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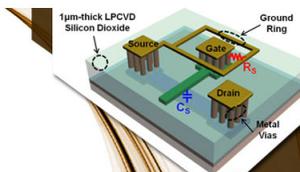
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Improved Kerr constant and response time of polymer-stabilized blue phase liquid crystal with a reactive diluent

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A polymer-stabilized (PS) blue phase liquid crystal (BPLC) with fast response time and large Kerr constant is investigated by doping a low molecular weight monomer (N-vinylpyrrolidone) into a conventional PS-BPLC consisting of BPLC, RM257, and 1,1,1-trimethylolpropane triacrylate. With this polymer network system, Kerr constant and the response can be improved simultaneously. Compared to the conventional PS-BPLC, Kerr constant of the proposed PS-BPLC can increase by 54% and the response time can decrease by 23% at the same time. The contrast ratio can be kept at a high level, over 1000:1 at $\lambda = 633$ nm. © 2013 American Institute of Physics. [<http://dx.doi.org/10.1063/1.4793416>]

Polymer-stabilized (PS) blue phase (BP) liquid crystals (PS-BPLCs) promise great potential applications in field sequential displays,^{1,2} three-dimensional (3-D) tunable photonic crystals,^{3,4} and phase modulator devices,⁵ owing to their interesting features, including sub-millisecond response time, optical isotropic dark status, no need for surface alignment layer, and periodic 3-D helical structure on the order of the visible wavelength. However, some issues, such as high driving voltage, residual birefringence, and hysteresis effect, must be solved before BPLCs can be widely applied.^{6,7} To improve the electro-optical performance of PS-BPLCs, several approaches have been demonstrated. The driving voltage can be reduced by protrusion electrodes,^{8,9} large Kerr constant BPLC materials, and vertical field switching (VFS) model.^{10,11} The hysteresis effect can be mitigated with weak electric field¹² and strong polymer network.¹³

According to Gerber's model,¹⁴ the Kerr constant (K) is approximated by the following equation:

$$K \approx \Delta n \Delta \epsilon \epsilon_0 P^2 / (k \lambda (2\pi)^2), \quad (1)$$

where Δn is the birefringence, $\Delta \epsilon$ is the dielectric anisotropy, P is the chiral pitch, and k is the effective elastic constant of the PS-BPLC. Several polar groups have been used to obtain a large Kerr constant by improving $\Delta \epsilon$ and Δn , which will undoubtedly result in an increased effective rotational viscosity (γ_1).¹⁰ The decay time of the PS-BPLCs is governed by γ_1 , k , and P , as shown in the following equation:

$$\tau \approx \gamma_1 P^2 / (k (2\pi)^2). \quad (2)$$

To improve the decay time, the PS-BPLC should show small effective rotational viscosity, short chiral pitch, and large elastic constant. By increasing the proportion of chiral dopant, the decay time of PS-BPLCs decreases, but the Kerr constant decreases due to small chiral pitch. With strong polymer network, the PS-BPLCs can reduce decay time and suppress

hysteresis, but the Kerr constant will inevitably decrease.^{10,15} Therefore, the existing material of PS-BPLCs cannot improve Kerr constant and decay time at the same time.

In this paper, a PS-BPLC material is investigated with a polymer network formed by N-vinylpyrrolidone (NVP, Jiangsu Hecheng Display Technology Co., Ltd. (HCCH)), RM257 (HCCH), and 1,1,1-trimethylolpropane triacrylate (TMPTA, HCCH). With this polymer network, Kerr constant and response time of PS-BPLC can be simultaneously improved due to the low interfacial energy and effective rotational viscosity of the PS-BPLC. Meanwhile, high contrast ratio (>1000:1) can also be achieved.

In our experiment, a nematic LC (HCBP-006, HCCH) was used as a LC host, whose physical properties are listed as follows: $\Delta n = 0.158$ at $\lambda = 633$ nm and 20 °C, $\Delta \epsilon = 34.2$ at 1 kHz and 20 °C, and clearing point $T_c = 80.5$ °C. In order to induce the blue phase, a high helical twisting power chiral compound (R5011, HCCH) was added into the LC host. In addition, the polymer network to broaden the temperature range of blue phase is formed by RM257 (di-acrylate monomer), NVP (mono-acrylate monomer), and TMPTA (tri-acrylate monomer). The chemical structures of the monomers are illustrated in Fig. 1. The IRG184 was added to the mixture as a photoinitiator.

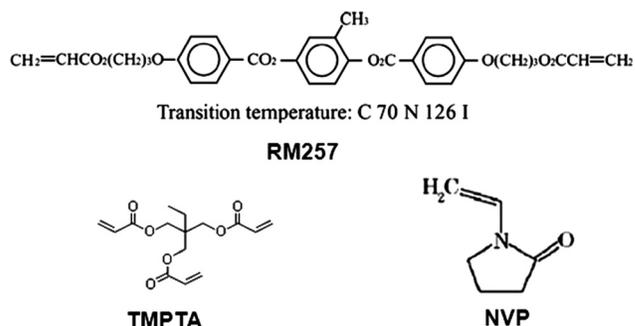


FIG. 1. Chemical structure of the monomers (RM257, TMPTA, and NVP).

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TABLE I. Summary of PS-BPLC precursors with different component ratios. T_c : the clearing point; T_{cho} : the phase transition temperature between blue phase and cholesteric phase.

Precursors	LC Host and R5011 (%)	NVP (%)	RM257 (%)	TMPTA (%)	IRG184 (%)	T_c - T_{cho} (°C)
A	91.5		4.95	3.0	0.45	67.1–61.1
B	91.5	1.15	3.80	3.0	0.45	62.0–54.0
C	91.5	1.65	3.30	3.0	0.45	59.8–50.8
D	91.5	2.4	2.55	3.0	0.45	56.2–46.2

For comparison, several precursors were prepared as listed in Table I, whose chiral pitches were controlled at 345 nm by adjusting the chiral concentration. To keep the total concentration of monomers from affecting the properties of PS-BPLC,⁷ we fixed the total concentration of the monomers at 7.95% by weight and the concentration of TMPTA at 3.0% by weight in the precursors. As shown in Fig. 1, NVP is a mono-acrylate monomer, and the conventionally used RM257 is a di-acrylate monomer. The polymer network formed with NVP and RM257 is more flexible than that formed only with RM257. For investigating the polymer system effect on the PS-BPLC, the relative concentration of NVP and RM257 in the precursors was adjusted to change the strength of the polymer network. In our PS-BPLC materials, the strength of polymer network decreases as the proportion of NVP increases and that of RM257 decreases in the precursor. After mixing, the precursors were filled into in-plane switching (IPS) cells in the isotropic phase on a temperature controller (HCS302, Instec Co.). The cell gap of IPS cell is 7.5 μm . The indium tin oxide electrode width is 7.5 μm and the electrode gap is 12.5 μm .

At a cooling rate of 0.2 °C·min⁻¹, the phase transition of our samples was observed under a polarized optic microscope (POM, XPL-30TF). Figure 2 shows the phase transition of sample A. The green color-spotted blue phase appears at about 67 °C in sample A (Fig. 2(b)). The sizes of these blue phase spots grow gradually with further decrease in temperature. The blue phase could be clearly identified from 67.1 °C to 61.1 °C. When the cell is cooled to 61.1 °C, the phase transition was observed from blue phase I to cholesteric (Cho.) phase (Fig. 2(d)). As shown in Table I, the clearing point, T_c , of the precursor decreases as the proportion of NVP increases and that of RM257 decreases, as a result of the low clearing point of NVP. The temperature range of blue phase, ΔT_{BP} , increases as the proportion of NVP increases and that of RM257 decreases. Compared with RM257, as a low molecular weight monomer, NVP is easier to fill into the disclination among the double twist cylinders (DTCs) to broaden the temperature range of blue phase.

The cells were irradiated at blue phase with chiral pitch at about 345 nm under ultraviolet light with an intensity of 3 mW·cm⁻² for 10 min. After polymerization, the clearing point of the PS-BPLC samples returns to 70 °C. The blue phases of the samples were observed when the temperature was cooling down to -30 °C. The inset in Figure 3(a) shows the texture of the PS-BPLC under POM at room temperature. The temperature range of blue phase in all the PS-BPLC samples is more than 100 °C. To measure the electro-optic properties of the PS-BPLC, a white light-emitting diode (LED) was used as a light source to avoid the diffraction of the IPS devices.^{15–17} The IPS cell applied with a 1 kHz square-wave AC signal was placed between two crossed polarizers. The transmittance was measured with a spectrometer (HR4000, Ocean optic Co.). The PS-BPLC reflects light in green regime owing to their Bragg reflection. To avoid the Bragg reflection, one can either change the pitch of PS-BPLC or shift the reference wavelength. In this paper, the reference wavelength of our IPS devices was set to 633 nm.

Figure 3(a) depicts the measured normalized voltage-dependent (V - T) curve of our IPS cells with different polymer network systems. The on-state voltage (V_{on}) of sample A, a conventional PS-BPLC, is about 110 V, which corresponds to an effective electric field about 4.3 V· μm^{-1} .

With the increase of NVP and decrease of RM257 in the precursor, V_{on} of their PS-BPLC decreases. The contrast ratio is defined as T_{on}/T_{off} , where T_{on} and T_{off} are the light intensities of $\lambda = 633$ nm at the turn-on and turn-off states, respectively. The measured contrast ratios of the samples after polymerization are all over 1000:1 at $\lambda = 633$ nm, indicating that the dark state is pretty good. According to the extended Kerr effect,¹⁸ the induced birefringence (Δn_{ind}) of PS-BPLCs is related to the electric field.

$$\Delta n_{ind} = \Delta n_s (1 - \exp[-(E/E_s)^2]), \quad (3)$$

where Δn_s is the saturated induced birefringence and E_s is the saturation electric field. In the weak field region, the Kerr constant is derived as

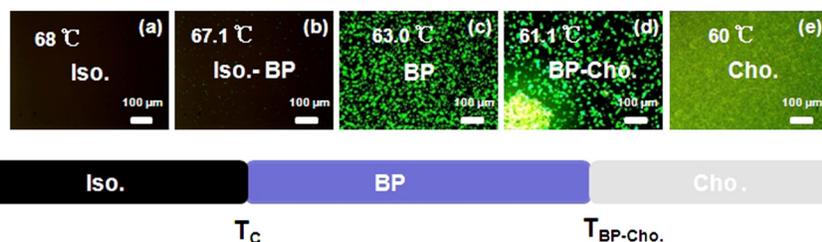


FIG. 2. The phase transition of sample A under POM at the cooling rate of 0.2 °C·min⁻¹ controlled by the temperature controller. Iso.: isotropic phase; BP: blue phase; and Cho.: cholesteric phase.

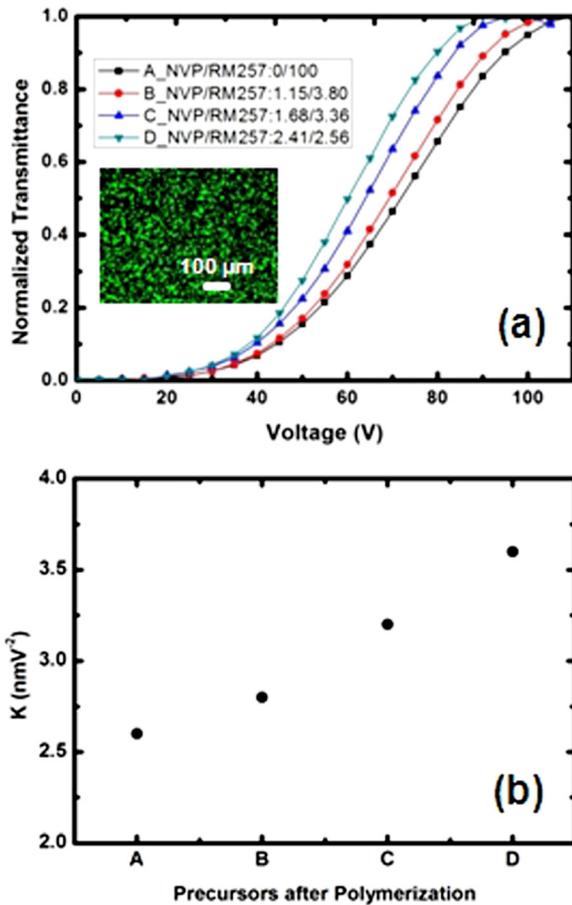


FIG. 3. (a) Voltage-dependent transmittance curves and (b) Kerr constant of PS-BPLC cells with different polymer network systems at $\lambda = 633$ nm.

$$K \approx \Delta n_s / (\lambda E_s^2). \quad (4)$$

The Kerr constant is obtained by fitting the V - T curves with the extended Kerr effect model.¹⁹ The electric field of our IPS devices was simulated with software TechWiz LCD (Sanayi System). Figure 3(b) shows the Kerr constant with different polymer network systems. Compared with sample A, the Kerr constant of sample D increases by 54%. As the concentration of NVP increases and that of RM257 decreases in the precursors, the Kerr constant of PS-BPLC increases.

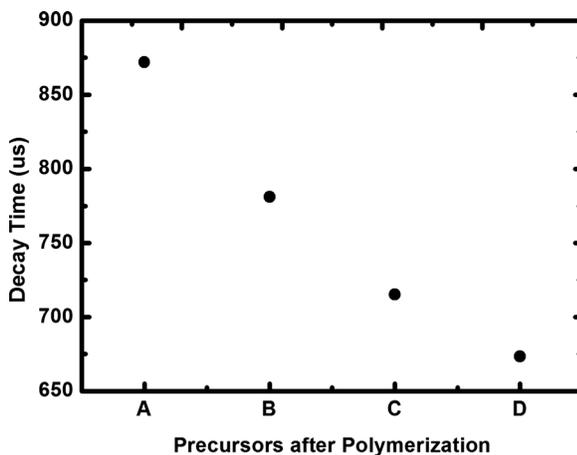


FIG. 4. Polymer network system depends on decay time at room temperature (~ 20 °C). $\lambda = 633$ nm.

Figure 4 shows the decay time with different polymer network systems. Compared with sample A, the decay time of sample D decreases by 23%. As the concentration of NVP increases and that of RM257 decreases in the precursors, the decay time of PS-BPLC decreases. Overall, the Kerr constant and the response time can be improved simultaneously with this polymer system. After polymerization, the polymer network increases the Kerr constant and decreases the response time of PS-BPLC due to low interfacial energy at the interface between the polymer network and DTCs.²⁰ In this material system, a reactive diluent can be formed by NVP and acrylic functional groups of the RM257 and TMPTA after polymerization. It can degrade the strength of polymer network and reduce the interfacial energy at the interface between the polymer network and DTCs that increase the Kerr constant. Meanwhile, it can diminish effective rotational viscosity of the material system resulting in decrease of response time of PS-BPLC.

Hysteresis is another key issue to solve before the wide application of PS-BPLC. In this letter, the relationship between hysteresis and polymer network was studied. To measure the hysteresis of our IPS devices, the IPS devices were driven by switching the applied voltage upwards to V_{on} and then downwards to zero. The hysteresis is defined as $\Delta V / V_{on}$, where ΔV is the voltage difference between the upward and downward scans at half of the peak transmittance. The hystereses of samples A, B, C, and D are 2.9%, 3.0%, 3.1%, and 3.2%, respectively. As the concentration of NVP increases and RM257 decreases in the precursor, the hysteresis of the resulting PS-BPLC increases slightly. This is because the low interfacial energy makes it difficult to recover the original alignment of the liquid crystal as the applied voltage is decreased.

In conclusion, by doping a low molecular weight cross-link monomer, NVP, into conventional polymer stabilization materials consisting of RM257 and TMPTA, a reactive diluent is formed among the polymer network. It can decrease the interfacial energy at the interface between the polymer network and DTCs that increase the Kerr constant and decrease the effective rotational viscosity of the material system resulting in decrease of decay time of PS-BPLC. Meanwhile, the contrast ratios of our samples are over 1000:1. However, the hysteresis increases slightly for the low interfacial energy. This study has a positive exploration for the application of the PS-BPLCs for color sequential displays and phase modulator devices.

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