Effect of Polymer Concentration and Composition on Blue Phase Liquid Crystals

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Abstract—Effect of polymer concentration and composition on the electro-optic properties of blue phase liquid crystal (BPLC) composites is investigated. By increasing the polymer concentration, a more stable structure and faster response time are obtained, while keeping a low hysteresis (∼3%). The major tradeoff is the increased operating voltage. Monomer ratio also plays an important role on the stability of the polymer-stabilized BPLC.

Index Terms—Blue phase (BP), liquid crystal (LC), polymer.

I. INTRODUCTION

BLUE PHASE liquid crystal (BPLC) has been studied for decades [1]–[3], however, the narrow temperature range limits its useful applications. Recently, with polymer stabilization, the temperature range of BPLC has been widened to more than 60 K [4]. The polymer-stabilized BPLC (PS-BPLC) has potential to become the next-generation display technology [5], [6] since it exhibits several revolutionary features, such as alignment-layer free, submillisecond response time [7], and wide viewing angle. However, the polymer concentration effect on the electro-optic properties of BPLCs has not been studied systematically.

In this paper, we investigate the polymer effect on the electro-optic properties of a self-assembled nano-structured BPLC composite. A PS-BPLC requires two kinds of monomers: mono-functional and di-functional monomers. We control the overall monomers concentration, as well as the ratio between the two monomers. Polymer effects on the residual birefringence, operating voltage, hysteresis, and response time of the PS-BPLC device are presented.

II. EXPERIMENT

We prepared a BPLC mixture consisting of 65 wt% Merck BL038 and 35 wt% chiral dopants (25% CB15 and 10% ZLI-4572). The phase transition temperature of the mixture is ISO 59.7 °C BP 57.4 °C N^* during the cooling process and N^* 59.0 °C BP 59.8 °C ISO during the heating process, where ISO represents isotropic phase, and N^* stands for chiral nematic phase. A monofunctional monomer C12A and a difunc-

TABLE I
MONOMER CONCENTRATIONS OF PRECURSORS

Overall monomer concentration (wt%)	Monomer ratio (RM257 : C12A)		
	1:1	2:1	3:1
9%	Sample 1	Sample 2	Sample 3
12%	Sample 4	Sample 5	Sample 6
15%	N/A	Sample 7	N/A

tional monomer RM257, as well as a small amount of photoinitiator (∼0.5 wt%) were added to the BPLC mixture. It was found that the concentration of RM257 needs to be higher than 4% in order to stabilize the blue phase lattice structure. On the other hand, the concentration of C12A should be lower than 6% otherwise blue phase cannot be observed in the precursor. It is believed that excessive C12A would suppress the formation of blue phase. To investigate the polymer effects, seven precursors with different monomer concentrations were prepared, as listed in Table I. These precursors were heated up to an isotropic phase and then filled into in-plane-switching (IPS) cells with 10 μm electrode width, 10 μm electrode gap, and 7.5 μm cell gap. Afterwards, UV light with 2 mW/cm^2 intensity was irradiated for 30 min. near the BP to chiral nematic transition temperature. After UV irradiation, PS-BPLC composites were formed. The clearing temperature of the PS-BPLC composites is ∼ 57 °C and we have not observed the blue phase to N* transition as we cool down our samples to 0 °C. Although green bluish color was observed under crossed polarizers, the PS-BPLC composites are transparent and optically isotropic for the probing light at $\lambda = 633$ nm. The wavelength effect of the optically isotropic LC has been studied before [8].

III. RESULTS AND DISCUSSION

A. Residual Birefringence

Fig. 1(a) shows the dark state of sample 2 under crossed polarizers when a voltage of 140 V is applied and then suddenly removed, and Fig. 1(c) represents the dark state after applying 190 V. The strong electric field distorts the blue phase structure and leads to light leakage. While the green and blue colors are the intrinsic colors of blue phase, the observed white and yellow stripes are due to the light leakage at the electrode gap. Light leakage degrades the device contrast ratio and needs to be minimized.

To investigate the optic axis direction of the residual birefringence, a $\lambda/4$ plate was inserted before the analyzer [9]. The
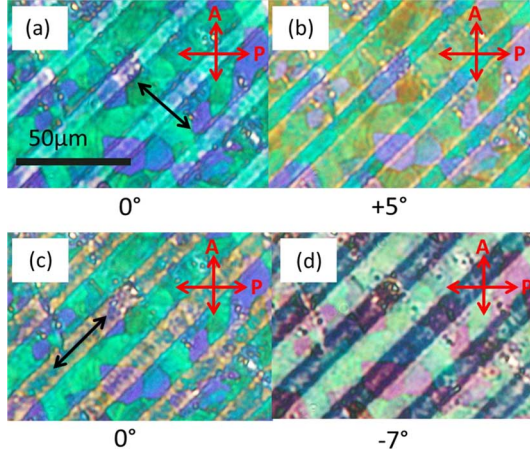
Fig. 1. Microscope photos of sample 2. (a) Voltage is removed from 140 V and under crossed polarizers. (b) Voltage is removed from 140 V and the analyzer is rotated by $+5°$. (c) Voltage is removed from 190 V and under crossed polarizers. (d) Voltage is removed from 190 V and the analyzer is rotated by $-7°$. (P: polarizer transmission axis. A: analyzer transmission axis. The black arrow represents the optic axis direction of the residual birefringence.)

Fig. 2. Microscope photos of IPS cells after driving. (a) Sample 1, (b) Sample 2. (c) Sample 3. (d) Sample 4. (e) Sample 5. (f) Sample 6. (g) Sample 7.

fast or slow axis of the $\lambda/4$ plate coincides with the transmission axis of the polarizer. The $\lambda/4$ plate compensates the phase retardation caused by the residual birefringence and converts the elliptically polarized light into an almost linearly polarized light. This linearly polarized light could be blocked by rotating the analyzer. As shown in Fig. 1(b), we rotated the analyzer by $+5°$ to compensate the residual birefringence. As a result, the white light leakage at the electrode gap is suppressed and only the original green and blue colors are observed. Similarly, in Fig. 1(d), we rotated the analyzer by $-7°$ to compensate the residual birefringence. For reference, we also find that when a small voltage is applied to the sample, i.e., the optic axis is along the electric field direction, we need to rotate the analyzer a positive angle to compensate the induced birefringence. Although the rotation angle is not accurate due to the non-uniform distribution of the residual birefringence, the positive sign implies that the residual birefringence of Fig. 1(a) has an optic axis along the electric field direction, which we call positive birefringence for simplicity; while the optic axis of the residual birefringence of Fig. 1(c) is perpendicular to the electric field direction, called negative birefringence. It is believed that there are two mechanisms contributing to the residual birefringence, perhaps caused by the polymer network distortion and blue phase lattice distortion. Due to the complexity of the material system, it is still not clear how the polymer network interacts with the liquid crystal. But from the observation we conclude that when the electric field is weak, the positive residual birefringence is dominant; and as the electric field increases the negative residual birefringence first appears at the electrode edges and then penetrates to the electrode gap region. When the electric field is sufficiently strong, the negative residual birefringence dominates.

All the seven prepared samples were examined under a polarized optical microscope after driving. Fig. 2 shows the morphologies of the seven samples under crossed polarizers. Comparing Fig. 2(b), (e), and (g), we find that the sample with higher polymer concentration has less residual birefringence, indicating a more stable structure. On the other hand,
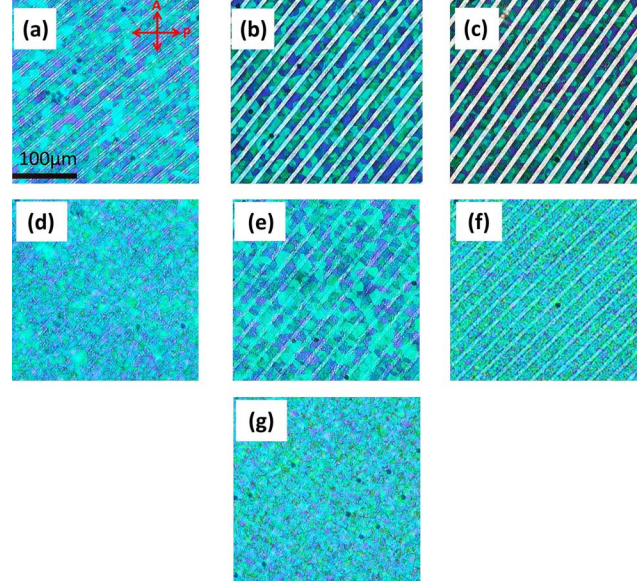
comparing Fig. 2(a), (b), (c), we find that sample 1 is more stable than samples 2 and 3. Similarly, sample 4 is more stable than samples 5 and 6 when we examine Fig. 2(d), (e), and (f). Therefore, the 1:1 ratio of RM257 and C12A gives a more stable structure. We also tried to prepare a sample with 4% RM257 and 6% C12A, but this sample shows severe phase transition after driving due to the low concentration of RM257.

B. VT Curves

We measured the voltage-dependent transmittance (VT) curves of our IPS cells by placing it between two crossed polarizers. To maximize transmittance, the electrode direction was oriented at $45°$ to the polarizer's transmission axis. A He-Ne laser ($\lambda = 633$ nm) was used as the light source. The cells were driven by a square-wave voltage with 1 kHz frequency. To get rid of the diffraction effect, we measured the VT curves under crossed polarizers and parallel polarizers, respectively, and then calculated the normalized transmittance as follows:

$$T_{\text{nor}}(V) = \frac{T_{\perp}(V)}{T_{//}(V) + T_{\perp}(V)}, \tag{1}$$

where $T_{\perp}$ is the transmittance under crossed polarizers and $T_{//}$ is that under parallel polarizers. Fig. 3 shows the normalized VT curves of these seven samples.

In Fig. 3, samples 1–3 have a lower on-state voltage (V_{on}, corresponding to the peak transmittance) than samples 4–7 due to the lower concentration of polymers. The contributions of lower polymer concentration are twofold: there are more liquid crystals, and the voltage shielding is less. As a result, the required driving voltage is lower. As to the monomer ratio effect, samples 4–6 have a similar on-state voltage. Therefore, V_{on} is insensitive to the monomer ratio, as long as the total polymer concentration is fixed. Similarly, samples 1–3 also have a similar on-state voltage. The fluctuation of the normalized transmittance is within the experimental error.
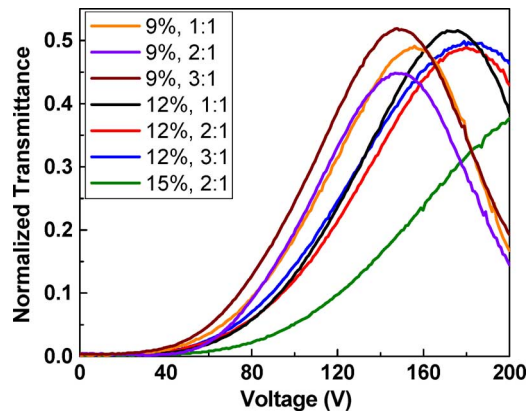
Fig. 3. Normalized VT curves of samples 1–7. $\lambda = 633$ nm and $T = 23$ °C.

TABLE II
MEASURED HYSTERESIS OF PREPARED SAMPLES

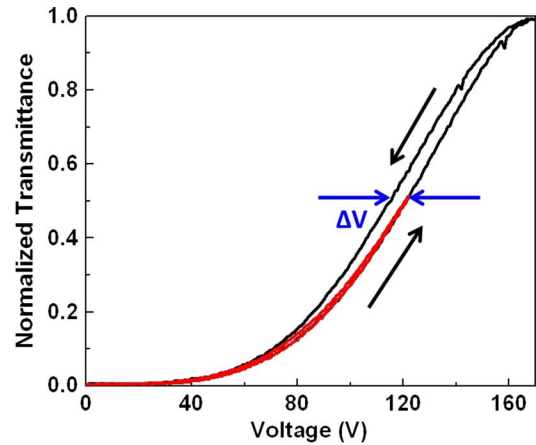| Overall monomer concentration (wt%)	Monomer ratio (RM257 : C12A)		
	1:1	2:1	3:1
9%	4.0%	3.0%	3.5%
12%	3.5%	3.0%	3.0%
15%	N/A	V_{on}>200V	N/A

Fig. 4. Voltage-dependent hysteresis loop for sample 4. Black line represents driving to the peak transmittance and red line stands for driving to 50% transmittance.

TABLE III
MEASURED DECAY TIME (MS) FOR PREPARED SAMPLES

Overall monomer concentration (wt%)	Monomer ratio (RM257 : C12A)		
	1:1	2:1	3:1
9%	0.44	0.68	0.84
12%	0.34	0.54	0.52
15%	N/A	0.30 (at 200V)	N/A

C. Hysteresis

Hysteresis affects gray scale control accuracy and needs to be suppressed [10]. To measure hysteresis, we drive the IPS devices by ascending the voltage to V_{on} and then gradually descending it to 0. Hysteresis is defined as $\Delta V/V_{on}$, where ΔV is the voltage difference between the forward and backward scans at half of the peak transmittance.

Table II lists the measured hysteresis of the IPS devices. The V_{on} of sample 7 is higher than 200 V, so its hysteresis was not measured. We found that hysteresis is relatively small (3%–4%) for all the samples investigated. Although samples 4–6 have a slightly smaller hysteresis than samples 1–3, the differences are within the experimental error. Therefore, hysteresis is insensitive to the overall monomer concentrations and monomer ratios for the investigated samples.

However, hysteresis is voltage dependent. If the voltage is too high, electrostriction effect would occur which could cause lattice deformation. As a result, the hysteresis loop will be amplified. Fig. 4 shows the hysteresis loop for sample 4, represented by the black line. For comparison, we took another measurement by driving the sample to half of the peak transmittance and then returning to the dark state gradually, indicated by the red line. In this way, the hysteresis is very small and can be considered as hysteresis free. This information is very important since most video images are in the vicinities of 50% gray levels [11].

D. Response Time

Submillisecond gray-to-gray response time is one of the most attractive features of PS-BPLC since it helps to reduce motion blur and enables color sequential displays using RGB LEDs. The latter is particularly favorable because it triples optical efficiency and resolution density. We measured the decay time for all the samples, and results are listed in Table III. Rise time is not included here because it is dependent on the driving voltage. The decay process was performed from V_{on} to $V = 0$. We calculated the decay time based on the transmittance change from 90% to 10% of the maximum transmittance. All the measurements were conducted at the room temperature (~ 23 °C).

Response time is highly related to the stability of the samples. For example, samples with 1:1 monomer ratio have a faster response time than the samples with 2:1 and 3:1 monomer ratios. A higher monomer concentration also gives a faster response time. Therefore, a more stable sample tends to have a faster response time.

E. Long-Term Stability

Long-term stability is a critical issue for the PS-BPLC devices. Here we prepared an IPS cell with Chisso JC-BP01M [12]. To evaluate the long-term stability, the sample was baked in an oven at 70 °C. Figs. 5 and 6 show the baking time dependent on-state voltage and response time. The measurements were conducted at room temperature (~ 23 °C) with 100 Hz driving frequency. Here the VT curves were measured under crossed polarizers but not normalized according to (1). Therefore, the on-state voltage is slightly lower than that reported in [12]. Overall speaking, both on-state voltage and response time
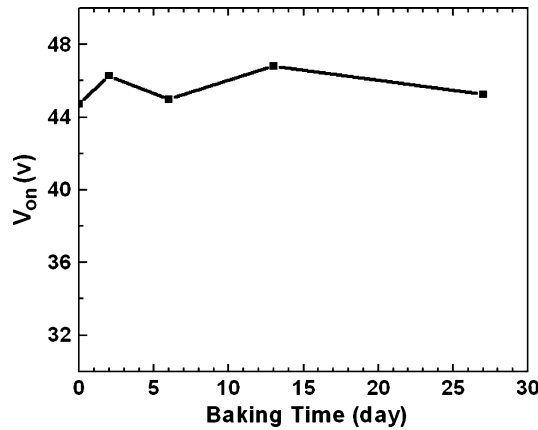
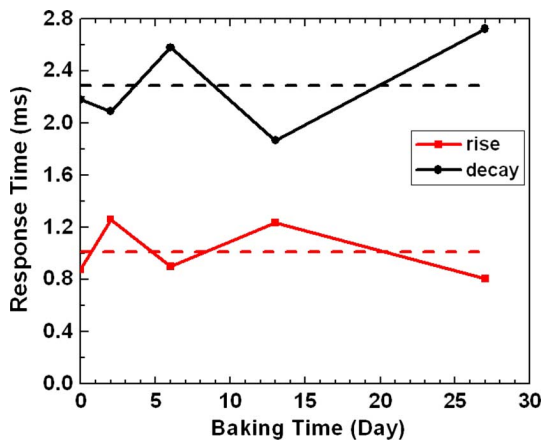Fig. 5. Baking time dependent on-state voltage.

Fig. 6. Baking time dependent response time. The dashed lines are averaged rise and decay time.

do not change much within one month of baking. The fluctuation of the response time is within 20%.

IV. CONCLUSION

Polymer-stabilized BPLC is emerging as next-generation display technology. Optimization of materials plays a crucial role for advancing the technology. Our experimental results indicate that, as the polymer concentration increases the network becomes more stable which in turn leads to smaller residual birefringence, faster response time, and higher operating voltage. Moreover, once the overall polymer concentration is fixed, samples with 1:1 monomer ratio forms a more stable structure than those with 2:1 and 3:1 monomer ratios. Hysteresis is insensitive to the polymer concentration and is relatively small for our systems. Our study will help guide future PS-BPLC material optimization.

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