

Azo Dye, Liquid Crystals Polymer Composite Photo-Alignment Layer For Modern Liquid Crystal Displays

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Abstract

In this article, a photoalignment layer, based on the azo dye and liquid crystal polymer (LCP) composite is proposed. The alignment layer offers easy processing and high photo and thermal stabilities. The high VHR (99.1%) and low RDC (30mV) have been achieved that is comparable with the conventional PI rubbing alignment layer. The proposed alignment layer shows low pre-tilt angle and small image sticking which is highly desirable for IPS display. Furthermore, the ability of multi-domain alignment has been demonstrated that shows a great potential to find applications in a range of electro-optical devices particularly those requiring in-plane LC director modulations.

Author Keywords

Azo dye; liquid crystal polymer; photoalignment; photo-stability.

1. Introduction

Recent few years have witnessed great progress made by azo-dye photoalignment on liquid crystal (LC) devices [1, 2], such as rewritable e-paper [3], IPS flat-panel displays and liquid crystal lens [4]. With several advantages, listed below, photoalignment possesses offer an edge over the conventional rubbing technique. Firstly, photoalignment is a non-contact process, which eliminates electrostatic charges as well as mechanical damage introduced by rubbing treatment. Secondly, photoaligning technique can realize controllable anchoring energy by varying irradiation energy. Furthermore, photoalignment techniques can also be applied on LC cells with sophisticated geometry and on processing system with high spatial resolution and curved surfaces, whereas a little can be done with traditional rubbing.

Several excellent properties of azo-dye alignment have been reported [5] viz. high anchoring energy at low irradiation energy, thin alignment layer but strong thermal-tolerance. However, the photo-stability problem still needs to be settled [6]. The re-orientation of azo-dye alignment is favorable for certain applications [2], nevertheless, for the display applications it is not desirable.

Several efforts have already been made to stabilize the azo dye photoalignment with LCP, including polymer azo dye composite [7], LCP layer on the top of the azo dye [8], and introduction of the polarizable moiety in the azo dye itself [4]. For the polymer composite azo dye alignment layer, it has been proposed to utilize azo dye and LCP mixture with a proper ratio to form a photo-stable photoalignment, but voltage holding ratio (VHR) and the residual DC (RDC) do not meet the industrial standards [9]. The LCP layer on the top of azo dye, an additional LCP

layer offers strong constraint on the thickness of LCP. Moreover the double layer structure increases the manufacturing cost. On the other hand, the introduction of the polymer unit in azo dye leads to poor alignment characteristics.

In this article, we demonstrated a method for stabilizing and optimizing the azo dye SD1 alignment by using LCP composite for the better parameters suitable for the industry. The process contains two-step irradiation: first for the SD1 alignment and second for the polymerization of LCP to build a robust network and then fix SD1 molecules one by one. Several experiments have been made to confirm the high thermal-tolerance and photo-stability. Additionally, the display-related parameters i.e. VHR, RDC and image sticking parameter were measured and meet the industrial standard. Furthermore, the proposed photoalignment layer is capable to offer multiple-domain alignment with high optical quality. Thus, this composite photoalignment layer has immense potential to be applied in various LC displays.

2. Experimental Results

In order to provide a perfect trapping for the azo dye molecules in the LCP network, two criteria have to be considered when choosing a proper LCP monomer. First, the phase separation between LCP and azo dye molecules should be avoided completely otherwise isolated domains of different materials would appear and restrict the stabilization of azo dye easy axis. The second crucial point is the size of LCP monomer that should be smaller or comparable to azo dye molecule.

In order to initiate the polymerization of LCP, a photo-initiator 2,2-Dimethoxy-2-phenyl-acetophenone was added. In addition, a commercially available azo dye, SD1 (DIC Corporation, Japan), was selected as the photoalignment material (Figure 1). As a polarized light beam optically pumps the azo dye layer so their oscillators increasingly absorb energy and orient themselves from the initial random position to the direction perpendicular to the polarization azimuth of the pumped light. SD1 can offer very large anchoring energy as well as small pretilt angle.

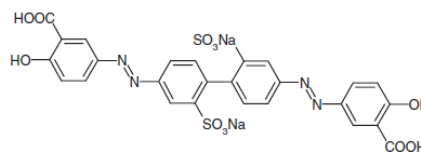


Figure 1. Chemical structure of azo dye SD1 molecule.

The LCP mixed in SD1 induces a screening effect on the aligning characteristic of pure SD1 and on the other hand, less concentration of the LCP offers poor stabilization for the azo dye easy axis. Therefore, the concentration of LCP in the solution needs an optimization to meet the tradeoff between the two processes. Therefore the mixtures with different concentrations of LCP have been studied and the process for the mixture preparation is described below. The N, N-dimethylformamide (DMF) is the solvent for both SD1 and LCP that offers excellent solubility. Nine different mixtures were prepared with LCP/SD1 wt/wt ratios: L1S9, L2S8...L5S5...L9S1. Here, L and S are referred as LCP and SD1, respectively. The numbers after L and S represent the wt/wt ratio value of LCP and SD1 in the mixture.

The mixture was directly spin coat onto the well-cleaned ITO glass plates to make the uniform thin layer as shown in Figure 2a. The ITO glass was then exposed to a polarized blue LED (90 mW/cm², 450 nm) for 2 minutes. SD1 molecules aligned themselves perpendicular to the polarization azimuth of the blue LED (Figure 2b). Afterwards, a linearly polarized DUV lamp (6 mJ/cm², 310 nm) was used to polymerize the LCP for 10 minutes (Figure 2c). Finally, the substrate was soft-baked on a 120°C hotplate for 20 minutes to dry out the left solvent.

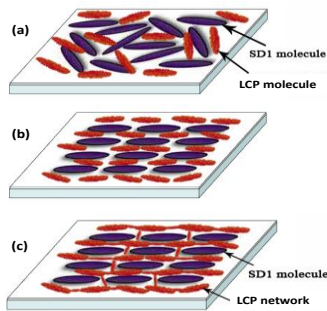


Figure 2. The aligning arrangement of SD1 and LCP molecules on each fabrication step: (a) after the spin coating of final mixture; (b) after first-step irradiation of polarized blue LED to align SD1; (c) after second-step exposure to DUV light for polymerize LCP to form a rigid network.

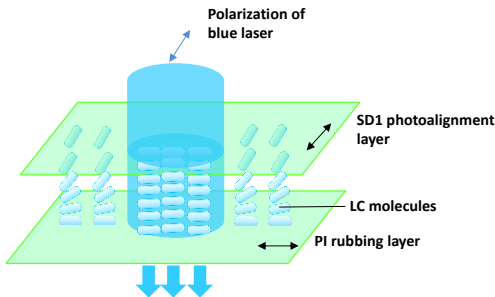


Figure 3. Framework of photo-stability test on 90° TN cells.

To test the alignment quality and photo-stability of proposed photoalignment layer, a 90° TN cell was fabricated by assembling one substrate with conventional rubbing PI substrate and other substrate with the proposed photoalignment substrate. The cell gap was precisely controlled at 5 μm by uniform spacers. Liquid crystal (MLC-6080, Merck Corporation) was

then filled into the empty cell by capillary action. Nine cells were made with different LCP/SD1 ratios i.e. L1S9, L2S8...L5S5...L8S2, L9S1. A polarized blue laser (5mJ/cm², 405 nm) was used to test the photo-stability characteristic. The polarization of the blue light beam was set to be parallel to the aligning of SD1. If the SD1 alignment direction is changed, then the exposed region would change from 90° TN cell to ECB-like cell (seen from Figure 3). Hence, the white state of the TN cell between the crossed polarizers would turn into gray or dark state. The contrast ratio before and after rewriting test were recorded and plotted in Figure 4. The increasing concentration of LCP largely improves the SD1 stability. For the samples with LCP/(LCP+SD1) lower than 0.5, the contrast ratio decreases considerably after rewriting, which is because of the weak trapping of the SD1 molecules offered by the low concentration of LCP. In case of LCP/(LCP+SD1) ratio larger than 0.5, the quantities of LCP is enough to form a robust network, but for very high concentration of LCP, i.e. 0.8 or 0.9, the alignment quality suffers due to the lack of SD1 molecules. For samples with LCP/(LCP+SD1) of 0.5~0.6 performed very well for both alignment and photo-stability.

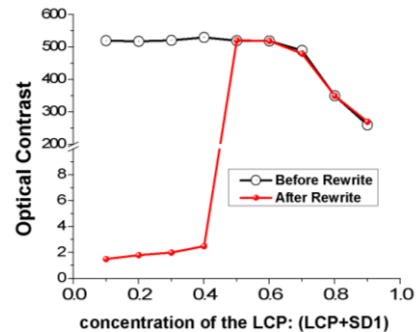


Figure 4. Contrast ratio of TN cells fabricated with different LCP/(LCP+SD1) ratios.

The Figure 5 shows photographs of three cells (L2S8, L5S5 and L8S2) after the photo-stability test, in which the contrast ratios and photo-stabilities performance were presented as a comparison. As mentioned above, for sample L2S8, due to the low concentration of LCP, a poor photo-stability was indicated by the gray spot within the re-exposed region either in black or white state, seen from Figure 5(a). Conversely, the high concentration LCP with insufficient SD1 molecules in sample L8S2 has an unfavorable alignment quality, which is reflected in the poor black and white state of the cell shown in Figure 5(c), respectively. On the other hand, for the cell with L5S5, both LC alignment and photo-stability are highly acceptable with extremely good optical states shown in Figure 5 (b).

Table 1. Results of VHR and RDC for different alignment layer.

	VHR,% (60Hz; 25°C)	VHR,% (60Hz; 65°C)	RDC,mV (60°C)
Pure SD1	91	85	80
L5S5	99.1	99	30
(PI 3744)	99.5	99.1	5

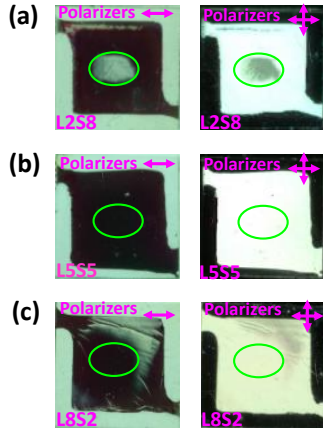


Figure 5. Tests on the purity of black/white states observed in crossed and parallel polarizers, respectively. (a), (b), and (c) represent the black/white state of sample L2S8, L5S5 and L8S2, respectively. The green circle is the region exposed to blue laser for photo-stability tests.

For the display applications of the photoalignment layer, several other parameters, i.e. VHR and RDC, are critically important to satisfy the TFT driving conditions. Therefore, the further study and optimization of these parameters have been performed only on the sample with optimized photo-stability and good alignment quality i.e. L5S5. Thus measured parameters are compared, with different alignment layers i.e. pure SD1 and polyimide, in Table 1. The VHR and RDC show huge improvements than that of the pure SD1. The VHR value of stabilized SD1 was above 99%, which is comparable to rubbing PI. The RDC value is found to be ~ 30 mV which is much smaller than that of pure SD1 (i.e. 80 mV).

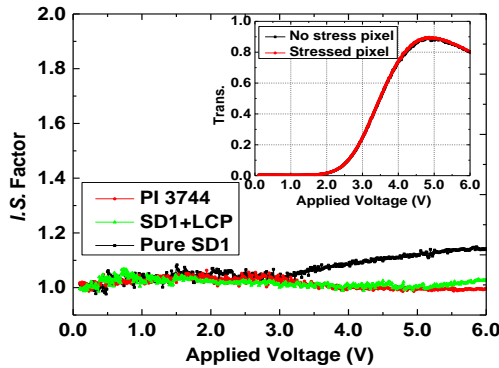


Figure 6. *I.S.* of three different alignment layers: PI 3744, pure SD1 and stabilized SD1 with 6V stress. The TVCs of stressed pixel (red) and non-stressed pixel (black) are indicated in the inset.

Furthermore, the image sticking parameters that is of great importance for the high-resolution displays viz. IPS or FFS, has been examined for the L5S5 alignment layer as a comparison with PI 3744 and pure SD1. Here, the image sticking parameter (*I.S.*) is evaluated commercially by comparing the gray scale or transmission for lower driving voltage of 2V as $I.S. = T_{\text{stress}} / T_{\text{no stress}}$. But here we also test *I.S.* factor on the voltages up to 2V as

shown in Figure 6. The stressed pixel is applied a 6V AC field with 30 Hz square signals for 6 hours but the non-stressed pixel is not. The *I.S.* values of three alignment layers differs slightly when the voltage is less than 3 V. Whereas, as the voltage increasing further pure SD1 loses its advantage, and the *I.S.* of stabilized SD1 is comparable to conventional PI rubbing. In particular, the *I.S.* for PI 3744, pure SD1 and stabilized SD1 at 2V is 1.032, 1.046 and 1.028, respectively. Also, the TVCs in the case $I.S. = T_{\text{stress at 6V}} / T_{\text{no stress}}$ of stabilized SD1 are measured and presented in the inset of Figure 6.

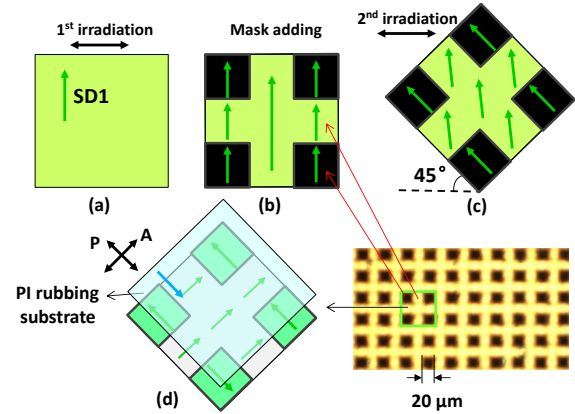


Figure 7. The fabrication process of multiple-domain cell.

In addition to the excellent performances for photo-stability, VHR, DRC and image sticking, the proposed photoalignment layer is capable to show the multi-domain alignment. In fact, nano-scale resolution achieved by photoalignment SD1 has already been reported [10], in which a minimum alignment domain size of 105 nm was obtained by means of interference pattern. Here, a cell with two alignment domains with characteristic domain size is $20\mu\text{m}$ has been fabricated in a single irradiation step. A half-wave plate is phase mask has been used to manipulate the polarization azimuth in the two different alignment areas. The half-wave plate was fabricated as follows: first, a substrate with pure SD1 film was irradiated by blue LED for unidirectional alignment (Figure 7a) and then an amplitude mask was covered on it (Figure 7b). Second, the substrate was rotated by 45° in plane, from the polarization plane azimuth from the 1st irradiation, to rotate SD1 45° in the exposed region (Figure 7c), while keep SD1 unchanged under the mask (shown in black color). Third, LCP was spin coated onto the two-domain SD1 film to form a retardation plate with two domains having easy axis mutually inclined at 45° , in plane. By controlling the thickness of the LCP, a half-wave phase pattern of 450 nm wavelength can be made, and can be used repeatedly. Thus prepared phase mask has been used to make a TN cell, which differs from before TN cells in the phase mask covering on the SD1 substrate when it exposed to UV light. This TN cell has two-alignment domains with mutually orthogonal alignment direction and $20\mu\text{m}$ characteristic domain size. The optical microphotograph is shown in Figure 7d.

3. Conclusion

In summary, a highly photo-stable photo-alignment layer with liquid crystal polymer composite was proposed and demonstrated. The proposed alignment layer is characterized by high VHR (99.1%), small RDC (30 mV), good thermal and

photo-stability. The low pre-tilt angle and small *I.S.* are the real advantages for high-resolution displays based on IPS or FFS electro-optical modes. Furthermore, the ability of multi-domain alignment offers several advantages for many modern display and photonic devices. Therefore, the proposed photoalignment layer with easy fabrication and high reproduction yield has great potential to find application in various LC devices.

4. Acknowledgement

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5. References

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