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Control of Pretilt Angle in Liquid Crystal and Photocurable Monomer System

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The pretilt angles of liquid crystals (LCs) could be controlled over the range, 0° to 90°, using LC/photocurable monomer (NOA65) mixture system through UV irradiation. The pretilt angles could be controlled using LC/NOA65 mixture in planar polyimide coated LC cell, by changing the mixture ratio ranging from 99.9/0.1 to 99.0/1.0 and UV irradiation time (10 and 20 min). Planar and tilted alignment was observed in LC/NOA65 mixture of 99.9/0.1 and 99.8/0.2, respectively, after UV irradiation for 20 min. Finally, homeotropic (or vertical) alignment was observed in weight ratio of over 99.7/0.3. The LC alignment behavior was well correlated with the wettability of the alignment films due to the surface morphology on the alignment layer surfaces by photopolymerization-induced phase separation. This study contributes to the latest efforts to develop new method for pretilt angle control.

Keywords Liquid crystal; phase separation; photocurable monomer; pretilt angle

1. Introduction

Continuous control of the pretilt angle of liquid crystal (LC), including intermediate pretilt angle between homogeneous planar and homeotropic (or vertical), has been extensively studied due to the scientific and technical interest in liquid crystal displays (LCDs). In particular, it is desired to improve image quality and electro-optical (E-O) performance. Recently, various techniques have been developed to control the continuous pretilt angle of LCs over a wide range on the alignment layer surfaces, so as to be applied in several LCD modes; rubbing of the polyimide surfaces [1, 2], irradiation of the photosensitive alignment layer with UV light [3], ion beam techniques using organic/inorganic alignment layer [4–7],

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blending and stacking of the alignment layers [8–16], nano/micro-structured patterns using lithographic techniques [17, 18], or nanoparticle-polyimide composites surface [19].

Recently, we found a novel method to obtain the homeotropic alignment using LC and photocurable monomer mixture systems, in which the homeotropic alignment was induced on the phase-separated polymer thin film through UV irradiation [20].

In this study we found that the pretilt angles could be continuously controlled further by changing the LC/photocurable monomer mixture ratio and UV irradiation time. Moreover, changes of the pretilt angles were found to be strongly related to changes of the surface properties. The surface properties of alignment layer films giving different pretilt angles were investigated using contact angle measurements and scanning electron microscopy (SEM). The electro-optical performance of the LC cells fabricated using UV treated alignment layer film is also included.

2. Experiment

2.1 LC Alignment Process and LC Cell Assembly

We prepared a mixture of a negative dielectric anisotropic LC, MLC-7026-000 (n_e = 1.5577, n_o = 1.4755, and $\triangle\varepsilon = -3.7$, Merck Co., Pyeongtaek, Korea) and photocurable monomer, NOA65 (Norland Products Inc., Cranbury Township, USA), in a weight ratio; 99.9/0.1, 99.8/0.2, 99.7/0.3, 99.6/0.4. 99.5/0.5, 99.4/0.6, 99.3/0.7, 99.2/0.8, 99.1/0.9, and 99.0/1.0. The pre-imidized alignment agent (RN-1720 as a planar alignment agent, Nissan Chemical Ind., Tokyo, Japan) film was fabricated by spin-coating (3000 rpm, 20 sec) onto indium-tin-oxide (ITO) coated glass substrates. The RN-1720 films were baked at fully baked at 230°C for 30 min. These polymer films were rubbed using a rubbing machine (RMS-50-M, Nam Il Optical Components Corp., Incheon, Korea). Antiparallel LC cells were fabricated using the rubbed polyimide films onto ITO coated glass slides substrates together antiparallel with respect to the rubbing direction using spacers with thicknesses of 50 μm. The LC and photocurable monomer mixtures were infiltrated into LC cell made from in planar polyimide coated antiparallel LC cell. The LC and photocurable monomer mixture cells were then exposed under an unpolarized UV light for 10 and 20 min at 30 mW/cm^2 ($\lambda\sim$365 nm). Pre-imidized alignment agent (SE-1211 as a vertical alignment agent, Nissan Chemical Ind., Tokyo, Japan) films were fabricated by spin-coating (3000 rpm, 20 sec) onto ITO coated glass substrates to compare electro-optical performance. The SE-1211 films were prebaked at 100°C for 30 min and then were fully baked at 250°C for 60 min. This polymer films also were rubbed using a rubbing machine. The cell was filled with MLC-7026-000, in isotropic state to avoid creating flow alignment by the capillary action. The manufactured LC cell was sealed with epoxy glue.

2.2 Instrumentation

For scanning electron microscope (SEM) and contact angle measurement, the sample was made by separating ITO coated glass substrates of LC cell and removing the LC on substrates. The contact angles of distilled water on the sample films were determined with a Kruss DSA10 contact angle analyzer equipped with drop shape analysis software. The cell gap was measured before filling the LC and photocurable monomer mixture using a spectrophotometer (S2000, Ocean Optics Inc., Dunedin, USA). The polarized optical microscopy (POM) images of the LC cell were taken using an optical microscopy

(ECLIPSE E600 POL, Nikon, Tokyo, Japan) equipped with a polarizer and digital camera. Electro-optical properties of the LC cells were investigated using optical apparatus equipped with a He-Ne laser, polarizer, analyzer, and a photodiode detector. The pretilt angle of LCs with respect to the planar direction in antiparallel LC cell was measured by modified crystal rotation method using PAMS series (Sesim Photonics Technology, Uiwang, Korea) [21]. The voltage-transmittance (V-T) was measured from the LC cell using the same method as that reported by others [22, 23]. The threshold voltage (V_{th}) in the V-T curve are defined as the voltages at which the transmittance was increased to 10% of the initial transmittance value [22, 23]. The rising (T_r) and falling (T_f) response times for the white-to-black and black-to-white changes, respectively, are defined as the time to transition from 10% to 90% transmittance and vice versa [22, 23]. The total response time (T_t) is determined by the average of T_r and T_f.

3. Results and Discussion

Figure 1 shows schematic diagram of LC cell manufacture process. First of all, indium-tin-oxide (ITO) coated glass substrates were coated with planar polyimide (RN-1720), and then baked (Fig. 1(a)). These glass substrates were rubbed one direction (Fig. 1(b)). LC cell was fabricated with this rubbed two substrate together antiparallel with respect to the rubbing direction, and then the LC and photocurable monomer (NOA65) mixture was infiltrated into this cell as shown in Fig. 1(c). In this state, LC mixture cell was irradiated by UV light. Then, the photocurable monomer is cured, and the LC and photocurable monomer mixture undergoes photopolymerization-induced phase separation in the vertical direction,

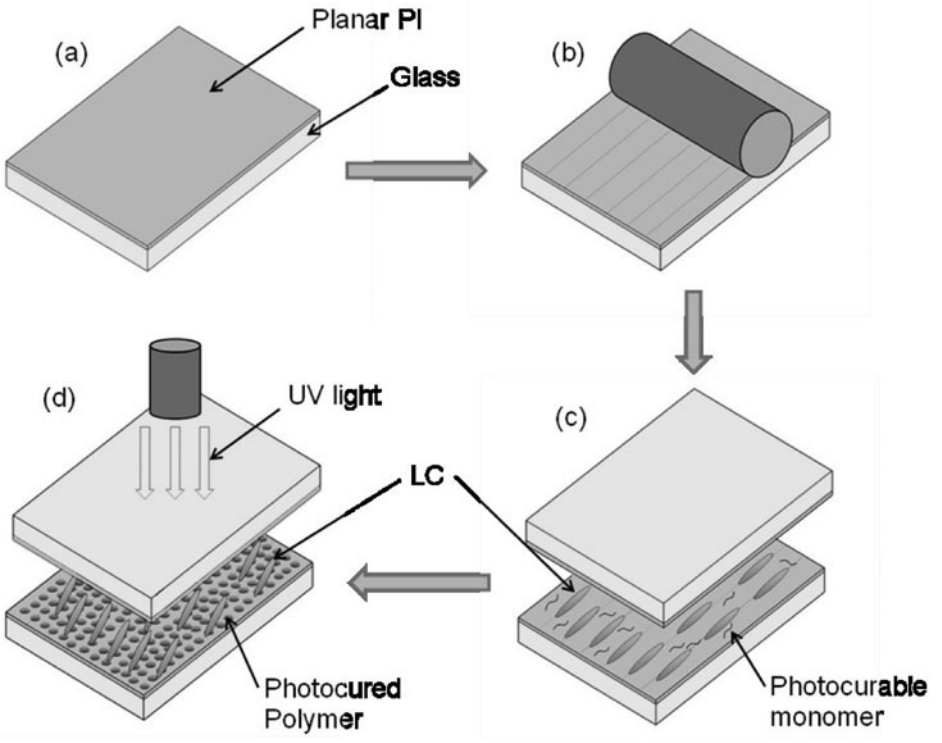

Figure 1. Schematic diagram of LC cell manufacture process.

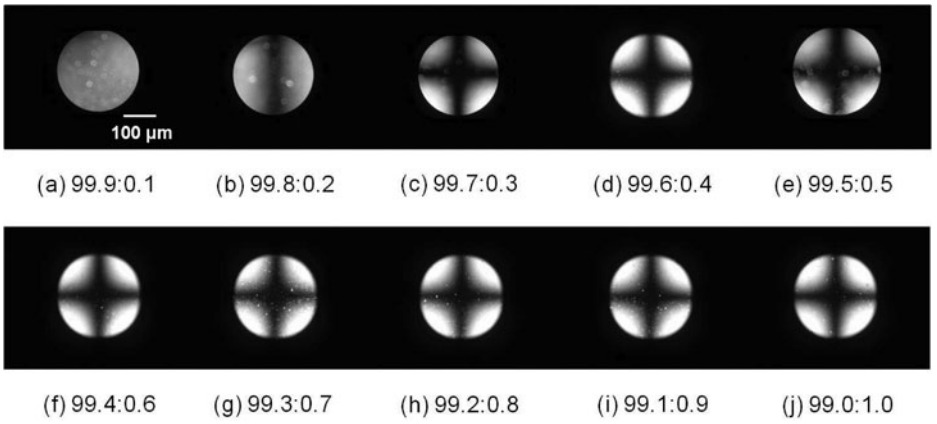

Figure 2. Conoscopic POM images of the LC/NOA65 cells fabricated with planar polyimide films onto glass substrates with an intensity of 30 mW/cm^2 ($\lambda\sim$365 nm) for 20 min under the following a weight ratio of the LC/NOA65; 99.9/0.1, 99.8/0.2, 99.7/0.3, 99.6/0.4. 99.5/0.5, 99.4/0.6, 99.3/0.7, 99.2/0.8, 99.1/0.9, and 99.0/1.0.

as described in previous paper [20]. At a certain UV irradiation condition, a NOA65 pattern forms on the polyimide films and the pretilt angles could be controlled on the surface composed of the planar polyimide region and phase separated NOA65 region as shown in Fig. 1(d).

Figure 2 shows conoscopic POM images of the LC/NOA65 cells fabricated with planar polyimide films onto glass substrates with an intensity of 30 mW/cm^2 ($\lambda\sim$365 nm) for 20 min under the following a weight ratio of the LC/NOA65; 99.9/0.1, 99.8/0.2, 99.7/0.3, 99.6/0.4. 99.5/0.5, 99.4/0.6, 99.3/0.7, 99.2/0.8, 99.1/0.9, and 99.0/1.0. At first, as shown in Fig. 2(a), homogeneous planar alignment was observed in NOA65 weight ratio of 0.1%. Tilted alignment was observed in NOA65 weight ratio of 0.2% as shown in Fig. 2(b). In the cases when NOA65 weight ratios are more than 0.3%, vertical alignments were observed as shown in Figs. 2(c)–(j). The maltese cross pattern in conoscopic POM images of the UV treated LC cells with a photoirradiation time of 20 min, shows a significant difference in LC orientation on the UV treated cell according to the mixing ratio of the LC/NOA65.

To investigate the dependence of UV irradiation time on LC alignment behavior, we decreased the UV irradiation time to 10 min. Fig. 3 shows conoscopic POM image of the LC cell according to the LC/NOA65 weight ratio for 10 min by UV irradiation. As shown in Fig. 3(a), planar alignment was observed in NOA65 weight ratio of 0.1%. Tilted alignment was observed in NOA65 weight ratio of 0.2% and 0.3% as shown in Figs. 3(b) and (c), respectively. However, the clear tilted alignment was not observed, because of incomplete phase separation between LC and NOA65 the interfaces for 10 min by UV irradiation. The photoproducts including monomer remained in the bulk LC might become defect image after UV exposure of 10 min. In the cases when NOA65 weight ratios are more than 0.4%, vertical alignments were observed as shown in Figs. 3(d)–(j).

Figure 4 shows the effect of the mixing ratio on the pretilt angle of the LC/NOA65 cells fabricated with rubbed planar polyimide (RN-1720) films. Previously, when antiparallel LC cells were prepared using rubbed RN-1720 films, the pretilt angle was found to be very low about 0°. On the other hand, UV irradiation can change from the planar alignment to tilted or vertical alignment using a larger weight percent of the NOA65 and a longer UV irradiation time. For example, as the weight percent was increased from 0.1% to 0.3%, the

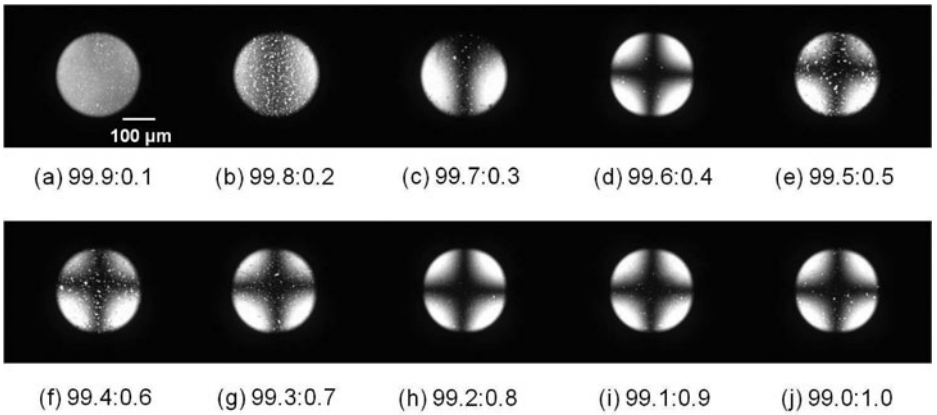

Figure 3. Conoscopic POM images of the LC/NOA65 cells fabricated with planar polyimide films onto glass substrates with an intensity of 30 mW/cm^2 ($\lambda\sim$365 nm) for 10 min under the following a weight ratio of the LC/NOA65; 99.9/0.1, 99.8/0.2, 99.7/0.3, 99.6/0.4. 99.5/0.5, 99.4/0.6, 99.3/0.7, 99.2/0.8, 99.1/0.9, and 99.0/1.0.

pretilt angles on the LC/NOA65 cell with UV irradiation for 10 min increased gradually from 0° to 85°. When the weight percent was increased to 0.4%, the pretilt angle increased drastically to approximately 90°. Moreover, when the irradiation time was 20 min, as the weight percent was increased from 0.1% to 0.2%, the pretilt angles on the UV treated LC/NOA65 cell increased gradually from 0° to 52°. When the weight percent was increased to 0.3%, the pretilt angle increased drastically to approximately 90°. Therefore, we could control the pretilt angle on the LC/NOA65 cells at appropriate UV irradiation time by changing the mixing ratio of LC/NOA65.

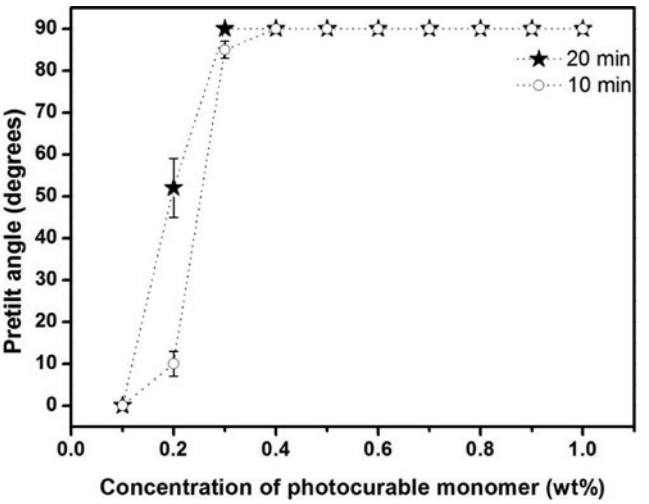

Figure 4. Pretilt angles of the UV treated LC/NOA65 mixture cells according to the mixing ratio of LC/NOA65 with an intensity of 30 mW/cm^2 for 20 min.

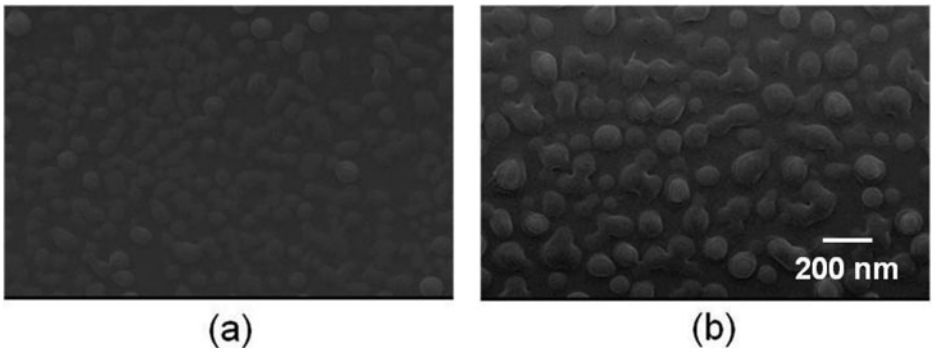

Figure 5. SEM images of the substrate of the LC/NOA65 ((a) 99.8/0.2 and (b) 99.7/0.3) mixture cell fabricated with planar polyimide films with an intensity of 30 mW/cm^2 for 20 min.

The surface morphology and wettability of the film were measured using scanning electron microscopy (SEM) (Fig. 5) and a contact angle measurement (Fig. 6), respectively, in order to confirm the mechanism of the pretilt angle control in the LC/photocurable monomer mixture cell via phase separation. The substrates of the LC cells were carefully separated and the LC on the substrates was selectively removed using solvents.

Figures 5(a) and (b) show the SEM images of the substrate of the LC/NOA65 (99.8/0.2 and 99.7/0.3) mixture cell with UV irradiation for 20 min, respectively. In those images, the gravel texture from the phase separated NOA65 can be observed at the substrate. The average height of gravel textures was about 20 nm. The substrate of the LC/NOA65 mixture cell are composed of the planar polyimide region and phase separated NOA65 region. However, noticeable difference in the SEM image was not observed according to the weight percent of the LC/NOA65, if any. To compare the surface morphology, we

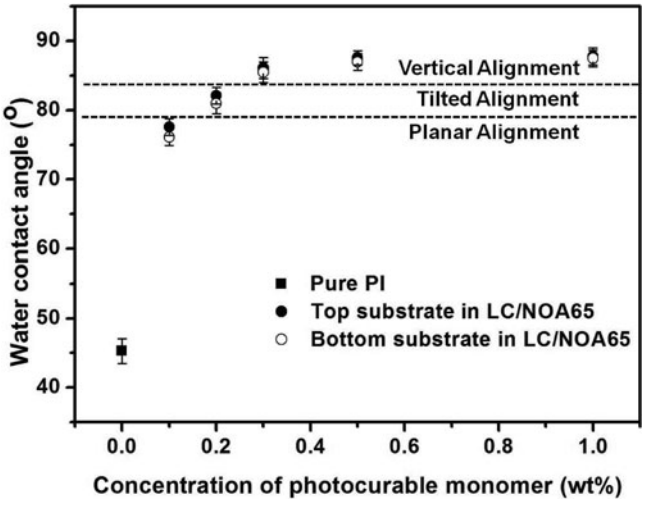

Figure 6. Water contact angles of the rubbed polyimide film and the top and bottom substrate of the LC/NOA65 mixture cell made from rubbed polyimide films according to the mixing ratio of LC/NOA65 with an intensity of 30 mW/cm^2 for 20 min.

performed a contrast experiment using substrates coated with rubbed planar polyimide film. The rubbed planar polyimide film is smooth without any noticeable patterns (data not shown). To investigate the mechanism of the pretilt angle control, it is essential to know the interaction between LC molecules and alignment layer surfaces. In this study we intentionally used a nematic mixture LC with a negative dielectric anisotropy, MLC-7026-000, because pretilt angle could not be controlled using pure LC such as 5CB and MBBA. Unfortunately, the detailed structures and compositions of this LC are not available from the company. Generally, LC molecules are composed of cyclic mesogenic structure such as phenyl and/or cyclohexyl groups, and polar terminal groups (positive LC, $\Delta\varepsilon > 0$) or polar lateral groups (negative LC, $\Delta\varepsilon < 0$) such as CN, F, or other dipolar groups[24]. Possibly the π-π and dipole-dipole interactions between the mesogenic groups of MLC-7026-000 and the aromatic, polar groups in the RN-1720, NOA65 would affect the pretilt angle of the LC molecules, respectively. These SEM results confirm that the gravel patterns on rubbed polyimide films were obtained through the phase separation process via UV irradiation. As a result, pretilt angle could be controlled in the LC/NOA65 cells due to the competition between NOA65 gravel region having vertical alignment characteristics via steric repulsions between LCs and protrusion surfaces and polyimide region having planar alignment characteristics via electronic interaction such as dipole-dipole interaction between LCs and polyimide surfaces, as reported by other group [12].

The water contact angles on the polymer films were measured according to the mixture ratio of LC and NOA65 in order to investigate the effect of wettability on the pretilt angle of LCs (Fig. 6). The water contact angles on the polymer films were determined in static mode. The water contact angle about 45.3° on the rubbed RN-1720 film was observed. The water contact angles on the substrates of the UV treated LC/NOA65 cells made from RN-1720 films for 20 min increased with increasing the NOA65 weight percent; They are 77.6 and 76.1, 82.1 and 81.0, 86.1 and 85.5, 87.6 and 87.0, 87.8 and 87.5° in water contact angles of the top and bottom substrates in 99.9/0.1, 99.8/0.2, 99.7/0.3, 99.5/0.5, and 99.0/1.0, respectively. In this system, polymer aggregates resulting from the phase separation of LC/NOA65 mixture via photopolymerization increase the surface roughness

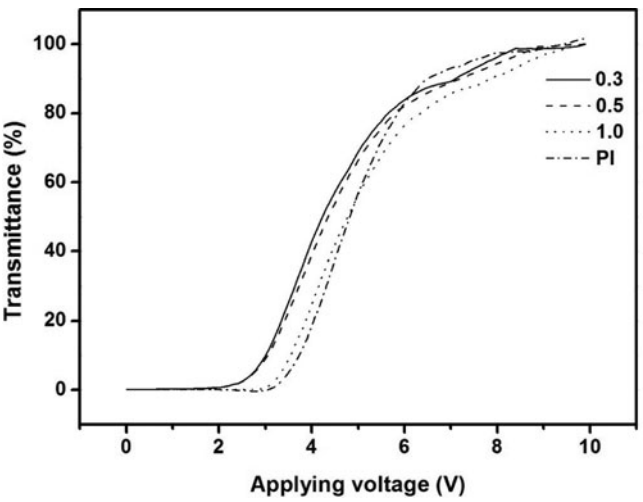

Figure 7. Voltage-transmittance (V-T) curve of the LC cells fabricated using the UV treated LC/NOA65 mixture and rubbed polyimide film with an intensity of 30 mW/cm^2 for 20 min.

Table 1. Threshold voltage and response time values of the LC cell

Sample	Threshold voltage (V) V_{th}	Response time (ms) T_r	T_f	T_t
LC/NOA65(99.7/0.3)	3.1	10.6	4.4	7.5
LC/NOA65(99.5/0.5)	3.2	10.6	3.2	6.9
LC/NOA65(99.0/1.0)	3.6	9.2	7.6	8.4
SE-1211	3.7	10.2	9.6	9.9

as previously shown in this manuscript and, thereby, induce a higher water contact angle. Alignment layer surfaces having water contact angles smaller than about 76.1° such as RN-1720 and 99.9/0.1 show planar alignment behavior, whereas the other alignment layer surface having water contact angle larger than about 85.5° such as 99.7/0.3, 99.5/0.5, and 99.0/1.0 show vertical alignment behavior. Alignment layer surfaces having intermediate water contact angle about 81.0–82.1° such as 99.8/0.2 show tilted alignment behavior. This trend is shown very well in Fig. 6. The changes in pretilt angle are strongly related to the changes in wettability on the phase separated photocured polymer films, as described previously [25–27]. Therefore, the pretilt angle on the UV treated polymer films depends strongly on the wettability of the polymer surfaces.

The electro-optical performance of the LC cells fabricated using the UV treated LC/NOA65 mixture cell for 20 min and rubbed polyimide film having vertical alignment characteristics (SE-1211 from Nissan Chemical Ind., Tokyo, Japan) was determined by measuring the voltage-transmittance (V-T) curve and response time values using the same condition (Fig. 7 and Table 1). In this study, same nematic LC with a negative dielectric anisotropy, MLC-7026-000, which shows a suitable switching behavior for vertical alignment (VA) mode, was used. The LC/NOA65 cell has a lower operating voltage and faster response time than those of the LC cell made from the rubbed polyimide film. For example, the V_{th} values (3.1–3.6 V) of the LC/NOA65 mixture cell were lower than that of the LC cell fabricated with the rubbed polyimide films (V_{th}: 3.7 V). The response times, T_t of 6.9–8.4 ms, for the LC/NOA65 mixture cell are faster than that, T_t of 9.9 ms, for the rubbed polyimide film. The electro-optical performance of the LC cell from the UV treated LC/NOA65 mixture was as good as or even better than that from the rubbed polyimide film, which suggests that these novel alignment films can be used for LC display applications. Therefore, we believe that these polymer films can be good candidates as an alignment layer for flexible LC display applications, such as VA mode.

4. Conclusions

The pretilt angle of liquid crystal (LC) was controlled using LC/photocurable monomer (NOA65) cells made from rubbed planar polyimide films by changing the mixing ratio and UV irradiation time. A lower pretilt angle was observed for the LC cells made from the UV treated polymer films with a smaller content of the NOA65 and shorter irradiation time. Pretilt angle could be determined by competition between polyimide having planar alignment characteristics (low pretilt angle) and phase separated NOA65 polymer having vertical alignment characteristics (high pretilt angle). The pretilt angle correlated well with the wettability of the alignment films due to the surface morphology such as gravel

patterns on the alignment layer surfaces by the UV irradiation process. Good electro-optical properties were observed for the LC cells made from the UV treated polymer films. For example, the V_{th} and response time of these LC cell were 3.1–3.6 V and 6.9–8.4 ms, respectively, indicating that these LC cells were similar to those fabricated from rubbed polyimide films, indicating that the LC cell can be used for LC display applications, including flexible displays.

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