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Polymer and azo-dye composite: a photo-alignment layer for liquid crystals
Qi Guo\textsuperscript{a}, A.K. Srivastava\textsuperscript{a}, V.G. Chigrinov\textsuperscript{a} & H.S. Kwok\textsuperscript{a}
\textsuperscript{a} State Key Laboratory on Advanced Displays and Optoelectronics Technologies, Hong Kong University of Science and Technology, Hong Kong
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Polymer and azo-dye composite: a photo-alignment layer for liquid crystals


State Key Laboratory on Advanced Displays and Optoelectronics Technologies, Hong Kong University of Science and Technology, Hong Kong

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In this article, we disclose a method to fabricate polymer-stabilised azo-dye photo alignment layers for liquid crystal. The idea includes the introduction of polymer network in the alignment layer, in optimal concentration, followed by two-step irradiation. The stabilised photo-alignment layer has been explored for different aspects of the display-related parameters, viz. anchoring energy, stability for various display-related environments as a function of concentration of monomer and irradiation, residual DC and voltage holding ratio. The composite photo-alignment layer offers well-suited parameters for the liquid crystal alignment and therefore could find application in a variety of modern photonic and display devices.

Keywords: photo-alignment; ferroelectric liquid crystals; azo-dyes

1. Introduction

Recently, photo-alignment, particularly for the ferroelectric liquid crystals (FLCs), got huge attention for a variety of applications in photonic and display devices. Excluding the mechanical contact with the aligning layer, the photo-alignment technique minimises mechanical damage and unwanted electric charging,[1–3] which is a serious issue for FLC devices.[4] Moreover, it is highly demanded for numerous developments when LC alignment is used on curved surfaces, or on the surfaces of microscopic scale.[5–7] It has been reported that photo-aligning azo-dyes, for which the easy axis can be altered by further exposure to blue light, could provide anchoring energy comparable to commercial polyimide (PI) film and show potential for a variety of applications, e.g. optical rewritable LC devices and alignment layers for FLC devices.[8–12]

The LC photo-alignment based on reorientation process of azo-dyes provides precise control on the anchoring energy of the alignment layer by varying irradiation energy that has been proven to be an excellent tool to achieve the good optical quality for the electrically suppressed helix FLCs (ESHFLC).[13] However, these photo-alignment layers based on reorientation process are not stable and can be destroyed by further exposure to light or thermal energy. Furthermore, such azo-dyes are highly sensitive to visible light, particularly to the blue light, which makes the problem even more difficult for display applications where such alignment layers are exposed to strong backlight, all the time. Considering these obstacles, the alignment stability of azo-dyes must be enhanced for the photo and thermal exposure to apply such photo-alignment technique in modern display devices.[14]

Several efforts have already been made to stabilise the azo-dye photo-alignment. In 2003, it has been proposed to add a reactive group, capable of being polymerised, to the dye molecule itself, but it results in poor anchoring energy. Moreover, a dual photo-reactive group in one copolymer structure was also explored by introducing a photo-crosslinking group.[15] However, these ideas took a long time to be implemented and a high cost of synthesis was involved; furthermore, the alignment quality of LCs was ruined because of additional groups. Recently, a liquid crystal polymer (LCP) layer was used to deposit on top of the azo-dye film. In spite of having a strong constraint on the layer thickness of LCP, it hardly could provide sufficient stabilisation to the azo-dye photo-alignment layer.[16] In another approach, a crosslinking material was added to the azo-dye material.[17] This approach provides good stability to the alignment layer but because of complex molecular structure optical quality is not good, particularly for FLC.

In this article, we disclose a polymer azo-dye composite photo-alignment layer for LCDs with the optimal concentration of the monomer and azo-dye in the mixture followed by a two-step irradiation: first for the alignment and second for the stabilisation of the photo-alignment layer that provides good alignment quality with anchoring energy comparable to pure azo-dye layer. The stability of thus prepared composite alignment layer has also been confirmed by testing photo, UV and thermal stabilities. Furthermore, the

*Corresponding author. Email: abhishek_srivastava_lu@yahoo.co.in

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display-related parameter for the alignment layer, i.e. residual DC (RDC) and voltage holding ratio (VHR), was measured and found in the acceptable range. Therefore, such composite photo-alignment layer has got immense potential to be applied in various modern display and photonic devices.

2. Experiment

Recently, it has been observed that good control on the anchoring energy provides an opportunity to optimise the optical characteristics of the displays, particularly for the ESHFFLCs.[18–20] Moreover, the anchoring energy for the azo-dye alignment layer can be tuned by the irradiation doses.[18,19] Therefore, to achieve the good optical quality, it is critically important to deal both process, i.e. alignment and stabilisation, separately. In simple words, it is better to have distinct absorption band for the photo-alignment azo-dye and stabilising monomer. Therefore, the azo-dye material SD1 (from Dainippon Ink and Chemicals Ltd, Tokyo, Japan) with absorption peak at 365 and 450 nm (Figure 1) has been used as the photo-alignment layer,[14] whereas the monomer RMM257 (from Merck, Darmstadt, Germany) with absorption peak at 300 nm (absorption spectrum is shown in Figure 1) has been chosen as the stabiliser. Furthermore, the concentration optimisation of monomer in the solution is needed to minimise the screening of the aligning characteristic of the pure SD1 and other addressing parameters. Therefore, to avoid such screening, the mixture preparation was done as follows. First, the solution of the photo-alignment material SD1 was dissolved in dimethylformamide (DMF) at a concentration 1% wt/wt (i.e. optimised for the FLCs) and termed as Sol–A [14,18]; thereafter, another solution of the monomer RMM257 and photo-initiator Igracure 651 (1% wt/wt of RMM257) were dissolved in the same solvent (DMF) at the concentration 1% wt/wt and was termed as Sol–B. Afterwards, five mixtures were prepared by mixing both the solutions in a volumetric ratio of 1:9, 3:7, 4:6, 5:5 and 7:3 for Sol–A and Sol–B, respectively. The proper miscibility of two solutions has been ensured by stirring (by means of magnetic stirrer) the mixture for 24 hrs.

Thereafter, the composite alignment film was prepared by coating the final solutions on the glass substrates followed by two-step irradiation process, as shown in Figure 2. The first irradiation with high-power (90 mW/cm²) polarised LED light (450 nm), with an optical filter to avoid 320 nm, for 10 min provides preferred easy axis to SD1 molecules with optimal anchoring energy that could be different for different FLC materials.[18] Just after the first irradiation for alignment, the same substrate has been irradiated second time by the polarised UV light ($\lambda = 320$ nm and intensity of 3 mW/cm²) with the optical filter to block light of $\lambda = 365$-450 nm, and the plane of polarisation is exactly the same as the first irradiation. The second exposure is used to create a polymer network to stabilise the SD1 photo-alignment layer. It has been observed that the 2 min irradiation by the polarised UV light is enough to provide good stability for the SD1 layer with acceptable aligning characteristic of the SD1. Therefore, the cell has been assembled by these substrates with several cell thicknesses ($d$) for different tests. The $d = 1.5$ µm was used to study the optical stability of the FLC layer whereas $d = 5$µm was used to study the electro-optical characteristics, viz. VHR, transmittance versus voltage response curve (TVC) and anchoring energy, for the composite alignment layer.

To test the stability of the alignment layer, the alignment quality of the sample has been compared before and after the exposure by photo, UV and thermal energy. The process flow to test the stability against the UV and photo energy has been shown in Figure 2. First, the cell has been fabricated with the alignment layer described above; thereafter, the cell was heated up to isotropic temperature (i.e. 100°C) and exposed to the polarised visible/UV light with the polarisation azimuth of the impinging light parallel to the easy axis of the fabricated cell. This irradiation pushes the easy axis of the alignment in an orthogonal direction. Therefore, if the alignment layer is not stable, the easy axis rotates and causes distortion and local defect in the alignment and thus decreases the contrast ratio of the FLC cell; however, if the alignment layer is stable, the contrast ratio does not have any effect on such exposures.

![Figure 1](image)(colour online) Absorption spectrums of photosensitive materials SD1 and monomer RMM257.
In addition to the photo-stability, thermal stability, optical contrast, anchoring energy and VHR are equally important parameters for a liquid crystal alignment layer. A schematic of the experimental arrangement for measurement of these parameters has been shown in Figure 3. These properties of cells were studied by placing the cell between the crossed polariser, and the whole set was illuminated.
by He–Ne laser (632 nm); thereafter, the electrically modulated optical signals were recorded by a photodetector.

The thermal stability of the alignment layer has been confirmed by comparing the TVC of nematic LC cells \( (d = 5 \mu m) \) made of pure and polymer-stabilised azo-dye alignment layer, after heating them at different temperatures till 230°C.[21] To measure the VHR in the same experiment, first a pulse of 5 V was applied to the cell for 60 µs and thereafter the transmittance was recorded against the time.[22,23] The same experiment arrangement was used for the contrast ratio and anchoring energy measurements. The detail measurement procedure is given in [12–23].

The fabricated polymer and azo-dye composite photo-alignment layer provide an opportunity to tune the anchoring energy that is of great interest, particularly for the ESHFLC materials. Therefore, most of the tests, viz. contrast ratio, anchoring energy and photo-stability, have been done on ESHFLC cells with \( d = 1.5 \mu m \) and on FLC-595. The FLC-595 is characterised by a spontaneous polarisation of \( P_S = 40 \) nC/cm\(^2\), a tilt angle of 21.3°, a rotational viscosity of 0.022 Pa·s, elastic constant of \( K_{22} = 1.65 \times 10^{-11} \) N and a helix pitch of \( P_0 = 0.72 \mu m \) at \( T = 22^\circ C \). The phase transition sequence of FLC-595 is given by \( Cr \rightarrow SmC^* \rightarrow SmA \rightarrow Iso \) at 22°C, 38°C and 72°C, respectively. On the other hand, tests related to the thermal stability, VHR and RDC measurement have been done on 5 µm thick cell nematic LC with the same alignment layer. The nematic LC MDA-01-4697 (from DIC) has been used for these tests. The phase sequence of this material is given by \( Cr \rightarrow N \rightarrow Iso \) at −20°C and 100°C, respectively.

3. Results

The phenomenon of the rewriteability of the easy axis of SD1 alignment layer has been elaborated by the optical textures (taken by the Olympus microscope under the crossed polarisers) of 1.5 µm thick FLC cell, as shown in Figure 4. Figure 4(a) shows the optical texture of the initial FLC cell with optimal anchoring energy for the pure SD1 alignment layer.[18] The two-domain structure reveals the best optical quality with maximum contrast ratio.[13, 20] The cell has been heated up to slightly above the isotropic temperature of the FLC material, and thereafter it has been exposed to the polarised blue light with polarisation azimuth parallel to the easy axis of the initial alignment. This irradiation attempts to manipulate the easy axis in a direction orthogonal to the initial direction. Afterwards, the cell has been cooled to room temperature, and the optical texture is shown in Figure 4(b). It is clear from the figure that the easy axis in Figure 4(b) is orthogonal to the initial easy axis (in Figure 4(a)). The whole process has been repeated with the orthogonally polarised light as compared to previous step. The easy axis of the SD1 alignment layer was manipulated again with relatively worse alignment and thus the worse optical quality. Thus, one can conclude here that the alignment by pure SD1 is not stable and can be altered by further irradiation.

The same test has also been done on the polymer and azo-dye composite alignment layer to test the stability. The photo-stability of the polymer and azo-dye composite layer has been evaluated by the exposure energy needed to rearrange the orientation of SD1 molecules for pure and composite mixture, and therefore the stability factor \( \alpha \) is defined as:

\[
\alpha = \frac{E_{\text{composite layer}}}{E_{\text{pure SD1}}}
\]

where \( E_{\text{composite layer}} \) is the exposure energy needed to rewrite RMM257/SD1 composite layer and \( E_{\text{pure SD1}} \) is the exposure energy needed to rewrite pure SD1.

Figure 4. (colour online) Microscopic picture of FLC textures (of size 150 µm × 80 µm) of pure SD1 layer – (a) without re-exposure; (b) re-exposure once; (c) re-exposure twice – and composite layer – (d) without re-exposure; (e) re-exposure once; (f) re-exposure twice.
The stability parameter has been plotted against the different mixture concentrations and respective optical textures of FLC-595 with \( d = 1.5 \) µm. From Figure 5, it is clear that the 4/6 mixture (i.e. 40% Sol-B and 60% Sol-A) shows least screening of the alignment characteristics of the pure SD1 and offers the good stability with \( \alpha \approx 20 \). The stability parameters for mixtures 5/5 and 7/3 are comparatively higher than that for mixture 4/6, but at the same time severe screening of aligning characteristic of the SD1 has been observed for the higher concentration of the Sol-B; therefore, mixtures with higher concentrations of the Sol-B have been left out of the scope of present work.

The inset in Figure 5 shows the stability test for the 4/6 mixture of the multiple exposure test, which is exactly the same as the test performed for pure SD1 described in Figure 4. One can observe that no change in the alignment quality has been observed for the composite alignment layer. Thus, it can be concluded that the polymer and azo-dye composite alignment layer, with mixture 4/6, shows good stability with acceptable alignment and thus better optical quality with \( \alpha = 20 \). Therefore, further tests and improvements have been done on the 4/6 mixture only.

Furthermore, the RMM257/SD1 composite alignment layer has also been tested for photo-stability issue in industrial environment. The UV stability and photo-stability of the stabilised SD1 layer, because of its photosensitivity, are critically important for the fabrication issues. Therefore, different exposure sources, i.e. blue LED with polarised light intensity of 40 mW/cm\(^2\), blue laser with polarised light intensity of 1 W/cm\(^2\) and white lamp with whole visible spectrum and non-polarised light of intensity 50 W/cm\(^2\), have been used to test the UV stability and photo-stability of the proposed alignment layer.

The contrast ratio (at two different operating voltages, i.e. 5 and 10 V) and the anchoring energy of the stabilised SD1 for photo-aligned FLC cell have been measured before and after exposure treatment and thereafter compared in Table 1. The contrast ratio and the anchoring energy coefficient \( W_Q \) for the RMM257/SD1 composite alignment layer is almost the same before and after the phototreatments, and deviation in values are within the experimental error limits. Thus, from Table 1, it can be advised that the alignment quality of RMM257/SD1 composite alignment layer after re-exposure maintains the same level and shows good photo and UV stability.

In addition to the photo-stability, temperature stability is also an important issue that is a big concern for manufacturers due to several high-temperature fabrication processes in the manufacturing line. To test the thermal stability of the fabricated polymer azo-dye composite photo-alignment layer, nematic LC cells with 5 µm thickness have been prepared with pure and composite SD1 alignment layer, and afterwards TVC, at room temperature, has been recorded before and after the thermal exposure. Figure 6 shows the TVC for pure and RMM257/SD1 composite photo-aligned nematic LC cells before and after thermal treatment at 180ºC and 230ºC for 2 h. For pure SD1 alignment layer, the TVC after the thermal exposure at 180ºC for 2 h repeats itself, which clearly suggests that the alignment layer is not affected by this thermal exposure. Whereas after the thermal exposure at 230ºC, the TVC is all deteriorated, which confirms the damaging of the SD1 alignment layer after the thermal exposure at 230ºC.

In the other hand, TVC, before and after the thermal exposure, for the RMM257/SD1 composite layer is

![Figure 5. (colour online) Stability factor and textures at different concentration ratios of composite layer RMM257/SD1. Inset shows the photo-stability of the optical texture of the composite alignment layer before (a) and after several irradiations (b) and (c) with different polarization azimuth of the irradiating light.](image-url)

| **Table 1. UV stability and photo-stability of composite 4/6 SD1 layer tested with FLC cells.** |
|-------------------|-------------------|-------------------|-------------------|-------------------|
|                  | Initial alignment | Blue LED 60 min   | Blue laser 10 s   | Lamp 30 h         | Lamp 3 days       |
| CR at 10 V       | 1550              | 1346              | 1142              | 1465              | 1436              |
| CR at 5 V        | 1423              | 1236              | 1049              | 1345              | 1321              |
| \( W_Q \) (J/m\(^2\)) | \( 5.42 \times 10^{-4} \) | \( 4.70 \times 10^{-4} \) | \( 3.99 \times 10^{-4} \) | \( 5.12 \times 10^{-4} \) | \( 5.02 \times 10^{-4} \) |
almost the same, and LC material degradation at high temperature can be attributed to the small deviation in the characteristics. However, the nature of the plot is the same that confirms that the RMM257/SD1 composite layer shows good thermal stability.

VHR is another important issue for the active matrix LCDs. We have measured the VHR for the similar 5 µm thick nematic cell. According to the widely accepted definition, the VHR is used to evaluate for the display frame time 16.7 ms. For this frame time, the VHR of the RMM257/SD1 composite layer for the optimal mixture (i.e. 4/6 mixture) is ~97% which is little bit lower than the industrial standard, i.e. ~99%. However, our prime target for the proposed RMM257/SD1 composite photo-alignment layer is field sequential colour display based on ESHFLCs with frame time ~5 ms. For this frame time, the VHR of the 4/6 mixture is ~99% as shown in Figure 7, which is widely accepted.[24]

As expected, because of mixing, the RDC of the stabilised SD1 by the polymer network is an issue and is found to be considerably larger than the pure SD1. The RDC of the composite alignment layer has been plotted against the different concentrations of the mixtures in Figure 8. The RDC decreases at higher concentrations of the monomer, but from the previous results we found that the 4/6 mixture provides the best electro-optical features. Therefore, for mixture 4/6-based alignment layer, the second exposure dose, i.e. for the stabilisation of the alignment layer, has been increased to increase the network density of
the polymer in the alignment layer and afterwards RDC was measured again, after making the same nematic cell of 5 \( \mu \)m thickness. The RDC for the 4/6 mixture has been plotted in the top-right insertion of Figure 8. The RDC of the stabilised SD1 layer with the irradiation dose of the 5.4 J/cm\(^2\) is \(\sim 0.01\) V, which is comparable to the conventional PI. Therefore, in the end, it is advised to increase the exposure doses of the second exposure, i.e. stabilisation, up to acceptable limits that in our case is 5.4 J/cm\(^2\). Furthermore, the stability parameter for the 4/6 mixture with increased irradiation dose for the stabilisation is \(\alpha \sim 24\) which is better than the previous measurement.

4. Conclusion

Here in this article, we proposed a stabilised azo-dye liquid crystal photo-alignment layer. The key point is the blending of a monomer with an azo-dye material followed by two-step irradiance. The stabilised SD1 alignment film shows comparable optical quality as that of a pure azo-dye material but with enhanced stability. The controllable anchoring energy along with good stability provides immense opportunity for the modern LC displays and photonic elements, particularly for the ESHFLCs. The RMM257/SD1 photo-alignment layer offers good UV, photo and thermal stability with good anchoring and optical quality. With proper treatment and large irradiation doses for the second step of stabilisation, the values of VHR and RDC are also found in the acceptable range. Thus, the RMM257/SD1 photo-alignment layer offers well-suited parameters with easy fabrication and therefore has the potential to find applications in a variety of modern photonic and display devices.

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**References**


