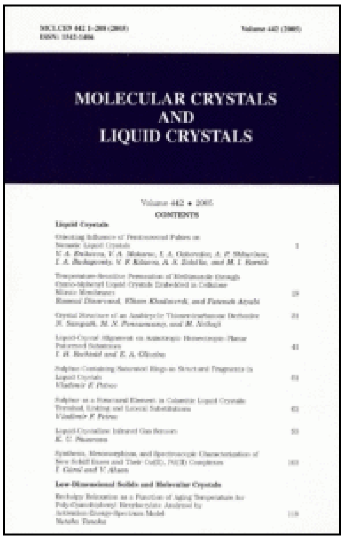

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Blue phase (BP) stability is dependent upon chemical structure as well as the physical properties of the chiral nematic liquid-crystal (LC) mixture. In this study, the dependence of blue phase temperature range on alkyl chain length was investigated in order to evaluate the relationship between blue phase stability and the molecular structures of four kinds of n-cyanobiphenyl (CB) homologue chiral nematic liquid-crystal mixtures composed of rod-like nematic LC. It was confirmed that blue phase temperature range was strongly dependent upon the length of the alkyl chain and the elastic constant in n-CB homologues chiral nematic LC mixtures.

Keywords Blue phase; chiral nematic liquid crystal; elastic constant; n-CB homologue; temperature range

Introduction

Blue phases (BPs) are liquid-crystal (LC) phases that appear in the temperature range between chiral nematic phase and isotropic liquid phase. BPs possess a three-dimensional cubic structure with lattice periods of several 100 nm in length [1–3] and therefore exhibit the selective Bragg reflections in the visible light range. BPs consist of a double-twist cylinder and three phases depending on the packing structure, such as blue phase 1 (BP-1), blue phase 2 (BP-2), and blue phase 3 (BP-3). BP-1 is a body-centered cubic structure, BP-2 a simple cubic structure, and BP-3 is an amorphous orientational structure. In general, BP-1, BP-2, and BP-3 are known to function depending on temperature and chirality.

BPs possess great potential as light modulators due to their allowance of the electrically controllable Bragg diffraction of visible light [4–7]. For practical applications, although blue phases hold potential as fast light modulators, their narrow

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temperature range, of less than a few degrees Kelvin, has always been a problem. Recently, Kikuchi *et al.* reported that the temperature range of blue phases could be successfully extended to more than 60 K through a polymer-stabilized blue phase [8]. More recently, Coles and Pivnenko reported that mixtures of three symmetric dimer homologues doped with a small percentage of a highly twisting chiral dopant showed the BP-1 of a very wide temperature range [9]. Furthermore, Yoshizawa *et al.* reported a novel T-shaped chiral oligomer with molecular biaxiality exhibiting a blue phase of wide temperature range [10]. However, the mechanism for the stabilization of BPs is not clear, and there have been few reports on low-molecular-weight chiral nematic LC mixtures composed of rod-shaped LCs [11].

In this study, the dependence of blue phase temperature range on alkyl chain length was investigated in order to evaluate the relationship between blue phase stability and molecular structure of four kinds of n-CB homologue chiral nematic liquid-crystal mixtures composed of rod-like nematic LC.

Experiment

Preparation of Sample

JC1041 (Chisso, Japan) and n-CB homologues (Aldrich) were used as nematic LC materials, and $ISO6OBA_2$ was used as chiral dopant as shown in Fig. 1. Four kinds of n-CB homologue LCs served as n-cyanobiphenyl compounds with $n = 5$, 6, 7, 8. The samples were prepared as (nematic LC1/nematic LC2/chiral dopant) mixtures in which nematic LC1 was the n-CB homologue LCs and nematic LC2 was JC1041.

Measurement of the Helical Twist Power of LC Mixtures

The helical twist power (HTP) corresponding to the molecular chirality was calculated by the equation $HTP = 1/(P \times C)$, where P is chiral pitch in the wedge cell with a $\tan\theta$ of 0.0083 as measured by a polarized optical microscope (POM; Nikon), and C is concentration of the chiral dopant of the chiral nematic LC mixture. The chiral dopant concentration of each chiral nematic LC mixtures was 0.4 wt% (n-CB:JC1041:$ISO6OBA_2 = 49.8:49.8:0.4$). The measurement temperature was $T_c - 10$ K for each chiral nematic LC mixture, where T_c was the phase transition

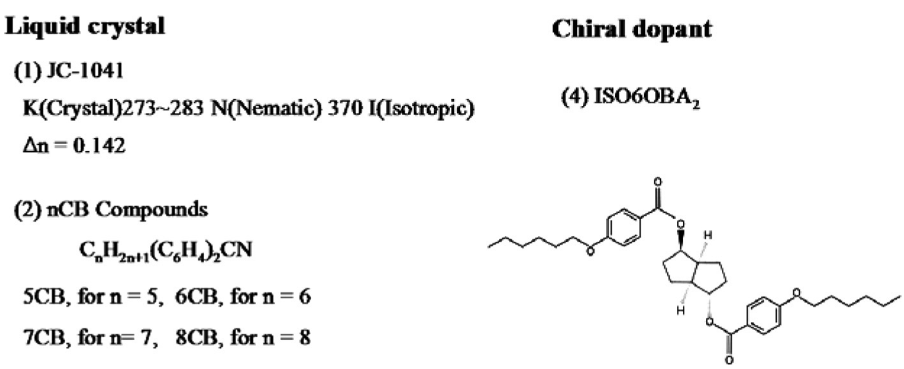


Figure 1. Chemical structures and physical properties of LCs and chiral dopant.

temperature from the chiral nematic phase to isotropic phase for each chiral nematic LC mixture.

Measurement of Elastic Constants (K_{11}, K_{22}, K_{33}) of LC Mixtures

The splay elastic constant (K_{11}), the twist elastic constant (K_{22}), and the bend elastic constant (K_{33}) were evaluated by measuring the curve between capacitance versus voltage of the nematic LC mixture without chiral dopant in a 10-μm sandwich cell with anti-parallel rubbed surface using EC-1 (Toyo Technica Co. Ltd., Japan). The measurement temperature was $T_c - 10\,\mathrm{K}$ for the four kinds of nematic LC mixtures. Furthermore, K_{22} was calculated by the measured K_{11} and K_{33} [12].

Evaluation of BP Temperature Ranges for the Four Kinds of n-CB Homologue Chiral Nematic LC Mixtures

The four kinds of chiral nematic LC mixtures were filled to vacant space of 10-μm gap sandwich cell without surface treatment. The four kinds of chiral nematic LC mixtures were composed of (n-CB:JC1041:ISO6OBA$_2$ = 46.25:46.25:7.5) wt% and were 7.5 wt%, which means that the chiral dopant concentration of the blue phase is reliably represented. The BPs are characterized by their lattice constants of several hundred nanometers derived from Bragg reflections of circularly polarized light, which were measured by ultraviolet (UV) reflection spectrometry and a POM observation texture.

The optical textures of the four 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 and heating ratio of the cell was set to 0.1 K/min.

The UV reflection spectra of the cells were measured by a multichannel photodetector (Hamamatsu photonics C4564-010G, Japan). A xenon lamp was used as the light source for the reflection spectra measurements.

Results and Discussion

The HTP and K_{11}, K_{22}, K_{33}, and K_{33}/K_{11} Values of the Four n-CB Homologue Chiral LC Mixtures

Table 1 shows the HTP as well as the K_{11}, K_{22}, K_{33}, and K_{33}/K_{11} values of the four n-CB homologue chiral LC mixtures at ($T_c - 10\,\mathrm{K}$). The magnitude of HTP decreased from 5CB to 6CB and from 7CB to 8CB but increased from 6CB to

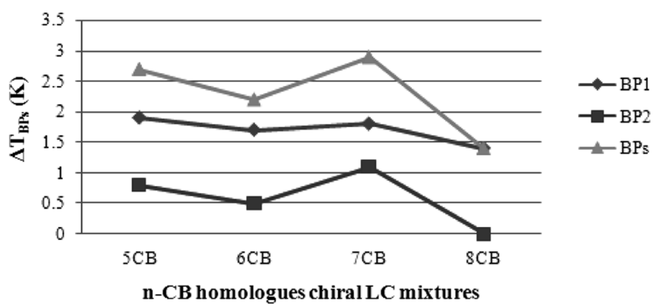
Table 1. Magnitude of HTP and the K_{11}, K_{22}, K_{33} values of four LC mixtures at ($T_c - 10\,\mathrm{K}$)

		Elastic constant (pN)			
LC mixture	HTP (μm^{-1})	K_{11}	K_{22}	K_{33}	K_{33}/K_{11}
5CB/JC1041	61.667	7.272	11.367	22.706	3.122
6CB/JC1041	43.508	6.171	6.305	11.187	1.813
7CB/JC1041	62.019	5.309	12.374	13.917	2.621
8CB/JC1041	60.265	5.740	7.857	12.552	2.217

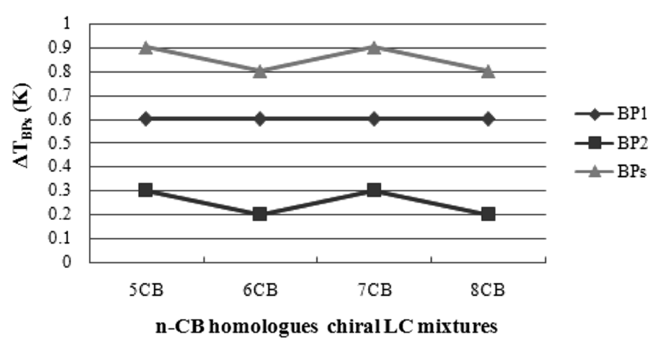
Table 2. Phase transition temperatures of the four n-CB homologue chiral nematic LC mixtures upon cooling and heating

	Phase transition temp. (K) on heating			Phase transition temp. (K) on cooling		
LC mixture	$T_{\text{Ch-BP1}}$	$T_{\text{BP1-BP2}}$	$T_{\text{BP2-Iso}}$	$T_{\text{Iso-BP2}}$	$T_{\text{BP2-BP1}}$	$T_{\text{BP1-Ch}}$
5CB/JC1041	318.05	318.65	318.95	318.95	318.15	316.25
6CB/JC1041	314.15	314.75	314.95	314.75	314.25	312.55
7CB/JC1041	319.35	319.95	320.25	320.25	319.15	317.35
8CB/JC1041	318.95	319.55	319.75	319.45		318.05

7CB for all four chiral nematic LC mixtures. In other words, when n is odd, the HTP is increased, whereas the HTP is decreased when n is even. Furthermore, the K_{22} value shares similar tendency as the K_{33}/K_{11} ratio, which decreased from 5CB and 7CB and increased from 6CB. These results indicate that the HTP is strongly dependent upon K_{22} and K_{33}/K_{11} for all four n-CB homologue chiral LC mixtures. In general, it is known 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]. Therefore, these results imply that the HTP and the K_{22} value corresponding to the molecular chirality of chiral nematic LC are proportional to the molecular aspect ratio, L/D, of the n-CB homologue chiral nematic mixtures.



(a)



(b)

Figure 2. BP temperature ranges of the four n-CB homologue chiral nematic LC mixtures upon (a) cooling and (b) heating at 0.1 K/min.

BP Temperature Ranges of the Four n-CB Homologue Chiral LC Mixtures

Table 2 shows the phase transition temperatures evaluated by the POM observation texture and UV reflection spectra of the four n-CB chiral LC mixtures upon cooling and heating at 0.1 K/min.

Figure 2 shows the temperature ranges of BPs (BP-1 + BP-2), ΔT_{BPs} of the four n-CB chiral LC mixtures upon (a) cooling and (b) heating. For cooling and heating, the ΔT_{BPs} of n-CB homologue chiral nematic LC mixtures fluctuated with changing alkyl length number, *n*, as shown in Figs. 2a and 2b. ΔT_{BPs} are decreased when *n* is even but are increased when *n* is odd. However, Fig. 2b shows that for heating, the ΔT_{BPs} was decreased by about two thirds compared to that for cooling. In particular, ΔT_{BP2} was more strongly dependent upon *n* when compared to ΔT_{BP1} for both heating and cooling. We need further study using different types of LCs to discuss the alkyl length dependence of ΔT_{BP1} and ΔT_{BP2}.

Relationship between the BP Temperature Ranges on Heating and the K_{22}, K_{33}/K_{11} Values of the n-CB Homologue Chiral LC Mixtures

Figure 3 shows the relationship between ΔT_{BPs} on heating and (a) K_{22} and (b) K_{33}/K_{11} of the n-CB homologue chiral nematic LC mixtures. We know that ΔT_{BPs} on heating strongly depends upon K_{22} as shown in Fig. 3a. This result is supported because the stability of BPs is increased with increasing K_{22} of LC molecules [14]. ΔT_{BPs} upon heating is also proportional to K_{33}/K_{11} as shown in Fig. 3b. Therefore,

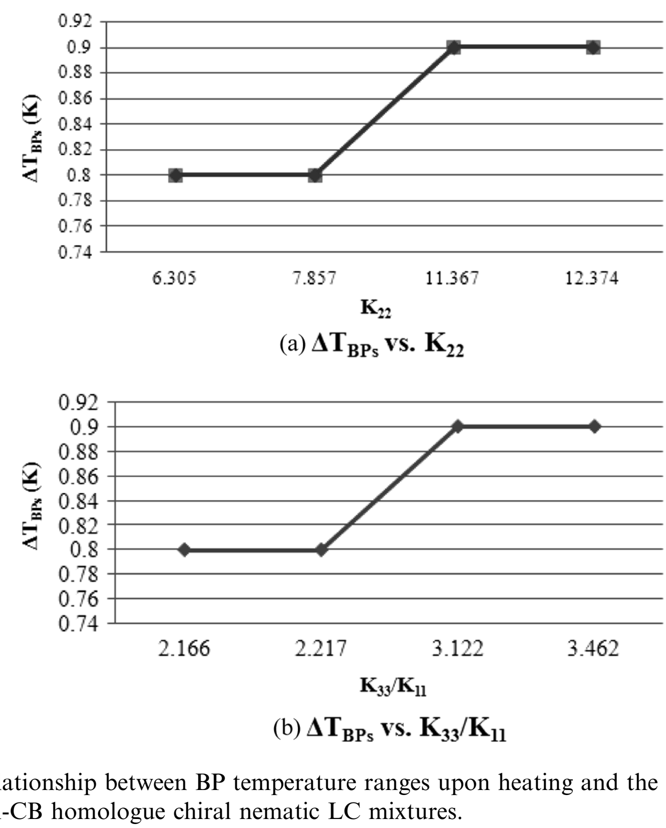


Figure 3. Relationship between BP temperature ranges upon heating and the (a) K_{22} and (b) K_{33}/K_{11} of n-CB homologue chiral nematic LC mixtures.

this result implies that the stability of BPs is dependent upon the molecular aspect ratio (L/D) related to K_{33}/K_{11} of the rod-like LC of the n-CB homologue chiral nematic LC mixtures.

Conclusions

It was confirmed that BP temperature ranges varied depending on whether the alkyl chains of n-CB homologue chiral nematic LC mixtures had an even or odd number of units. It was also confirmed that BP temperature ranges were strongly dependent upon the elastic constant, K_{22}, corresponding to molecular chirality as well as K_{33}/K_{11}, which corresponds to the molecular aspect ratio, L/D, of n-CB homologue chiral nematic LC mixtures.

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