One Step Stabilized Azo Dye Photoalignment for Mass Production

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Abstract

A novel azo dye stabilization method was presented that only requires single-shot UV light exposure. The proposed photoalignment layer offers highly acceptable thermal and photo-stability, as well as low pre-tilt angle (0.2 °) and low image sticking (1.01). Also, high VHR (99%) and low RDC (<10mV) comparable to that of PI rubbing have been achieved. Furthermore, the ability of multi-domain alignment has been demonstrated that shows a great potential in a wide range of electro-optical devices.

Author Keywords

Azo dye; stabilization; photoalignment.

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 offers 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 [5-7] 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. 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 liquid crystal polymer (LCP), including polymer azo dye composite [8], LCP layer on the top of the azo dye as a passivation film [4]. For the polymer azo dye composite, it has been proposed to utilize azo dye and LCP mixture with a proper ratio to form a photo-stable layer which, however, requiring two times exposure with different light sources[9]. On one hand, two light sources will dramatically increase the manufacturing cost, on the other hand, two-time exposure complicates the process flow and consumes longer time for mass production.

In this article, we demonstrated a one-step exposure method to stabilize and optimize the azo dye SD1 alignment by introducing a photo initiator (dominated as P.I.) to accelerate the polymerization of LCP monomer for the superior parameters for commercial usage. The process only contains single-step irradiation: 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 carrying photo-initiator has immense potential to be applied in various LC displays.

2. Experiments

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.

For one thing, 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 to the direction perpendicular to the polarization azimuth of the pumped light. Also, SD1 offers large anchoring energy as well as small pretilt angle.

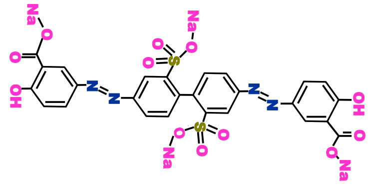

Figure 1. Chemical structure of azo dye SD1 molecule.

For the other thing, to initiate and accelerate the polymerization of LCP, a photo-initiator 2,2-Dimethoxy-2-phenyl-acetophenone was added. To achieve single shot exposure, the wavelength to be chosen for light exposure should be located on the overlapping absorption region to make sure considerable speed of SD1 alignment and LCP polymerization, respectively. From this point of view, the wavelength 365nm is a good choice since both absorption are relatively high.

The key for our single step technique is to find a proper concentration of P.I., azo dye and LCP monomer in the solution preparation. The ideal case is the aligning speed of SD1 should be faster than the polymerization speed of LCP during the single-shot exposure. Otherwise, the film will poorly align due to the failure rotation of SD1 molecules after LCP is fully polymerized. Therefore, the concentration of P.I. in the final recipe has to be properly chosen and it is proven again that 365nm is a good option, where SD1 absorption is much higher than photo initiator.

The minimum energy to photo-align pure SD1 molecules at 365nm is 50mJ/cm^2. For the blending case, more energy (at least three times) is needed. This is because each SD1 molecule is surrounded by several LCP monomers which consume more energy for polymerization due to the increasing distance between each LCP monomer. The response of the process depends on P.I. concentration and the blending ration of SD1 as well as the LCP monomer. From the selecting condition yielding optimal alignment quality in our previous work [9], both S5R5 and S4R6 (Here, S and R refer to SD1 and LCP, respectively and the number after S and R means the wt/wt ratio of SD1 and LCP.) were selected for our single shot experiment with varying concentrations of P.I..

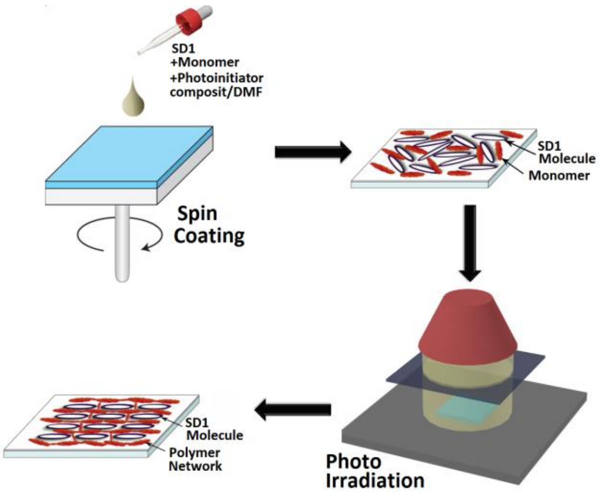

Figure 2. Fabrication process of single-shot exposure.

An overview of our process is shown in Figure 3. The recipe was directly spin coat onto the well-cleaned ITO glass plates to make a uniform thin layer. The substrate was then exposed to a polarized UV lamp (1.1mW/cm^2, 365nm) for different dosages. At the beginning, 3 to 5 minutes irradiation is for SD1 aligning perpendicular to the polarization azimuth of the UV lamp. Then LCP polymerization started to work where LCP continuously form a rigid polymer network to trap the aligned SD1 molecules one by one. Finally, the substrate was soft-baked on a 120˚C hotplate for 10 minutes to dry out the left solvent. Figure 3 shows the dependence of light dosage on the concentration of photo initiator. It drops intensely at the beginning and gradually reaches saturation when P.I. concentration is up to 50%. Though the dosage required tends to be small (<1000mJ) at high P.I. concentration, the alignment turns to be poor as seen from the low contrast of S5R5 and S4R6 (Figure 4).

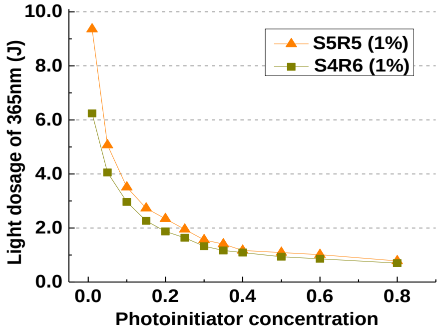

Figure 3. Light dosage dependence on P.I. concentration for S5R5 and S4R6 recipes, respectively.

3. Parameters Testing

3.1 Photo-stability tests

To test the photo-stability, TN cells were fabricated by assembling substrate with rubbing PI and the other with our proposed photoalignment layer. The cell gap was 5µm; the LC-mixture MLC-6080 from Merck was filled into the cell by capillary action. After the initial contrasts of the cells were measured, they were then exposed to a polarized blue laser (5mJ/cm^2, 405 nm) to check the stability of SD1 in the network. The cells were positioned with blue laser polarization parallel to the direction of SD1 (Figure 4). After 5 minutes the contrast were checked again. The resultant contrasts before and after photo stability test of S5R5 and S4R6 are shown on Figure 5. The contrast drops rapidly when P.I. exceeds 40%. This is because too much P.I. will double enhance the polymerization speed of LCP before SD1 molecules fully align themselves. For P.I. concentration below 20%, a mass of UV dosage is required which is not desirable in mass production. Therefore, P.I. concentration ranging from 20% to 40% is a reasonable operating window for single-shot exposure. Also, S5R5 performs better at contrast value in above window.

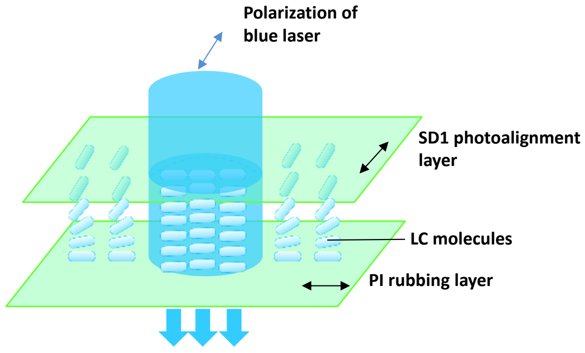

Figure 4. Framework of photo-stability test.

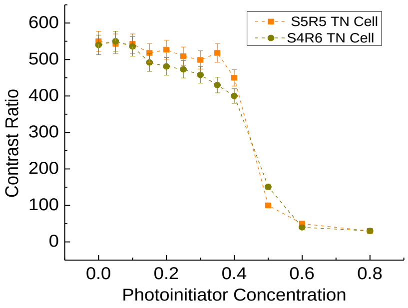

Figure 5. Contrast ratio dependence on the P.I. concentration in the recipes.

3.2 RDC, VHR and Image Sticking Tests

For photoalignment layer to be applied on display, several parameters, i.e. VHR and RDC, are critically important under certain TFT driving condition. Further optimization was done on L5S5 recipe. The 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 and also comparable to rubbing PI, i.e. VHR value of S5R5 was above 99% at high degree. RDC (<10 mV) is much smaller than that of pure SD1 (i.e. 80 mV).

Table 1. Parameters comparison on PI 3744, S5R5 and pure SD1.

	PI 3744	**S5R5**	**Pure SD1**
RDC (60ºC)	5mV	8mV	80mV
VHR (60ºC)	99.87%	99.0%	85%
Polar anchoring	3.76x10^{-3} J/m^{2}	2.5x10^{-3} J/m^{2}	8.1x10^{-4} J/m^{2}
Azimuthal anchoring	4.7x10-4 J/m^{2}	0.55x10-4 J/m^{2}	~5x10^{-5} J/m^{2}
I.S.	1.032	1.01	1.046

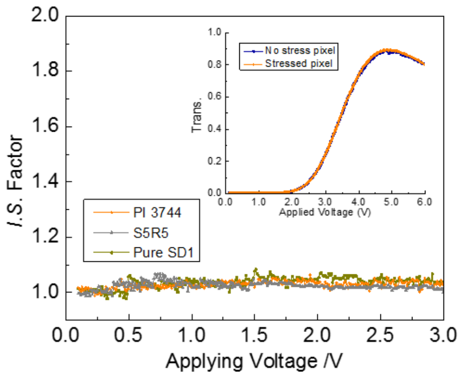

Figure 6. *I.S.* of PI 3744, pure SD1 and S5R5 with 6V stress for 6 hours. The TVCs of stressed pixel and non-stressed pixels is in the inset.

In addition, image sticking is of great importance for high-resolution displays viz. IPS or FFS. 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_{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 within 2V. In particularly, the *I.S.* for PI 3744, pure SD1 and S5R5 at 2V is 1.032, 1.046 and 1.028, respectively. Also, the TVCs after image sticking test of S5R5 with and without stress measured and presented in the inset of Figure 6.

3.3 Multi-domain aligning with ultra-high resolution

In addition to the excellent performances for photo-stability, VHR, DRC and image sticking, the proposed photoalignment layer is also capable of multi-domain alignning. In fact, nano-scale resolution achieved by photoalignment SD1 has been reported before [10], in which a minimum alignment domain size of 75nm was obtained by means of interference pattern. With high-resolution grayscale achieved by controlling the spatial resolution of dark and white pixels by Schadt in 1995 [11], picture with very fine alignment at the boundary can be obtained using our S5R5 recipe. As seen from Figure 7, the performance of S5R5 is much better than rubbing PI.

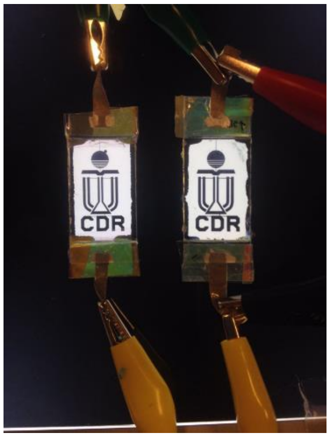

Figure 7. “CDR” logos made by conventional rubbing PI (left) and S5R5 alignment recipe (right).

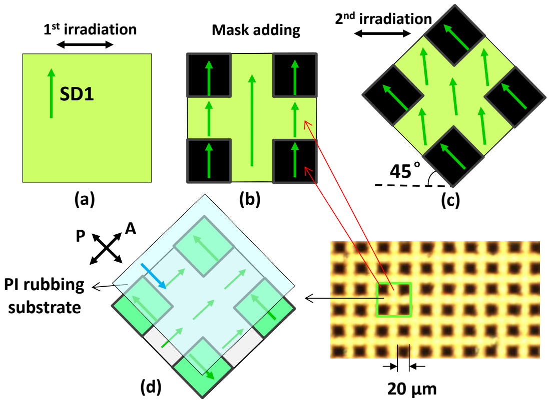

Figure 8. The fabrication process of multiple-domain cell.

A TN-sample of two-domain with domain size 20μm was fabricated by single shot exposure. Before the sample fabrication, a half-wave plate was made as follows: first, a substrate with pure SD1 film was irradiated by a blue LED for SD1 aligning (Figure 8a) and then the substrate was covered by an amplitude mask (Figure 8b). In the next step, the substrate was rotated by 45 ° for second exposure which realigns SD1 in the exposed region (Figure 8c). And then, a LCP spin-coating to form a dual domain SD1 aligning was followed. By controlling the thickness of the LCP, a half-wave phase pattern of 450 nm wavelength was obtained, which can repeatedly be used as a retarder mask. With this mask, multi-domain LC cells can be fabricated by covering the mask on the substrate when exposed to the UV lamp, which differs from before TN cells in the phase mask covering on the SD1 substrate when it exposed to UV light. The resultant optical microphotograph of two-domain is shown in Figure 8d.

4. Conclusion

In summary, an ultra-effective azo dye stabilization through single-shot exposure has been proposed and demonstrated. The alignment layer is characterized by high VHR (99.0%), small RDC (<10mV), good thermal and photo stability. The low pre-tilt angle (0.2 °) and small *I.S.* (1.01) are the real advantages for high-resolution displays based on IPS or FFS electro-optical modes. Furthermore, the ability of high resolution multi-domain 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.

5. Acknowledgement

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6. References

[1] V. Finnemeyer, D. Bryant, R. Reich, H. Clark, S. Berry, C. Bozler, O. Yaroshchuk, L. Lu, and P. Bos. J. Appl. Phys. **118**, 034501(2015).

[2] A. Muravsky, A. Murauski, V. Chigrinov and H. S. Kwok, SID Sym. Dig. Of Tech, **39**, 915(2008).

[3] A. Muravsky, A. Murauski, V. Chigrinov, and H. S. Kwok, IEICE Trans. Electron., **E91**–C, N.10,1576-1580 (2008).

[4] M. Tseng, C. Lee, O. Yaroshchuk, A. Srivastava, V. Chigrinov, H. S. Kwok, SID Symposium Digest of Technical Papers,**46**,997-1000(2015).

[5] R. Nersisyan, N. V Tabiryan, D. M. Steeves, B. R. Kimball, V. G. Chigrinov, and H. S. Kwok, *Appl. Opt.*, **49**,1720(2010).

[6] S. Furumi and K. Ichimura, *Adv. Funct.Mater.*,**14**,247(2004).

[7] D. Matsunaga, T. Tamaki and K. Ichimura, *J. Mater. Chem.*,**13**, 1558(2003).

[8] Qi Guo, *A. Srivastava*, V. Chigrinov, and H. S. Kwok, *Liquid crystals*, **41(10)**, 1465**(**2014).

[9] C. L. Meng, M. C. Tseng, C. Y. Lee, A. Srivastava, Vladimir G. Chigrinov and Hoi-Sing Kwok. SID, **47(1)**, 1566–1569(2016).

[10] E. Shteyner, A. Srivastava,V. Chigrinov,and H. S. Kwok, Soft Mattr,**9**, 5160-5165 (2013).

[11] M. Schadt, H. Seiberle, A. Schuster and S.M. Kelly, Jpn. J. Appl. Phys. Lett. **34**, 764L-767L(1995).