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Electro-optical properties of photochemically stable polymer-stabilized blue-phase material

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Polymer-stabilized blue-phase liquid crystal (BPLC) comprising fluorinated compounds with high resistivity and photochemical stability is demonstrated. The Kerr constant, driving voltage, and response time of this BPLC are measured using an in-plane switching liquid crystal cell. At 20 °C, the measured total response time is faster than 0.7 ms and Kerr constant is 2 nm/V². This fluorinated BPLC material is a promising candidate for next-generation photonic and display devices, because it can be used in active matrix addressed devices. © 2014 AIP Publishing LLC.

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I. INTRODUCTION

Liquid crystalline blue phase is a promising material for fast-response displays,^{1–3} three-dimensional lasers,^{4,5} and new photonic devices.⁶ It exhibits several revolutionary features in comparison to conventional nematic materials, such as sub-millisecond response time,^{7,8} optically isotropic dark state, and no need for surface alignment layer. There are, however, a few remaining challenges that need to be overcome: hysteresis, high operating voltage, and thermal instability.

Three blue phases BPI, BPII, or BPIII exist between cholesteric and isotropic phase in a very narrow temperature range (from 0.1 K to 5 K). It is proposed⁹ that blue phase has periodic cubic lattice of double twist cylinders in which the LC director rotates spatially about any radius of the cylinder and is parallel to the axis at the centre of the cylinder. The twist in each cylinder can be right- or left-handed, twisting to 45° at the boundary. Matching these tubes in three-dimensional space is impossible, which induces disclinations or defects in molecular arrangement. The blue phase occurs due to the balance between defects and local energy minimum of LC director and is a frustrated system. The structures of BPI and BPII have been identified in many experiments and theories.¹⁰ BPI has body-centred cubic symmetry, BPII has simple cubic structure, and BPIII is amorphous with the short distance order of double twist alone. In frustrated systems, different terms in the free energy dictate different molecular arrangements, and the competition between them results in a more complex structure.¹¹ Defects in blue phase make the structure less stable, thus, blue phase exists in a narrow temperature range.

To widen the blue phase range, several methods have been explored, such as adding nanoparticles,¹² bent-shaped molecules,¹³ T-shaped molecules,¹⁴ polymer network,¹⁵ or combining several methods together.¹⁶ The great majority of reported and measured blue phase systems are stabilized by a polymer network with a LC host having cyano compound to increase dielectric anisotropy. Usually, 4-cyano-4'-pentylbiphenyl (5CB),^{17,18} 4-cyano-4'-(2-methyl)butylphenyl

(CB15),^{19,20} and cyanoesters²¹ are mentioned. In our recent work,^{22,23} we demonstrated that the presence of 5CB has entailed reduction of BP temperature range and clearing point. Additionally, it complicates the temperature control of BP material doped with polymer precursor during UV exposure.

In this paper, we report a polymer-stabilized blue phase (PSBP) system comprising fluorinated compounds with high resistivity and high photochemical stability. They can be applied to devices addressed by an active matrix due to their high voltage holding ratio (VHR).^{24–26} The reported system should be useful for display and non-display applications, such as spatial light modulators, photonic crystal fibers, and lasers.

II. EXPERIMENTS

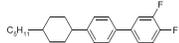
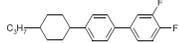
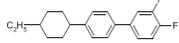
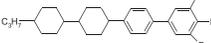
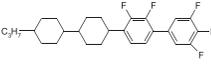
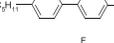
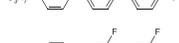
A. Preparation of PSBP

The nematic LC host we employed is mixture 1911 whose major compositions are fluorinated terphenyls, biphenyl, cyclohexylbiphenyls, and bicyclohexylbiphenyl. Table I lists the compound structures, phase transition temperatures, and concentrations. Compounds 1–3 were provided by Valiant Fine Chemicals and compounds 4–10 were synthesized in our laboratory. Some properties of mixture 1911 are as follows: melting point below –20 °C, clearing point 82 °C, birefringence $\Delta n = 0.174$ at 589 nm, dielectric anisotropy $\Delta \epsilon = 8.5$ at 1 kHz, and bulk viscosity $\eta = 30$ mPas, all measured at 20 °C.

We prepared a blue phase precursor, we blended two chiral dopants: biphenyl-4,4'-dicarboxylic acid bis-(1-methylheptyl) ester and [1,1';4',1'']terphenyl-4,4'-dicarboxylic acid bis-(1-methylheptyl) ester (both synthesized in our laboratory²⁷) as well as two reactive acrylates: 1,4-bis-[4-(3-acryloyloxypropoxy) benzoyloxy]-2-methylbenzene (from CHEMOS), 1,1,1-tri-(acryloyloxymethyl)-propane (from SARTOMER), and photoinitiator 2-hydroxy-2-methyl-1-phenylpropan-1-one (from SIGMA-ALDRICH) at 6.3 wt. %, 6.3 wt. %, 6.0 wt. %, 4.0 wt. %, and 0.5 wt. % concentrations, respectively, to mixture 1911. Out of all the components only difunctional acrylate has nematic phase, neither the mono-functional acrylate nor the chiral dopants exhibit mesophase.

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TABLE I. Formula of components of the nematic host mixture 1911.

No.	Formula	Phase sequence	Concentration in mole fraction (%)
1		Cr 65.1 N 108.2 Iso	20.9
2		Cr 67.6 N 98.6 Iso	7.8
3		Cr (60.9 N) 69.0 Iso	7.0
4		Cr 103.8 N 263.0 Iso	11.4
5		Cr 89.2 N 233.6 Iso	2.7
6		Cr 41.4 Iso	13.3
7		Cr 87.7 SmA 95.6 N 132.5 Iso	7.6
8		Cr 75.4 N 87.9 Iso	6.6
9		Cr 62.3 Iso	13.7
10		Cr 69.2 Iso	9.0

The mixture of nematic host, chiral dopants, and polymer precursor was heated to 70 °C to dissolve all components and then it was filled into an empty cell at the same temperature (the mixture was at an isotropic state). To measure the electro-optical properties of the material, we used an IPS cell with following geometry: cell gap of 7.5 μm, indium tin oxide electrode width of 10 μm, and electrode gap of 10 μm.

The phase transition temperatures were determined by a polarizing optical microscope OLYMPUS BX51 equipped with a LINKAM THMS600 heating stage. The temperature was controlled with an accuracy of ±0.1 K. The precursor exhibits blue phase between 47.8 °C and 52.4 °C. To stabilize the precursor, we heated the cell to 70 °C, then cooled down to 47.7 °C (the cooling rate was 1 K/min), and exposed to UV light. The temperature in which the cell was irradiated was 0.1 °C below the transition from cholesteric to blue phase to avoid the transition to isotropic phase, which is possible due to the heating during UV curing. Photo-polymerization was performed using a metal halide lamp (Hamamatsu Photonics LC6; λ ~ 365 nm) with 10 mW/cm² intensity for 30 min at 47.7 °C. After polymerization, the cell was cooled down with 1 K/min cooling rate. As observed from an optical microscope, the polymer-stabilized composite shows a stable blue phase from less than -30 °C to 54.3 °C (isotropic phase). Figure 1 shows the observed microscopic texture at 23 °C.

The voltage-dependent transmittance (VT) of filled IPS cell was measured with a He-Ne laser (λ = 633 nm) by applying 100 Hz signal with rectangular waveform. The induced birefringence Δ*n*_{ind} is related to wavelength λ, electric field *E*, and Kerr constant *K* as

$$\Delta n_{ind} = \lambda K E^2. \quad (1)$$

However, we fit the VT curves with the extended Kerr effect model²⁸ because the induced birefringence should be

saturated in the strong electric field region according to Eq. (2), where Δ*n*_{sat} represents the saturated induced birefringence and *E*_s is saturated electric field

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

In the weak field region, Eq. (2) can be expanded and reduced to Kerr effect (Eq. (1)) with the following relation:

$$K = \Delta n_{sat} / (\lambda E_s^2). \quad (3)$$

III. RESULTS AND DISCUSSIONS

Figure 2 shows the normalized VT curves from 10 °C to 50 °C. As the temperature increases, the on-state voltage (*V*_{on}) increases as well. Since Kerr constant depends on the on-state voltage, the VT curves measured at each temperature were fitted with extended Kerr effect model. The Kerr

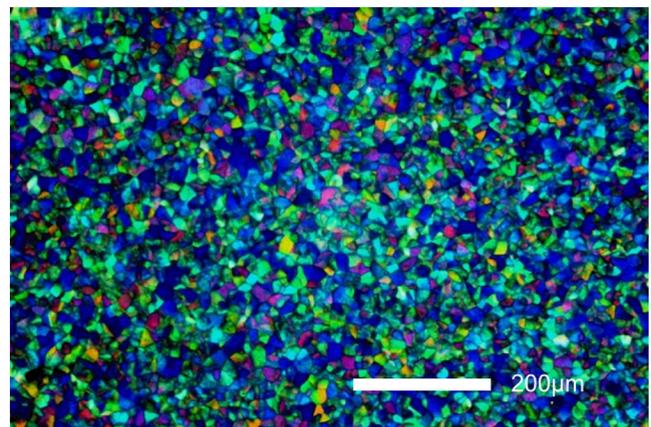


FIG. 1. Polarized optical microscope image of PSBP at ~23 °C.

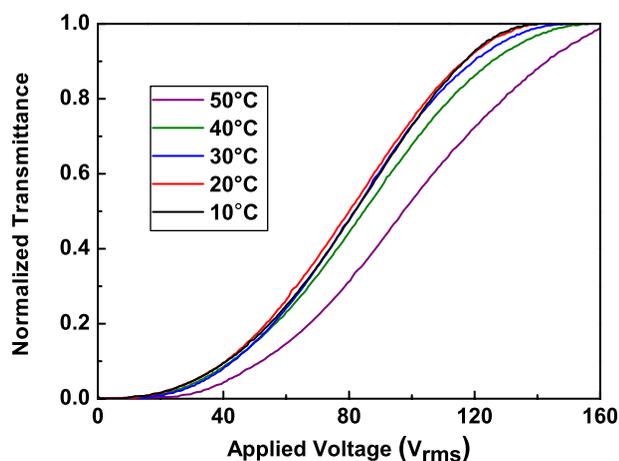


FIG. 2. The VT curves of PSBP measured in an IPS cell at different temperatures, $\lambda = 633$ nm. IPS cell: Electrode width = $10 \mu\text{m}$, electrode gap = $10 \mu\text{m}$, and cell gap = $7.5 \mu\text{m}$.

constants obtained at each temperature are shown in Fig. 3. The Kerr constant tends to saturate at low temperatures.²⁹ The highest Kerr constant was 2.1 nm/V^2 at 10°C , while the lowest Kerr constant of 1.4 nm/V^2 was observed at 50°C , which is close to the clearing point. A typical Kerr constant of a polymer-stabilized BP composite is about 1 nm/V^2 .^{30,31} However, some BP materials with an extraordinarily large Kerr constant ($K > 13.7 \text{ nm/V}^2$) have been reported by using a nematic host with a very large dielectric anisotropy ($\Delta\epsilon > 100$).^{32,33} The development goal for the PSBP materials is to increase Kerr constant to lower the driving voltage. To enhance Kerr constant, a liquid crystal with high birefringence and large dielectric anisotropy is strongly desirable.

Fast response time is one of the several outstanding features of BP in comparison to conventional nematic materials. It is less than 1 ms and is independent of the cell gap. Fast response time makes PSBP applicable to devices working in longer ranges of electromagnetic radiation (infrared, gigahertz, and terahertz frequency range), where the required LC layer is thicker. Response time was measured by applying a voltage corresponding to the maximum transmittance and then removed instantaneously. The optical signals were recorded by a photodiode detector and displayed in a digital

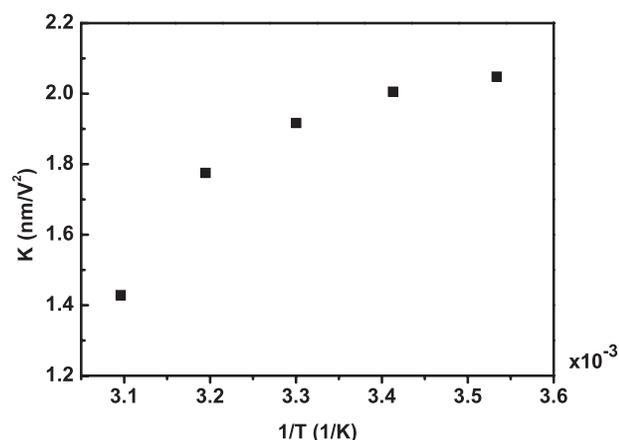


FIG. 3. Temperature dependent Kerr constant of PSBP obtained by fitting with extended Kerr model.

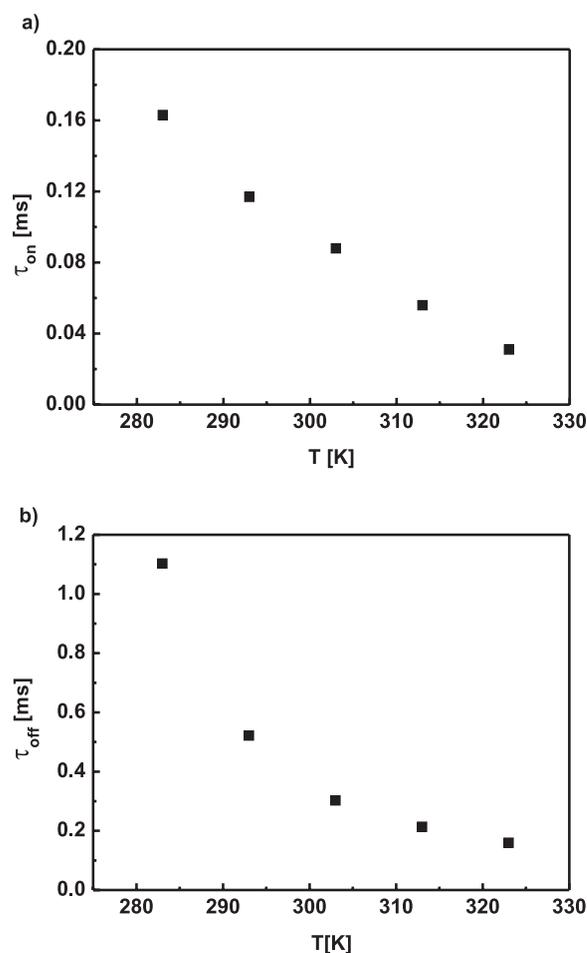


FIG. 4. Measured temperature dependent (a) rise time and (b) decay time.

oscilloscope. Both rise time (τ_{on}) and decay time (τ_{off}) were measured as the transmittance changes from 10% to 90%. Figures 4(a) and 4(b) show the measured temperature dependent rise time and decay time, respectively.

The sum of rise time and decay time is in the range from 1.266 ms (283 K) to $191 \mu\text{s}$ (323 K). At room temperature (293 K), rise time is $117 \mu\text{s}$ and decay time is $522 \mu\text{s}$. These times are slightly shorter than those published in the literature by other groups.^{34,35} The response time of a PSBP depends on the type of polymer network, LC host, and chiral dopants employed. Generally, it decreases with increased degree of crosslinking, but the trade-off is increased operation voltage.

High chemical and photochemical stability of fluorinated liquid crystals opens many new applications where UV light and visible light with high intensity are used. What is more, compounds with fluorine substituents have high resistivity, which does not change after UV illumination, in contrast to the compounds with cyano or isothiocyanato groups. The VHR of nematic base mixture 1911 is 99% and it slightly decreases to 98% after UV exposure. In contrast, the VHR is only 60% for cyano mixture like E7 and it decreases to 51% after UV exposure.

IV. CONCLUSIONS

We have demonstrated a polymer-stabilized blue phase composite based on a nematic mixture comprised fluorinated

compounds, which are chemically and photo-stable. The voltage holding ratio is very high $VHR = 98\%–99\%$ and does not change after UV exposure. Proposed material has Kerr constant $K = 2 \text{ nm/V}^2$ at 20°C and $\lambda = 633 \text{ nm}$. The corresponding on-state voltage is $130 \text{ V}_{\text{rms}}$ in an IPS cell with $10 \mu\text{m}$ electrode width and $10 \mu\text{m}$ electrode gap. The total response time ($\tau_{\text{on}} + \tau_{\text{off}}$) is only $640 \mu\text{s}$ measured at 20°C by applying a voltage corresponding to the maximum transmittance. Since the presented fluorinated materials exhibit a high resistivity in contrast to other cyano materials used in BP systems, we believe our materials have potential for widespread application in next-generation displays and photonic devices.

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