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Enhanced surface anchoring energy for the photo-alignment layer with reactive mesogens for fast response time of liquid crystal displays

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Abstract

We propose a method for enhancing the surface anchoring energy in photo-alignment (PA) through a two-step ultraviolet (UV) exposure process using reactive mesogens (RM) for fast response time characteristics of liquid crystal displays. We establish the azimuthal alignment direction through the first linearly polarized UV exposure process, as the conventional PA method does. We then achieve the stable alignment and strong surface anchoring energies of our method through the second unpolarized UV exposure process, which polymerizes the RM monomers within the vertical alignment layer. As a result, the fast response time characteristics are remarkably improved, and thermal stability is obtained.

(Some figures may appear in colour only in the online journal)

1. Introduction

Liquid crystal displays (LCDs) have been studied and used for a wide range of display applications, such as mobile phones, monitors and television sets, due to their superior display performance, including high transmittance and high contrast ratio with low power consumption. For high image quality, uniform alignment is one of the most important factors. Many alignment methods have been developed to obtain uniform alignment of LCs, including directional rubbing of polymer films, evaporation of silicon monoxide (SiO_x), ultraviolet (UV) exposure of photopolymers, ion beam treatment on polymer substrates, and surface modification with surfactants or micro-groove patterns [1–5]. Among these methods, the rubbing method is the most widely used and provides the best electro-optic performance of LC switching with good thermal stability [6, 7]. However, the corresponding impurities, electrostatic charges and mechanical damage may result in deterioration in the quality of LC switching. Additionally,

it is very difficult to achieve multi-domain alignment of the LCs [8].

To overcome these problems, non-contact alignment methods have been developed, especially the photo-alignment (PA) method, which has various advantages compared with the rubbing process. In the PA method, homogeneous alignment of the LCs can be achieved using anisotropic polymer films. The anisotropic distribution of the PA layer is generated by illumination with polarized UV light. However, the PA method still has other problems, such as weak surface anchoring energies and unstable pretilt angles, which cause slow response times and reverse tilt domains [9–13]. A photosensitive polyimide (PI) is known to produce homogeneous alignment of the LC molecules perpendicular to the linearly polarized (LP) UV light, due to chemical reactions of photo-degradation [14]. The LPUV light breaks the PI backbones lying parallel to the UV polarization at the surface, revealing the PA effects [15–17]. The surface anisotropy that arises from the preferential bond breaking by a LPUV light perpendicular

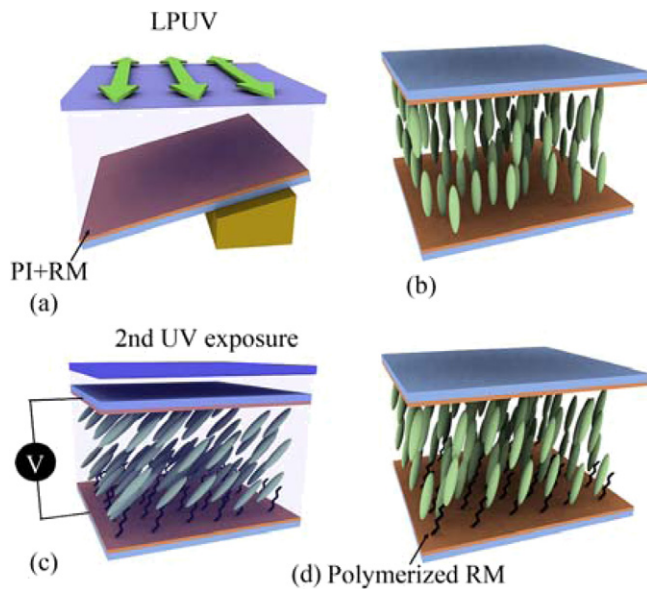


Figure 1. Schematic diagrams of the proposed two-step PA method.

to the PI backbones is small. Consequently, the azimuthal anchoring energy of an LC layer attached to this surface would also be small [18].

In our previous work, we reported the surface-controlled patterned vertical alignment (SC-PVA) mode with fast response time achieved by using a PI alignment layer mixed with UV-curable reactive mesogens (RMs) [19]. The vertical alignment (VA) PI layers with RM monomers were exposed to UV light under an applied electric field, and the RM monomers within the VA layer were polymerized along the LC directions, which were determined by the oblique electric field's one with patterned electrodes. In this case, the directionally polymerized RMs produced a rotational preference in the azimuthal direction during switching of the LC molecules. As a result, the response time could be reduced because direct switching occurred without a reorientation process of the LC molecules in the PVA mode.

In this paper, we propose an advanced PA method with strong anchoring energies achieved through a two-step UV exposure process using a mixture of VA-PI-alignment material and RMs. The azimuthal direction of the LC molecules is established through the first UV exposure step, and then the surface anchoring energies are enhanced by the second UV exposure step, which polymerizes the RM monomers within the alignment layer along the LC directors. As a result, fast response time characteristics are achieved in the VA mode.

2. Experimental

Figure 1 shows the schematic diagrams of the proposed PA process. In our study, we used cleaned glass substrates coated with indium tin oxide (ITO) for electrodes. For alignment materials, we prepared a mixture of a vertical polyimide (VPI) material (AL60101, JSR) whose chemical bonds are dissociated in the direction of (LPUV) light, an RM monomer (RM 257, Merck) with 2 wt%, and a photo-initiator (IRGACURE 651 from Ciba Chemicals) that can enhance the

photoreactivity according to UV light. The mixture was spin-coated on both ITO glasses at the rate of 1000 rpm for 10 s, and then 3000 rpm for 20 s. The alignment layer was pre-baked at 80 °C for 10 min followed by curing at 180 °C for 1 h. To induce the alignment direction of the LC molecules, the prepared alignment layers were irradiated with the obliquely incident LPUV light for 15 min as the first UV exposure step, as shown in figure 1(a). The LPUV light establishes the azimuthal direction of the LC molecules by dissociating the polymer chains of the VPA material, and the obliquely incident condition at 30° to the alignment surface is provided for the pretilt angle of the LC molecules. Subsequently, two substrates were assembled with a 3 μm glass spacer, and the nematic LC, MLC 6610 ($\Delta\epsilon = -3.1$, $\Delta n = 0.0996$, E Merck), was injected (figure 1(b)). At this state, the pretilt angle was almost 89.7°, which is not enough to provide unidirectional alignment without reverse tilt domains under an applied switching voltage, as the conventional PA method does using only photo-polymers. To increase the pretilt angle and surface anchoring energy, we exposed the second-step UV light onto the PA-VA LC cell with applied voltage, as shown in figure 1(c). The RM monomers within the VPI layer were thereby completely polymerized along the LC direction, depending on the applied voltage. After removing the applied voltage, the VA LC cell had an increased pretilt angle.

3. Results and discussion

In our studies, we established the azimuthal angle of LC molecules for the uniform alignment of LC molecules using LPUV exposure onto the alignment-mixture layer with VPI and RMs. The used VPI is a positive type whose polymer chains are dissociated with the parallel direction to the polarized axis of the LPUV light. After exposure to the LPUV light, non-dissociated polymer chains perpendicular to the absorption axis of the LPUV generate the anisotropy that induces the alignment direction of the LC molecules near the layer. Figure 2 shows the anisotropy of the alignment layer surface using its retardation. Surface anisotropy is induced after the first UV exposure process; however, it is not large enough to determine the LC direction under the applied voltage, as conventional PA methods do. To increase the surface anisotropy, we introduce the second UV exposure process after the LC filling process under the applied voltage. When an electric field is applied to the VA LC cell, the LC molecules fall down to the alignment substrate, with a long stabilizing time, along the azimuthal angle, which was determined through the first UV process, and the RM monomers within the VPI alignment layer align along the LC molecules. The RM monomers are dissolved in the LCs, and they are movable due to the liquid crystalline property of the RM [18, 20]. Subsequently, the cell is exposed to the unpolarized UV light, causing the RM monomers to be polymerized within the alignment layer along the LC directors. By measuring the retardation of the alignment layer, we detach the top and bottom substrates of the VA LC cell and washed the LC out by hexane. The directionally polymerized RM

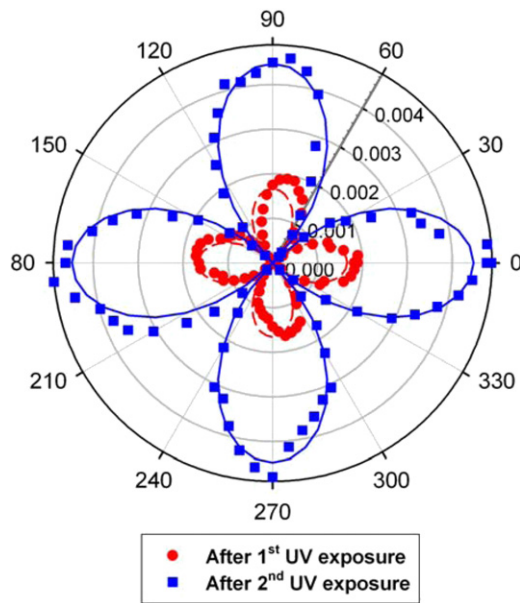


Figure 2. Birefringence of the alignment layer after the first LPUV exposure process, and after the second UV exposure process.

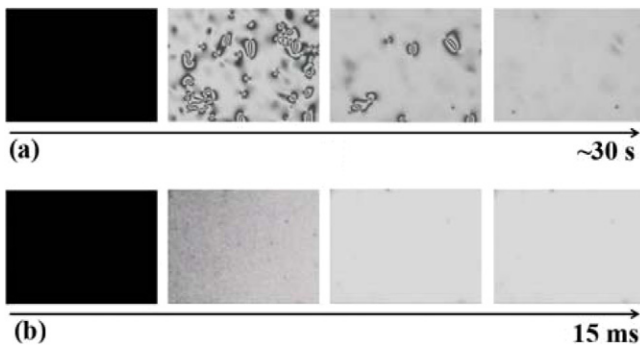


Figure 3. Time-resolved microscopic textures for the photo-aligned VA mode sample (a) after the first LPUV exposure process and (b) the second UV exposure process.

polymers after the second unpolarized UV exposure increase the surface anisotropy to about five times larger than the alignment layer after the first LPUV exposure process, as shown in figure 2.

Figure 3(a) shows the time-resolved microscopic textures under crossed polarizers for the LC cell after the first LPUV exposure process. When 10 V is applied, the LC molecules fall down to the substrate oriented in various directions, and then they reorient to the alignment direction after a long time. The measured pretilt angle is about 89.7°. Therefore, when the voltage is applied, it is easy to observe disclination lines and reverse tilt domains in the whole area of the sample during the reorientation of the LC molecules. However, the second-UV-exposed sample shows the direct falling down process due to the induced pretilt angle from the directionally polymerized RMs, as shown in figure 3(b). We obtained a uniform texture without any disclination lines and reverse tilt domains, and the reorientation time for stabilization of the LC molecules was dramatically enhanced (reduced). In the experiment, the response times of the VA samples before and after the second

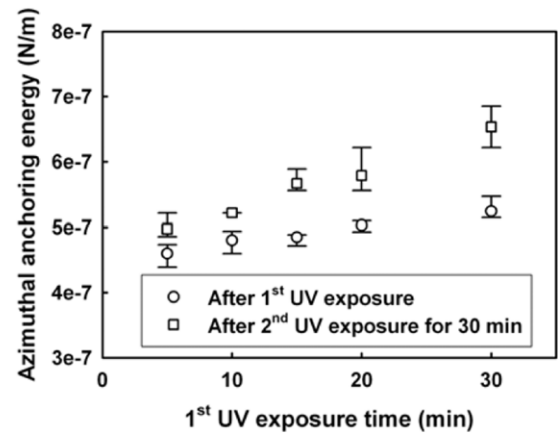


Figure 4. Azimuthal surface anchoring energies as a function of the first LPUV exposure time. The two-step PA-VA cell undergoes the second UV exposure for 30 min.

UV exposure process were 30 s and 15 ms, respectively, and the measured pretilt angle was 87°.

For uniform alignment of LC molecules, a strong surface anchoring energy is essential as are pretilt angles. Figure 4 shows the azimuthal anchoring energies depending on the UV exposure time for the LC cells. We measured the azimuthal anchoring energy using a twisted LC cell [21]. After the first UV exposure of the cell, the azimuthal anchoring energies increase slightly with increasing UV exposure time. That is because the surface anisotropy is increased by the remaining perpendicular PI polymers, after breaking the polymers that are parallel to the LPUV light. The increase in the anchoring energy between 5 min and 10 min exposure times was about 13.8%, which is too small for aligning the LC molecules unidirectionally. However, after the second UV exposure process for 30 min, the azimuthal anchoring energy was increased by about 31.3% compared with the VA LC cell with 5 min UV exposure. That is because the directionally polymerized RMs formed through the second UV exposure process create a high surface anisotropy, as shown in figure 2, which strongly anchors the LC molecules. Figure 5 shows the voltage–transmittance characteristics. The threshold voltages of the two VA LC cells before and after the second UV exposure process are about the same, because the absolute values of surface anchoring energies are small. However, due to the well-defined azimuthal angle, the transmittance of a cell after the two-step UV exposure process is higher than the cell after only one-step UV illumination.

Figure 6 shows the response time characteristics of our two-step PA-VA cell as a function of applied voltage, compared with the conventional rubbed VA cell. The response time of the PA-VA cell with the first UV exposure is very long (~30 s) due to the reorientation process of the LC molecules. We compare the response time characteristics of our proposed two-step PA-VA cell with those of the conventional rubbed VA cell. When applied voltages are less than 6 V, the rising time is almost the same between the PA-VA cell and the rubbed VA cell, as shown in figure 6(a). However, when the applied voltage is larger than 6 V, the rising time characteristics are remarkably improved. For the rubbed VA cell, the measured

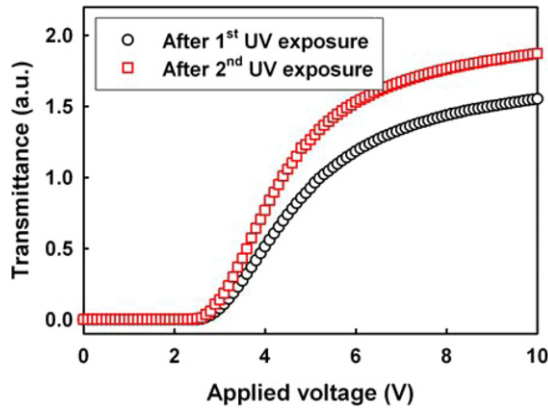


Figure 5. V - T characteristics comparing the VA LC cell before and after the second UV exposure process.

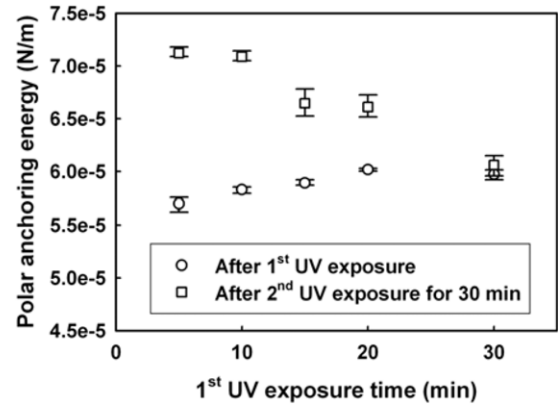


Figure 7. Polar surface anchoring energies as a function of the first LPUV exposure time. The two-step PA-VA cell undergoes the second UV exposure for 30 min.

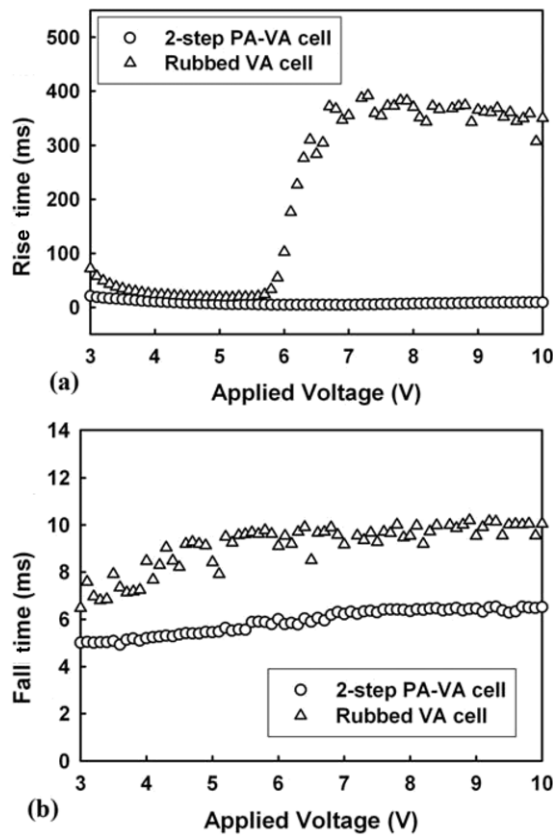


Figure 6. Response time characteristics for rubbed VA cell and two-step PA-VA cell as a function of applied voltage: (a) rising time and (b) relaxation time.

pretilt angle and the azimuthal anchoring energy are 89° and $5.2 \times 10^{-7} \text{ N m}^{-1}$, respectively. These values are not enough to determine the falling direction when a high electric field is applied. So, the LC molecules are aligned unidirectionally after the reorientation process; as a result, the response time becomes very low [19]. The falling time characteristics are also improved in our two-step PA-VA cells, as shown in figure 6(b). At 6 V, the fall times of our PA-VA cell and the rubbed VA cell are 6.0 ms and 9.7 ms, respectively. The difference is due to the polar anchoring energy strength. Figure 7 shows the measured polar anchoring energy as a function of exposure

time of the first UV. After the first UV exposure process, the polar anchoring energy of the VA cell is slightly increased with increasing exposure time. However, after the second UV exposure for 30 min, the anchoring energies are decreased as a function of the exposure time of the first UV exposure. That is because the too-large UV light energies destroy the polymer chains of the VA materials. For this reason, our first and second UV exposure times are 10 min and 30 min, respectively, to achieve high display performance including response time, contrast ratio and transmittance. For the rubbed VA cell with the same process conditions (i.e. the same LC and alignment material), the measured polar anchoring energy is $5.41 \times 10^{-5} \text{ N m}^{-1}$. Although the anchoring energy depends on the rubbing strength, from the response time of 24 ms at 5 V, we could consider that the corresponding anchoring energy is strong enough to generate a fast switching in the VA cell. The polymerized RMs in the alignment layer for our two-step PA-VA cell increase the polar anchoring energy to 1.3 times stronger than that of the rubbed VA cell, and the anchoring energy of the PA-VA cell after the first UV exposure is the same as that of the conventional PA cell. As a result, the rise and fall times of our two-step PA-VA cell are 4.7 ms and 6.0 ms, respectively, under an applied 6 V, and this is fast enough for moving pictures. However, the polar and azimuthal anchoring energies are not so high to compare the planar alignment materials. We believe that these problems could be overcome by increasing the concentration of RMs in the alignment layer and controlling the first UV exposure times within the range of maintaining the display performance [22].

For application of LCDs, the electrical characteristics of alignment materials are very important. We measured the voltage holding ratio (VHR) and residual direct current (RDC) for the proposed PA-VA cell with $1 \text{ cm} \times 1 \text{ cm}$ electrode area, using the commercial equipment (6254, Toyo corp., Japan). For measuring the VHR, 60 Hz ac square voltage was applied with $60 \mu\text{s}$ duration. For the RDC, we applied 5 V dc voltage for 1 h, and then measured during 10 min. The measured VHR value was 98.9%, and that is acceptable for TFT LCD applications [23]. However, the RDC value was somewhat

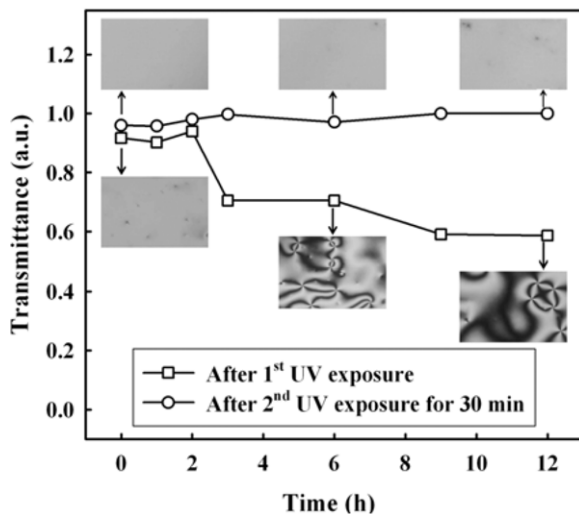


Figure 8. Stability of LC alignment as a function of heating time at 100 °C for the VA cell with the first LPUV exposure and the two-step PA method.

high (529 mV). For increasing the RDC characteristics, we should optimize the UV irradiation conditions and develop alignment materials.

Figure 8 shows the thermal stability as a function of the annealing time at 100 °C. The inset boxes in figure 8 show microscopic textures under crossed polarizers at each testing condition. For PA-VA cells with only the first UV exposure, as in the conventional PA method, the uniform textures collapse, and the LC molecules have random azimuthal directions that generate four-brush ($s = \pm 1$) defects after 3 h annealing time. In contrast, the textures of our two-step PA-VA cell maintain a uniform appearance over the testing conditions.

4. Summary

We propose an advanced PA method using a two-step UV exposure process on the alignment layers which are mixed with PI and RMs. Through the first LPUV exposure process, we establish the azimuthal falling direction of the LC molecules with an applied voltage. The RMs mixed within the polyimide alignment layer are directionally polymerized through the second UV exposure process, and the polymerized RMs are able to increase the pretilt angles and the surface anchoring energies. As a result, we achieved a fast response time and thermal stability for the PA-VA LC mode.

Acknowledgments

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