# Stabilizing blue phase liquid crystals with linearly polarized UV light

Daming Xu<sup>\*a</sup>, Jiamin Yuan<sup>a</sup>, Martin Schadt<sup>b</sup>, Jing Yan<sup>a, c</sup>, Shin-Tson Wu<sup>a</sup>

<sup>a</sup>College of Optics and Photonics, University of Central Florida, Orlando, Florida 32816, USA;

<sup>b</sup>High-Tech Consulting, Liestalerstrasse 77, 4411 Seltisberg, Switzerland;

<sup>c</sup>Display Center, School of Electronic Science and Engineering, Southeast University, Nanjing,

China

# ABSTRACT

Polymer-stabilized blue-phase liquid crystal (PS-BPLC) has become an increasingly important technology trend for information display and photonic applications. BPLC exhibits several attractive features, such as reasonably wide temperature range, submillisecond gray-to-gray response time, no need for alignment layer, optically isotropic voltage-off state, and large cell gap tolerance when an in-plane switching (IPS) cell is employed. However, some bottlenecks such as high operation voltage, relatively low transmittance, and noticeable hysteresis and prolonged response time at high field region for IPS mode, still remain to be overcome before widespread application of BPLC can be realized. To reduce operation voltage, both new BPLC materials and new device structures have been investigated. In this paper, we demonstrate the stabilization a photopolymer-embedded blue phase liquid crystal precursor using a linearly polarized UV light for first time. When the UV polarization axis is perpendicular to the stripe electrodes of an IPS cell, anisotropic polymer networks are formed through the linear photo-polymerization process and the electrostriction effect is suppressed. As a result, the measured hysteresis is dramatically reduced from 6.95% to 0.36% and the response time shortened by ~2X compared to unpolarized UV exposure. To induce larger anisotropy in polymer networks for mitigating the electrostriction effect, high-intensity linearly polarized UV exposure is preferred. It is foreseeable this method will guide future BPLC device and material development as well as manufacturing process. The dawn of BPLCD is near.

Keywords: Blue phase liquid crystal, LCD, Kerr effect, electrostriction effect, hysteresis, linear photo-polymerization

# **1. INTRODUCTION**

Polymer-stabilized blue phase liquid crystal (PS-BPLC)<sup>1</sup> is a very prospective technology for next-generation display<sup>2, 3</sup> and photonic applications.<sup>4-6</sup> Unlike mainstream nematic liquid crystals,<sup>7-9</sup> BPLC is a self-assembly nanostructure electro-optic medium exhibiting several attractive features. Firstly, it possesses self-assembly process to form threedimensional lattice structure without the need of an alignment layer (e.g. polyimide); secondly, it exhibits microsecond response time<sup>10</sup> resulted from nanoscale (typically  $\sim 100$  nm) double-twisted cylinder diameter and short coherence length; and thirdly, its three-dimensional lattice structure lead to optically isotropic voltage-off state. Since no surfactant is required to generate uniform molecular alignment for PS-BPLC, the device fabrication process can be greatly simplified. On the other hand, fast response time is particularly appealing as it not only reduces motion image blurs<sup>11</sup> but also enables color-sequential display using RGB LED backlight with negligible color breakup.<sup>12, 13</sup> By eliminating spatial color filters, both optical efficiency and resolution density are tripled. High optical efficiency helps to reduce power consumption while high resolution density is particularly desirable for the future Ultra High Definition Television. Moreover, with an isotropic voltage-off state, PSBPLC is able to achieve high contrast ratio and wide view.<sup>14</sup> After a decade of extensive efforts, major technical challenges of PS-BPLCs have gradually been resolved. For example, by using large Kerr constant BPLC materials<sup>15-17</sup> and implementing device structures with enhanced penetrating fields<sup>18-20</sup>, the operation voltage has been reduced from 50V to below 10V. Meanwhile, high transmittance (> 80%) can be achieved through optimizing the refraction effect of the non-uniform electric fields.<sup>21</sup> Moreover, an over 3000:1 contrast ratio has been demonstrated by compensating the polarization rotation effect of PS-BPLC cells.<sup>22, 23</sup>

In terms of the device configuration, both in-plane-switching (IPS)<sup>18-20</sup> and vertical field switching<sup>24, 25</sup> modes have been developed. Between these two, IPS is more commonly employed because of its simpler backlight system and fabrication. However, for IPS cells, hysteresis and prolonged response times, especially in the high field region, remain as technical challenges.<sup>26, 27</sup> This is due to the electric field generated by the IPS electrodes are non-uniform; in particular, the field at

Emerging Liquid Crystal Technologies X, edited by Liang-Chy Chien, Harry J. Coles, Hirotsugu Kikuchi, Ivan I. Smalyukh, Proc. of SPIE Vol. 9384, 93840H · © 2015 SPIE · CCC code: 0277-786X/15/\$18 · doi: 10.1117/12.2081459 the edge of the electrodes are very strong. According to prior studies, up to three electric field-induced effects occur in PS-BPLCs when electric field increases: 1) local LC director reorientation within the double-twist cylinder of BPLC governed by Kerr effect;<sup>28</sup> 2) lattice distortion induced by electrostriction effect;<sup>29</sup> and 3) phase transition to a LC phase with lower symmetry.<sup>30</sup> The typical response time of the Kerr effect is in the submillisecond range, but the latter two processes usually take several milliseconds or even longer to accomplish. When the electric field is below a critical field ( $E_c$ ), the Kerr effect dominates, which means the response time is fast and the hysteresis is negligible. However, if the electric field exceeds  $E_c$ , electrostriction would gradually develop,<sup>31, 32</sup> causing both hysteresis and response time to increase dramatically. Hysteresis should be suppressed as it affects the accuracy of grayscale control. Meanwhile, if the response time of BPLCs increases into the millisecond range, then a major advantage of PS-BPLC over nematic LCs would be lost. Therefore, there is an urgent need for suppressing the electrostriction effect in order to achieve submillisecond response time and hysteresis-free PS-BPLC devices.

In this paper, we propose an approach for suppressing the electrostriction effect by polymerizing photopolymers with linearly polarized UV light instead of conventional unpolarized UV. We found linear photo-polymerization  $(LPP)^{33}$  can induce an anisotropic polymer network in the bulk of BPLCs, generating anisotropic electrostriction with respect to the direction of applied electric fields. By setting the polarization direction of the crosslinking UV light perpendicular to the stripe electrodes of an IPS cell, the electrostriction effect is dramatically suppressed. As a result, the hysteresis diminishes from 6.95% to 0.36% and the response time is improved by a factor of two, as compared to unpolarized UV curing.

# 2. EXPERIMENT

To form polymer network for stabilizing the BPLC lattice, two types of monomers are commonly used:<sup>3</sup> a di-functional (e.g. RM257) monomer is mixed with a mono-functional [e.g. dodecyl acrylate (C12A)] or a tri-functional monomer [e.g. 1,1,1-trimethylolpropane triacrylate (TMPTA)]. The chemical structures of these exemplary monomers are depicted in Fig. 1. Conventionally, unpolarized UV light was used to conduct the polymerization process of monomers in PS-BPLC. However, it is known that the photo-crosslinking mechanism of monomers depends on the polarization of UV light.<sup>33, 34</sup> For instance, the crosslinking probability of a dichroic acrylate moiety is greater when exposed to UV light whose polarization axis is parallel to the double bonds instead of perpendicular. Therefore, by crosslinking double bonds of monomers with a linearly polarized UV light, anisotropy can be induced in the polymer networks. From previous study, it was found that the severity of electrostriction mainly depends on the soundness of polymer network.<sup>31</sup> Hence, by controlling the UV polarization axis with respect to the direction of the stripe electrodes of an IPS-BPLC cell, the formed anisotropic polymer network could result in anisotropic electrostriction correspondingly.



Figure 1. Chemical structures of monomers employed in our PS-BPLC.

In our experiments, we employed a large  $\Delta \varepsilon$  nematic LC host JC-BP07N (JNC, Japan) whose physical properties are:  $\Delta n = 0.162$  at  $\lambda = 633$  nm,  $\Delta \varepsilon = 302$  at 100 Hz and 22°C, and  $T_c = 87^{\circ}$ C.<sup>35</sup> The BPLC precursor consists of 86.53 wt. % JC-BP07N, 2.82 wt. % chiral

dopant R5011 (HCCH), 6.31 wt. % RM257 (Merck), 4.02 wt. % C12A (Sigma Aldrich) and 0.32 wt. % photoinitiator. The BPLC precursor was heated to an isotropic phase and then filled into IPS cells with cell gap  $d \sim 7.3 \,\mu\text{m}$ . The cells comprise interdigitated pixel electrodes on the bottom substrates (electrode width  $w = 8 \,\mu\text{m}$ , spacing  $l = 12 \,\mu\text{m}$ ) without polyimide alignment layer. Next, the cells were place on a Linkam temperature controllable stage, cooled to a temperature close to the chiral nematic and blue phase transition temperature, and then illuminated with UV light for 15 min ( $\lambda \sim 365$  nm, intensity 8 mW/cm<sup>2</sup>). After UV exposure, the nanostructured BPLC composite was self-assembled. In the next step, the IPS cell was sandwiched between two crossed polarizers and a He-Ne laser was used as a probing beam ( $\lambda = 633$  nm). The voltage-dependent transmitted light was focused by a lens so that different diffraction orders could be collected by the detector.

# 3. RESULTS AND DISCUSSION

## 3.1 Effect of UV polarization

In order to investigate the effect of UV polarization on the electro-optic properties of PS-BPLCs, we first prepared three IPS samples exposed under different UV polarization conditions. The directions of UV polarization were parallel and perpendicular to the stripe electrodes in Sample 1 and 2, respectively; whereas Sample 3 was cured by unpolarized UV light. Since temperature cooling rate and curing temperature play a very important role in determining the properties of polymer network,<sup>36, 37</sup> we kept these two parameters identical for all three samples. A linear UV polarizer is placed between UV light source and BPLC cell in all polarized-exposure experiments, as shown in Fig. 2.



Figure 2. Experimental setup of curing process of LPP-stabilized BPLC cell.

Some prior studies reported the electrostriction effect could be characterized by measuring the shift of Bragg reflection wavelength.<sup>38</sup>, <sup>39</sup> In those experiments, the results were measured using LC cells with homogeneous alignment, in which the deformation of cubic lattice caused by the vertical electric field would shift the Bragg reflection wavelength. In contrast, the IPS cells employed in transmissive BPLCD do not have any alignment layers, and the electric field is mainly in the horizontal plane. Thus, the shift in Bragg reflection wavelength is very small and therefore difficult to detect. Nevertheless, the degree of electrostriction effect causes noticeable hysteresis and increased response time.<sup>31</sup> Accordingly, in order to evaluate the degree of electrostriction, we measured and compared the hysteresis as well as response time of these three samples. The hysteresis was measured by increasing the voltage to their individual peak transmittance and then sweeping it back to zero. To measure the rise time, we applied a voltage to the BPLC sample

and recorded the transmittance change by a digital oscilloscope. Similarly, to measure decay time we removed the on-state voltage of the BPLC sample instantaneously and recorded the transmittance change.

#### 3.1.1. Hysteresis

Figure 3 depicts the measured hysteresis loop of Samples 1-3, and the numerical values of their operation voltage and hysteresis are listed in Table 1. From the table we can find that Sample 2 (UV polarization is perpendicular to the stripe IPS electrodes) exhibits a much smaller hysteresis than Sample 3 (cured by unpolarized UV light).



Figure 3. Hysteresis loops of Samples 1-3 (Solid lines: forward driving, dashed lines: backward driving).

	Sample 1	Sample 2	Sample 3
$V_{on}\left(\mathrm{V}\right)$	51.8	56.2	53.0
Hysteresis	7.56%	0.36%	6.95%
$ au_{rise}$ (µs)	674.6	456.8	524.7
$ au_{decay}$ (ms)	4.34	1.90	3.72
$t_1$ (ms)	0.51	0.27	0.39
$t_2 (\mathrm{ms})$	6.47	3.78	5.98
B/(A+B)	43.8%	16.9%	38.7%

Table 1. Measured operation voltage, hysteresis, response time, fitted time constants and contribution of electrostriction effect of Samples 1-3.

The physical mechanism underlying the observed difference is explained as follows. In the BPLC precursor containing C12A and RM257 monomers, the directional LPP photoreaction is parallel to the polarization axis of the incident linearly polarized UV radiation. As a result, the formed polymer network is more rigid along the UV polarization axis.<sup>33, 40</sup> The LPP-induced anisotropy in polymer networks of Samples 1 and 2 are sketched in Figs. 4(a) and 4(b), respectively. In Sample 2, the polymer network is formed along the UV polarization direction; that is, parallel to the direction of the applied electric field, as Fig. 4(b) depicts. Therefore, the polymer network is more robust against electric field-induced deformation or distortion along the LPP direction, leading to a suppressed electrostriction effect and a reduced hysteresis. In contrast, for Sample 1, in which the UV polarization parallel to the stripe electrodes, the polymer network is mainly formed along the electrode direction, as shown in Fig. 4(a), and thereby it is less robust along the direction of the applied electric field. Consequently, the polymer network is more likely to be distorted or deformed by the

applied electric field in the configuration of Fig. 4(a), resulting in more severe electrostriction. This is indeed observed in Sample 1, which exhibits the largest hysteresis (7.56%) as depicted in Fig. 3.



Figure 4. LPP-induced polymer network in (a) Sample 1 and (b) Sample 2.

#### 3.1.2. Dynamic response

On the other hand, among Samples 1-3, Sample 2 exhibits the fastest rise and decay times while Sample 1 is the slowest, as Table 1 lists. To explain the difference, the double relaxation model was used to characterize the decay process.<sup>31</sup> This model well reveals the contributions of Kerr effect and electrostriction effect on the electro-optic properties of a PS-BPLC device. In the following experiments, each cell was driven to its own peak transmittance after which the voltage was instantaneously removed. The transient transmittance change was recorded by a digital oscilloscope. The measured change in transmittance *T* is related to the phase retardation  $\varphi$  by:

$$T = \sin^2(\varphi/2). \tag{1}$$

The black solid line in Fig. 5 shows the measured transient phase retardation of Sample 2 during the decay process. Then the experimental data was fitted with following double relaxation equation:<sup>31</sup>

$$\varphi(t) = Ae^{-t/t_1} + Be^{-t/t_2}, \tag{2}$$

where  $t_1$  and  $t_2$  are the average decay time constants while A and B are the phase retardations due to Kerr effect and electrostriction, respectively. The double exponential equation is commonly used to characterize a two mechanism-involved dynamic process.<sup>41</sup>



Figure 5. Transient decay process of Sample 2 at 56.2V.

The fitting curve (magenta solid line) in Fig. 5 indicates that Eq. (2) well describes the decay process of the phase retardation. The fitted time constants and the contribution of electrostriction effect, which is described by B/(A + B) in our model, are also included in Table 1.<sup>31</sup> All the values of  $t_1$  lie in the submillisecond range while those of  $t_2$  are around several milliseconds. These results correspond well with the previously reported response time of fast Kerr effect and the slow electrostriction effect. Please note here that Sample 2 exhibits the fastest response time. This is due to the suppression of electrostriction by polarized crosslinking, which can be seen from the smallest B/(A + B) ratio of Sample 2. However, from Fig. 4 the non-planar electric field at the edges of planar stripe electrodes is still quite strong,<sup>32</sup> therefore the electrostriction effect is yet not negligible (16.9%). Nevertheless, compared to Sample 3 which is stabilized by unpolarized UV light, this ratio is reduced by more than 2X. By using protruded electrodes instead of planar electrodes,<sup>32</sup> the on-state voltage would drop to below 10V and the electrostriction effect should be completely suppressed. As a result, the response time should be in the submillisecond range over the entire driving voltage range.

## 3.2 Effect of UV illumination intensity

Meanwhile, the illumination intensity of polarized UV light affects the rate and the anisotropy of the crosslinking process. Thus, UV intensity also plays an important role in the LPP process. Using LPP-photoalignment, which employs polarized UV light to induce anisotropic LC-surface alignment,<sup>33</sup> as an analogy, the induced surface anchoring of LPP-photoalignment is related to the intensity of the activating UV light.<sup>42</sup> This trend applies to polarized UV-polymerized PS-BPLC as well.

In order to investigate the effect of illumination intensity, we prepared two more samples using different UV exposure intensities in addition to Sample 2 for comparison. The UV dosage for all three samples was the same: 8 mW/cm<sup>2</sup> for 15 min, 4 mW/cm<sup>2</sup> for 30 min, and 2 mW/cm<sup>2</sup> for 60 min. The measured hysteresis loops of these three samples are plotted in Fig. 6 and the numerical values of their operation voltages, hysteresis, and response times are listed in Table 2. As we can see, when UV exposure intensity increases, the response time becomes faster while the hysteresis is reduced, indicating that the electrostriction is suppressed. This trend is similar to the LPP process of azo-type monomers, in which the diffusion rate of linearly polarized pre-polymers is proportional to the illumination power according to a diffusion model of photopolymers.<sup>42</sup> Hence, here we use this model as an analogy to explain the correlation of UV intensity and LPP-induced anisotropy in PS-BPLC. The higher diffusion rate under stronger UV illumination power expedites the anisotropic polymerization process, and accordingly results in a larger anisotropy of polymer networks. Consequently, a stronger polymer network is formed along the electric field direction, thus suppressing electrostriction. In analogy, lower UV illumination power lead to smaller anisotropy of polymer networks. Hence, a linearly polarized UV light with strong intensity is preferred in LPP-stabilization in order to induce a large anisotropy in the polymer networks of PS-BPLCs for the purpose of suppressing electrostriction effect.



Figure 6. Hysteresis loops of IPS cells under different UV illumination intensities (Solid lines: forward driving, dashed lines: backward driving).

UV Intensity	$V_{on}$	Hysteresis	$ au_{rise}$ (µs)	$ au_{decay}$ (ms)
$2 \text{ mW/cm}^2$	53.2V	6.79%	860.5	3.67
$4 \text{ mW/cm}^2$	54.0V	3.40%	594.5	2.78
8 mW/cm <sup>2</sup>	56.2 V	0.36%	456.8	1.90

Table 2. Measured operation voltage, hysteresis and response times of IPS cells under different UV illumination intensities.

#### 3.3. Monomer selection

Besides the RM257 and C12A monomer combination discussed above, we also investigated the effect of LPP on the electro-optic properties of PS-BPLCs by using another monomer combination, namely the di-functional monomer RM257 and the tri-functional monomer TMPTA. The blue phase precursor consists of 86.90 wt. % JC-BP07N, 2.81 wt. % chiral dopant R5011, 5.98 wt. % RM257, 3.99 wt. % TMPTA and 0.32 wt. % photoinitiator. This time, we also prepared three IPS samples under different UV curing conditions. The directions of UV polarization were parallel and perpendicular to the stripe electrodes in Sample 4 and 5, respectively; whereas Sample 6 was illuminated by unpolarized UV light. All three samples were polymerized with the same UV dosage with: 8 mW/cm<sup>2</sup> for 15 minutes.



Figure 7. Measured hysteresis loops of Samples 4-6 (Solid lines: forward driving, dashed lines: backward driving).

The measured hysteresis loops of these three samples are plotted in Fig. 7, and the numerical values of their operation voltage, hysteresis as well as response time are listed in Table 3. Compared to the combination of RM257 and C12A, the samples comprising RM257 and TMPTA exhibit much faster response time. This results from the fact that the tri-functional monomer TMPTA has three photo-crosslinking double bonds, which can form much stronger polymer network than the mono-functional monomer C12A. Nevertheless, these three samples do not exhibit large differences in terms of operation voltage, hysteresis and response time under different UV polarization directions. This is because the three photo-crosslinking double bonds of TMPTA are along different directions, thus rendering their polymer networks more likely to be isotropic no matter which direction is the UV light polarized along. Therefore, in order to use of the LPP-stabilization for the purpose of suppressing electrostriction effect, the combination of monomer-functional and di-functional monomers should be chosen.

	V <sub>on</sub>	Hysteresis	$ au_{rise}$ (µs)	$ au_{decay}$ (µs)
Sample 4	57.2 V	4.37%	362.9	958.4
Sample 5	58.0 V	3.97%	369.3	810.7
Sample 6	58.0 V	4.14%	345.8	871.5

Table 3. Measured operation voltage, hysteresis, and response time of Samples 4-6.

## 4. CONCLUSION

In conclusion, we propose a method to suppress the electrostriction in PS-BPLCs via polymerizing photopolymers with linearly polarized UV light. By illuminating the mono-functional monomer C12A and the di-functional monomer RM257 with linearly polarized UV light, anisotropic polymer networks are formed, resulting in anisotropic electrostriction. Linear polarization of the cross-linking UV light perpendicular to the stripe electrodes strongly suppresses electrostriction. The resulting hysteresis of the driving voltage is reduced from 6.95% to 0.36% and the response times improve by a factor of two. To induce a larger anisotropy in the polymer network which further reduces the electrostriction effect, a more powerful linearly polarized UV exposure is required.

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