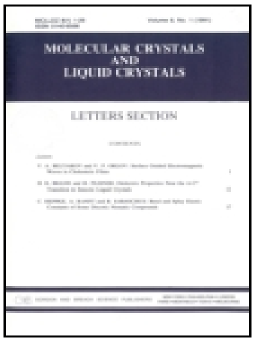

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Effects of Host Liquid Crystal Composition on the Stability of Liquid Crystalline Blue Phases

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The temperature range of blue phase liquid crystal can be extended through the use of polymer stabilization. In this work, the mixing condition for the host liquid crystal mixture containing E8, PE-5CNF, and CPP-3FF; and the monomer UCL-011 and the chiral dopant NYC-22133L was investigated. Typically, the operating temperature for displays should be in the range of −40 to +80°C. The chiral dopant and monomer tend to lower the clearing temperature; thus, the host LC should have a high BP-Iso clearing temperature. In this work, optimization of the ratio of the host liquid crystal with respect to the monomer was carried out. It was found that a ratio of 5:3:2 for E8: PE-5CNF: CPP-3FF gave a polymer stabilized blue phase of ∼50.4°C. Driving voltage and electro-optic hysteresis was also investigated, yields a conclusion that a trade-off between driving voltage and hysteresis exists for the PSBPLC mixture that was investigated.

Keywords Blue phase liquid crystals; driving voltage; host liquid crystal; hysteresis; polymer stabilization

1. Introduction

Blue phase liquid crystals (BPLCs) are attractive candidates for next generation display and photonic applications because they exhibit advantages such as optical isotropy, sub-millisecond response time and a reflective band switched by external fields [1–3]. The structure of blue phase is significantly different from the other liquid crystal phases, since it possesses a self-assembled three dimensional cubic lattice structure [4–8]. Blue phases appear in a highly twisted chiral nematic liquid crystal [9]. Since high chirality lead to twist the molecules in all lateral direction it is guided to form an organized double twist cylinder structure within a stable area. The BP can be divided into three types (BPI, BPII, and BPIII) depending on the chirality of the LC. The BPIII phase has an almost similar structure to the isotropic phase [10], whereas BPI and BPII are made out of double twist cylinders

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packed in cubic lattices [11]. In its basic from, its three dimensional helical double twisted cylinder structure causes formation of it disclination lines which decreases its stability and thus limits its temperature range to approximately 1–2°C.

In order to ensure applicability of the BP phases in displays or photonic applications, a wide and stable temperature range is desirable. In 2002, Kikuchi et al. [12–14] and his group developed a unique mechanism to stabilize the BP structure by means of polymer network which results a large temperature range (more than 60°C) of BPLC. This polymer addition causes the cross-linking of the polymer network, which is selectively concentrated in the disclination cores. Separately, in 2005, Coles and Pivnenko [15] extended the temperature range of BPLC to approximately 50°C by developing bimesogenic materials. Bimesogenic liquid crystals are formed by separating two terminal mesogenic groups by a flexible alkyl chain spacer. These nontraditional shaped dimer compounds show large flexoelectric properties and Coles and Pivnenko assumed that this strong flexoelectric polarization arising close to disclination line may thermally stabilize the blue phase structure with large temperature range. Another way of widening the temperature range of BPLCs is through incorporation of nanoparticles (NPs), where the NPs accumulate in the lattice disclination lines of the blue phase and hence stabilize the overall cholesteric blue structure. Systematic high-resolution calorimetric studies have found that the mixing of surface-functionalized NPs with LC can lead in the stabilization of BPIII in a wide temperature window, approaching a range of 20°C [16]. Moreover, in 2012, Dierking et al. [17] reported a variety of mechanisms including some hybrid systems (combining two methods) such as polymer stabilize bent core doped systems and polymer stabilized NP fillers to stabilize the BPLC.

From the viewpoint of display applications, low power consumption, fast response time, and high transmittance are desirable from the LC material [18–20]. In particular, fast response time is an issue. The BPLC exhibits some unique features such as sub-millisecond response time (which is $\sim 10 \times$ faster than a typical nematic) [21], the alignment layer in the device is not required; and it is optically isotropic thereby providing excellent dark state and wide viewing angle without any compensation films [22]. Thus, BPLCs possess potential for next generation displays application such as 3D and large-screen LC displays. However, in order to render commercialization of BPLCs possible, it must possess a wide temperature range from -40 to $+80$°C and operating voltage below 50 V.

In particular, a low driving voltage is a key barrier to commercialization of BPLC display and photonic devices; lowering the driving voltage is tackled through either introduction of novel electrode structures [22–24] or modification of the properties of host LC, polymer, and chiral material component of BPLC mixture. In a typical BPLC mixture, the components are the host LC, monomer and chiral dopant. In this paper, the effect of the ratio of the host LC to the monomer and chiral dopant are investigated through the evaluation of the LC phases upon polymer stabilization; and its resulting driving voltage and electro-optic properties. In order to optimize the host LC ratio, the chiral dopant and monomer weight percentage were not changed.

2. Experimental Details

2.1. Materials

The room temperature BPLC mixture was achieved using the following materials; E8, PE-5CNF (4-Cyano-3-fluorophenyl 4-pentyl benzoate, LCC Corporation, Japan), and CPP-3FF (4-(trans-4-*n*-propyl cyclohexyl)-3',4'-difluoro-1,1'-biphenyl, LCC Corporation, Japan) as

Table 1. Chemical composition of room temperature samples

Sample no.	Host LC mixing ratio	Host LC (wt%) E8	PE-5CNF	CPP-3FF	Chiral dopant NYC-22133L (wt%)	Monomer UCL-011 (wt%)
1	2:4:4	15.9	31.7	31.7	12.9	7.7
2	2:5:3	15.9	39.7	23.8	12.9	7.7
3	3 : 3.5 : 3.5	23.8	27.8	27.8	12.9	7.7
4	3:4:3	23.8	31.7	23.8	12.9	7.7
5	4:3:3	31.7	23.8	23.8	12.9	7.7
6	4:4:2	31.7	31.7	15.9	12.9	7.7
7	5:3:2	39.7	23.8	15.9	12.9	7.7
8	5:2:3	39.7	15.9	23.8	12.9	7.7
9	5 : 2.5 : 2.5	39.7	19.8	19.8	12.9	7.7

the host liquid crystal, NYC-22133L as the chiral dopant and UCL-011 (DIC Co.) as the monomer. During mixing, the mixture was stirred for more than 5 h at the isotropic temperature. The temperature range of a PSBPLC system is very much dependent on host LC mixing ratio, because each host LC possess different characteristics such as Kerr constant, viscosity, and isotropic temperature. Therefore, nine mixing conditions (altering only the host LC ratio) of the BPLC materials were studied. The details of the LC mixing ratio are listed in Table 1.

All the mixtures were injected in sandwich-type cell made with plain ITO glass substrates. Table 2 shows the cell fabrication conditions of the BPLC cell. This type of cell structure was used to identify the phase transition temperature of BPLC under the polarizing optical microscope (POM).

2.2. *Electro-Optic Measurement*

BPLCs are self-organized structures and thus the BP does not need any mechanical alignment which is typically induced by rubbing processes for other LC phases such as nematics and smectics. Thus, for PSBPLC cells, the alignment and rubbing process can be eliminated. All the BPLC mixtures were filled in a sandwich-type cell (using two substrates) where plain glass was used as the top substrate and the bottom substrate contained interdigitated ITO (indium tin oxide) electrodes as shown in Fig. 1(a).

Table 3 represents the fabrication conditions of the cell. An interdigitated electrode of the profile shown in Fig. 1(b) is used in order to provide an in-plane electric field for switching. The cell parameters are as follows: electrode line 25 μm, electrode spacing 10 μm, and cell gap 10 μm. UV irradiation (wavelength = 365 nm) was used on all samples in order to polymerize the UCL-011 monomer. The UV irradiation intensity was

Table 2. Cell making condition

Substrate	Glass substrate with ITO
Substrate size	25 × 15 × 1.1 [mm]
Alignment film	No alignment film
Spacer	10 μm

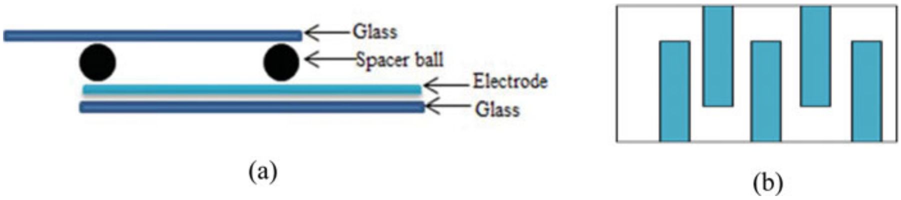

Figure 1. Structure of (a) BPLC cell, (b) interdigitated electrode.

1.5 mW/cm^2 and the irradiation time was 20 min. Before polymer stabilization, the cell was observed under POM to identify the BP texture and phase transition temperature. The sample is heated from chiral nematic to blue phase, and then the precursor was left to be exposed to UV at the BPI temperature range to form polymer stabilize blue phase. Finally, after photopolymerization the cell cooled down at room temperature to confirm the LC phase using the POM.

In order to calculate transmittance T, the sample cell was placed between crossed Nichols. All electro-optical measurements were carried out at 25°C by using a temperature controller hot stage.

3. Results and Discussion

3.1. Temperature Range

The phase transitions for the nine mixing conditions are listed in Table 4, where sample no. 1–7 were successfully polymer stabilized. Sample no. 8 and 9 did not show the BP, assuming those mixing conditions were not suitable to achieve PSBPLC. The failed cases (Sample no. 8 and 9) also indicated that there is a minimum amount of PE-5CNF of 3wt% which was required to exhibit the BP.

The three different host LC possess three different isotropic temperatures. Thus, the objective of varying the composition ratio of host LC is to achieve a higher positive BP-Iso temperature as well as the widest possible temperature range. For sample no. 1 and 2, the ratio of the E8 was fixed but the ratio between the PE-5CNF and CPP-3FF were varied. Gradually, the E8 ratio was increased (sample no. 3–9) in the mixture whilst the PE-5CNF and CPP-3FF ratios were changed. Additionally, in sample 1, PE-5CNF and CPP-3FF showed the same ratio; whilst in sample no. 2 they have different ratios. Finally, four groups of mixtures were studied which included samples such as sample no. 1 and

Table 3. Cell making condition for V-T measurement

Substrates	Interdigitated	Blank glass	Electrode width	Electrode Gap
Size	25 × 22 × 1.1 [mm]	25 × 15 × 1.1 [mm]	25 [mm]	10 [mm]
Alignment process	None			
Spacer	10 [μm]			

Table 4. Phase transition temperatures of BPLC mixtures (before and after stabilize) are determined by polarizing optical microscope studies

	Transition temperature (−C) before			Transition temperature (−C) after		
Sample no.	N*→BPI	BPI→ISO	ΔT (°C)	N*→BPI	BPI→ISO	ΔT (°C)
1	33	35.4	2.4	<-10	32.9	> 42.9
2	27.5	29.8	2.3	<-10	29.7	> 39.7
3	33.7	36.7	3	<-10	27.8	> 37.8
4	30.4	33.4	3	<-10	27.3	> 37.3
5	31.3	35.2	3.9	<-10	31.5	> 41.5
6	31.5	34.4	2.9	<-10	28.5	> 38.5
7	33.4	36.2	2.8	<-10	40.4	> 50.4

2 (group 1), 3 and 4 (group 2), 5 and 6 (group 3), and 7–9 (group 4); where the ratio of E8 in each group is 2, 3, 4, and 5, respectively. Moreover, for each group the ratio of PE-5CNF and CPP-3FF were either equal or biased. However, the other mixing conditions were attempted to optimize the best ratio of host LC. Furthermore, evaluation of the most dominant host LC to achieve a wide temperature PS-BPLC was conducted.

Prior to polymer stabilization, the blue phase temperature range was identified through polarized optical microscopy. Referring to the Table 4, the lowest temperature range of the blue phase at this stage existed within a temperature window of 2.3°C before stabilization. After polymer stabilization, POM observations indicated that the highest BP-Iso transition temperature of the polymer stabilized mixture was 40.4°C (referring to Table 4). Currently, the BP-N* phase transition temperature is limited by the lower temperature unit of the hot stage at −10°C. Thus, a minimum observable temperature of −10°C was defined. Therefore, taking this into consideration, the overall blue phase range for the mixture after polymer stabilization was found to be more than 50.4°C. Fig. 2 shows a comparison texture of sample 7 using polarized optical microscopy before and after polymer stabilization.

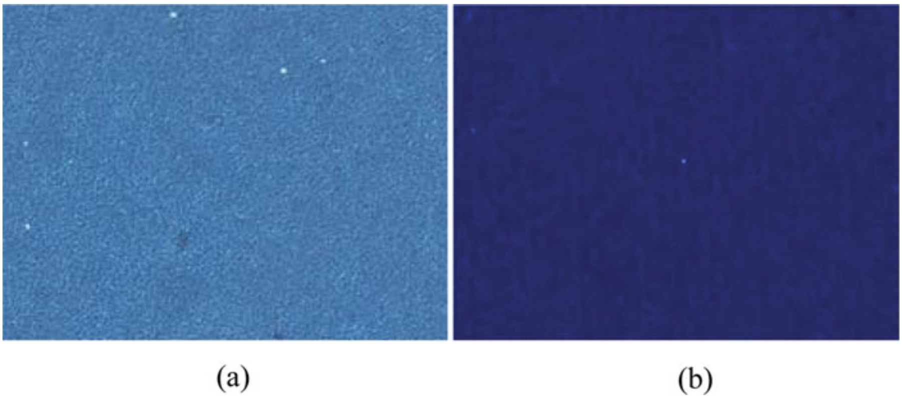

Figure 2. Polarizing optical microscope image of room temperature PSBPLC. (a) Before polymer stabilization at 33.9°C and (b) After polymer stabilization at 30.3°C.

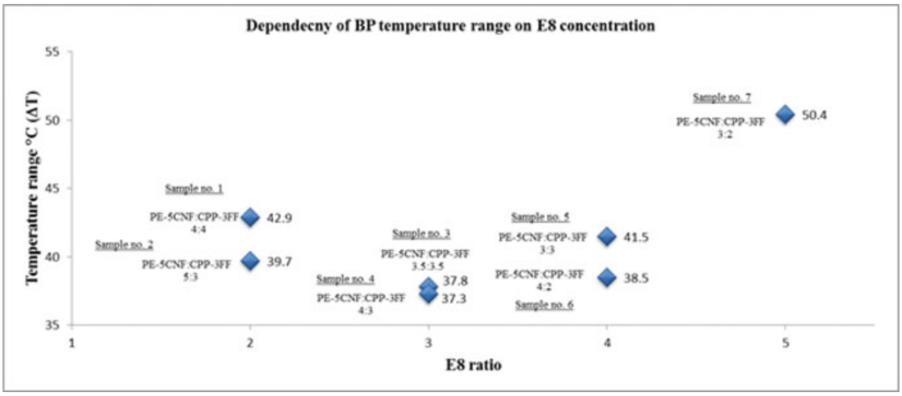

Figure 3. Dependency of BP temperature range on host LC.

From Table 4, it is clear that the percentages of host liquid crystal played a vital role in widening the BP temperature range. Samples no. 7 and 1 showed the highest temperature range. It is believed that CPP-3FF contributes most to the widening of the temperature range, even though sample no. 7 possessed the lowest ratio of CPP-3FF. It is an assumption that sample 7 would have been limited to around −20°C. Observation of the PSBPLC texture under POM indicated that BP texture seemed to be vanishing at −10°C for sample no 7, whereas for sample no. 1, it still showed a strong BP texture at −10°C. Thus, the BP range is expected to have a lower $N^* \rightarrow BPI$ for sample no. 1, compared to sample no. 7.

Figure 3 represents the dependency of the BP temperature on host LC, where the BP temperature range is plotted as a function of the ratio; E8 vs. PE-5CNF and CPP-3FF. The lowest BP temperature range (∼37.3°C) was observed when the ratio of the E8, PE-5CNF, and CPP-3FF was 3:4:3. It was also observed that the temperature range of BP changed when the ratio of PE-5CNF and CPP-3FF was changed. Furthermore, when the ratio of the E8 and CPP-3FF was 2 and 3, respectively, the BP temperature range was ∼39.7°C but when the CPP-3FF ratio increased from 3 to 4, the temperature range increased up to ∼42.9. The same results were obtained for the other groups of mixtures. For every group of mixture, when the ratio of PE-5CNF was decreased and ratio of the CPP-3FF was increased, the BP temperature range increased which again establishes the hypothesis that the ratio of CPP-3FF is the dominant factor to extend the BP temperature range.

3.2. Characterization of Electro-Optical Properties

The room temperature mixture (sample no. 1 and no 5) demonstrates promising electro-optic performance. In general, for both mixtures, low driving voltage (<80 V) and high transmission (∼45%) have been achieved for the room temperature BPLC. The electro-optic characteristics were investigated for sample no. 1 and 5 where the ratio of PE-5CNF and CPP-3FF increased one unit in sample no. 5. Fig. 4 depicts the VT curves of the PSBP LC cell using sample no. 1 as shown in Table 1. It was observed that VT curves began to saturate at ∼79 V. Fig. 5 illustrates the VT curves of PSBP LC cells using sample no. 5. Here, the $V_{\max}$ was found at ∼78 V. It was also observed that sample no. 1 showed slightly lower hysteresis compared to sample no. 5, which indicated that as the $V_{\max}$ increased, the hysteresis decreased. Furthermore, the driving voltage decreases as the percentages of PE-5CNF and CPP-3FF decreased in the host LC mixture but again the tradeoff is in

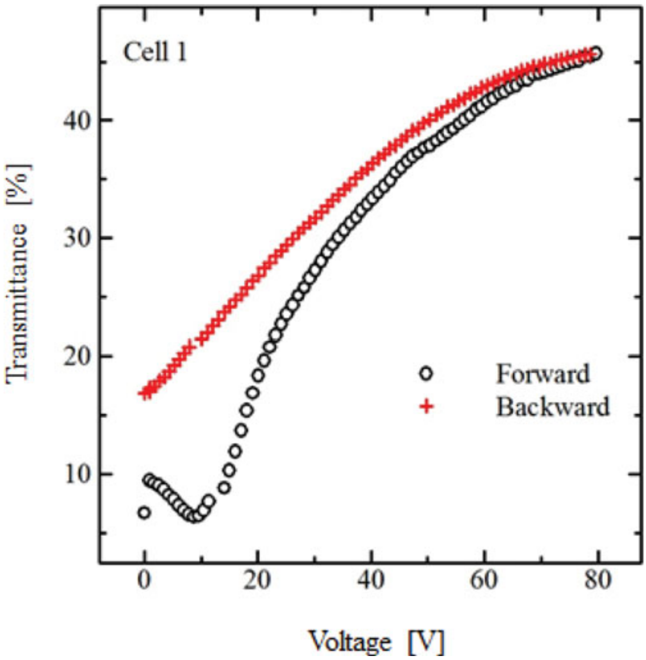

Figure 4. V-T graph of sample no. 1.

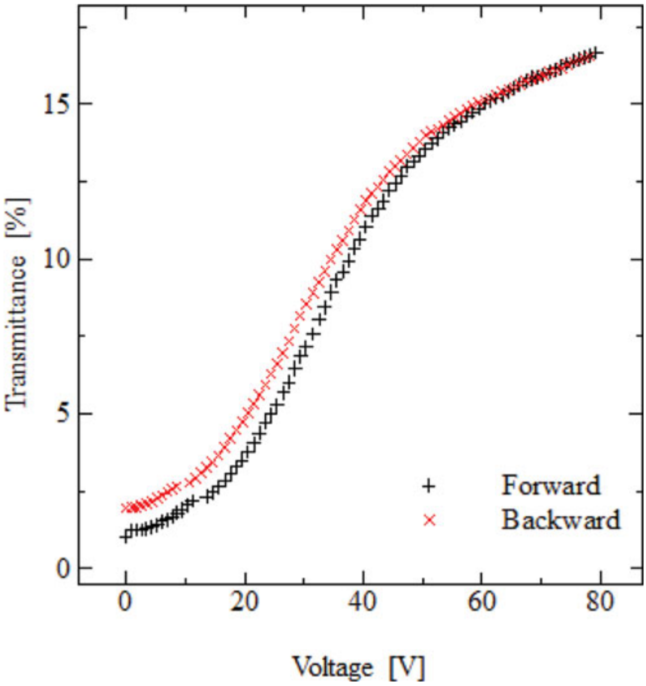

Figure 5. V-T graph of sample no. 5.

increased hysteresis. This investigation confirms that tuning in host LC ratio led to change in the materials electro-optic parameters. Overall, the room temperature of the blue phase mixture shows good potential for electro-optic applications given its wide blue phase range and electro-optic performance.

4. Conclusion

The present work focuses on stability of polymer stabilize BPLC based on host LC ratio. It was found that the BPLC temperature range and electro-optical properties such as driving voltage and hysteresis is very much dependent on host LC mixing ratio. The host LC materials used in this study consisted of a mixture E8, PE-5CNF and CPP-3FF. The BP temperature range was extended to approximately 50.4°C and found to be at 5:3:2 (E8: PE-5CNF: CPP-3FF) ratio of these three host LC mixture. As a summary, it is expected that the CPP-3FF plays an important role compare to the other host LC in achieving broad temperature range and reduction in the hysteresis. Moreover, the mixtures present BPLC in room temperature and demonstrate promising electro-optical properties such as lower driving voltage ($\sim$78 V) and low hysteresis which could lead to the future generation displays and switching applications.

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