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Yuan Chen
University of Central Florida

Jin Yan
University of Central Florida

Jie Sun
University of Central Florida

Shin-Tson Wu
University of Central Florida

Xiao Liang

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Authors

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A microsecond-response polymer-stabilized blue phase liquid crystal

Yuan Chen,¹ Jin Yan,¹ Jie Sun,¹ Shin-Tson Wu,^{1,a)} Xiao Liang,² Shih-Hsien Liu,³
Pao-Ju Hsieh,³ Kung-Lung Cheng,³ and Jyh-Wen Shiu⁴

¹College of Optics and Photonics, University of Central Florida, Orlando, Florida 32816, USA

²Department of Chemistry, Tsinghua University, Beijing 10084, China

³Material and Chemical Research Laboratories, Industrial Technology Research Institute, Hsinchu, Taiwan

⁴Display Technology Center, Industrial Technology Research Institute, Hsinchu, Taiwan

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A polymer-stabilized blue-phase liquid crystal (BPLC) with microsecond response time is demonstrated using a vertical field switching cell. The measured decay time is $39\ \mu\text{s}$ at room temperature (21°C) and then decreases to $9.6\ \mu\text{s}$ at 44.3°C . Such a response time is 1-2 orders of magnitude faster than that of a typical BPLC device. The responsible physical mechanisms are the collective effects of short pitch length, strong polymer network, and low viscosity through temperature effect. The on-state voltage of our BPLC device is $44.2\ \text{V}$, hysteresis is below 0.7% , and contrast ratio is over $1300:1$. © 2011 American Institute of Physics. [doi:10.1063/1.3662391]

Polymer-stabilized blue-phase liquid crystal (PS-BPLC)¹⁻⁵ has opened a gateway for next-generation display and photonic applications^{6,7} because of its revolutionary features, such as submillisecond response time, no need for surface alignment layer, and optically isotropic dark state. However, high operation voltage and hysteresis still hinder its widespread applications. To reduce operation voltage, three approaches are commonly practiced: (1) to develop BPLC materials with a large Kerr constant (K) because the on-state voltage is inversely proportional to $\sqrt{K}$,⁸ (2) to implement protrusion electrodes so that electric field can penetrate deeply into liquid crystal (LC) bulk,^{8,9} and (3) to use vertical field switching (VFS) mode which generates uniform longitudinal electric fields.¹⁰

Kerr constant is related to the birefringence (Δn), dielectric anisotropy ($\Delta\epsilon$), elastic constant (k), and pitch length (p) of the LC host as¹¹

$$K \approx \Delta n \cdot \Delta\epsilon \frac{\epsilon_0 p^2}{\lambda k (2\pi)^2}. \quad (1)$$

To obtain a large K , a LC host with $\Delta\epsilon \approx 94$ and $\Delta n \approx 0.17$ has been developed by Chisso (JC-BP01M).¹² Based on Eq. (1), a large $\Delta\epsilon$ helps to lower the operation voltage. However, to achieve such a large $\Delta\epsilon$, several polar groups have to be used, which would undoubtedly result in an increased rotational viscosity (γ_1). The decay time of a BPLC is governed by rotational viscosity, elastic constant, and pitch length as¹¹

$$\tau = \frac{\gamma_1 p^2}{k (2\pi)^2}. \quad (2)$$

From Eq. (2), three approaches can be considered for improving response time: (1) to reduce pitch length by increasing chiral concentration, (2) to increase elastic constant by strengthening polymer network, and (3) to reduce viscosity by operating the cell at an elevated temperature. However, each approach has its pros and cons. In approach

(1), reducing pitch length by increasing chiral concentration could lead to a higher operation voltage [as described in Eq. (1)] and lower clearing temperature of the BPLC composite. For example, CB-15 is a chiral compound; its clearing point is 4°C . Adding CB-15 to a BPLC mixture would dramatically lower the clearing temperature, which is undesirable for practical applications. In approach (2), a strong polymer network helps to reduce response time and suppress hysteresis, but its operating voltage would be inevitably increased. In approach (3), elevated temperature would substantially reduce rotational viscosity, but the tradeoffs are reduced Kerr constant and increased operation voltage. Therefore, a delicate balance between abovementioned parameters needs to be taken.

In this letter, we experimentally demonstrate a microsecond-response PS-BPLC device using a VFS cell instead of commonly employed in-plane-switching (IPS) cell. In an IPS cell, the strong fringing field near the electrode edge could cause lattice distortion locally, which in turn increases the response time and hysteresis. In contrast, VFS mode has uniform longitudinal field which would effectively avoid the lattice distortion and improve the response time. At room temperature (21°C), the measured decay time is $39\ \mu\text{s}$, but at 44.3°C , the decay time drops to $9.6\ \mu\text{s}$. The on-state voltage of our BPLC device is $44.2\ \text{V}$ which corresponds to $K = 0.6\ \text{nm/V}^2$, hysteresis is below 1% , and contrast ratio is over $1300:1$.

In the experiment, we prepared a nematic LC host designated as JM2069-145 (ITRI, Taiwan). It is a multi-component mixture comprising of cyano-biphenyl and terphenyl compounds. Its physical properties are listed as follows: $\Delta n = 0.215$ at $\lambda = 633\ \text{nm}$, $\Delta\epsilon = 50$ at $1\ \text{kHz}$ and 21°C , and clearing temperature $T_c = 80^\circ\text{C}$. In order to induce chirality into the host nematic LC, we mixed 93 wt. % JM2069-145 with 7 wt. % of a high helical twisting power ($HTP \approx 100/\mu\text{m}$) chiral compound (Formula I-2 in Ref. 13). Blue phase was found from 57°C to 62°C during the heating process. From the chiral concentration and HTP , we estimated that the pitch length is about $140\ \text{nm}$. 10 wt. % of photocurable monomers [6 wt. % RM257 (Merck) + 4 wt. %

^{a)}Electronic mail: swu@mail.ucf.edu.

TMPTA (1,1,1-Trimethylolpropane Triacrylate, Sigma Aldrich] and 0.85 wt. % of photoinitiator were blended with 89.15 wt. % of the BPLC mixture to form the precursor. The chiral nematic/BP transition temperature is lowered to 40.5 °C during heating and 36.1 °C during cooling. Next, we injected the LC/monomers mixture into a VFS cell in an isotropic phase. The VFS cell was comprised of two ITO (indium tin oxide) glass substrates (but without polyimide alignment layer), and its cell gap was 5.27 μm . Afterwards the cell was placed on a Linkam heating/freezing stage controlled by a temperature programmer (Linkam TMS94). The cell was cooled to BP phase and then cured at 37.5 °C with a UV light ($\lambda = 365 \text{ nm}$) with intensity of 2 mW/cm^2 for 30 min. After UV irradiation, polymer-stabilized BPLC nanocomposites were self-assembled. The clearing temperature of the polymer-stabilized BPLC was measured to be 62 °C, similar to that of the BP host. The texture of the BPLC under crossed polarizer is shown in Fig. 1(a). We intentionally increased the illumination intensity of the microscope in order to see the small platelet structures of the blue phase.

Figure 1(b) depicts the measurement setup. A linearly polarized He-Ne laser ($\lambda = 633 \text{ nm}$) was used as probing beam. In order to acquire phase retardation, the laser beam was incident on the VFS cell at an 80° oblique angle. The VFS cell was immersed in a glass container filled with glycerol ($n = 1.47$), so that the beam could enter the LC layer at a large angle due to the refractive index match between the glass and glycerol. The container was placed between two crossed polarizers, and the light transmittance was measured by a photodiode detector (New Focus Model 2031) and recorded digitally by a LabVIEW data acquisition system (DAQ, PCI 6110).

A 1-kHz square-wave AC signal was applied to the VFS cell. Figure 2(a) depicts the measured voltage-dependent transmittance (VT) curve. From Fig. 2(a), the first transmission peak occurs at $V_p = 44.2 \text{ V}$, which corresponds to an electric field of 8.39 $\text{V}/\mu\text{m}$. In the voltage-off state, blue phase is optically isotropic. The contrast ratio is defined as T_p/T_{dark} , where T_p is the peak transmittance at V_p and T_{dark} is the dark state light leakage at $V = 0$. Our measured contrast ratio is over 1300:1, indicating that the dark state is pretty good due to the short pitch length of the BPLC. As voltage increases, the induced birefringence increases as described by the following extended Kerr model:¹⁴

FIG. 1. (Color online) (a) Microscopic image of the PS-BPLC under crossed polarizers and (b) experimental setup for electro-optic measurement of the VFS cell.

FIG. 2. (Color online) (a) Voltage dependent transmittance of the BPLC cell. Dots represent the experimental data, and the red solid line is the fitting curve by extended Kerr model; (b) Hysteresis loop.

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

where Δn_s is the saturated induced birefringence and E_s is the saturated electric field. Through fitting,⁴ we obtained the Kerr constant $K = \Delta n_s / (\lambda E_s^2) = 0.6 \text{ nm}/\text{V}^2$. By contrast, the Kerr constant of our BPLC is about 12× smaller than that of JC-BP01M (also in a VFS cell). Substituting Δn , $\Delta \epsilon$, and p of these two BPLCs into Eq. (1), we find that the elastic constant of our BPLC is 3.5× larger than that of Chisso's JC-BP01M. The increased elastic constant is believed to originate from the employed TMPTA. A strong polymer network helps to reduce hysteresis and response time.

Hysteresis affects gray scale accuracy of a BPLC device and should be minimized. To measure hysteresis, we drove the VFS cell by ascending the voltage to V_p and then gradually descending it to 0. Hysteresis is defined as $\Delta V/V_p$, where ΔV is the voltage difference between the forward and backward scans at half of the peak transmittance, shown in Fig. 2(b). For this cell, the measured $\Delta V/V_p$ is only 0.68%. Although the maximum electric field is as strong as 8.39 $\text{V}/\mu\text{m}$, the hysteresis is still negligible, indicating the polymer network is quite stable.¹⁵ If the cell is driven to 31 V (i.e., 50% of the peak transmittance) and then back to zero (result not shown), then hysteresis is too small ($<0.1\%$) to be detected by our measurement system. Due to the uniform distribution of electric field, the VFS cell has a much smaller hysteresis than IPS cell.¹⁰

Fast response time is probably the most attractive feature for BPLC. Both rise time and decay time were measured between 10% and 90% transmittance change. The measured decay time at room temperature (21 °C) is 39 μs , and rise

time is 46 μs . We believe that the fast response time originates from the short pitch length and strong polymer network. Based on Eq. (2), the decay time is proportional to p^2 , so a shorter pitch length would lead to a faster response time. On the other hand, TMPTA is a tri-functional monomer, while the normally used EHA (ethylhexyl acrylate) or C12A (Refs. 16 and 17) are mono-functional monomers. The cross-link between TMPTA and RM257 is much stronger, resulting in increased elastic constant k which in turn shortens the response time through Eq. (2).¹⁸

In addition, the decay time decreases as the temperature increases, as described by following equation:¹⁹

$$\tau \approx B \cdot \frac{\exp(E_a/K_B T)}{(1 - T/T_{c_BP})^\beta}, \quad (4)$$

where B is a proportionality constant, E_a is the activation energy, K_B is the Boltzmann constant, and T_{c_BP} is the clearing point of the PS-BPLC. Equation (4) is derived based on the order parameter S as described in Ref. 19, and the denominator $(1 - T/T_{c_BP})^\beta$ is the approximated expression for S using Haller's semi-empirical equation.²⁰ This approximation is valid only for the temperature not too close to T_{c_BP} (e.g., $T_{c_BP} - T > 1^\circ\text{C}$). Although Eq. (4) has three unknowns (B , E_a , and β), β can be obtained by measuring the temperature dependent birefringence of the LC host JM2069-145 or the BPLC composite.²¹ The Δn of the LC host was measured through phase retardation of a homogeneous cell sandwiched between two crossed polarizers. The experimental detail has been described in Ref. 22. The birefringence is related to the order parameter S as²³

$$\Delta n = \Delta n_o S \approx \Delta n_o (1 - T/T_c)^\beta, \quad (5)$$

where Δn_o denotes the birefringence at $T = 0\text{ K}$. Figure 3(a) shows the measured temperature dependent Δn of our LC host at $\lambda = 633\text{ nm}$. Through fitting, we found $\Delta n_o = 0.350$ and $\beta = 0.267$.

Next, we measured the temperature dependent decay time of our BPLC cell. Because our VFS cell was immersed in a glycerol container, so we placed the whole container on a heating stage. Results are depicted in Fig. 3(b). As the temperature increases from 25.4 $^\circ\text{C}$ to 44.3 $^\circ\text{C}$, the peak voltage increases slightly from 44.2 V to 50 V because of the reduced Kerr constant. Meanwhile, the decay time is reduced from 32.8 μs to 9.63 μs . We used the same β value to fit the decay time data by Eq. (4) and found quite good agreement. From the fitting, we obtained $E_a = 613.5\text{ meV}$ and $B = 7.35 \cdot 10^{-10}\text{ }\mu\text{s}$. This activation energy is smaller than that of Chisso's JC-BP01M whose $\Delta\epsilon \approx 94$, Kerr constant is 7.5 nm/V^2 , but its response time at 23 $^\circ\text{C}$ is 870 μs in a 5.74 μm VFS cell.^{10,12}

In conclusion, we demonstrated a microsecond-response and "hysteresis-free" ($\leq 0.68\%$) polymer-stabilized BPLC device. The decay time at room temperature is 39 μs and is reduced to 9.64 μs as the temperature increases to 44.3 $^\circ\text{C}$. The peak voltage is 44.2 V and the contrast ratio is over 1300:1. With these attractive features, our PS-BPLC exhibits great potential for next generation high speed display and photonics devices.

FIG. 3. (Color online) (a) Temperature dependent Δn of the LC host JM2069-145 and (b) temperature dependent decay time for the VFS PSBP cell. Blue dots: experimental data; Red line: fitting curve.

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