

Effects of monomer/liquid crystal compositions on electro-optical properties of polymer-stabilized blue phase liquid crystal

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Abstract: A polymer-stabilized blue phase liquid crystal is one of the candidates for the next-generation display material. In this study, effects of monomer/liquid crystal compositions on electro-optical characteristics of polymer-stabilized blue phase liquid crystals were investigated. By optimizing monomer/liquid crystal compositions, lower operating voltage, reduction in hysteresis and residual birefringence were achieved. However, some technical issues remain to be overcome.

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1. Introduction

Blue phases (BPs) are found in highly chiral liquid crystals (LCs) in a narrow temperature range (typically less than a few kelvin) between the high temperature isotropic phase and the low temperature cholesteric phase [1–5]. The very small temperature range over which blue phases have been thermodynamically stable limits their technological applications. Recently, Kikuchi and associates proposed a new type of polymer stabilization effect to increase the stability range of BPs to as much as 60 K including room temperature for potential technological applications [6]. They also showed that the temperature range of BP can be enhanced by means of monomer/LC compositions such as monomer types, monomer concentration, and monomer ratio. Moreover, Hisakado *et al.* investigated an effect of monomer compositions on response time of the polymer-stabilized blue phase liquid crystal (PSBP LC) [7]. Since then PSBP LC is emerging as a next-generation display material because it offers several attractive features such as: (i) no requirement for any alignment layer [7], (ii) optically isotropic dark state for wide and symmetric viewing angle [7,8], and (iii) sub-millisecond response time [6,9]. However, high operating voltage [10], residual birefringence, and hysteresis [11,12] are crucial issues to be resolved. To reduce operating voltages, there are three approaches viz. (a) to develop new host LC mixtures with a large Kerr constant [13], (b) to design electrode shape, structure and dimension for generating strong and deep-penetrating electric fields [14–18], and (c) to optimize the monomer/LC compositions (monomer types, monomer concentration and monomer ratio) and the process [6,19,20]. The purpose of this study is to investigate the effects of monomer/liquid crystal compositions on electro-optical properties of PSBP LC by using a new host LC mixture. Here we also present the effect of exposure wavelength to photo-polymerize the monomer in BP on operating voltage, hysteresis, residual birefringence, and response time of PSBP LC.

2. Experimental

We prepared the blue phase LC mixture JC-BP03C consisting of 94.7 wt% of JC-BP03N (Chisso Petrochemical Co. Ltd., $\Delta n \sim 0.167$ at 30°C) and 5.3 wt% of chiral dopant, BP-CD3 (Chisso Petrochemical Co. Ltd.), thereby forming cholesteric pitch of ~ 160 nm. The phase transition temperature of JC-BP03N is N 352.25–353.35 Iso upon heating where N represents nematic phase and Iso stands for isotropic phase. Monofunctional monomers used were dodecyl acrylate (C12A, Wako) and dodecyl methacrylate (C12M, Wako). Difunctional monomers used were PLC (acrylate type) and PLCM (methacrylate type) (Chisso Petrochemical Co. Ltd.). The chemical structures and physical parameters of JC-BP03N, BP-CD3, PLC and PLCM are not available because of commercial confidentiality. A small amount (~ 0.4 wt%) of 2,2-dimethoxy-2-phenyl acetophenone (DMPAP, Aldrich) was added to the solution as a photoinitiator. To investigate the effects of monomer/LC compositions, four precursors were prepared as shown in Table 1. In order to obtain an in-plane electric field, a glass substrate with inter-digitated electrodes made of chromium having electrode width of 5 μm and electrode distance of 10 μm (Alone Co. Ltd.) without any alignment layer was used. The counter substrate was a bare glass substrate. The nominal cell gap is 8–18 μm .

The cells were filled with precursors by capillary action in the isotropic phase. We cooled down the cells from the isotropic to chiral nematic phase (N^*). Then, we heated the cells from the chiral nematic phase to the blue phase (BPI) to measure the transition temperature as shown in Table 2. Polarizing optical microscopy (Nikon, Eclipse, LV100POL, Japan) was used to characterize the LC textures. The cells were then exposed (from the bare glass substrate side at normal incidence) to ultraviolet (UV) light of 1.5-10 mW/cm² for 3-20 min at the temperature slightly higher than N^* -BPI transition temperature. With regard to exposure condition, 1.5 mW/cm² is referred to as “low intensity” exposure and 5-10 mW/cm² is referred as “high intensity” exposure in this paper. Note that the exposure dose was set to be 1.8 J/cm². The light sources used in the photopolymerization experiments were UV lamp (deep UV 500, Ushio), and light emitting diodes (LEDs) ($\lambda = 365, 375, 395$ nm) (Hamamatsu Photonics K. K.). The temperature range of PSBP LC after photopolymerization was shown in Table 2. To characterize electro-optical properties, a He-Ne laser ($\lambda = 633$ nm) was used as a light source and PSBP LC sample cell was adjusted between the crossed polarizers so that the electrode direction made an angle of 45° with respect to both their axes. The cells were driven by 100 Hz square waves at 50% duty cycle. The ascending and descending voltages scanning from $V = 0$ V to $V > V_{\max}$ were performed for each sample. Here, V_{\max} is defined as a voltage at the maximum transmittance of the voltage-dependent normalized transmittance curve. Note that all electro-optical measurements were performed at 26°C.

Table 1. Compositions of BP LC Samples

Samples	C12A (wt%)	PLC (wt%)	C12M (wt%)	PLCM (wt%)	JC-BP03N + BP-CD3 (wt%)
precursor 1	6	5	0	0	89
precursor 2	4	4	0	0	92
precursor 3	0	0	6	5	89
precursor 4	0	0	4	4	92

Table 2. Phase Transition Temperature of BP and PSBP LC Samples

Samples	Phase transition temperature before photopolymerization (K)	Phase transition temperature after photopolymerization (K)
precursor 1	N*302.65-303.75 BPI	N*283.15 BPI 338.15 Iso
precursor 2	N*317.75-318.35 BPI	N*283.15 BPI 338.15 Iso
precursor 3	N*309.15-309.65 BPI	N*273.15 BPI 338.15 Iso
precursor 4	N*315.55-316.45 BPI	N*273.15 BPI 338.15 Iso

3. Results and discussion

3.1 Operating voltage

Operating voltage, V_{\max} is defined as a voltage at the maximum transmittance of the voltage-dependent normalized transmittance (VT) curve. Figure 1 illustrates typical VT curves of PSBP LC cells using the four precursors shown in Table 1. Here, photopolymerization was performed by UV lamp having an intensity of 10 mW/cm². Figure 2 shows exposure wavelength-dependent V_{\max} of PSBP LC cells at 26°C. The lowest value of V_{\max} of ~35 V was achieved when the precursor 2 was exposed by UV lamp of 365 nm. The noticeable dependency on exposure wavelength was found in PSBP LC cells of precursors 1, 3 and 4. V_{\max} of PSBP LC cells using precursors 3 and 4 tends to decrease at exposure wavelength of 395 nm while that of PSBP LC cells using precursor 1 (LED, high intensity exposure) tends to increase towards longer exposure wavelength. However, this tendency was not found in PSBP LC cells using precursor 2. It was observed that increasing monomer concentration led to the higher operating voltage, V_{\max} . With the same monomer concentration (8 wt% or 11 wt%), V_{\max} of PSBP LC cells using precursors 1 or 2 was almost less than that of PSBP LC cells using precursors 3 or 4, respectively. By optimizing monomer/LC compositions and exposure wavelength, V_{\max} can be reduced to 35 V/10 μ m.

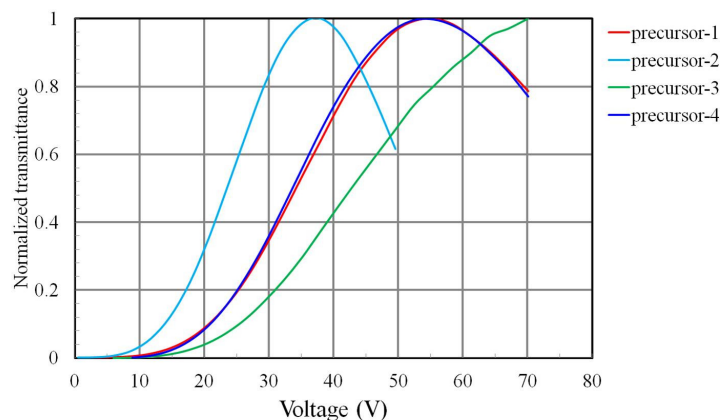


Fig. 1. Typical VT curves of PSBP LC cells prepared using four precursors. In-plane-switching cell with electrode distance of 10 μm was used.

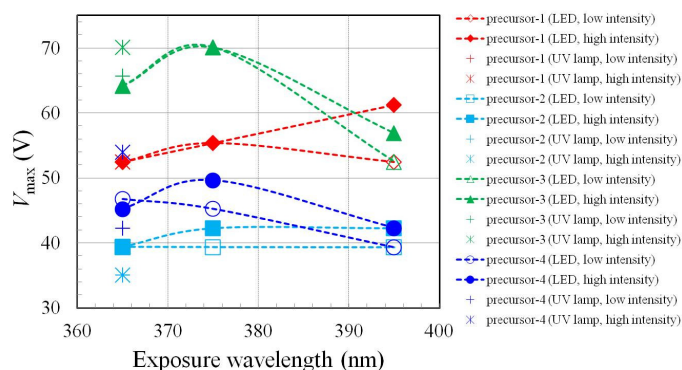


Fig. 2. Exposure wavelength-dependent V_{max} of PSBP LC cells prepared using four precursors.

3.2 Hysteresis and residual birefringence

Hysteresis is defined as the ratio of voltage difference at half-maximum transmittance (ΔV_{T50}) between the ascending and descending VT curves to V_{max} . In symbol, $\text{hysteresis} = \Delta V_{T50}/V_{\text{max}}$. As the V_{max} decreased, the hysteresis increased, that is, a trade-off between V_{max} and hysteresis was observed as shown in Fig. 3(a). It was also found that increasing monomer concentration resulted in decreasing hysteresis. With the same monomer concentration (8 wt% or 11 wt%), hysteresis of PSBP LC cells using precursors 1 or 2 was almost larger than that of PSBP LC cells using precursors 3 or 4, respectively. Hysteresis of precursor 2 showed a decreasing trend towards longer exposure wavelength while that of precursors 3 and 4 exhibited an increasing trend towards longer exposure wavelength. However, hysteresis of precursor 1 was nearly independent on exposure wavelength as depicted in Fig. 3(b).

Residual birefringence is defined as the remaining transmittance of the descending operation at 0 V after application of an electric voltage. The trade-off between V_{max} and residual birefringence was observed as illustrated in Fig. 4(a) like the relationship between V_{max} and hysteresis. It was found that increasing monomer concentration led to decreasing residual birefringence. With the same monomer concentration (8 wt% or 11 wt%), residual birefringence of PSBP LC cells using precursors 1 or 2 was almost larger than that of PSBP LC cells using precursors 3 or 4, respectively. Residual birefringence of precursors 1, 3 and 4 showed a slightly increasing trend towards longer exposure wavelength while that of

precursor 2 exhibited a decreasing trend towards longer exposure wavelength as depicted in Fig. 4(b).

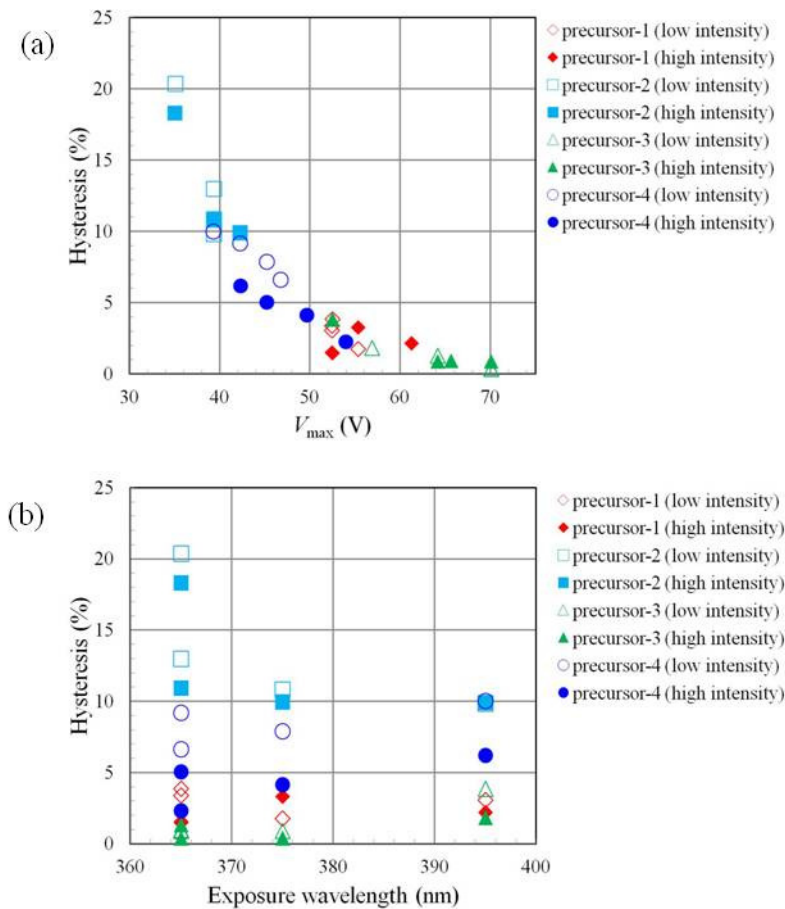


Fig. 3. Hysteresis of PSBP LC cells using four precursors as a function of V_{\max} and exposure wavelength.

3.3 Response time

The rise time is defined as the time difference between 10% and 90% of the maximum transmittance upon on-electric field. The decay time is defined as the time difference between 90% and 10% of the maximum transmittance upon off-electric field. Note that response time was determined under an applied voltage of $V \leq V_{\max}$ at 26°C. The relationship between V_{\max} and rise time is shown in Fig. 5(a). It was observed that increasing monomer concentration resulted in a shorter rise time. With the same monomer concentration (8 wt% or 11 wt%), the average rise time of PSBP LC cells using precursors 1 or 2 was nearly the same as that of PSBP LC cells using precursors 3 or 4, respectively. Rise time of all precursors showed a decreasing trend towards longer exposure wavelength with some exceptions as depicted in Fig. 5(b).

The trade-off between V_{\max} and decay time was observed as indicated in Fig. 6(a). It was found that increasing monomer concentration resulted in a shorter decay time. With the same monomer concentration (8 wt% or 11 wt%), the average decay time of PSBP LC cells using precursors 1 or 2 was nearly the same as that of PSBP LC cells using precursors 3 or 4,

respectively. Decay time of all precursors showed a decreasing trend towards longer exposure wavelength with a few exceptions as shown in Fig. 6(b).

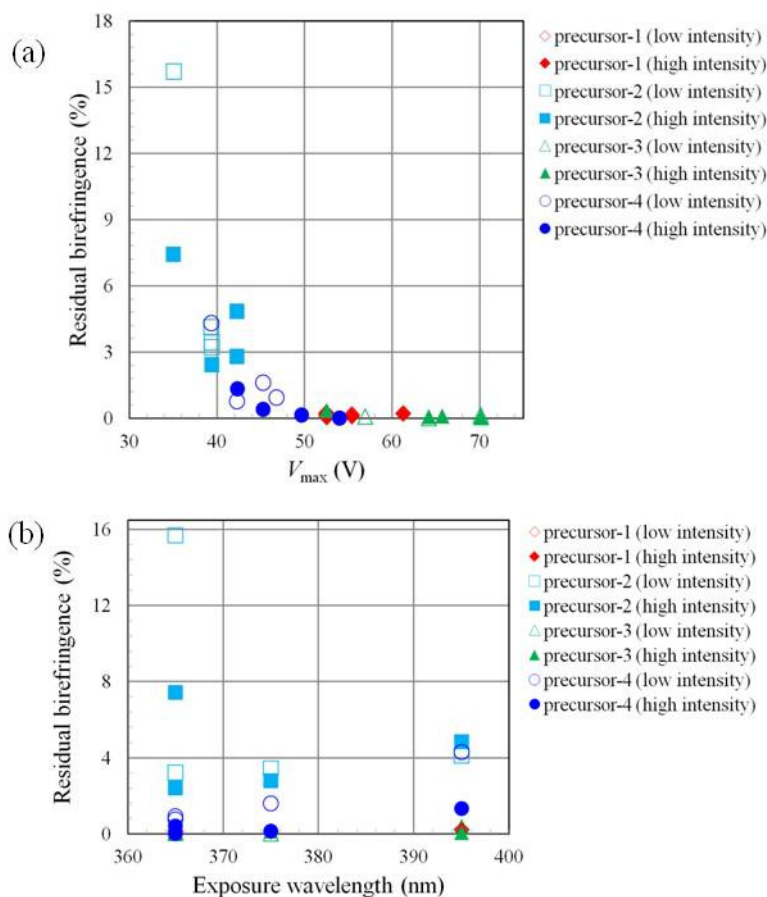


Fig. 4. Residual birefringence of PSBP LC cells using four precursors as a function of V_{\max} and exposure wavelength.

3.4 Discussion

The preliminary results of exposure wavelength effects on the electro-optical properties of PSBP LC are encouraging. It was reported that there is a relation between the structure of polymer network formed in the bulk and/or at the interface of electrode and electro-optical properties of PSBP LC [12,21]. The complex nature of mechanism of formation of polymer network influenced by a number of factors such as exposure wavelength, intensity of UV light, copolymerization reactivity ratio of two different monomers, curing temperature has not yet been clearly understood. Further experimental investigations are necessary to clarify and elaborate the mechanism of formation of polymer network and exposure wavelength-dependent electro-optical properties of PSBP LC. Based on our detailed experimental results as mentioned in Table 3, it was found that the choice of a light source (UV lamp or LED) for photopolymerization and exposure conditions was composition-dependent.

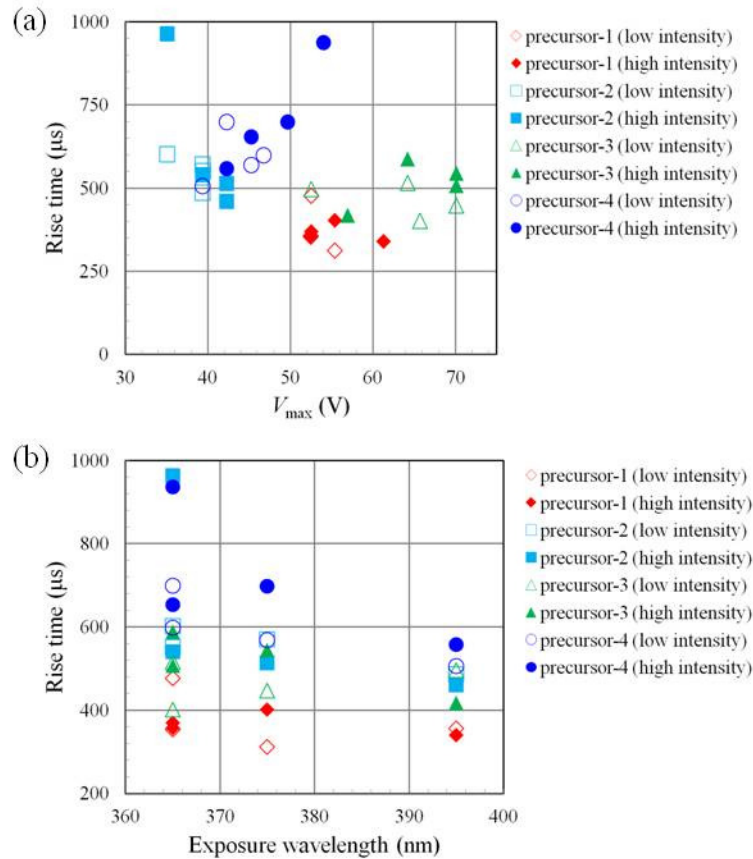


Fig. 5. Rise time of PSBP LC cells using four precursors as a function of V_{\max} and exposure wavelength.

Hysteresis and residual birefringence were applied voltage-dependent. In this study, ascending and descending voltages scanning from $V = 0$ V to $V > V_{\max}$ were performed for VT curves. Even in the “upper limit” of applied voltage, hysteresis and residual birefringence can be reduced to 0.37% and 0.001%, respectively by optimizing monomer/LC compositions. The different scenarios of the hysteresis and the residual birefringence would be observed by applying voltages from $V = 0$ V to $V < V_{\max}$. By controlling an applied electric field, *i.e.* checking whether the electric field E exceeds a critical electrical field E_c or not, the hysteresis and the residual birefringence can be optimized.

From the viewpoint of response time, it is preferable to use host LC mixture of low viscosity [22]. On the one hand, the new host LC mixture used in this study has a relatively high viscosity due to its large dielectric anisotropy ($\Delta\epsilon$), but on the other hand, host LC mixture with a large Kerr constant is required to reduce a high operating voltage [13,23]. Since there is a trade-off between the Kerr constant and the response time, it is needed to synthesize a novel host LC mixture in order to compromise between dielectric anisotropy and viscosity. Nonetheless, in this study, rise and decay times can be reduced to 312 μs and 1.3 ms, respectively under an applied voltage of $V \leq V_{\max}$ at 26°C by optimizing the monomer/LC compositions. Moreover, rise time is dependent on the applied voltage [24] and both rise time and decay time are temperature dependent. Voltage and temperature dependent response time of PSBP LC cells prepared using four precursors will be published elsewhere.

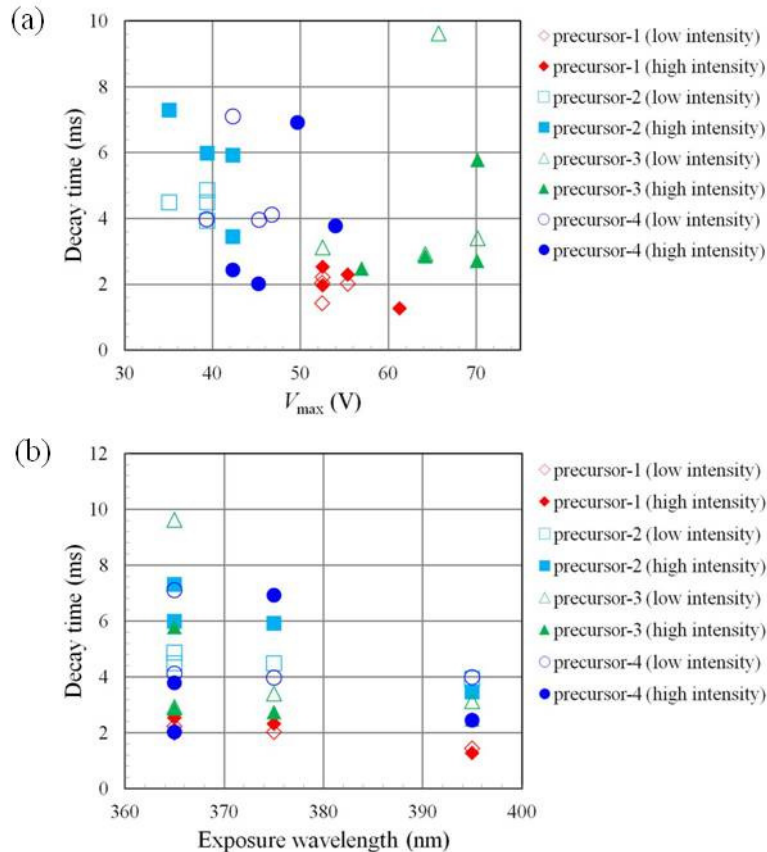


Fig. 6. Decay time of PSBP LC cells using four precursors as a function of V_{\max} and exposure wavelength.

Among four precursors, either precursor 1 or precursor 4 has a proper balance of operating voltage, hysteresis, residual birefringence and response time as summarized in Table 4. However, voltage holding ratio (VHR) of precursor 4 is higher than that of precursor 1. It is important to consider electrical characteristics (VHR, ion density) of PSBP LC cells for mass production. Moreover, precursor 4 showed a wider temperature range up to the low temperature region by comparison with precursor 1 as mentioned in Table 2. So, our next technical challenge is the stability of PSBP LC in the low temperature region.

4. Conclusions

Effects of monomer/liquid crystal compositions on electro-optical properties of the polymer-stabilized blue phase liquid crystals were investigated. It was found that increasing monomer concentration led to higher operating voltage, smaller hysteresis, smaller residual birefringence and shorter response time. With the same monomer concentration (8 wt% or 11 wt%), hysteresis and residual birefringence were sensitive to monomer compositions while rise and decay times almost did not depend on monomer compositions. Among four precursors, the precursor 4 (8 wt% of C12M and PLCM) would be the one having a proper balance of operating voltage, hysteresis, residual birefringence and response time. By optimizing monomer/liquid crystal compositions and matching of monofunctional and difunctional monomers, lower operating voltage and reduction in hysteresis and residual birefringence were achieved. The remaining technical issues to be overcome are the relatively slow response time and the low temperature stability.

Table 3. Detailed Results of PSBP LC Samples

Samples	UV lamp	LED (365 nm)	LED (375 nm)	LED (395 nm)	Parameters
	low/high intensity	low/high intensity	low/high intensity	low/high intensity	
Precursor-1	52.47/52.5 0.14/0.043	52.49/52.48 0.18/0.16	55.38/55.38 0.15/0.09	52.47/61.26 0.23/0.21	V_{\max} (V) Residual birefringence (%) Hysteresis (%)
	3.37/1.47	3.85/1.52	1.75/3.29	3.07/2.17	Hysteresis (%)
	353/369	476/357	312/402	356/340	Rise time (μ s)
	2.1/2	2.2/2.5	2/2.3	1.4/1.3	Decay time (ms)
Precursor-2	35.1/35.04 15.69/7.42	39.39/39.38 3.21/2.41	39.38/42.28 3.44/2.79	39.37/42.28 4.11/4.84	V_{\max} (V) Residual birefringence (%) Hysteresis (%)
	20.36/18.29	12.97/10.9	10.82/9.93	9.83/9.89	Hysteresis (%)
	601/963	551/540	570/513	486/460	Rise time (μ s)
	4.5/7.3	4.9/6	4.5/5.9	3.9/3.4	Decay time (ms)
Precursor-3	65.68/70.12 0.09/0.034	64.19/64.19 0.07/0.008	70.1/70.09 0.0082/0.15	52.51/56.92 0.35/0.061	V_{\max} (V) Residual birefringence (%) Hysteresis (%)
	0.94/0.37	0.9/1.31	0.9/0.39	3.85/1.83	Hysteresis (%)
	402/507	515/588	447/544	496/418	Rise time (μ s)
	9.6/5.8	2.9/2.9	3.4/2.7	3.1/2.5	Decay time (ms)
Precursor-4	42.28/54 0.77/0.001	46.75/45.23 0.92/0.4	45.25/49.6 1.6/0.14	39.34/42.3 4.29/1.32	V_{\max} (V) Residual birefringence (%) Hysteresis (%)
	9.2/2.28	6.61/5.04	7.87/4.13	9.99/6.2	Hysteresis (%)
	698/936	598/653	569/697	506/558	Rise time (μ s)
	7.1/3.8	4.1/2.03	3.96/6.92	3.98/2.45	Decay time (ms)

Table 4. Summarized Results of PSBP LC Samples

Samples	V_{\max} (V)	Residual birefringence (%)	Hysteresis (%)	Rise time (μ s)	Decay time (ms)
Precursor-1	52.47-61.26	0.043-0.23	1.47-3.85	312-476	1.3-2.5
Precursor-2	35.04-42.28	2.41-15.69	9.83-20.36	460-963	3.4-7.3
Precursor-3	52.51-70.12	0.008-0.35	0.37-3.85	402-588	2.5-9.6
Precursor-4	39.34-54	0.001-4.29	2.28-9.99	558-936	2.45-7.1

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