

Investigation of host Liquid Crystal composition on Polymer stabilised Blue Phase properties

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Abstract

Polymer stabilised blue phase liquid crystals (PSBPLCs) have been investigated for photonics and display applications for the following reasons: optical isotropy in the dark state, ease of fabrication due to the omission of the alignment layer, and sub-millisecond response length. Major barriers to the commercialisation of PSBPLCs are: hysteresis, residual birefringence, and most significantly, high driving voltage. We have chosen to lower the driving voltage through optimization of the mixture (host LC, chiral dopant and monomer). In this paper, investigation of the contribution of the host liquid crystal to the phase stability and electro-optic characteristics of the PSBP will be discussed. The following cases have been investigated: a) A three component host liquid crystal (E8, PE-5CNF (4-Cyano-3-fluorophenyl 4-pentyl benzoate) and CPP-3FF (4-(trans-4-n-propyl cyclohexyl)-3',4'-difluoro-1,1'-biphenyl), LCC Corporation, Japan). For a ratio of E8:PE-CNF:CPP-3FF of 5:3:2, a large BPI window of $>50.4^{\circ}\text{C}$ and low hysteresis was achieved, but the driving voltage was 79V, and b) A single host liquid crystal, 8OCB with chiral dopant CB15. For a ratio for 8OCB:CB15 of 1:1, this mixture demonstrated a significantly lower driving voltage of 65V, but exhibited a smaller BPI window of $>27^{\circ}\text{C}$. Decrease in the ratio of 8OCB:CB15 also induced the presence of a BPII phase in the mixture. A single host liquid crystal has the advantage of simplicity of composition, and lowered driving voltage. However, the hysteresis and blue phase temperature range needs to be optimised. This investigation concludes upon the suggestion of liquid crystal characteristics which optimises the blue phase temperature range, low hysteresis, switching times and driving voltage.

Keywords: polymer stabilised blue phase liquid crystal, hysteresis, driving voltage, electro-optic effect, switching time.

1. Introduction

The blue phases (BP) of liquid crystals are a set of phases that exist between the isotropic and cholesteric phases of certain liquid crystalline materials. It exists in a fairly small temperature range, typically around 1 to 2 K. BP liquid crystals are optically isotropic and have double helix cubic arranged in a cubic superstructure [1]. The periodic lattice structure of BP is comparable to the wavelength of visible light, typically of a pitch comparable to that of blue light, hence the name "blue phase". In 1969, Saupé was the first to describe the BP as a cubic structure [2]. Further identification of the structure of blue phases revealed a three-dimensional lattice of cylindrical liquid crystal "logs" interspersed with a corresponding lattice of disclination lines [2, 3]. The BP can be divided into three types (BPI, BPII and BPIII) depending on the chirality of the LC. The BPIII phase has in almost similar structure to the isotropic phase, whereas BPI and BPII are made out of double twist cylinders packed in cubic lattices. It can be understood as the stacking of cylindrical "double twist tubes", in which the director rotates about any radius of a cylinder. The disclination lines arising from this three-dimensional fluid crystal lattice is the reason for the small temperature

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range of the blue phases, as they are relatively unstable. Blue phases possess the advantages of sub-millisecond response time, no requirement for alignment layers, and wide viewing angles, and thus promise potential electro-optic applications such as large area displays and tunable lasers [4, 5]. However, their development is impeded by this small temperature range, and high driving voltage. The stability of the blue phases are usually improved in the following three ways: polymer stabilisation [6], nanoparticle stabilisation [7], and use of unconventional liquid crystals such as liquid crystalline dimers and novel shaped liquid crystals [8, 9]. In particular, polymer and nanoparticle stabilisation operate on the same principle: filling up the space in the disclination lines should reduce the free energy costs of the defects, thereby stabilising the phase. Two significant milestones which were achieved in broadening the blue phase temperature range were by Kikuchi in 2002, who, through polymer stabilisation expanded the blue phase temperature range up to 60°C; and Coles and Pivnenko who presented a broad-temperature blue phase of approximately 50°C. that existed at room temperature using liquid crystal dimers [8]. By 2008 Samsung demonstrated a blue phase liquid crystal display (BPLCD) prototype at the Society for Information Display's annual conference [10]. More recently, an interest in flexible blue phase displays has emerged, due to the fact that an alignment layer is not needed for the device architecture of BPLC [11, 12], such as the bendable single substrate BPLC developed by Kimura et al [13].

For commercialization of PSBPLCs in electro-optic and photonics applications, the key challenges that lie ahead are in terms of high operating voltage, low transmittance (~75%), poor dark state, switching hysteresis induced by chirality in the BP mixture, and inconsistent gray levels due to the presence of the polymer networks. This work addresses two of the issues, i.e. high operating voltage and electro-optic hysteresis, through comparison of a three-mixture liquid crystal host vs a single liquid crystal host. Current practice is to employ a mixture LC host in order to tune the PSBPLC properties; in this work, a single host LC is employed in order to simplify the overall PSBPLC composition and improve its electro-optic characteristics.

2. Experimental details

2.1 Materials

The widening of the blue phase was achieved through polymer stabilisation in two cases; 1) a three host LC mixture and 2) a single host LC mixture. For the three host LC mixture the following materials were used to achieve a room temperature PSBPLC mixture: E8, CPP-3FF (4-(trans-4-n-propyl cyclohexyl)-3',4'-difluoro-1,1'-biphenyl, LCC Corporation, Japan) and PE-5CNF (4-Cyano-3-fluorophenyl 4-pentyl benzoate, LCC Corporation, Japan) as the host liquid crystal, NYC-22133L as the chiral dopant and UCL-011 (DIC Co.) as the monomer. On the other hand, for a single host LC based PSBPLC mixture, 8OCB, CB15 and UCL-011 were used as host LC, chiral dopant and monomer respectively to prepare the room temperature BPLC mixture. The chemical structure of 8OCB and CB15 are shown in Fig 1. Moreover, the phase transition temperatures of these materials are shown in Table 1.

For each of these cases, the BP of the unpolymerised mixture is first identified using Polarising Optical Microscopy (POM). The samples were temperature controlled using hotstage, Linkam (LTS420). After having identified the blue phase range, the mixture was irradiated with a UV light ($\lambda = 365$ nm) of irradiation intensity 1.5 mW/cm^2 for 20 min, in order to polymerise the UCL-011 monomer within the blue phase temperature window. The mixture was then left to cool down to room temperature. POM was then again used to identify the phase transition temperatures of the polymer stabilised mixture, and define the broadened blue phase temperature range.

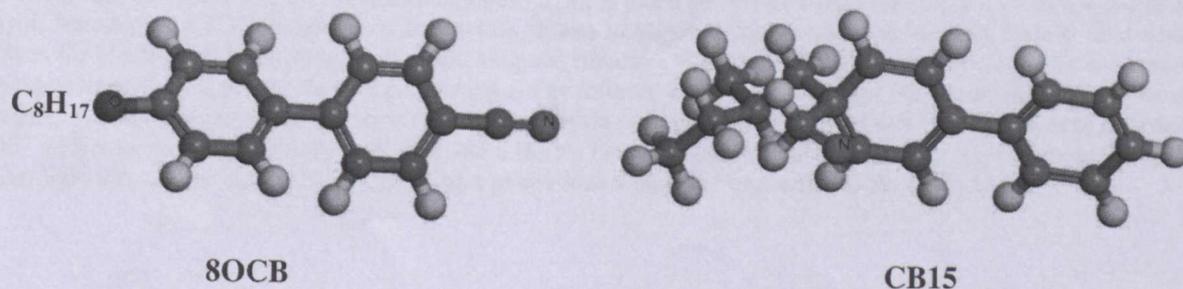


Figure 1: Chemical structure of 8OCB, 8CB and CB15

Table 1: Phase transition temperature of 8OCB, 8OCB, and CB15

Material	Cr→SmA (°C)	SmA→Nematic (°C)	Nematic→Iso (°C)
8OCB	54	67.1	80
CB15	4.0	-54	-30

For the three host LC mixtures, seven mixing conditions are detailed here, where the percentage of host LCs were altered whilst keeping constant the amount of chiral dopant and monomer. The mixing conditions for this mixture are shown in Table 2.

Table 2: Mixing conditions

Condition No.		1	2	3	4	5	6	7
Host LC (wt%)	E8	15.9	15.9	23.8	23.8	31.7	31.7	39.7
	PE-5CNF	31.7	39.7	27.8	31.7	23.8	31.7	23.8
	CPP-3FF	31.7	23.8	27.8	23.8	23.8	15.9	15.9
Chiral Dopant (wt%)	NYC-22133L	12.9	12.9	12.9	12.9	12.9	12.9	12.9
Monomer (wt%)	UCL-011	7.7	7.7	7.7	7.7	7.7	7.7	7.7

Initially, 8OCB was mixed with same chiral dopant (NYC-22133L) used in three host LC mixture but the BP could not be observed, thought to be due to the insolubility of 8OCB with NYC-22133L. According to Figure 1 which depicts the molecular structures of 8OCB and CB15, 8OCB contains the CN group, thus it is believed that a chiral dopant (CB15) with the CN group will be appropriate for the solution. The optimized mixing condition is shown in Table 3.

Table 3: Mixing conditions

Name	Ideal value		Experimental value	
	weight[mg]	ratio[wt%]	weight[mg]	ratio[wt%]
8OCB	50	45.45	53	46.37
CB15	50	45.45	50.6	44.27
UCL-011	10	9.09	10.7	9.36

All the mixtures were injected in sandwich-type cell made with plain ITO glass substrates (dimension-25×15×1.1 [mm]). The substrates were untreated as the BP does not require any alignment to guide the molecules. The phase transition temperatures for all the mixtures were identified by using this type of cell structure.

2.2 Electro-optic measurement

The cell structure for the BPLC, as shown in Figure 2 (a), is much simplified due to the elimination of the alignment layer. Interdigitated ITO electrodes of dimensions shown in Figure 2 (b), provide the in-plane electric field which drives the electro-optic switching. Upon switching, the directors from the isotropic state to an aligned state parallel to the electric field applied. The cell parameters are as follows: electrode line 25µm, electrode spacing 10 µm and cell gap ~10 µm. During the observation of the electro-optic response, the cell was placed between crossed polarizers (45° with respect to the electrode direction) and a He-Ne laser was used as the optical input. Optical response of the laser light through the cell was captured using a photodiode which was connected to the oscilloscope.

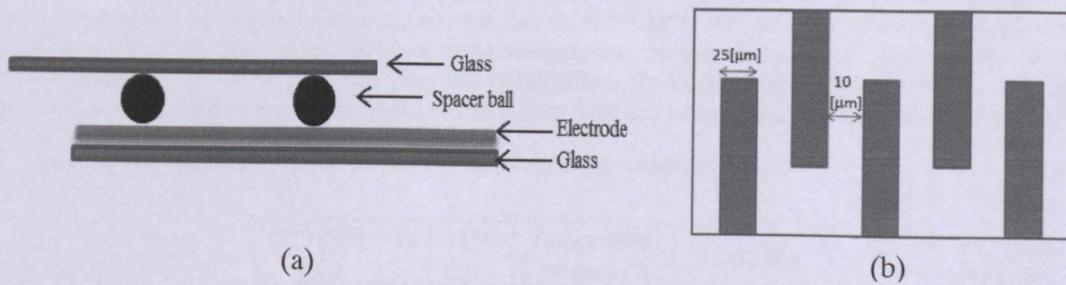


Figure 2: Structure of (a) BPLC cell (b) Interdigitated electrode.

3. Results and discussion

3.1 Temperature range

The BP temperature ranges for the three host LC (seven mixing conditions) are shown in Table 4. Given that the three component LC host mixtures possess different isotropic transition temperatures, tuning of the composition of the mixtures is required in order to achieve both a high positive BPI-Iso transition temperature, and also the widest BP temperature range. Referring to Table 4, it can be seen that the widest temperature range was achieved for Condition No. 7, where a BP range of $>50.4^{\circ}\text{C}$, assuming that the BPI-Iso transition temperature for this condition was 40.4°C , and the minimum observable temperature for this mixture was -10°C . It was also observed that the component, CPP-3FF proved to be the most dominant in determining the overall phase temperature of the mixture. The textures for the BP for the case of the three host mixture for Condition No. 1, the resulting blue phase can be seen in Figure 3.

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

Condition No.		1	2	3	4	5	6	7
Before Stabilisation ($^{\circ}\text{C}$)	$\text{N}^* \rightarrow \text{BPI}$	33	27.5	33.7	30.4	31.3	31.5	33.4
	$\text{BPI} \rightarrow \text{Iso}$	35.4	29.8	36.7	33.4	35.2	34.4	36.2
	ΔT	2.4	2.3	3	3	3.9	2.9	2.8
After Stabilisation ($^{\circ}\text{C}$)	$\text{N}^* \rightarrow \text{BPI}$	< -10	< -10	< -10	< -10	< -10	< -10	< -10
	$\text{BPI} \rightarrow \text{Iso}$	32.9	29.7	27.8	27.3	31.5	28.5	40.4
	ΔT	>42.9	>39.7	>37.8	>37.3	>41.5	>38.5	>50.4

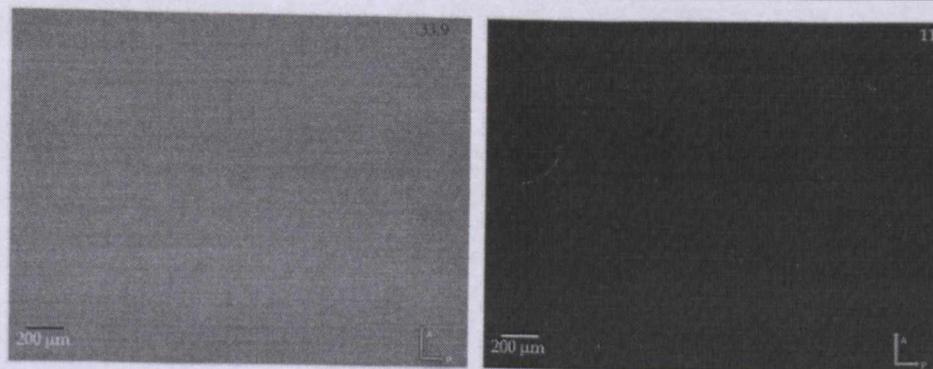


Figure 3: Polarized Optical Microscope (POM) image of room temperature PSBPLC. (a) Before polymer stabilisation at 33.9°C and (b) After polymer stabilisation at 11°C .

For the single host liquid crystal case, Figure 4 represents the POM images of the BP for the mixture listed in Table 3. Before stabilisation, the following transitions were recorded: N* 39°C BPI 40°C Iso. However, in this condition, BPII was not observed. The photo-polymerisation temperature of the sample was chosen to be in the BPI temperature range, i.e. at 39.5 °C. Before polymer stabilisation, the temperature range of BPI was 1°C and after polymer stabilisation the temperature range was successfully widened to more than 27°C, as tabulated in Table 5.

Table 5: Phase transition temperature of BPLC before and after stabilisation

N*→BPI (°C)	BPI→ISO (°C)	Temperature range (°C)	Condition
39	40	1	Before stabilisation
<10	37	>27	After stabilisation

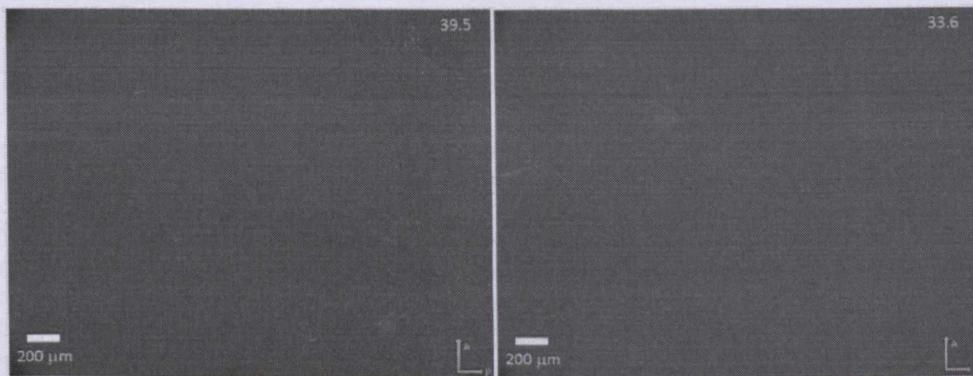


Fig 4: POM image: (Left) BPI on heating before stabilised reflectance mode (right) BPI on cooling after stabilised transmission mode

Having successfully achieved the blue phase using 8OCB as the base, the composition was further optimized. The mixing ratios are shown in Table 6. From this table, it is noted that the Sample 5 which contains the ratio of (0.6:1) for 8OCB:CB15 shows both BPI and BPII. After UV irradiation, the BPI-Iso transition temperature was increased from 4.6°C to 13.8°C. Moreover, BPII was observed before polymer stabilisation while cooling (Iso 28.3°C BPII 26.7°C BPI 23.7°C N*), believed to be due to the high percentage (60 wt%) of chiral dopant which increased the chirality of mixture. On the other hand, after polymer stabilisation, the BPI-Iso temperature dropped below the room temperature (23.8°C), due to the low weight percentage (40 wt%) of host LC in the mixture. Thus, it is noted that Sample 3 of the original composition explored still shows the widest temperature range, which will then be investigated further for its electro-optic characteristics.

Table 6: Optimized mixing conditions of host LC and chiral dopant for single host LC mixture

Sample	8OCB (% wt)	CB15 (% wt)	Comments	N*→BPI (°C)	BPI→Iso (°C)	ΔT (°C)
1	60	40	BP did not appear	N/A	N/A	N/A
2	55	45	BP did not appear	N/A	N/A	N/A
3	50	50	BPI appear	<10	37	>27
4	45	55	BPI appear	<10	29.4	>19.4
5	40	60	BPI and BPII appear	<10	23.8	>13.8

The POM images of the BP texture of the optimized single host mixture from Table 6 (Sample 5) is shown in Figure 5.

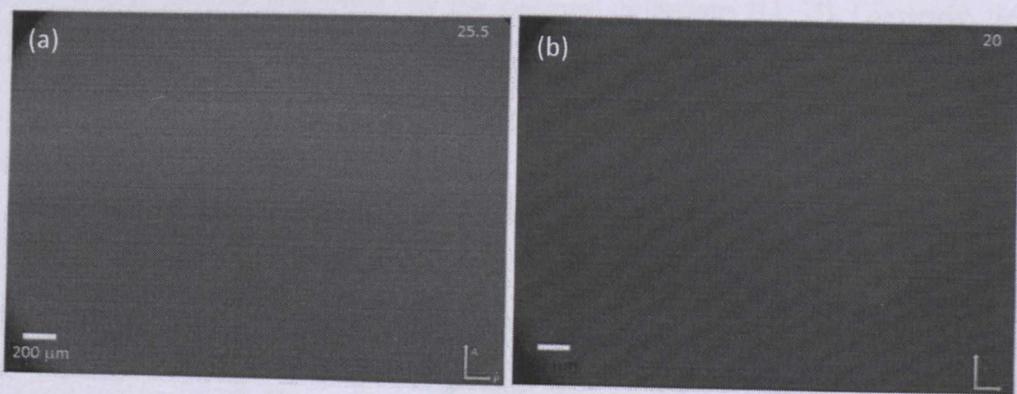


Figure 5: POM image of BPLC for the optimized single host mixture (a) before UV irradiation (b) after UV irradiation.

3.2 Electro-optical (Voltage vs Transmittance) performance

The room temperature mixtures (at 25 °C) for Condition No. 1 and No. 5 have been characterized for their electro-optic performance, as shown in Figure 6. Whilst for Condition No. 7 showed the widest BP range, it showed some anomaly in the BP range for before and after stabilisation. Thus, the next two widest compositions for the BP, Condition No. 1 and No. 5, were selected for their electro-optic properties. For Condition No. 1, the V-T curve began to saturate at 79 V, and for Condition No. 5, at 78 V. Furthermore, Condition No. 1 showed slightly lower hysteresis compared to Condition No. 5, which indicated a tradeoff between the switching voltage and hysteresis. The transmission for Condition No. 1 is far superior at ~45%, compared to Condition No. 5 which had a transmission of 18%.

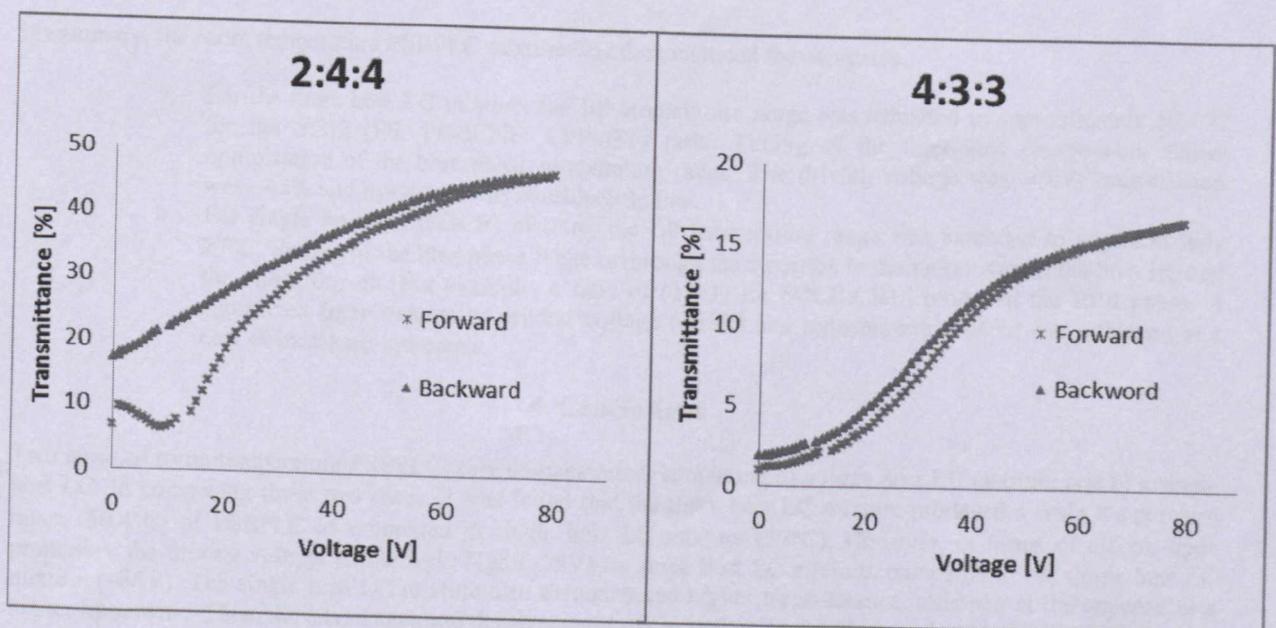


Figure 6: V-T graph of Condition No. 1 (Left), Condition No. 5 (right)

For the single host mixture containing 8OCB (listed in Table 3), the switching voltage and transmittance are significantly better than the three host mixture, at a voltage of $\sim 65\text{V}$ and a transmittance of $\sim 66\%$ is shown in Figure 7. The driving voltage of $\sim 65\text{V}$ is comparatively low compared to literature [14, 15]. Conversely, the residual birefringence and hysteresis is relatively high.

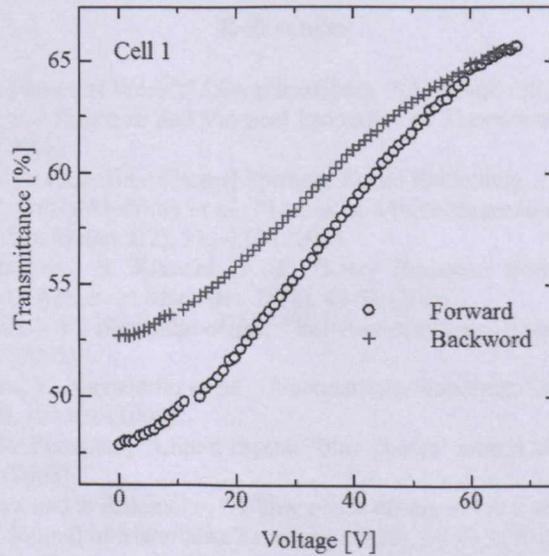


Figure 7: V-T graph (ratio of 1:1 for 8OCB:CB15)

In summary, the room temperature PSBPLC mixture was demonstrated for two cases:

- For the three host LC mixture, the BP temperature range was extended to approximately 50.4°C for the 5:3:2 (E8: PE-5CNF: CPP-3FF) ratio. Tuning of the three-host components allows optimisation of the blue phase temperature range. The driving voltage was $\sim 78\text{V}$, transmission was $\sim 45\%$ and hysteresis was considerably low.
- For single host LC (8OCB) mixture, the BP temperature range was extended to approximately 27°C . Tuning of the blue phase range is through the variation in the ratio between the host LC and the chiral dopant. For example, a ratio of (0.6:1) for 8OCB:CB15 produced the BPII phase. A significant improvement of driving voltage ($\sim 65\text{V}$) and transmission ($\sim 66\%$) was achieved at a cost of increased hysteresis.

4. Conclusions

Two types of room temperature PSBPLC were demonstrated, containing a) a three host LC mixture, and b) a single host LC. In comparing these two cases, it was found that the three host LC mixture produced a wide temperature range (50.4°C) of PSBPLC as compared to single host LC mixture (27°C). However, in terms of electro-optic properties, the driving voltage is relatively high ($\sim 79\text{V}$) for three host LC mixture, compared to the single host LC mixture ($\sim 65\text{V}$). The single host LC mixture also demonstrated higher transmittance, although at the expense of a higher hysteresis. Thus, the advantages and disadvantages of the two cases are compared, with the eventual aim that should an optimal single liquid crystal host be identified, it will contribute towards developing a simpler mixture for the PSBPLC which promises potentially lower driving voltage and higher transmissivity.

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