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A hysteresis-free polymer-stabilised blue-phase liquid crystal

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We report a polymer-stabilised blue-phase liquid crystal (BPLC) in an in-plane-switching (IPS) cell with negligible hysteresis and good stability. Long ultraviolet (UV) wavelength and top-side (no IPS electrode) exposure create uniform polymer network, which in turn helps to suppress hysteresis. The effect of photoinitiator is also investigated. Although a BPLC precursor without photoinitiator requires a higher UV dosage to stabilise the polymer network, it is favourable for keeping high resistivity and reducing image sticking.

Keywords: blue-phase liquid crystal; UV curing; hysteresis free

1. Introduction

Polymer-stabilised blue-phase liquid crystal (PS-BPLC) [1–3] is a promising candidate for next generation display and photonic technology.[4–6] After one decade of extensive effort, most technical challenges of PS-BPLC have been gradually solved. In order to reduce the driving voltage to below 10 V, new liquid crystal (LC) host materials with a large Kerr constant have been developed,[7–9] innovative electrode structures with deeper penetrating field have been introduced,[5,6,9] and vertical-field-switching display mode has also been proposed.[10] High transmittance can be obtained by optimising the electrode dimension.[11] And finally, contrast ratio can be improved significantly after correcting the polarisation rotation effect of a PS-BPLC cell.[12,13]

However, hysteresis and long-term stability remain a challenge to PS-BPLC. In principle, a higher monomer concentration helps to produce sturdier polymer network which is favourable to suppress hysteresis, but the trade-off is increased driving voltage.[14] Nevertheless, there has been limited investigation on the impact of ultraviolet (UV) curing condition upon polymer morphology and hysteresis. [15–18] Besides, most BPLC precursors contain some photoinitiator in order to facilitate the polymerisation process.[8,19] However, photoinitiator introduces additional ions to the BPLC system, which not only lowers the resistivity but also causes image sticking. Therefore, it is important to investigate whether we can produce a high-performance PS-BPLC without photoinitiator.

In this paper, we investigate the UV curing process of BPLC by varying the exposure wavelength and dosage with and without a photoinitiator. We find that through optimising the UV exposure conditions it is possible to fabricate a hysteresis-free, high-stability PS-BPLC device without using photoinitiator.

2. PS-BPLC cured at $\lambda = 385$ nm

The recipe of the BPLC precursor used in our experiment is listed as follows: LC host 84.10 wt% HTG-135200-100 (HCCH, China), chiral dopant 4.00% R5011 (Sigma Aldrich), and two monomers: 7.11% RM257 (HCCH, China) and 4.79% C12A (Sigma Aldrich). In this study, we did not use any photoinitiator; we will show some results with photoinitiator in Section 4. The precursor was filled into an in-plane-switching (IPS) cell, which has no surface rubbing treatment. In an IPS cell, the top substrate has no electrode, but the bottom substrate has interdigitated stripe indium tin oxide (ITO) electrodes: the electrode width is 8 μm and electrode gap is 12 μm. The cell gap was controlled at 7.5 μm by spacer balls.

In experiments, we prepared two identical BPLC cells but exposed UV light from different sides, as Figure 1 shows. Sample 1 was exposed from the top substrate side (no electrode), whereas sample 2 was from the bottom side (with IPS electrodes). Two UV wavelengths were used in our studies: $\lambda = 365$ nm (mercury lamp) and $\lambda = 385$ nm (UV LED). For convenience, let us abbreviate the shorter UV wavelength ($\lambda = 365$ nm) as SUV and longer UV ($\lambda = 385$ nm) as LUV. The results shown in Figure 1 were conducted at LUV with intensity ~8 mW/cm^2 and exposure time ~40 minutes.

Next, we measured the voltage-dependent transmittance (VT) curves of both samples. The IPS cell was sandwiched between two crossed polarisers, and
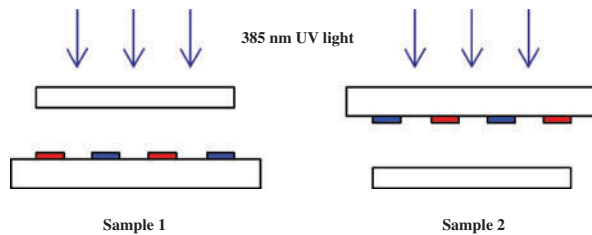
Figure 1. (colour online) Two UV exposure directions: sample 1 is exposed from the top substrate side (no electrode) and sample 2 is from bottom side (IPS electrode). LUV λ = 385 nm.

driven with 1 kHz AC voltage signal. A He–Ne laser (λ = 633 nm) was used as a probing beam. Figure 2 shows the measured results.

From Figure 2, the peak voltages of samples 1 and 2 are almost the same (109.4 V_{rms} vs. 110 V_{rms}). By fitting these VT curves using extended Kerr model, we obtained the Kerr constant K ~ 2.9 nm/V^2 for both samples 1 and 2.[20] However, sample 1 has a smaller hysteresis than sample 2 (0.3% vs. 1.8%), even though both samples are fully cured. This difference, although not significant, could originate from the non-uniform polymer network of sample 2. In sample 2, the ITO electrode blocks a portion of the incident UV light before it reaches the BPLC layer. Therefore, the polymer network in sample 1 will be more uniform and more rigid than in sample 2, which results in a smaller hysteresis for sample 1.

We also prepared some similar samples but cured at smaller UV dosages, such as 4 mW/cm^2 for 40 minutes and 8 mW/cm^2 for 10 minutes. Our test results
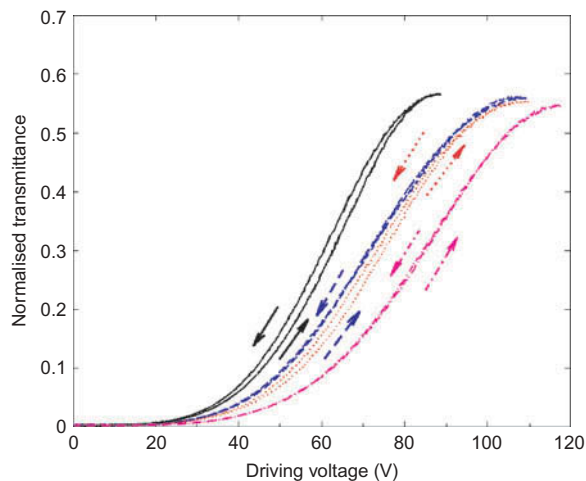

Figure 2. (colour online) Measured VT curves of samples 1–4: blue dashed lines are for sample 1, red dotted lines are for sample 2, black solid lines are for sample 3, and magenta dash-and-dot lines are for sample 4.

indicate that these samples were not fully cured. Thus, for the LUV light source, we need a higher dosage (8 mW/cm^2 for 40 minutes) to fully cure the IPS BPLC samples.

3. PS-BPLC cured by λ = 365 nm

It has been reported before that the wavelength of a UV light source affects the electro-optical property of a PS-BPLC.[15] So in this section, we compare the curing effect with SUV (λ = 365 nm) from a mercury lamp. Again, we prepared two identical IPS BPLC cells: samples 3 and 4. The UV dosage was controlled at 8 mW/cm^2 for 10 minutes. Sample 3 was exposed from top side, whereas sample 4 from bottom side; similar to the curing directions of samples 1 and 2, respectively. The measured VT curves of samples 3 and 4 are also included in Figure 2.

From Figure 2, we notice that different UV exposure directions result in remarkably different VT characteristics of samples 3 and 4, although both samples are fully cured. Sample 3 has a much lower peak voltage (88.8 V_{rms}) than sample 4 (118 V_{rms}). The fitted Kerr constant of samples 3 and 4 is K = 4.46 nm/V^2 and 2.52 nm/V^2, respectively. Besides, sample 3 shows a much larger hysteresis than sample 4 (2.9% vs. 0.8%).

Please note that samples 3 and 4 were fully cured under 8 mW/cm^2 for 10 minutes. This dosage is only 25% of that we employed to cure samples 1 and 2 using λ = 385 nm. Such a dramatically different behaviour is believed to originate from the UV penetration depth inside the BPLC layer.

The absorption of a LC composition is determined by the conjugation length of each individual component.[21] We measured the transmission spectrum of our BPLC precursor. In experiment, we made a LC cell (cell gap = 22 μm) using two UV transparent BaF_2 substrates. No ITO or alignment layer was used. We first heated the sample to an isotropic state and measured its transmission spectrum. Next, we cooled the sample to blue phase I (BP-I) state and measured its transmission spectrum again. The measured results are normalised to the transmission spectrum of an empty BaF_2 cell, as shown in Figure 3.

In Figure 3, the blue line represents the measured data in an isotropic state, where the scattering loss is negligible so that the optical loss is mainly due to the absorption of BPLC precursor. In the visible spectral region, the BPLC sample is highly transparent. As the wavelength decreases to below ~370 nm, the transmittance declines (i.e., absorption increases) sharply. The red dashed lines in Figure 3 represent the measured data in a BP-I state. Clearly, the Bragg reflection of the BPLC sample appears at λ_B ~ 460 nm (which
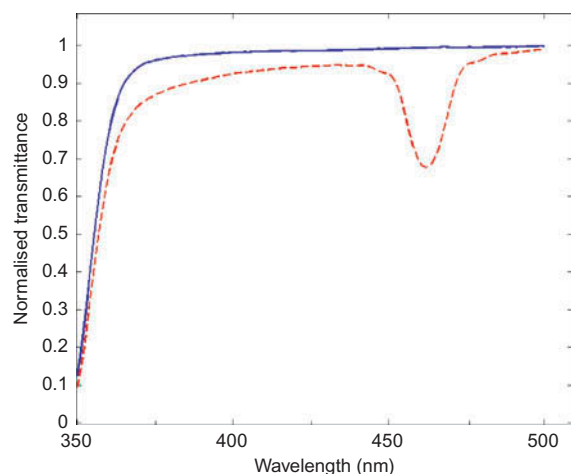
Figure 3. (colour online) Measured transmission spectrum of BPLC precursor in an isotropic state (blue solid line) and BP-I state (red dashed lines).

depends on the chiral concentration) and some light scattering loss is observed. From the blue curve, we find that the absorption coefficient at $\lambda = 365$ nm is ~4× higher than that at $\lambda = 385$ nm. These data explain well why we need 4× higher dosage at $\lambda = 385$ nm in order to fully cure the sample than that cured at $\lambda = 365$ nm. It is also noticed from Figure 3 that the absorption of the precursor in the visible region is smaller than that at 385 nm. This is also consistent to the experimental results reported in [17] in which the PS-BPLC cured with a visible light exhibits a more symmetric current–voltage (I–V) curve than that cured with a UV light.

As Figure 3 shows, the employed BPLC precursor has much stronger absorption at $\lambda = 365$ nm than that at 385 nm. As a result, the SUV light intensity decays exponentially as it traverses the BPLC cell and the

polymer network distribution inside the cell will not be uniform.[22] Upon UV exposure, more monomers will be attracted to the entrance side and these monomers will cross-link more quickly. Thus, the polymer network concentration will be denser near the top substrate, as Figure 4 illustrates. On the other hand, LUV can penetrate the BPLC cell more deeply because of its weaker absorption. As a result, the polymer network is more uniform.

As shown in Figure 4, sample 3 was cured with its top substrate (no electrode) facing SUV. Thus, a denser and more rigid polymer network is formed near the top substrate, whereas the polymer network near the IPS electrodes is looser. On the contrary, sample 4 has denser polymer network near the IPS electrode, as Figure 4 depicts. Moreover, the electric field in an IPS cell is mainly concentrated near the electrodes and its penetration depth depends on the electrode dimension.[5] Based on these mechanisms, sample 3 should have a lower operation voltage but larger hysteresis than sample 4.[16] Indeed, these phenomena are observed experimentally. In the case of LUV exposure, less UV energy is absorbed by the monomers, so a higher dosage is required to stabilise the BPLC samples. The merit is that the LUV light intensity is more uniform across the LC cell and so does the polymer network. Therefore, no matter from which direction the cell is cured, the driving voltage remains more or less the same (samples 1 and 2).

4. Impact of photoinitiator
A photoinitiator is a chemical compound that decomposes into free radicals when exposed to UV light. These free radicals play an important role to promote polymerisation reactions. Therefore, it helps lower the
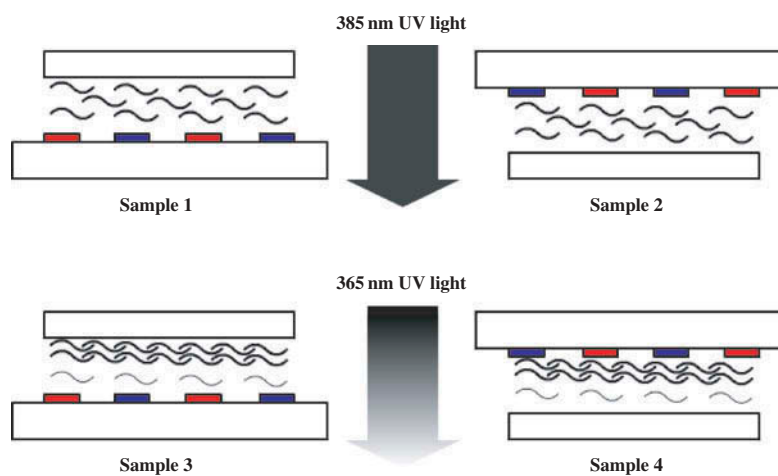

Figure 4. (colour online) Polymerisation of BPLC cells under different UV exposure conditions.

UV exposure dosage. But on the downside, it introduces extra ions to the LC system, which could cause unfavourable image sticking problem. Therefore, the amount of photoinitiator should be controlled carefully.

In the above-mentioned BPLC samples 1–4, we did not use any photoinitiator. In this section, we report the impact of photoinitiator in the polymerisation process of BPLC. In our experiment, we mixed a small amount of photoinitiator Darocur 1173 (Ciba) to our BPLC precursor mentioned in Section 2 and then exposed different UV lights to cure the precursor. We prepared two samples: BPLC-1 containing 99.8 wt% precursor and 0.2 wt% photoinitiator, and BPLC-2 containing 97.9 wt% precursor and 2.1 wt% photoinitiator. Samples 5 and 6 are the IPS cells filled with BPLC-1 and BPLC-2, respectively, and cured under the same conditions: $\lambda = 365$ nm, 8 mW/cm^2 intensity, top-side exposure for 10 minutes.

Figure 5 depicts the measured VT curves of sample 3 (no photoinitiator), sample 5 (0.2%), and sample 6 (2.1%) under same UV exposure conditions. As the photoinitiator concentration increases, the hysteresis varies from 2.9% (sample 1) to 1.4% (sample 5) and 1.7% (sample 6), but the peak voltage increases from 90 V$_{rms}$ to ~95 V$_{rms}$. These results can be explained as follows. The photoinitiator promotes the polymerisation process so that even a low-intensity UV near the bottom of the cell can still cross-link the monomers. Thus, for the samples exposed from the top substrate, photoinitiator helps increase the polymer concentration near the bottom electrodes, which in turn leads to a higher driving voltage but a lower hysteresis.

We also cured an IPS cell filled with BPLC-1 (0.2% photoinitiator) under LUV (385 nm). The dosage was 8 mW/cm^2 × 10 minutes. This dosage is only 1/4 of the previous dosage we used to cure samples 1 and 2. With the help of photoinitiator, such a low dosage can still stabilise the BPLC. The on-state voltage of this sample is similar to that of samples 1 and 2. This result confirms that a small amount of photoinitiator indeed speeds up the curing process of BPLC precursor at $\lambda = 385$ nm.

In summary, we find that LUV not only improves polymer network uniformity but also suppresses hysteresis. But to fully cure the BPLC precursor, a higher exposure dosage is needed. Photoinitiator improves the curing speed for LUV and polymer network uniformity for SUV. But for LUV, the improvement of curing speed may not be worthwhile because photoinitiator introduces extra ions to the LC system, which lowers the resistivity and causes image sticking. Therefore, from device performance viewpoint, following curing conditions are preferred: (1) to employ a LUV, (2) to expose light from the top substrate (no
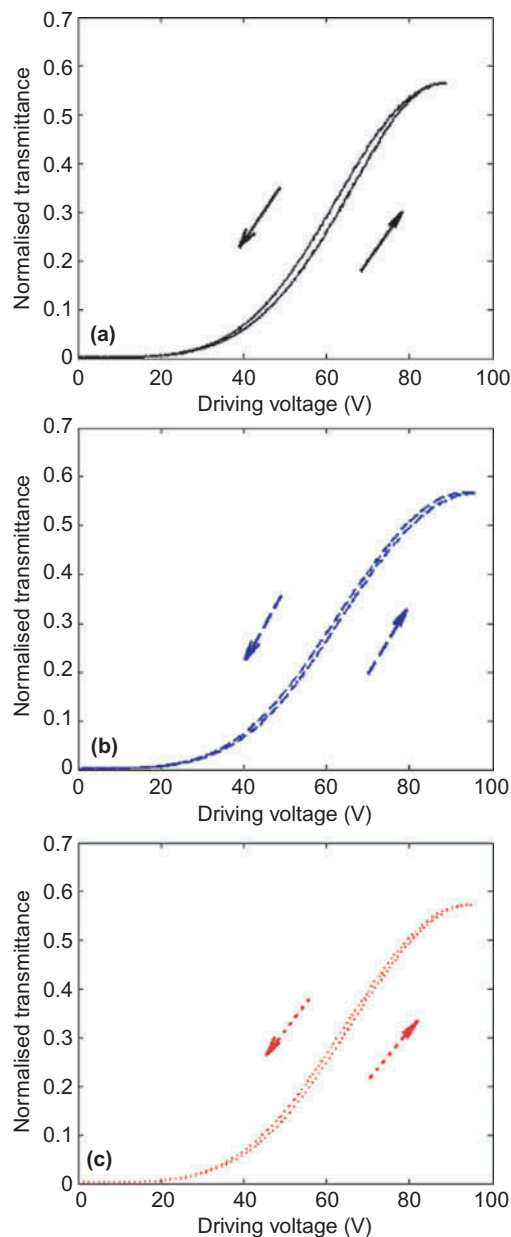

Figure 5. (colour online) Measured VT curves of three PS-BPLC samples: (a) black solid line is for sample 3 (no photoinitiator); (b) blue dashed lines are for sample 5 (0.2% photoinitiator); (c) red dotted lines are for sample 6 (2.1% photoinitiator). UV lamp: $\lambda = 365$ nm, top exposure. Probing wavelength $\lambda = 633$ nm.

electrode), and (3) to avoid using photoinitiator while tolerating the increased exposure dosage.

5. Hysteresis-free PS-BPLC

Based on the approaches discussed above, we prepared another BPLC sample with optimal curing conditions. We filled the precursor without photoinitiator into an IPS cell and cured by a 385-nm UV light from
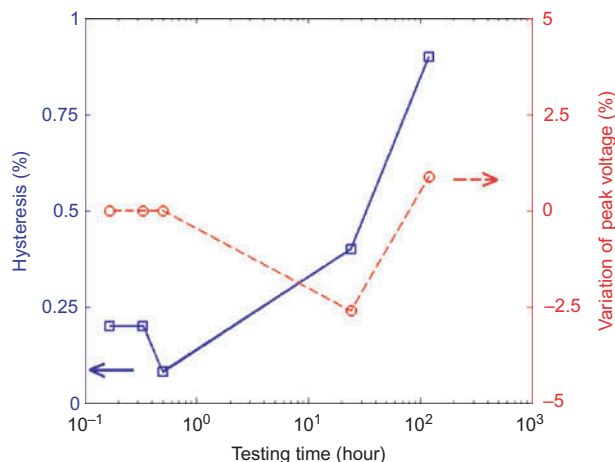
Figure 6. (colour online) Aging test of a PS-BPLC sample cured under optimised curing conditions. Blue open squares show the hysteresis variation during the test. Red open circles represent the peak voltage variation of the sample during the test.

top side. The UV intensity was 16 mW/cm^2 and exposure time was 40 minutes. An aging test was taken to evaluate the long-term stability of this sample. We applied the peak driving voltage (~115 V) upon the same sample for 10 minutes, 20 minutes, 30 minutes, 24 hours and 120 hours, respectively, and then measured its VT curve after each test. The measured results are plotted in Figure 6 – the peak voltage of this sample has a small variation of 2.5%. The hysteresis also varies slightly, but is within 1%. We also notice that the residual transmittance after aging test remains at 0.05%, corresponding to CR ~ 1200:1. These results prove that this PS-BPLC sample has quite good stability. Although the driving voltage of this sample is still high compared to other reported BPLC materials, our main objective here is to demonstrate a polymerisation process which can lead to hysteresis-free device with good long-term stability.

6. Conclusion

We have investigated the impact of UV curing conditions on the hysteresis and stability of a PS-BPLC. UV wavelength, exposure direction and dosage, and photoinitiator all play important roles determining the stability of a PS-BPLC composite. Using a long UV wavelength, high exposure dosage, and no photoinitiator we demonstrated a hysteresis-free BPLC device with very good stability.

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