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Reducing driving voltage and securing electro-optic reliability of in-plane switching liquid crystal display by applying polysulfone photoalignment layer with photo-reactive mesogens

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Newly synthesised photocurable polysulfone (PSCMh) was applied as a photoalignment layer of in-plane switching liquid crystal display (IPS LCD). When the linear polarised ultraviolet light (LPUVL) was irradiated on the typical calamitic nematic liquid crystals on the PSCMh alignment layer, the liquid-crystal director was aligned perpendicular to the LPUVL. Based on the experimental results, it was realised that IPS LCD photoaligned by PSCMh with additional polymer layer associated with reactive mesogen (RM) showed a low driving voltage with reduction of 0.2 V compared to the rubbed cell and also excellent electro-optic reliability such as alignment stability, residual direct current and voltage holding ratio compared to the purely photoaligned cell. Therefore, it was concluded that the polymer stabilisation of PSCMh with RM was effective for improving IPS LCD performances.

Keywords: photocrosslinkable polysulfone; in-plane switching cell; reactive mesogen; electro-optic characteristics

1. Introduction

Since the advent of touching displays, in-plane switching (IPS) or fringe-field switching (FFS) liquid crystal display (LCD) among various LCD modes has been ubiquitous due to the excellent electro-optic characteristics, such as wide-viewing angle, high contrast and viewing angle independent colour values.[1–4] However, to expand its application territory especially in portable display market, we have to solve the higher driving voltage and the slower dynamic response time of in-plane switching liquid crystal display (IPS LCD) compared with twist nematic (TN) LCD.

Contact-free technology of photoalignment,[5–10] as one of the attractive alternatives to rubbing method, has met with a lot of interest for efficient liquid crystal (LC) alignment of various LCD applications. In general, LC photoalignment involves light exposure onto the thin photoreactive polymer film to form the surface anisotropy, which results in the molecular orientational long-range order of nematic LCs (NLCs). Depending on the anisotropic interfacial chemical and physical interactions between polymer substrate and NLCs, the degree of orientational ordering (director axis) of NLCs is determined and controlled. Since the non-contact LC photoalignment does not induce the electrostatic charge and the undesired mechanical damage leading to degradation of LCD quality, this technology has attracted a lot of scientists and

engineers for the LCD application. Despite the high application potential of photoalignment for LCD, it results in weak anchoring with NLCs compared with its rubbing-alignment counterpart,[11–14] which increases the driving voltage and decelerates response time of IPS LCD. Additionally, weak anchoring interactions between alignment layer and NLCs cause the insufficient LC alignment stability as well as the pronounced image sticking effect.[15–17] In order to overcome these limitations, the current photoaligning materials [18–24] need to be further improved. The recently introduced polymer-surface stabilisation by reactive mesogen (RM) [25,26] and photoaligning stabilisation [27–31] can be promising candidate methods for the enhancement of surface anchoring. Nevertheless, the switching stability of electro-optic characteristics of photoaligned IPS LCD with electric field stress still needs to be improved. Furthermore, when we develop the photoalignment materials, we should consider their thermal stability and chemical resistance to many solvents and chemicals, which are closely related to alignment performance during the practical manufacturing process for LCDs.[23]

Therefore, we demonstrated in the present study novel photocrosslinkable polysulfone (PSMCh) with high film photoreaction extent up to 78.5% in the absence of photoinitiator as LC photoalignment, which has good thermal stability up to 320°C and

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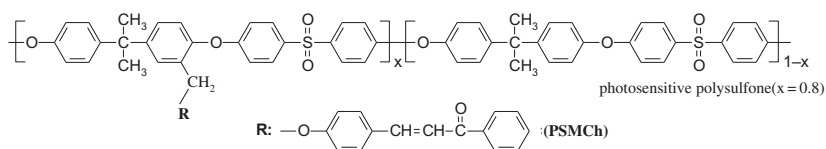


Figure 1. Chemical structure of novel photocrosslinkable polysulfone (PSMCh).

superior chemical resistance with weight loss less than 4% after photocrosslinking.[32] We had further investigated the electro-optic characteristics of IPS LCDs, which were fabricated by various PSMCh alignments: such as mechanical rubbing alignment, a simple photoalignment and a photoalignment with polymerised RM. Based on the experimental results, we realised that IPS LCD photoaligned by photocurable polysulfone (PSCMh) with RM showed a lower driving voltage as well as a higher electro-optical reliability, such as residual direct current (RDC) and voltage holding ratio (VHR), compared with its counterparts.

2. Experimental

The new polysulfone containing highly photosensitive chalcone (PSMCh) was synthesised from commercially available polysulfone with chloromethyl methyl ether by chemical chloromethylation method and subsequent esterification process by reacting chloromethylated polysulfone with 4-hydroxychalcone. The number of chalcone substitution per each 2,2'-position of bisphenol-A moieties was controlled to be 0.8, which was confirmed by $^1\text{H-NMR}$ spectroscopy and thermogravimetric analysis. The structure of PSMCh was given in Figure 1. The detailed synthesis process and structure characterisation as well as properties of the obtained PSMCh had been described elsewhere.[32]

The 1 wt% PSMCh solution in cyclohexanone was spin-coated on different substrates such as bare glass and glass with an interdigitated electrode made of transparent indium tin oxide (ITO), and the films were baked at 180°C for 1 hour to remove the solvent. The linear polarised ultraviolet light (LPUVL) was generated from a high-pressure Hg lamp through a polarising prism. The UV dose applied was measured using a photometer (International, IL1350) with a photodiode sensor (SED 240). The PSMCh-coated substrates were vertically irradiated to LPUVL at 365 nm with an intensity of 1.0 mW/cm^2 for 30 min. The pretilt angles of LC molecules on the UV irradiated and rubbed surface of PSMCh films were measured to be 0.2° and 2° by crystal-rotation method.[33]

The direction of LC photoalignment through the angle dependence of the polarised absorbance of LC cells containing dichroic dye was carried out with a

plane polariscope equipped with a linearly polarised He-Ne laser (632.8 nm) as a function of rotational angle. The LC cells with cell gap of $30\text{ }\mu\text{m}$ were assembled with two irradiated PSMCh-coated substrates. A nematic LC with positive dielectric anisotropy ($\Delta\epsilon = +7.4$) from Merck Co. containing 1 wt% dichroic dye (Disperse Blue 14, Jeonju, Korea; Aldrich) was injected into the cells in its isotropic phase by capillary action and cooled down slowly to remove the flow effect.

Figure 2 showed a schematic illustration of IPS samples fabricated with rub-aligned (a) and photoaligned (b) methods used in this study. The rub-aligned IPS cell was in the horizontal direction to align the LC director at an angle of 8° with respect to the electrode direction. The LPUVL direction for photoaligned IPS cells was perpendicular to rubbing direction at an angle of 82° with respect to electrode direction because photoaligned LC director was perpendicular to the LPUVL direction. For experiment, we prepared one rub-aligned and two photoaligned IPS samples with an electrode width (w) of $4\text{ }\mu\text{m}$ and electrode distance (D) of $4\text{ }\mu\text{m}$. The LC was filled into the rubbed and one photoaligned IPS cells, and the

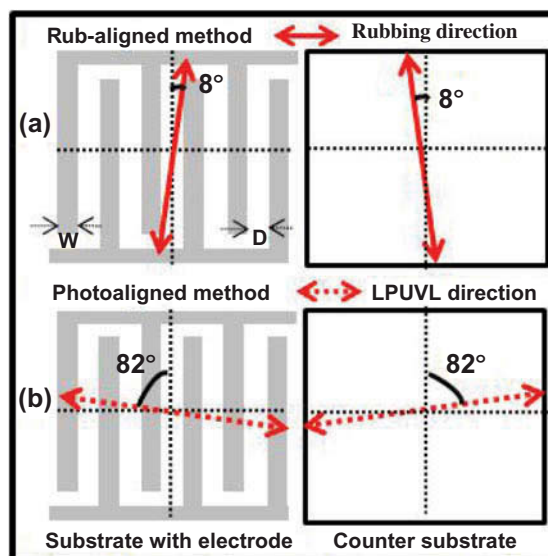


Figure 2. (colour online) Schematic illustration of IPS cell structure with rub-aligned (a) and photoaligned (b) methods.

other photoaligned IPS cell was injected with LC mixed with small amount of RM257 from Merck Co. (0.1 wt%) and photoinitiator (1 wt% compared to RM257) at isotropic phase by capillary action, respectively. The cell gaps were 3.5 μm for all cells and the optic axis of LC director in rub-aligned cell with pure LC (Case 1), photoaligned cell with pure LC (Case 2) and photoaligned cell with RM-mixed LC (Case 3) were controlled to be 8.2°, 7.8° and 8.1°, respectively. Initially, the RM molecules were aligned along the photoaligned LC orientation before UV exposure because of low RM concentration.[28,29] After filling, the cell with Case 3 was irradiated under unpolarised UV for 30 min with an intensity of 1.5 mW/cm^2 and then the RM molecules were polymerised at the interface of alignment layer and LC molecules along the placed original homogeneous state while an additional polymer layer was finally formed over photoaligning surface.[28–30]

After sample fabrication, the switching textures of dark and white state of IPS cells were investigated using a polarised optical microscope (POM, Nikon DXM1200, Tokyo, Japan) in transmittance mode with and without voltage. Electro-optic measurements such as voltage-transmittance and response time were carried out with LCMS-200 (Sesim Photonics Technology Co., Uiwang-si, Korea) with applying a square wave voltage of 60 Hz with an increasing step of 0.1 V. The electric characteristics of VHR and RDC voltage were evaluated using an LCR meter 4284A (Agilent Technologies, Santa Clara, CA, USA). The pulse width, frame frequency and data voltage of VHR measurements were 40 μs , 60 Hz and 1.0 V, respectively. Values measured at different temperatures of 25°C, 50°C and 70°C were averaged. In RDC measurements, DC voltage was applied to the LC cells by tuning the voltage from -10 to +10 V with a step bias voltage of 0.1 V/s, and the RDC was defined as the voltage difference divided by 2 between voltage increasing and decreasing process at 50% of maximal capacitance.

3. Results and discussion

Figure 3 illustrates a polar diagram of LC cells fabricated from PSMCh film exposed to LPUVL for 1.8 J/cm^2 . Under UV irradiation, the PSMCh undergoes two distinct photo-induced processes of *trans-cis* photoisomerisation and [2 + 2] photocycloaddition.[6,8] The diagram indicates that the LC molecules are aligned homogeneously on the film surface perpendicular to the electric vector of LPUVL, which is greatly related to the anisotropic *trans-cis* photoisomerisation process.[5,6,8] Similar polar diagrams are obtained for the other LC cells fabricated from films with various exposure doses. From these polar diagrams, the saturation

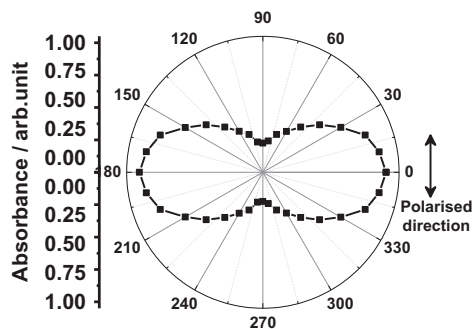


Figure 3. Polar diagram of photoaligned LC cell fabricated from PSMCh film.

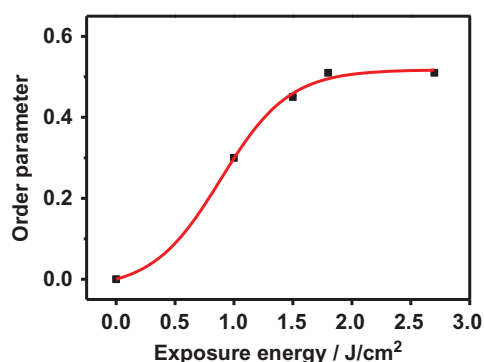


Figure 4. (colour online) Order parameter of photoaligned LC cell fabricated from PSMCh film.

dose for a perfect alignment is estimated by calculating an order parameter S . The order parameter S is defined as $S = (A_{\perp} - A_{\parallel}) / (A_{\perp} + 2A_{\parallel})$, where A_{\parallel} and A_{\perp} denote the absorbance of dichroic LC cells for a polarised probe light with the electric vector parallel to and perpendicular to the direction of LPUVL, respectively. Figure 4 shows the change in S with LPUVL irradiation of the PSMCh alignment layer. With different LPUVL irradiation time S has positive values all the time. S initially increases logarithmically with exposure energy, and saturates to be 0.51 after 1.8 J/cm^2 . These results indicate that LPUVL exposure induces anisotropic photoreaction in the film, causing the polymer chains to orient enough to induce a homogeneous LC alignment on the surface.

To investigate the effect of anchoring energy onto switching, we simulate IPS device at first using LCD master software (Shintech, Yamaguchi, Japan). For the simulation, we use a nematic LC with positive dielectric anisotropy ($\Delta\epsilon = +7.4$, $K_{11} = 11.7$ pN, $K_{22} = 5.1$ pN, $K_{33} = 16.5$ pN) and IPS structure with $w = 4$ μm , $D = 4$ μm and $d = 3.5$ μm . Figure 5 illustrates the computer simulation results of transmittance characteristics of IPS devices with respect to the voltage for varied azimuthal anchoring with 10^{-5} J/m^2 , 10^{-4} J/m^2 and 10^{+3} J/m^2 .

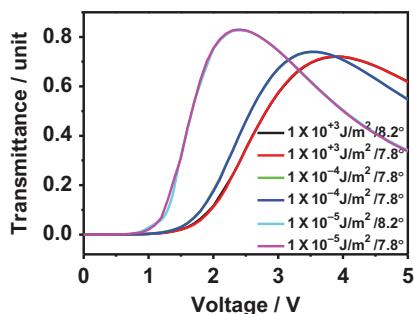


Figure 5. (colour online) Simulated voltage-dependent transmittance curves of IPS mode as a function of surface anchoring energy (the labelled arabic numerals in the picture indicate IPS LC optic axis).

Significant reduction nearly by 38% in the driving voltage is observed when the azimuthal anchoring energy is reduced from 10^{+3} to 10^{-5} J/m^2 , indicating that LC molecules are easily twisted along the field direction with weaker anchoring energy than that with strong anchoring energy, causing the reduction of driving voltage.

For IPS LC cell in consideration of cell surface boundary condition, the implicit dependence of threshold voltage (V_{th}) and anchoring energy (W) is given by [13]

$$\xi_C = -\frac{\xi_E^{\text{th}}}{\tan \xi_E^{\text{th}}} \quad (1)$$

where $\xi_E^{\text{th}} = V(d/D)(\epsilon_0 \cdot \Delta\epsilon/K_{22})^{1/2}$ is the dimensionless electric field, and $\xi_C = Wd/K_{22}$ is the anchoring parameter on the surface. Equation (1) gives V_{th} as a function of surface anchoring strength of the LC (W), cell gap (d) and distance (D) between the interdigitated electrodes. With this dependence, we can describe the effect of the decrease in anchoring for the V_{th}

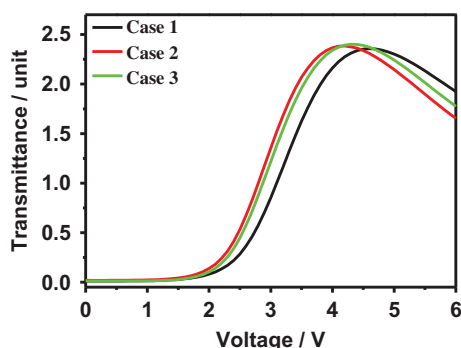


Figure 6. (colour online) Measured voltage-dependent transmittance curves of rub-aligned (Case 1), photoaligned (Case 2) and RM-coated photoaligned (Case 3) IPS cells.

reduction. Figure 6 shows measured voltage-dependent transmittance (V - T) curves of three IPS samples with different aligning methods of mechanical rub (Case 1), photoalignment (Case 2) and RM-coated photoalignment (Case 3). We clearly observe that threshold voltages (V_{th} , defined as the voltage which exhibits the 10% of maximum transmittance) of Case 2 and Case 3 are lower than that of Case 1, which are reduced with 0.2 and 0.1 V compared to that of Case 1, respectively, in experiment. Additionally, the driving voltages (V_{op} defined as the voltage which exhibits the maximum transmittance) of Case 2 and Case 3 shown in V - T curves are totally shifted with reduction of 0.3 and 0.2 V in comparison with Case 1. Note here that the LC optic axis of the fabricated IPS cell has slight variation below 0.4° . In order to confirm if the difference in V - T curves comes from the difference in an initial optic axis, we performed computer simulations. As clearly shown in Figure 3, V_{th} shift below 0.05 V is caused rather than the whole changes in V - T curves. Therefore, it is quite clear from Equation (1) that W decreases in sequence of Case 1, Case 3 and Case 2 according to the decreased V_{th} and W is enhanced by the polymerisation process of mixing RM compared to the pure photoalignment. The POM images of three IPS samples represented in Figure 6 show the defect-free dark states and comparable field driving switching behaviours. The switching images (Figure 7) further confirm that driving voltages (V_0 , V_{10} , V_{50} and V_{90}) of Case 3 at different grey scales (T_0 , T_{10} , T_{50} and T_{90}) are intermediate between Case 1 and Case 2, which are lower than that in Case 1 and higher than that in Case 2 due to the sequential decreases of anchoring forces of Case 1, Case 3 and Case 2.

Normally, the response time of IPS LCD depends on cell gap d , rotational viscosity γ and twist elastic constant K_{22} . In consideration of different anchoring forces, the response times of three cases are not only dependent on d , γ and K_{22} , but also related to the surface anchoring energy (W). Therefore, the modified rising and decaying times have been shown in the following forms [12–14]:

$$\tau'_{\text{rising}} = \frac{\gamma}{\epsilon_0 |\Delta\epsilon| E^2 - \frac{\pi^2 K_{22}}{d^2 + \frac{4d}{W}}} \quad (2)$$

$$\tau'_{\text{decaying}} = \frac{\gamma}{K_{22} \pi^2} \left(d^2 + \frac{4dK_{22}}{W} \right) \quad (3)$$

Equations (2) and (3) indicate that the decaying time becomes slower and the rising time becomes faster with the decreasing of W . Figure 8 represents

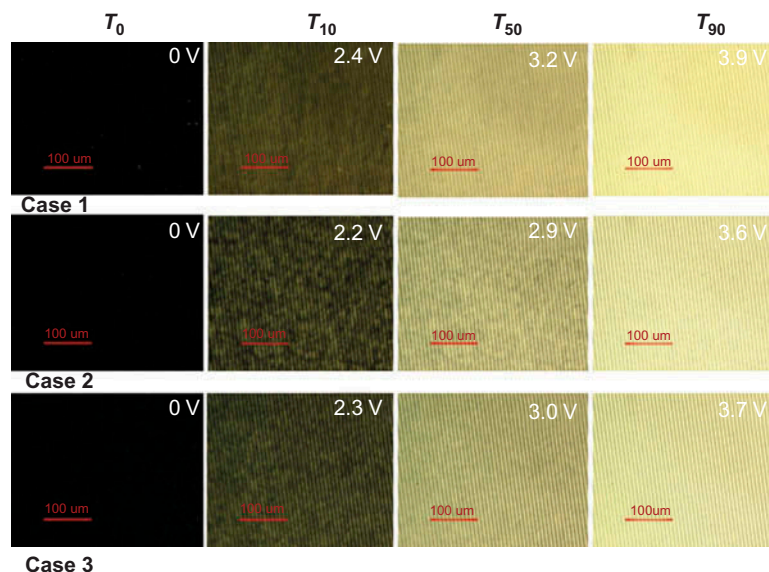


Figure 7. (colour online) Polarising optical microscopic images of rub-aligned (Case 1), photoaligned (Case 2) and RM-coated photoaligned (Case 3) IPS cells.

the measured voltage-dependent response time of the above mentioned IPS cells at varied applied voltages from V_{th} to V_{op} . The average rising time of Case 3 is slightly faster than Case 1, and decaying time of Case 3 becomes slower than that in Case 1, which is approximately 3% slower. In comparison with Case 2, however, the rising and decaying situations in Case 3 react slower and faster, which are close to 8% slower and 40% faster. The measured response time also clearly confirms the change in surface anchoring energy such that W is reduced in sequence of Case 1, Case 3 and Case 2, and W can be improved by the polymerised RM network instead of pure photoaligning layer allowing stronger π - π stacking interaction or dipole interaction with LC molecules.

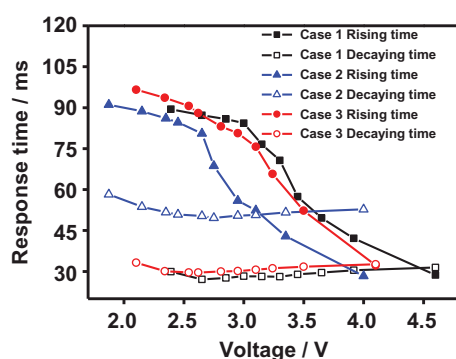


Figure 8. (colour online) Measured voltage-dependent response curves of rub-aligned (Case 1), photoaligned (Case 2) and RM-coated photoaligned (Case 3) IPS cells.

Now, in order to test stability of LC anchoring, the 60 Hz square wave AC field stress is applied onto three IPS cells with applying voltage of V_{90} at 3.9 V (Case 1), 3.6 V (Case 2) and 3.7 V (Case 3) for 20 hours at room temperature (V_{90} defined as the voltage which exhibits the 90% of maximum transmittance). Figure 9 shows the measured V - T curves of three IPS samples before and after the field stress. As clearly shown in Figure 9(a), the field stress onto Case 2 leads to shift of V - T curves about 0.2 V at T_{50} , while Case 1 does not exhibit any noticeable change. Here, the obvious drift of the easy axis does not occur even if the anchoring is weak, which is mainly attributed to the light-induced [2 + 2] photocycloaddition [6,8] with high crosslinking reaction up to 78.5% for stabilising surface ordering and contributing to stability of LC photoalignment.[8, 34] Interestingly, as shown in Figure 9(b), Case 3 shows comparable results to Case 1 without exhibiting noticeable shift in V - T curves even after the field stress. The possible reason may come from the stabilisation of photoaligned orientation ordering due to W enhancement through further photo-crosslinking of RM molecules on surface of alignment layer.

In general, the image quality and reliability of LCD device not only relate to the alignment properties such as surface anchoring energy but also to their electrical characteristics. For advanced thin-film transistor-LCD with photoalignment technology, the high VHR and low RDC values of the devices in addition to excellent alignment characteristics are required in order to achieve a high-performance display with high

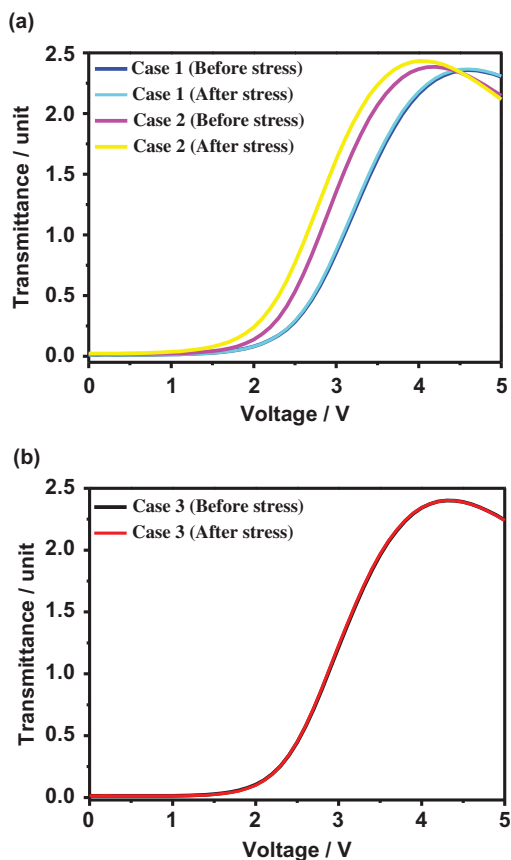


Figure 9. (colour online) Measured voltage-dependent transmittance curves of IPS cells before and after field stress: (a) cells with rubbing-alignment (Case 1) and photoalignment (Case 2) and (b) RM-coated photoalignment (Case 3).

contrast and low image sticking. Table 1 shows electrical characteristics of the IPS cells with different alignment methods. The measured VHR values of Case 1, Case 2 and Case 3 at 25°C are found to be 93%, 84% and 89%. The RDC values of Case 1, Case 2 and Case 3 are 0.10, 0.25 and 0.05 V, respectively. From these results, we can confirm that UV irradiation induced photoaligned surface exhibits highest ion

Table 1. Electrical characteristics of residual direct current (RDC) voltage and voltage holding ratio (VHR) in the rubbed-aligned (Case 1), photoaligned (Case 2), and RM-coated photoaligned (Case 3) IPS cells.

| Samples | RDC (V) | VHR (%) | | |
|---------|---------|---------|------|------|
| | | 25°C | 50°C | 70°C |
| Case 1 | 0.05 | 93.2 | 81.9 | 71.8 |
| Case 2 | 0.25 | 83.5 | 66.7 | 48.0 |
| Case 3 | 0.10 | 88.9 | 74.7 | 58.2 |

amount compared to other alignment methods, and the cell with polymerised RM layer on photoalignment surface has reduced ions trapped at the interfaces, which helps reducing the RDC voltage and increasing VHR. To further verify why the RDC voltage of the photoaligned IPS cell is the largest one and its VHR value is the lowest one among three IPS cells, we calculate the surface energy of each alignment layer through measuring their contact angles by using diiodomethane (CH_2I_2) and distilled water (H_2O). The polar, dispersion and total surface energies are calculated from the result of contact angle measurements by using the Owens–Wendt geometric mean equation,[35] which is suitable for obtaining the surface energy of most of the polymers. The Owens–Wendt geometric mean equation is given as

$$\begin{aligned} \gamma_1(1 + \cos \theta_1) &= 2 \left(\sqrt{\gamma_1^d \gamma_s^d} + \sqrt{\gamma_1^p \gamma_s^p} \right) \\ \gamma_2(1 + \cos \theta_2) &= 2 \left(\sqrt{\gamma_2^d \gamma_s^d} + \sqrt{\gamma_2^p \gamma_s^p} \right) \end{aligned} \quad (4)$$

where γ_s is the surface energy of the alignment layer, γ_1 , γ_2 , θ_1 and θ_2 are the surface energies and contact angles of distilled water and diiodomethane, respectively. Superscripts *d* and *p* are dispersion energy and polar energy, respectively.

The measured θ_1 (H_2O) and θ_2 (CH_2I_2) of the rubbed alignment layer, photoalignment layer and RM-coated photoalignment layer are 74° and 23°, 75° and 26° and 65° and 30°, respectively. Surface energies of distilled water and diiodomethane are obtained from the literature.[35] Table 2 shows the calculated surface energy components of three IPS samples. The total surface energy is slightly decreased in the order of photoaligned layer > rubbed layer > RM-coated photoaligned layer. While the dispersion energies of the three samples are similar to each other, the polar energy term of photoaligned layer shows a significant difference compared to that of rubbed layer and RM-coated photoaligned layer. The highest polar energy of the photoaligned layer is estimated to be 8.0 mN/m, resulting from UV-irradiation induced generation of

Table 2. Surface energy components of the rubbed-alignment layer, photoaligned layer, RM-coated photoaligned layer (unit: mN/m).

| Samples | Dispersion | Polarity | Surface energy |
|---------|------------|----------|----------------|
| Case 1 | 44.2 | 8.0 | 52.4 |
| Case 2 | 45.8 | 3.7 | 49.5 |
| Case 3 | 46.0 | 4.3 | 49.2 |

polar groups such as carbonylated and hydroxylated oxidative derivatives on the degradable polysulfone surface as a consequence of chain scissions.[36,37] The lowest polar energy value of the RM-coated photoaligned layer estimates to be 3.7 mN/m because the polymerised RM layer covering the photo-aligned polysulfone surface effectively reduces the exposure of surface polar groups to the IPS cell while retaining the homogeneous LC orientation.

4. Conclusion

A LC photoalignment layer utilising novel photocrosslinkable polysulfone with good thermal stability and chemical resistance was proposed and its electro-optic characteristics in IPS LCD were investigated by varying LC alignment methods, such as mechanical rubbing alignment, photoalignment and RM-coated layer on photoalignment. All the IPS LCD cells exhibited good homogeneous LC alignment with a good dark state but the IPS LCD cell with a photoalignment layer with additional polymer layer from RM showed an excellent alignment stability under voltages stress as well as a superior electro-optic reliability compared with the photoaligned IPS LCD cells. Therefore, it was concluded that the polymer stabilised photoalignment technology using RM has great potential for high performance IPS LCD.

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