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Electro-Optical Properties in Polymer-Stabilized Blue Phase of *n*-OCB Homologue Chiral Nematic Liquid Crystal Mixtures

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*In this study, the chemical structures and physical property dependencies of the electro-optical properties were investigated in polymer-stabilized blue phase (BP) using the four kinds of 4-*n*-alkyloxy-4'-cyanobiphenyl (*n*-OCB) homologue chiral nematic LCs. It was confirmed that the optical response time and Kerr coefficient in polymer-stabilized BP was varied with the molecular parity as determined by the alkyl chain length of the *n*-OCB homologue chiral nematic LC mixtures.*

Keywords K_{33}/K_{11} ; Kerr coefficient; *n*-OCB homologue; optical response time; polymer-stabilized BP

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 in chiral nematic LC. BPs possess a three-dimensional cubic structure with lattice periods of several hundreds nanometer in length [1–3]; therefore, they exhibit the selective Bragg reflections in the visible and ultraviolet (UV) light range. The BP is optically isotropic due to a three-dimensional symmetric structure of molecules in a state without an electric field, and then enters to anisotropic phase due to the one directional alignment of molecules upon application of an electric field, which has several hundreds of microseconds of response time due to the Kerr effect [4].

For practical applications, although blue phases hold potential as fast light modulators, their narrow temperature range of less than a few degrees Kelvin has always been a problem. Recently, the polymer-stabilized blue phase (PS-BP) with a wide temperature range greater than 60 K including room temperature reported as a high performance optical switch with high speed electro-optical response time of the order of 10^{-4} s [5–7]. However, so far, there are few reports about the relationship between the electro-optical properties and the chemical structures or the physical properties in the blue phase [8, 9].

In this study, the chemical structures and physical properties dependencies of the electro-optical properties were investigated in polymer-stabilized BP using the four kinds of *n*-OCB homologue chiral nematic LCs.

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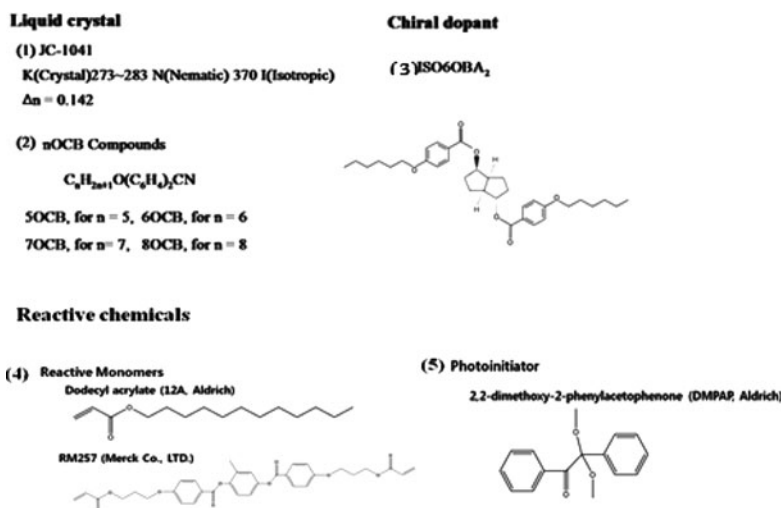


Figure 1. Chemical structures and physical properties of LCs, chiral dopant, reactive monomer, and photoinitiator.

2. Experiment

2.1 Preparation of Sample

JC1041 (Chisso Corp., Tokyo, Japan) and 4-*n*-alkyloxy-4'-cyanobiphenyl (*n*-OCB) homologues (Sigma-Aldrich Corp., St. Louis, MO, USA) were used as nematic LC materials, and ISO6OBA₂ was used as a chiral dopant as shown in Fig. 1. Four kinds of *n*-OCB homologue LCs served as compounds with $n = 5, 6, 7, 8$.

For the polymer stabilization of the blue phase, RM257 (Merck & Co. Inc., Whitehouse Station, NJ, USA) and dodecyl acrylate (DA, Sigma-Aldrich Corp.) were used as a reactive monomer and 2,2-dimethoxy-2-phenyl-acetophenone (DMPAP, Sigma-Aldrich Corp.) was used as the photoinitiator as shown in Fig. 1.

2.2 BP Polymer Stabilization and Evaluation of BP Temperature Range for the Four Kinds of *n*-OCB Homologue LC Mixtures

The four kinds of *n*-OCB chiral nematic LC mixtures were filled to the vacant space of a 10 μm gap sandwich cell without surface treatment. For the low molecular BP (LM-BP) without polymer, the four kinds of 7.5 wt% chiral nematic LC mixtures were composed of (*n*-OCB:JC1041:ISO6OBA₂ = 46.25:46.25:7.5) in weight ratio. Where 7.5 wt% means the chiral dopant weight percent in the LC mixtures.

For the polymer stabilization BP (PS-BP), the four kinds of chiral nematic LC mixtures, two kinds of reactive monomer, and a photoinitiator were mixed such as (*n*-OCB:JC1041:ISO6OBA₂:RM257:DA:DMPAP = 42.6:42.6:7.5:3.5:3.5:0.3) in the weight ratio, were done by UV light irradiation when the four kinds of LC mixtures maintained a blue phase. UV light was irradiated for 15 min. and the light intensity was 600 mW/cm².

The BPs temperature range was characterized by polarizing optical microscope (POM) observation texture. The optical textures of the eight cells such as LM-BP and PS-BP were

observed by a POM equipped with a hot stage calibrated to an accuracy of ± 0.1 K (Linkam LK-600PM) under crossed Nicols. The cooling and heating ratio of the cell was set to 1 K/min.

2.3 Measurement of Elastic Constants (K_{11} , K_{33}) of *n*-OCB Homologue Nematic LC Mixtures

The splay elastic constant (K_{11}), and the bend elastic constant (K_{33}), were evaluated by measuring the curve between the capacitance versus the voltage of the *n*-OCB nematic LC mixture without chiral dopant in a 10 μm gap sandwich cell with an antiparallel rubbed surface using EC-1 (Toyo Technica Co. Ltd). The measurement temperature was $T_c - 10$ K for the four kinds of *n*-OCB nematic LC mixtures.

2.4 Measurement of Electro-Optical Properties of *n*-OCB Homologue Chiral Nematic LC Mixture

The sandwich type electrode cell was prepared to measure the electro-optical properties of BP LC mixtures. The top glass did not have any surface treatment and the bottom glass was patterned with an in-plane ITO electrode, which was 10 μm wide on the same plane. The two glasses were attached by a light curing adhesive and kept at a 10 μm gap with a PET film as a spacer. The four kinds of *n*-OCB homologue chiral nematic LC mixtures were injected into the electrode cell during the isotropic phase to prevent flow alignment. The BP polymer stabilization was done by UV light irradiation of *n*-OCB homologue chiral nematic LC mixtures when the LC was maintaining a blue phase.

The electro-optical response time was evaluated by measurement of the time whose transmittance is changed from 10% to 90% upon voltage on (rising time), or from 90% to 10% upon voltage off (decay time) at $T_c - 10$ K in the cell. The sample cell was placed between two polarizers and the mutual polarizing directions were adjusted to provide the maximum contrast between on and off electric voltages. The frequency was 1.0 kHz. During the measurement of the electro-optic response, the squared AC electric voltage was applied for 1 s until saturation and averaged over 30 times. A He-Ne laser ($\lambda = 633$ nm) was perpendicular to the sample cell. The transmitted light was detected by a photo diode (New Focus 1621 M) and recorded with a digital storage oscilloscope (LeCroy WP950).

The Kerr coefficient was evaluated by the extended Kerr model [10, 11] through measurement of the relationship between the transmittance and the square of applied voltage at $T_c - 10$ K, where the T_c means clearing point temperature to be isotropic phase from BP.

3. Results and Discussion

3.1 BP Temperature Ranges of *n*-OCB Homologue LM-BP and PS-BP

Figure 2 shows the temperature ranges of BP, $\Delta T_{\text{BP}s}$ (BP-1 + BP-2), $\Delta T_{\text{BP}s}$ of the four *n*-OCB chiral nematic LC mixtures of LM-BP and PS-BP upon heating. $\Delta T_{\text{BP}s}$ for both LM-BP and PS-BP increased when *n* was even but decreased when *n* was odd. Namely, the BP temperature ranges of LM-BP and PS-BP were dependent upon the molecular parity in the *n*-OCB homologue chiral nematic LC mixtures.

In particular, the temperature range from BP to the isotropic phase on heating was extended to a few degrees above $T_{\text{BP} \rightarrow \text{Iso}}$ before polymer stabilization and also $T_{\text{Ch} \rightarrow \text{BP}}$ was

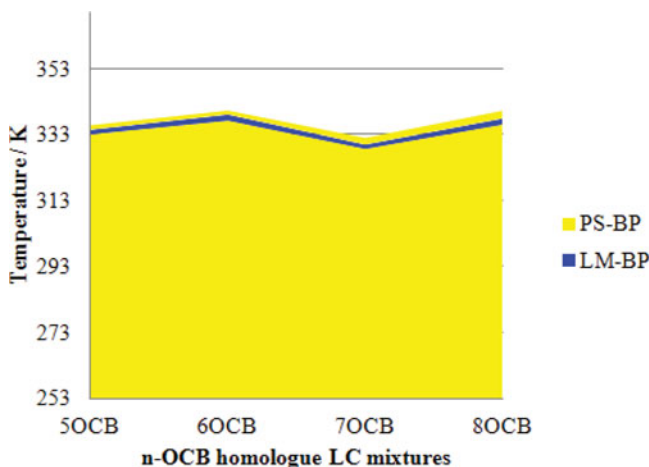


Figure 2. BP temperature ranges of the four *n*-OCB homologue LM-BP and PS-BP.

lowered to 253 K. Namely, these indicate that the ΔT_{BP} s of PS-BP in four kinds of *n*-OCB homologue were extended over 60 K. Also, the BP before polymer stabilization showed BP-1 and BP-2, but PS-BP only presented BP-1 after the polymer stabilization.

3.2 Elastic Constant and Kerr Coefficient of *n*-OCB Homologue LC Mixtures

Table 1 shows the measurement results of K_{11} and K_{33} of *n*-OCB homologue nematic LC mixtures as well as the molecular aspect ratio, which is the length over diameter (L/D) of the four *n*-OCB homologue nematic LCs evaluated by the space filling model enclosing molecule in the ellipsoid [12]. The K_{33}/K_{11} increased from 5OCB to 6OCB and from 7OCB to 8OCB, but decreased from 6OCB to 7OCB for four nematic LC mixtures as shown in Table 1. Furthermore, the L/D value exhibited a similar tendency in that it increased from 5OCB and 7OCB and decreased from 6OCB. Therefore, we can know that the elastic constant ratio of K_{33}/K_{11} is dependent upon the molecular aspect ratio, L/D of *n*-OCB homologue nematic LC mixtures from the results of Table 1. These results are supported by the fact that the ratio of K_{33}/K_{11} is related to the molecular aspect ratio, length over diameter (L/D) of the rod-like LC mixtures [13, 14]. Furthermore, it is known that in the

Table 1. K_{11} , K_{33} , K_{33}/K_{11} , and L/D values of the four kinds of *n*-OCB homologue nematic LC mixtures

LC mixture	Elastic constant (pN)			Aspect ratio L/D
	K_{11}	K_{33}	K_{33}/K_{11}	
5OCB/JC1041	3.469	5.034	1.451	2.453
6OCB/JC1041	3.304	5.915	1.790	2.941
7OCB/JC1041	3.214	4.555	1.417	2.568
8OCB/JC1041	3.280	5.799	1.768	2.608

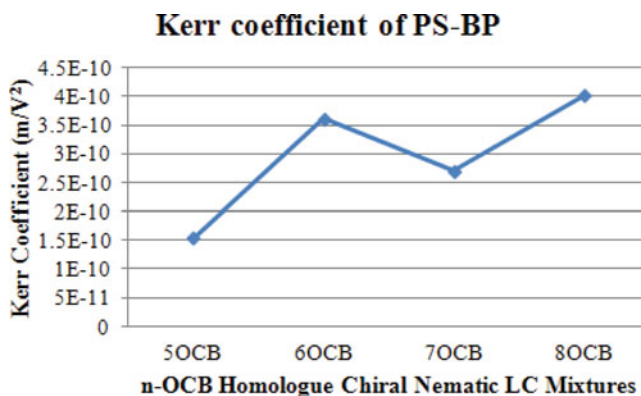


Figure 3. Measurement results of the Kerr coefficient of four kinds of *n*-OCB PS-BP LC mixtures.

case of *n*-OCB homologue LCs the end alkyl chains of even number align better along the direction of the rigid biphenyl core part than those of odd number [15].

Figure 3 shows the measurement results of the Kerr coefficient in regard to the four kinds of PS-BPs on the basis of the transmittance-voltage curve at $T_c - 10$ K. For even alkyl numbers such as 6OCB and 8OCB, PS-BP shows high Kerr coefficient, but for odd alkyl numbers such as 5OCB and 7OCB, it shows a low Kerr coefficient. It can also say that the Kerr coefficient is approximately dependent upon the molecular aspect ratio L/D and the K_{33}/K_{11} of the *n*-OCB PS-BP from Table 1 and Fig. 3. However, we need further study on the molecular structures and the physical properties of PS-BP after polymer stabilization because Kerr coefficient is not perfectly proportional to the L/D and K_{33}/K_{11} .

3.3 Electro-Optical Response Time of *n*-OCB Homologue PS-BP

Figure 4 shows the measurement results of rising time and decay time of four kinds of *n*-OCB homologue PS-BPs. The rising time increased when *n* was odd and decreased when *n* was even, while the decay time is not nearly dependent upon the number of alkyl chains in the four kinds of PS-BP *n*-OCB LCs as shown in Fig. 4. We can say that the rising time of

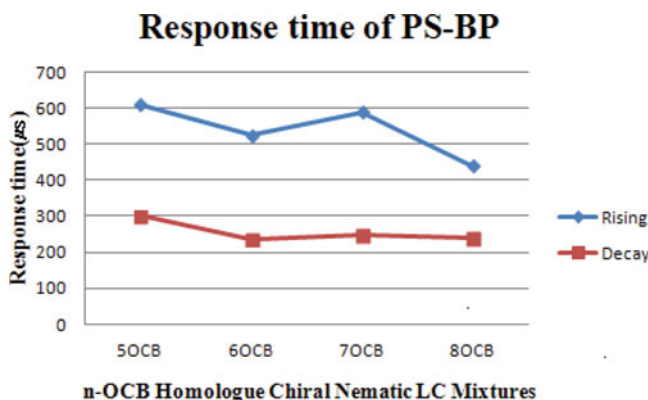


Figure 4. Measurement results of rising time and decay time of four kinds of *n*-OCB PS-BP LC mixtures.

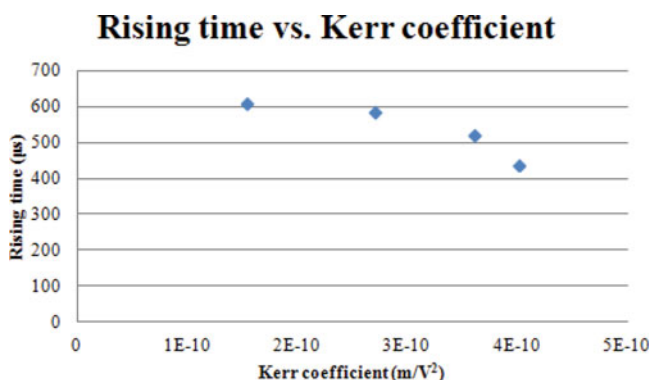


Figure 5. Relationship between the rising time and the Kerr coefficient in four kinds of *n*-OCB PS-BP LC mixtures.

PS-BPs was changed with molecular parity, whereas the decay time did not nearly change with the molecular parity in the PS-BP of *n*-OCB homologues LC mixtures.

Figure 5 shows the relationship between the rising time and the Kerr coefficient in the *n*-OCB homologue PS-BP LC mixtures. We know that the rising time is strongly dependent upon the Kerr coefficient in the PS-BPs. Therefore, this result imply that the rising time is more strongly dependent upon the Kerr coefficient related to electric field whereas the decay time is affected by multifactors such as viscosity, elastic constant, and electric field in *n*-OCB homologue PS-BP LC mixtures.

4. Conclusions

It was confirmed that the rising time and the Kerr coefficient of PS-BP were dependent upon the molecular parity as determined by the alkyl chain length of the *n*-OCB homologue chiral nematic LC mixtures. Also, it was confirmed that the rising time was more strongly dependent upon the Kerr coefficient compared to the decay time in the PS-BP of *n*-OCB homologue chiral LC mixtures.

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