability of polymer-walls formation technique for application of flexible LCDs, we observed the properties of the trial LC cell in operation as an optical-modulation device. Here, we focused on three properties: maintaining the LC orientation to the rubbing direction, the bonding effect of both substrates on the polymer walls, and driving of the LC by applying a voltage to the electrodes. Microscopic image of the LC cell, exposed to UV irradiation at 5°C are shown in Fig. 9.

Figure 9(a, b) show polarized microscope images of LC cells after formation of polymer wall structure. The extinction position of the LC in the pixel areas consists with the rubbing direction, which confirms that the LC was orientated toward the rubbing direction even after photopolymerization of monomer. The LC was orientated parallel to the rubbing direction after formation of the polymer walls. Therefore, we found that some of the LC in contact with the polymer walls showed birefringence perpendicularly to the rubbing direction. This is attributed to a change in the orientation of the LC at polymer walls interface because of their anchoring force.

Figure 9(c) shows a polarized microscope image of LC cell while we pressed cell top with a finger in order to confirm that the polymer-walls structure connected the upper and lower substrates in the LC cell. Some LC flowed from the cracks of the polymer wall, so the cell gap changed locally. However, at the point where continually connected polymer wall is formed, the behavior of LC fluidity beyond the walls cannot be observed. This means that upper

and lower substrates was bonded by polymer walls. Moreover, the result of observation after press was much same as Fig. 9(a), which was microscope image before press. Hence, this polymer-walls structure has resistant for pressure added from the top. It is necessary to be improved so that the polymer wall structure is connected continually.

Finally, we confirmed voltage driving of LC in the cell. When applied voltage is 20 V, we obtained a black-colored image because LC molecules inside polymer wall is aligned toward vertical direction, as shown in Fig. 9(d). Hence, we concluded that the binding effect of LC was weak at the LC/polymer interface because decreasing the temperature promoted phase separation of the LC and monomer.

These results show that control of the monomer aggregation by utilizing of surface wettability like a lattice-patterned CYTOP/polyimide film is useful for bonding spacer of flexible LCDs.

6. Conclusions

We proposed that fabrication of the LC cell having pattern composed of the highly hydrophobic fluororesin and hydrophilic polyimide on substrate in order to promote phase separation between LC and monomer. The mixture of LC and monomer is separated by difference in wettability on the substrate surface and their varying compatibility as a function of temperature. By means of proposed method, we achieved that significant suppression of residual LC on the wall areas and promotion of LC aggregation on the pixel areas are possible. As a result, the monomer and LC aggregation was concentrated on the wall areas and on the pixel areas, respectively. The reasons are that fluororesin repels LC molecules and low temperature increased the separation among LC and monomer molecules. The reorientation of LC was maintained despite of applied voltage. In addition, polymer-walls structure could be partitioned into individual pixels by UV irradiation to the entire LC-cell surface. For more exact phase separation of the LC and the monomer, the development of materials to coated on the substrate surface will be necessary. Furthermore, as our future problem, we are going to analyze the residual monomer, oligomer or polymer in the pixel areas. We expect that this polymer-walls formation method is effective for developing high-quality flexible LCDs.

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