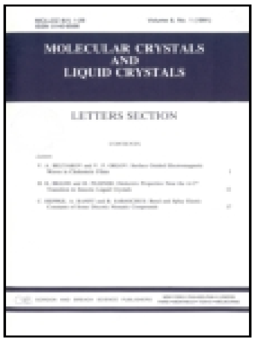

Molecular Crystals and Liquid Crystals

ISSN: 1542-1406 (Print) 1563-5287 (Online) Journal homepage: http://www.tandfonline.com/loi/gmcl20

Effect of Reactive Monomer Concentration on Electro-Optical Properties in Polymer-Stabilized Blue Phase Liquid Crystals with Identical Chiral Dopant Concentrations

Gihwan Lim, Jae-Hyun Hwang, Hirotsugu Kikuchi & Sung-Kyu Hong

To cite this article: Gihwan Lim, Jae-Hyun Hwang, Hirotsugu Kikuchi & Sung-Kyu Hong (2015) Effect of Reactive Monomer Concentration on Electro-Optical Properties in Polymer-Stabilized Blue Phase Liquid Crystals with Identical Chiral Dopant Concentrations, Molecular Crystals and Liquid Crystals, 609:1, 54-60, DOI: 10.1080/15421406.2014.956398

To link to this article: http://dx.doi.org/10.1080/15421406.2014.956398

Mol. Cryst. Liq. Cryst., Vol. 609: pp. 54–60, 2015
Copyright © Taylor & Francis Group, LLC
ISSN: 1542-1406 print/1563-5287 online
DOI: 10.1080/15421406.2014.956398

Effect of Reactive Monomer Concentration on Electro-Optical Properties in Polymer-Stabilized Blue Phase Liquid Crystals with Identical Chiral Dopant Concentrations

GIHWAN LIM,[1] JAE-HYUN HWANG,[2] HIROTSUGU KIKUCHI,[1] AND SUNG-KYU HONG[3,*]

[1]Institute for Materials Chemistry and Engineering, Kyushu University, Kasuga, Fukuoka, Japan
[2]Department of Food Industrial Management, Dongguk University-Seoul, Jung-gu, Seoul, South Korea
[3]Department of Chemical & Biochemical Engineering, Dongguk University-Seoul, Jung-gu, Seoul, South Korea

The effects of reactive monomer concentration on electro-optical properties were investigated using polymer-stabilized blue phase (PS-BP) liquid crystals (LCs) with different reactive monomer concentrations but identical chiral dopant concentrations. We found that the driving voltage was increased with increase in the reactive monomer concentration, whereas the switching hysteresis and Kerr coefficient were decreased with increase in the reactive monomer concentration in PS-BP LCs with identical chiral dopant concentrations. In addition, we found that the activation energy of electro-optical rising time was increased with increase in the reactive monomer concentration, whereas that of electro-optical decay, time was slightly decreased with increase in the reactive monomer concentration in PS-BP LCs.

Keywords Blue phase polymer stabilization; driving voltage; optical response time; reactive monomer concentration; switching hysteresis

1. Introduction

Blue phases (BPs) are liquid crystal (LC) phases that appear in the temperature range between the chiral nematic and isotropic liquid phases for chiral nematic LCs under high chirality conditions. BPs have a three-dimensional cubic structure with lattice periods of several hundred nanometres in length [1–3], and therefore exhibit selective Bragg reflections in the visible and ultraviolet (UV) wavelength ranges. BPs are optically isotropic due to the cubic symmetry of their molecular arrangement in the absence of an electric field. However, BPs become optically anisotropic due to the unidirectional anisotropy of

---

[*]Address correspondence to Sung-Kyu Hong, Department of Chemical & Biochemical Engineering, Dongguk University-Seoul, 3 Pil-dong, Jung-gu, Seoul, Korea 100-715. E-mail: hsk5457@dongguk.edu

Color versions of one or more of the figures in the article can be found online at www.tandfonline.com/gmcl.

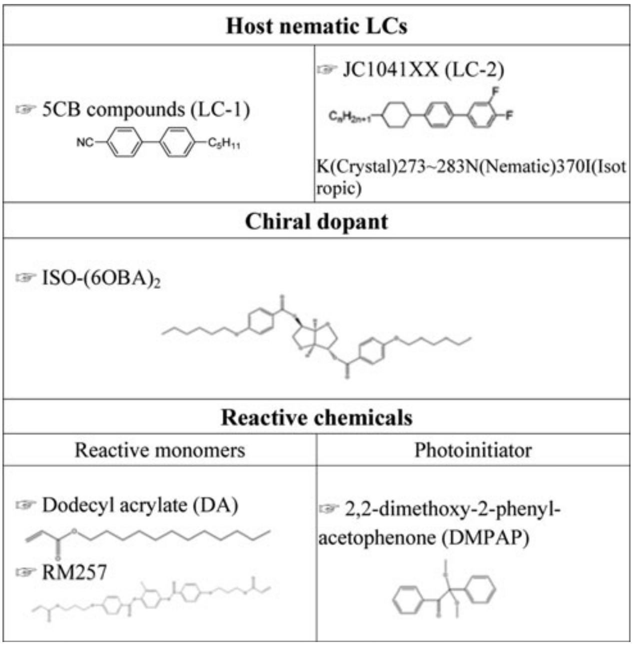

Figure 1. Chemical structures and physical properties of host nematic LCs, chiral dopant, reactive monomers, and photoinitiator.

molecular alignment in an applied electric field, with a response time of several hundred microseconds due to the Kerr effect [4]. For practical applications, although BPs hold potential as fast light modulators [5–10], their narrow temperature range of less than a few degrees Kelvin has always been a problem.

Recently, the polymer-stabilized BP (PS-BP), with a wide temperature range of more than 60 K that includes room temperature, was reported as a high-performance optical switch with a fast electro-optical response time of the order of 10^{-4} s [11]. However, the polymer stabilization of BP resulted in a high driving voltage and large switching hysteresis compared with low molecular weight BP without polymer stabilization. In order to achieve low driving voltages in PS-BP, the implementation of protrusion electrodes [12] and a vertical field switching mode [13] in terms of device structures and the development of new host nematic LC mixtures [14,15] and the optimization of the composition of reactive monomers and host nematic LCs [16,17] in terms of materials have been studied extensively. In this study, the transmittance against applied voltage, switching hysteresis, Kerr coefficient, and activation energy of optical response time were investigated using various PS-BP LCs with different reactive monomer concentrations but identical chiral dopant concentrations and reactive monomer species.

2. Experimental

2.1. Sample Preparation

As shown in Fig. 1, LC-1 of 4-cyano-4′-alkyl biphenyl (5CB) (Sigma-Aldrich Corp., St. Louis, MO, USA) and LC-2 of JC1041XX (JNC Co., Tokyo, Japan) were used as host

Table 1. Chemical composition of five kinds of chiral nematic LC mixtures with different reactive monomer concentrations

Sample	JC-1041XX+5CB(1:1)	ISO $(6OBA)_2$	DA	RM257	DMPAP
0 wt%	92.5	7.5			
8 wt%	84.5	7.5	4.0	4.0	0.5
10 wt%	82.4	7.5	5.0	5.0	0.5
12 wt%	80.6	7.5	6.0	6.0	0.5
14 wt%	78.4	7.5	7/0	7.0	0.5

nematic LC materials, and ISO-$(6OBA)_2$ was used as a chiral dopant. Here JC1041XX was nematic LC mixtures comprising single compounds with different carbon number, *n*. For the polymer stabilization of BP, RM257 (Merck & Co. Inc., Whitehouse Station, NJ, USA) and dodecyl acrylate (DA, Sigma-Aldrich Corp.) were used as reactive monomers, and 2, 2-dimethoxy-2-phenyl-acetophenone (DMPAP, Sigma-Aldrich Corp.) was used as a photoinitiator, as shown in Fig. 1.

Prior to the polymer stabilization of BP LC, four kinds of chiral nematic LC mixtures with different reactive monomer concentrations were prepared with the same 7.5 wt% chiral dopant (ISO-$(6OBA)_2$) dissolved in a mixture of 5CB:JC1041XX:RM257:DA:DMPAP, as listed in Table 1. Also, 7.5 wt% chiral dopant (ISO-$(6OBA)_2$) dissolved in a mixture of 5CB and JC1041XX without reactive monomers was prepared as a reference sample as listed in Table 1. Hereinafter, the sample names refer to the reactive monomer concentrations used (i.e., 0 wt%, 8 wt%, 10 wt%, 12 wt%, and 14 wt%).

2.2. *Evaluation of BP Temperature Range for Five Kinds of BP LC Cells*

Each temperature range for a low molecular weight BP LC cell without polymer and four kinds of PS-BP LC cells was characterized by the observation of texture made through a polarizing optical microscope (POM) (Nikon Co. Ltd.). The optical textures of five kinds of cells were observed by a POM equipped with a hot stage calibrated to an accuracy of ±0.1 K (Linkam LK-600PM, UK) under crossed Nicols. The cooling ratio of each cell was set to 1 K/min, and the lower observable temperature limit of POM was 253 K upon cooling.

2.3. *Measurement of Electro-Optical Properties for Four Kinds of PS-BP LC Cells*

A sandwich-type in-plane switching electrode cell was prepared to measure the electro-optical properties of four kinds of PS-BP LC mixtures. The top bare glass was not surface-treated, and the bottom Cr-coated glass was patterned with a distance of 10 μm in plane. The two glasses were attached by a UV light-curing adhesive and kept in a 10-μm gap with a PET film as a spacer. Cell gap of the vacant sandwich cell was measured by observing interference peak generated from vacant space between the two glasses using UV-Vis spectrometer, and the cells within a cell gap variation of 10 ± 0.5 μm were only used in this study. The chiral nematic LC mixtures were injected into vacant spaces of the sandwich-type electrode cell at the isotropic phase to prevent flow alignment. BP polymer stabilization was accomplished by UV exposure with a maximum wavelength of 365 nm on the 5CB:JC1041XX:ISO-$(6OBA)_2$:RM257:DA:DMPAP chiral nematic LC mixtures,

Table 2. Phase transition temperature of five kinds of BP LC cells upon cooling using POM under crossed Nicols

Sample	$T_{\mathrm{Iso}\rightarrow\mathrm{BP}}$	$T_{\mathrm{BP}\rightarrow\mathrm{Ch}}$	ΔT_{BP}
0 wt%	318.0	315.1	2.9 K
8 wt%	316.6	none	>60 K
10 wt%	316.3	none	>60 K
12 wt%	314.5	none	>60 K
14 wt%	312.0	none	>58 K

while the LC maintained a BP I. UV light irradiation was maintained for 15 min, with a light intensity of 600 mW/cm^2.

A He–Ne laser ($\lambda = 633$ nm) was positioned perpendicular to the sandwich cell to measure the electro-optical properties of PS-BP cells. The light transmitted through the cell according to applied voltage was detected by a photodiode (New Focus 1621M) and recorded with a digital storage oscilloscope (LeCroy WP950). The switching hysteresis of each PS-BP cell was defined as the voltage difference between voltage-up and voltage-down at transmittance 40% (T-40).

The Kerr coefficient of each PS-BP cell was evaluated by the extended Kerr model [18,19] through measurement of the relationship between transmittance and square of the applied voltage. The measurements of transmittance against applied voltage, switching hysteresis, and the Kerr coefficient for four kinds of PS-BP cells were performed at 293 K. The electro-optical response time was evaluated by the measurement of time during which the transmittance changed from 10 to 90% with voltage on (rising time) or from 90 to 10% with voltage off (decay time) in the cell. In particular, to achieve activation energies of the response time, the temperature dependencies of the response time for four kinds of PS-BP cells were measured between 243 K and 308 K. When the electro-optical response time was measured, a squared AC electric voltage with a frequency of 1.0 kHz was applied for 1 s over 30 times to the cell.

3. Results and Discussion

3.1. BP Temperature Ranges of Five Kinds BP LC Cells with Different Reactive Monomer Concentrations

Table 2 shows the phase transition temperature of a low molecular weight BP LC sample (0 wt%) and four kinds of PS-BP LC samples (8 wt%, 10 wt%, 12 wt%, and 14 wt%) upon cooling. We observed that the phase transition temperatures from the isotropic phase to BP, $T_{\mathrm{Iso}\rightarrow\mathrm{BP}}$, were lowered with increase in the reactive monomer concentrations of four kinds of PS-BP LC samples, as shown in Table 2. In particular, the phase transition temperatures from the isotropic phase to BP were abruptly lowered above 12 wt% of reactive monomer concentration. These may be due to the increase of unreacted monomer as the concentration of reactive monomer was increased in the PS-BP LC samples. Furthermore, phase transitions between the BP and chiral nematic phases were not observed, even though the temperature was lowered by 253 K. Therefore, we observed wide BP temperature ranges of more than 58 K in all four kinds of PS-BP LC samples compared with 0 wt% sample of low molecular weight BP without reactive monomer.

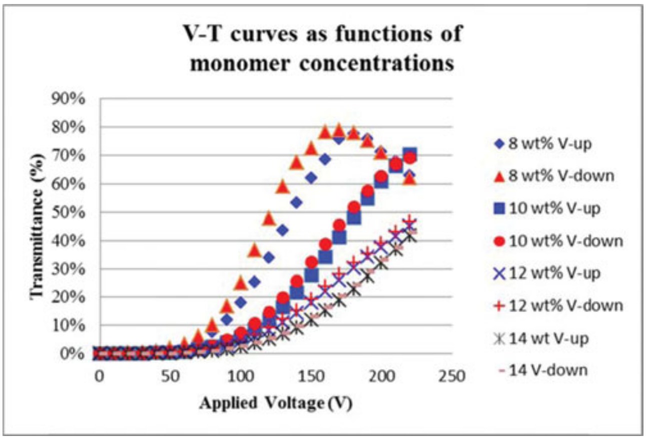

Figure 2. Transmittance results with respect to applied voltage for four kinds of PS-BP LC cells.

3.2. Electro-Optical Properties of Four Kinds PS-BP LC Cells with Different Reactive Monomer Concentrations

Figure 2 shows the experimental results of light transmittance (T) against applied voltage (V) for PS-BP LC cells with four reactive monomer concentrations of 8 wt%, 10 wt%, 12 wt%, and 14 wt% upon voltage-up and voltage-down. Unfortunately, it was not possible to define the quantitative driving voltage of each PS-BP cell because maximum transmittances were not observed in 10 wt%, 12 wt%, and 14 wt% PS-BP cells except 8 wt% sample under 220 V possible to be exerted by our experimental equipment. From Fig. 2, we found that the V-T curves of PS-BP cells were right-shifted with increase in the reactive monomer concentration in PS-BP cells. In other words, the driving voltages of PS-BP LC cells were increased with increase in the polymer ratio generated from reactive monomers dissolved in host nematic LCs by UV curing during polymer stabilization. In general, PS-BP LC is known as the polymer/LC composite, in which the disclination line of BP LC was surrounded by polymer chain [11]. Therefore, the PS-BP LC comprising polymer/LC can be treated as a binary dielectric composite which the external applied AC electric voltage is distributed to BP LC and polymer, and it can be understood by comparing the series-connected dielectric model of composite of BP LC and polymer upon application of an AC electric field [20,21]. Using this model, the external applied electric field E_{EXT} could be approximated by Equation (1), where ϕ is the volume ratio of LC in the composite of polymer and LC:

$$E_{\mathrm{EXT}} = \varphi E_{\mathrm{LC}}\,(\varphi) + (1 - \varphi) E_p(\varphi), \tag{1}$$

where $E_{\mathrm{LC}}(\varphi)$ and $E_P(\varphi)$ are the electric fields distributed to the LC and polymer regions, respectively. As a result, if the E_{EXT} is constant, it can be said that the E_{LC} in PS-BP is decreased with increase of polymer ratio $(1 - \varphi)$. In other words, decrease of LC ratio (φ) in PS-BP on the basis of Equation (1) and then the higher voltage should be applied to PS-BP cell to have the same transmittance for the higher polymer ratio of PS-BP cell. Moreover, it was considered that the increase of polymer ratio in the PS-BP cell resulted in the increase of the anchoring energy of LC molecules due to the increase of polymer interface, which was connected to an increase in the driving voltage of PS-BP [22,23].

Table 3. Switching hysteresis and the Kerr coefficients of four kinds of PS-BP LC cells

Sample	Switching hysteresis (V) at $T-40$	Kerr coefficient (m/V^2)
8 wt%	13.1	5.89234E-11
10 wt%	6.3	4.51809E-11
12 wt%	4.5	2.97053E-11
14 wt%	1.9	2.90286E-11

Table 3 shows the results of switching hysteresis at 40% transmittance (T–40) and the Kerr coefficient for four kinds of PS-BP LC cells estimated from Fig. 2. The values of switching hysteresis of four kinds of PS-BP LC cells were decreased with increase in reactive monomer concentrations in PS-BP LC cells as shown in Table 3. These results imply that a rigid polymer network with high elasticity was generated in PS-BP LC cells as the concentration of reactive monomer dissolved in the host nematic LC increased. As a result, it is considered that this polymer network may play a role in reducing switching hysteresis in PS-BP cells in the presence of an electric field.

The Kerr coefficients for four kinds of PS-BP LC mixtures were inversely proportional to the reactive monomer concentrations in PS-BP LC cells as shown in Table 3. These results are considered with the increase of anchoring energy according to the increase of polymer interface generated from reactive monomer [23].

Table 4 shows the activation energies for the rising and decay times for four kinds of PS-BP LC cells depending on monomer concentration. While the activation energy of rising time largely increased when the monomer concentration was increased, the activation energy of decay time was slightly decreased with increase in the monomer concentration of four kinds of PS-BP LC mixtures. These results imply that the increase of activation energy of rising time and the decrease of activation energy of decay time are due to the increase of anchoring energy between polymer and BP-LC according to increase of polymer interface generated from reactive monomer.

Table 4. Activation energies for rising and decay times as functions of reactive monomer concentrations for four kinds of PS-BP LC cells

Sample	Activation energy (J/mol)	
Polymer 8 wt%	Rising	24.59
	Decay	17.94
Polymer 10 wt%	Rising	19.66
	Decay	12.49
Polymer 12 wt%	Rising	24.62
	Decay	10.81
Polymer 14 wt%	Rising	50.49
	Decay	8.85

4. Conclusions

We found that the driving voltage was increased with increase in reactive monomer concentration, whereas the switching hysteresis and the Kerr coefficient were decreased with increase in reactive monomer concentration in PS-BP with identical chiral dopant concentrations.

Moreover, we found that the activation energy of rising time was increased with increase in reactive monomer concentration, whereas that of decay time was decreased with increase in reactive monomer concentration in PS-BP.

Acknowledgments

We give thanks to JNC Co. Ltd. for providing the nematic mixture JC1041XX.

Funding

This work was supported by Dongguk University-Seoul Research Fund 2014.

References

[1] De Gennes, P. G., & Prost, J. (1995). *The Physics of Liquid Crystals*, Clarendon Press: Oxford, UK.
[2] Crooker, P. P. (2001). *Chirality in Liquid Crystals*, Springer: New York, NY.
[3] Higashiguchi, K., Yasui, K., & Kikuchi, H. (2008). *J. Am. Chem. Soc.*, *130*, 6326–6327.
[4] Kerr, J. (1875). *Philos. Mag.*, *50*, 337–348.
[5] Dmitrienko, V. E. (1989). *Liq. Cryst.*, *5*, 847–851.
[6] Gerber, P. R. (1985). *Mol. Cryst. Liq. Cryst.*, *116*, 197–206.
[7] Coles, H. G., & Gleeson, H. F. (1989). *Mol. Cryst. Liq. Cryst.*, *167*, 213–225.
[8] Heppke, G., Jerome, B., Kitzerow, H. S., & Pieranski, P. (1989). *J. Phys. (Paris)*, *50*, 2991–2998.
[9] Wenyi, C., Antonio, M., & Peter, P. M. (2002). *Nature Mater.*, *1*, 111–113.
[10] Shibayama, S., Higuchi, H., Okumura, Y., & Kikuchi, H. (2013). *Advanced Functional Mater.*, *23*, 2387–2396.
[11] Kikuchi, H., Yokota, M., Hisakado, Y., Yang, H., & Kajiyama, T. (2002). *Nature Mater.*, *1*, 64–68.
[12] Rao, L., Ge, Z., Wu, S. T., & Lee, S. H. (2009). *Appl. Phys. Lett.*, *95*, 231101.
[13] Cheng, H. C., Yan, J., Ishinabe, T., & Wu, S. T. (2011). *Appl. Phys. Lett.*, *98*, 261102.
[14] Rao, L. Yan, J., Wu, S. T., Yamamoto, S., & Haseba, Y. (2011). *Appl. Phys. Lett.*, *98*, 081109.
[15] Chen, Y., Xu, D., Wu, S. T., Yamamoto, S., & Haseba, Y. (2013). *Appl. Phys. Lett.*, *102*, 141116.
[16] Mizunuma, T. *et al.* (2011). *Optical Materials Express*, *1*, 1561–1568.
[17] Oo, T. N. *et al.* (2011). *Optical Materials Express*, *1*, 1501–1510.
[18] Yan, J. *et al.* (2010). *Appl. Phys. Lett.*, *96*, 071105.
[19] Yan, J., Jiao, M., Rao, L., & Wu, S. T. (2010). *Optics Express*, *18*, 11450–11455.
[20] Miyamoto, A., Kikuchi, H., Kobayashi, S., Morimura, Y., & Kajiyama, T. (1991). *Macromolecules*, *24*, 3915–3920.
[21] Lim, G., Kikuchi, H., & Hong, S.-K. (2014). *Polymer J.*, *46*, 337–341.
[22] Fukuda, J.-I., & Žumer, S. (2013). *Phys. Rev. E*, *87*, 042506.
[23] Zhu, J.-L. *et al.* (2014). *Liquid Cryst.*, *41*, 891–896.