Enlargement of blue-phase stability for rod-like low-molecular-weight chiral nematic liquid crystal mixtures

Beomjong Kim\textsuperscript{a}, Yeon Jung Um\textsuperscript{a}, Seongun Jeon\textsuperscript{a}, Hirotugu Kikuchi\textsuperscript{b} and Sung-Kyu Hong\textsuperscript{a}\textsuperscript{*}

\textsuperscript{a}Department of Chemical & Biochemical Engineering, Dongguk University-Seoul, Seoul, 100-715 Korea; \textsuperscript{b}Institute for Materials Chemistry and Engineering, Kyushu University, Fukuoka 816-8580, Japan

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In this study, we investigated the enlargement of liquid crystal (LC) blue-phase (BP) temperature range using the rod-like low-molecular-weight cyano phenyl-type chiral nematic LC with various core group and chiral dopant concentrations. Also, the electro-optic response time was investigated for them. We found that the BP temperature range was strongly dependent upon the core structure and the chiral dopant concentration for the chiral nematic LC mixtures having the same terminal group. Also, we found a stable BP with a wide temperature range (more than 6 K), including a BP-isotropic coexistence state over 13.5 K upon heating and cooling processes and very fast response time (less than 1 ms), by using the cyano phenyl-type chiral nematic LC mixture with a high molecular aspect ratio and a high chiral dopant concentration.

Keywords: liquid crystal; blue phase; temperature range; rod-like chiral nematic liquid crystal; core group; concentration of chiral dopant

1. Introduction

Blue phases (BPs) are liquid crystal (LC) phases that appear in the temperature range between the chiral nematic phase and isotropic liquid phase for a chiral nematic LC under high chirality conditions. BPs basically consist of a double-twist cylinder and show three kinds of phase, blue phase I (BP I), blue phase II (BP II) and blue phase III (BP III), as functions of temperature and chirality. BP I and BP II possess a three-dimensional cubic structure with lattice periods of several hundred nanometres in length \cite{1} and therefore exhibit selective Bragg reflections in visible and ultraviolet (UV) light. Furthermore, BPs present very fast electro-optic response times of less than 1 ms due to the Kerr effect upon an applied electric field. \cite{5} Therefore, BPs are applicable to high-performance optical devices, \cite{6-14} and it is possible to fabricate a low-cost high-performance LC display without optical compensating film and surface alignment of LC, since BPs are optically isotropic in the absence of an external electric field.

However, due to their narrow temperature range typically less than a few degrees, the practical application of BPs had always been difficult. Recently, the polymer-stabilised blue phase (PS-BP) with a wide temperature range (greater than 60 K), including room temperature, was reported as a high-performance optical switch doped with highly twisting chiral dopant \cite{16} and a T-shaped chiral LC, \cite{17} respectively. More recently, Kutnjak et al. reported a wide temperature range of about 20 K through BP III stabilisation, using a hydrophobic surface-treated CdSe nanoparticle. \cite{18}

However, there are few reports related to a BP with a wide temperature range (more than 10 K) and a fast response time (less than 1 ms) using the rod-like low-molecular-weight chiral nematic LC mixtures without stabilisation by polymer and nano particles.

In this study, we investigated the enlargement of BP temperature range using the rod-like low-molecular-weight cyano homologue chiral nematic LCs with various core groups and chiral dopant concentrations. Also, the electro-optic response time was investigated for the cyano homologue chiral nematic LC mixture.

2. Experimental procedures

2.1 Preparation of chiral nematic LC mixtures

Two kinds of cyano LC-1s having different core group with same terminal group such as a cyano and a pentyl, and a JC1041XX (LC-2; JNC Co. Ltd., Tokyo, Japan) were used as host nematic LCs, and ISO-(6OBA)\textsubscript{2} was used as a chiral dopant as shown in Figure 1. Two kinds of cyano homologue LC-1s were 4-cyano-4’-pentylbiphenyl (5CB; Sigma-Aldrich Corp., St. Louis, MO, USA) and 4-cyano-4’-pentyl-p-terphenyl (5CT;
Alfa Aesar, Ward Hill, MA, USA). In particular, 5CT was mixed with 5CB as the half weight ratio to lower the phase transition temperature between BP and isotropic phase, because 5CT had very high $T_c$ more than 500 K. Here, the $T_c$ means the clearing temperature to become isotropic phase. In general, a chiral nematic LC can be prepared by mixing a nematic LC with a chiral dopant. Thus, in this study, nine kinds of chiral LC mixtures such as samples 1 – 9 with different chiral dopant concentration of 7.5 – 13 wt% were prepared as shown in Table 1. In particular, for the samples 2 – 5, the weight ratio of host nematic LCs for 5CT:5 CB:JC1041XX was 25:25:50, while for the samples 6 – 9, the weight ratio of the host nematic LCs for 5CT:5CB:JC1041XX was 35:35:30.

### 2.2 Evaluation of BP temperature range for each chiral nematic LC mixture

Each chiral nematic LC mixture was filled into the vacant space of a 10-μm gap glass-sandwiched cell without surface treatment. The BP temperature range was evaluated based on temperature dependence of the optical texture changes observed by polarising optical microscope (POM; Nikon, Tokyo, Japan) under crossed Nicols, and their lattice constants of several hundred nanometers were derived from the Bragg reflections of circularly polarised light, as determined by UV–Vis reflection spectrometry. The temperature of each cell was precisely controlled with a hot stage which was calibrated to an accuracy of ±0.1 K (Linkam LK-600PM). The cooling and heating ratio of the cell was set to 0.2 K/min. The UV–Vis reflection spectra of the cells were measured using a multi-channel photo detector (Hamamatsu photonics C4564-010G). A xenon lamp was used as the light source for the reflection spectra measurements.
2.3 Evaluation of electro-optic response time for sample 9 chiral LC mixture

The sample 9 [13 wt% chiral dopant ISO-(6OBA)$_2$ in 5CT/5CB/JC1041XX (35/35/30)] chiral nematic LC mixture was injected into the vacant space of the in-plane switching cell, where a bare top glass and 4 μm indium tin oxide electrode-patterned bottom glass were assembled with a 5-μm spacer. The electro-optic response time of the cell was evaluated by measurement of the time required for transmittance to be changed from 10% to 90% upon the application of voltage (rising time) or from 90% to 10% upon voltage off (falling time) at five different temperatures from 358.0 K to 369.7 K. During the measurement of the electro-optic response time, a square wave AC electric voltage of 1.0 kHz was applied 20 times for 1 s each. A He–Ne laser ($\lambda = 633$ nm) was incident on the sample cell perpendicular to the cell surface. The transmitted light through the cell was detected by a photo diode (New Focus 1621M) and was recorded with a digital storage oscilloscope (LeCroy WP950).

3. Results and discussion

3.1 BP temperature range for each chiral LC mixture

Figure 2 shows the molecular aspect ratio of length/diameter (L/D) values for the two host nematic LCs, 5CB and 5CT. The L/D values of the two host nematic LCs were approximately evaluated to be 2.03 for 5CB and 2.60 for 5CT on the basis of the space filling model enclosing the molecule in an ellipsoid [19] as shown in Figure 2. Here, the molecular models for 5CB and 5CT were depicted using ChemDraw 3D (cambridgesoft).

Figure 3 shows the optical textures observed by POM for two kinds of the chiral nematic LC mixtures with 7.5 wt% chiral dopant: the sample 1 [7.5 wt% chiral dopant ISO-(6OBA)$_2$ in 5CB/JC1041XX(50/50)] chiral nematic LC mixture and the sample 2 [7.5 wt% chiral dopant ISO-(6OBA)$_2$ in 5CB/5CT/ JC1041XX(25/25/50)] chiral nematic LC mixture upon cooling process at 0.2 K/min under crossed Nicols. In the case of the sample 1, BP II showing...
dark blue (100) plane reflection was observed during 0.6 K range from 318.9 K to 318.3 K, as shown in Figure 3(1-a). After further cooling, a platelet texture of BP I was observed during 1.4 K range from 318.3 K to 316.9 K, as shown in Figure 3(1-b), and a focal conic texture of chiral nematic phase (N*) began to appear from 316.9 K as shown in Figure 3(1-c). BPs were observed in a temperature range of 2.0 K between 318.9 K and 316.9 K upon cooling process for the sample 1. On the other hand, in the case of sample 2, a platelet texture BP I surrounded with black cracks was observed during 4.5 K range from 372.2 K to 367.7 K as shown in Figure 3(2-a). Here, the black cracks in the BP I texture domains were confirmed as isotropic phases (Iso) because the brightness of the black cracks was not almost changed even though the sample cell was tilted with respect to the vertical direction from POM stage. After further cooling, a complete platelet-shaped BP I texture without an isotropic phase was observed during 1.2 K from 367.7 K to 366.5 K, as shown in Figure 3(2-b). BP including coexistence state with an isotropic phase was observed in a temperature range of 5.7 K between 372.2 K and 366.5 K upon cooling process. In particular, the sample 2 presented a stable BP-isotropic coexistence state over a wide temperature range compared to the sample 1 even though the complete BP I range without BP-isotropic coexistence state was slightly decreased compared to sample 1. In other words, BP could be stabilised through the BP-isotropic coexistence state for the sample 2. Therefore, it is shown that the 5CT/5CB/JC1041XX/ISO-(6OBA)2 chiral LC mixture including the 5CT with high L/D presents a wider BP temperature range including the stable BP-isotropic coexistence state than the 5CB/JC1041XX/ISO-(6OBA)2 chiral LC mixture including only 5CB with low L/D.

Also it is suggested that the BP temperature range is more strongly dependent upon the core group molecular structure than the terminal group molecular structure of host nematic LC in cyano homologue chiral LC mixtures, since it was previously reported that the BP temperature ranges were changed from 1.2 K to 2.9 K upon cooling process for chiral LC mixtures of cyanobiphenyl homologue nematic LCs with different terminal alkyl or alkoxy chain length.[20-23]

Figure 4 shows the phase diagrams by POM observation for the samples 2 – 9 as functions of chiral dopant concentration for mixtures of 5CT/5CB/JC1041XX/ISO-(6OBA)2 upon cooling and heating process at 0.2 K/min. BP I and BP I-isotropic phase coexistence state were observed for the samples 2 – 9 on POM observation. Also, the phase transition temperatures were lowered with increasing chiral dopant concentration for the samples 2 – 9 as shown in Figure 4. The observed phase diagrams were classified into five regions: isotropic phase (iso), BP I + Iso, BP I, chiral nematic phase and N* + BP I, as can be seen in Figure 4. Interestingly, the temperature ranges of BP I-Iso coexistence states were almost independent of the chiral dopant concentration but strongly depended on the constituent of host nematic LCs, 5CT/5CB/JC1041XX, in the chiral LC mixture. For example, for the samples 2 – 5 (5CT/5CB/ JC1041XX = 25/25/50), the temperature ranges of BP I-Iso coexistence states ranged approximately 4.5 – 4.6 K upon heating, and 4.6 – 4.9 K upon cooling as shown in Figure 4(1-a) and (1-b). On the other hand, for the samples 6 – 9 (5CT/5CB/ JC1041XX = 35/35/30), those of a temperature range of the coexistence state were approximately 9.5 – 10.2 K upon heating and 9.7 – 10.7 K upon cooling, as shown in Figure 4(2-a) and (2-b). These results indicate that the temperature ranges of BP I-Iso coexistence states increased with an increase of 5CT ratio among the host nematic LCs. From this result, it is suggested that the rotational mobility around short axis of host nematic LC molecules is constricted with increase of the ratio of 5CT with higher L/D compared to the ratio of 5CB and JC1041XX in chiral LC mixture; as a result, the competition state between the maintaining BP and the transition to isotropic phase is maintained for a long temperature range.

Also, the temperature range of BP I without an isotropic phase (complete BP I) was dependent upon the chiral dopant concentration. For example, for the samples 2 – 5, the temperature ranges of BP I were 0.9 K upon heating and 1.2 K upon cooling for 7.5 wt% of chiral dopant, 1.4 K upon heating and 1.6 K upon cooling for 8 wt% of chiral dopant, 1.4 K upon heating and 1.8 K upon cooling for 8.5 wt% of chiral dopant and 1.8 K upon heating and 2.6 K upon cooling for 9 wt% of chiral dopant as shown in Figure 4(1-a) and (1-b). On the other hand, for the samples 6 – 9, the temperature ranges of BP I were 0.9 K upon heating and 1.2 K upon cooling for 10 wt% of chiral dopant, 2.0 K upon heating and 2.8 K upon cooling for 11 wt% of chiral dopant, 2.4 K upon heating and 3.6 K upon cooling for 12 wt% of chiral dopant and 3.0 K upon heating and 4.5 K upon cooling for 13 wt% of chiral dopant as shown in Figure 4(2-a) and (2-b). The complete BP I temperature ranges were strongly dependent upon the chiral dopant concentrations in all cases of 5CT/5CB/JC1041XX/ISO-(6OBA)2 chiral LC mixtures.

Figure 5 shows the observed POM photographs for the sample 9 [13 wt% chiral dopant ISO-(6OBA)2] in 5CT/5CB/JC1041XX upon cooling and heating
processes. During the cooling process, BP-isotropic phase coexistence states were observed during 10.7 K from 372.6 K to 361.9 K, as shown in Figure 5(1-a)–(1-c). Through further cooling, a complete platelet texture of BP I without an isotropic phase was observed during 4.5 K from 361.9 K to 357.4 K, as shown in Figure 5(1-d), and then a phase transition from BP to chiral nematic phase was observed from 357.4 K to 356.1 K, as shown in Figure 5(1-e). For the cooling process of sample 9, BP was observed in a temperature range of 16.5 K between 372.6 K and 356.1 K. On the other hand, during the heating process of the sample 9, a phase transition from chiral nematic phase to BP was observed during 1.0 K from 358.6 K to 359.6 K, as shown in Figure 5(2-a). Through further heating, complete BP I without an isotropic phase was observed during 3.0 K from 359.6 K to 362.6 K, as
shown in Figure 5(2-b), and then BP-isotropic phase coexistence states were observed during 10.1 K from 362.6 K to 372.7 K, as shown in Figure 5(2-c)–(2-e). For the heating process, BP including BP-isotropic phase coexistence state was observed during 14.1 K between 358.6 K and 372.7 K.

Figure 6 shows the UV–Vis reflection spectra for the sample 9 upon heating process. Here the UV–Vis reflection spectra were measured after holding the sample for 15 min at each temperature to prevent effect of thermal hysteresis. A strong reflection peak appeared during 13.5 K between 357.6 K and 371.1 K at 372 – 448 nm which could be assigned as Bragg diffraction from (100) plane of the cubic lattice in BP I. These results indicate the sample 9 presented BP I over 13.5 K even though including the BP-isotropic coexistence state. In particular, stable BP I which have high reflective peak intensities maintained during 6 K over 360.5 – 366.5 K. In addition, the reflection peak is shifted towards the longer wavelength.

Figure 6. (colour online) Observed UV–Vis reflection spectra of sample 9 upon heating.
from 372 nm to 448 nm with increasing temperature. This could be due to the increase of chiral pitch according to the increase of temperature. However, we could not observe the reflection peak from BP II on the basis of the lattice constant in UV-Vis reflection spectra of Figure 6. The weak intensity peaks of less than 360 nm might be due to the interference of two glasses of cell. Every reflection spectra change depending on temperature alteration was reversible upon cooling and heating. In conclusion the sample 9 [13 wt% of chiral dopant ISO-(6OBA)$_2$] in 5CT/5CB/JC1041XX mixture presents a wide stable BP I more than 6 K with including BP-isotropic coexistence state over 13.5 K from the results of Figures 5 and 6.

3.2 Electro-optic response time for sample 9 chiral nematic LC mixtures

Figure 7 shows the measurement results of electro-optic response time for the sample 9 at various temperatures. It was clear that the sample 9 had very fast response times of less than 1 ms at five different temperatures from 358 K to 369.7 K. In particular, the total response times at the region of BP I + Iso were slower than those at the region of single BP I but showed fast response times of less than 1 ms at three temperatures over 364.2 K – 369.7 K. This result indicates that the BP + Iso coexistence state of the sample 9 had the fast electro-optic response time similar with conventional BP.

Conclusions

Firstly, we found that stable BP was presented during wide temperature range (more than 6 K) with including BP-isotropic coexistence state over 13.5 K upon heating and cooling, as well as a very fast response time of less than 1 ms by using the rod-like low-molecular-weight cyano chiral nematic LC mixture with the high molecular aspect ratio and the high chiral dopant concentration. Also, we found that the BP temperature ranges were strongly dependent upon the core structure and the chiral dopant concentration for cyano phenyl type chiral nematic LC mixtures having same terminal group.

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Supplemental data

Supplemental data for this article can be accessed here.

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