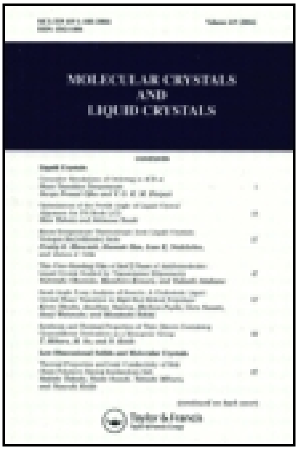

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Optically Isotropic Chiral Liquid Crystals Induced by Polymer Network and Their Electro-Optical Behavior

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The optical and electro-optical properties of the optically isotropic liquid crystalline composites prepared by in-situ photo-polymerization of cross-linking monomers in the isotropic phase and the blue phase of the chiral liquid crystals were investigated. In the composites prepared in the isotropic phase, no typical platelet textures corresponding to blue phase I and blue phase II were seen, and no reflection peaks were observed around the wavelength where the polymer-stabilized blue phase should exhibit reflection. A large Kerr constant, being relatively insensitive to temperature, was obtained for composites even in a temperature range where a liquid crystal used exhibits chiral nematic phase. The response time of Kerr effect was on the order of tens to hundreds of microseconds.

Keywords: blue phase; chiral; Kerr effect; liquid crystal; optically isotropic phase; polymer

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1. INTRODUCTION

Recently, LCDs have been widely used in television because of the development of new display modes such as in-plane switching (IPS) [1,2], vertical alignment (VA) [3], optically compensated bend (OCB) [4], etc. However, LCDs with fast response are still required from the view points of the motion video images.

The Kerr effect is one of the electric birefringence in an optically isotropic substance, the magnitude of the electric birefringence, $\Delta n(E)$, can be expressed by Eq. (1) [5].

$$\Delta n(E) = \lambda K E^2 \tag{1}$$

where $\Delta n(E)$ is the electric birefringence, λ is the wavelength of light, E is the applied electric field, and K is the Kerr constant. An anomalously large Kerr constant is observed just above nematic–isotropic phase transition temperature, T_{NI}. This is because the isotropic phase has nematic-like short-range ordering on a distance scale defined by a coherence length, ξ. The ξ of nematic liquid crystals in an isotropic phase diverges as temperature decreases to the temperature T^* which is a critical temperature where ξ diverges infinitely, actually slightly below the nematic-isotropic transition temperature, T_{NI}. In general, T^* is about 1 K lower than T_{NI}. The temperature dependence of ξ can be expressed by Eq. (2) based on the Landau-de Gennes theory [6].

$$\xi^2 \sim (T - T^*)^{-1}, \quad (T > T^*) \tag{2}$$

Below T_{NI} the domain size of nematic liquid crystals becomes infinite.

The Kerr constant of liquid crystals in an isotropic phase can be expressed as follows:

$$K \sim (T - T^*)^{-1} \sim \xi^2 \tag{3}$$

The magnitude of Kerr constant of liquid crystals also diverges as temperature decreases to T^*, and in a small temperature range, just above T_{NI}, has been observed to reach more than 100 times in comparison with nitrobenzene, $K_{\mathrm{nitrobenzene}} = 2{-}4 \times 10^{-12}\ \mathrm{mV}^{-2}$ [7,8]. Since such an anomalously large Kerr effect is associated with pretransitional fluctuation of the isotropic phase, it inevitably disappears in a temperature range below T_{NI}. The response time of nematic liquid crystals in an isotropic phase is much shorter ($\sim 1\,\mu\mathrm{s}$) than that in nematic phase ($5 \sim 100\,\mathrm{ms}$). Though the fast response of the Kerr effect in an isotropic phase of nematics is attractive, the steep temperature dependence and magnitude of Kerr constant are problems considering practical application in electro-optics, especially LCDs.

The optically isotropic liquid crystal could be one of the candidates to overcome the problems mentioned above. Blue phases are liquid-crystalline phases that generally appear in a very small temperature range between a chiral nematic phase and an isotropic phase [9]. There are three types of blue phases; BP I, BP II and BP III. Because of the structural symmetry, blue phases are optically isotropic. Recently, blue phases with a wide temperature range were developed. The one is so-called polymer-stabilized blue phase (PSBP), where the polymer network makes an important rule to stabilize blue phase [10]. The other is liquid crystal composed of dimeric molecules with high flexoelectric coefficients [11]. The PSBP shows large Kerr response with a wide temperature range [12]. Additionally the optically isotropic (polymer/chiral liquid crystal) composites show large Kerr effect, being relatively insensitive to temperature due to the suppression of ξ below T^* [13,14]. In this study we investigate the optical and electro-optical properties of optically isotropic liquid crystalline composites prepared by in-situ photo-polymerization of cross-linking monomers in the isotropic phase and blue phase of chiral liquid crystals.

2. EXPERIMENTAL

The liquid crystal materials used in this study were a nematic mixture (JC1041-XX, Chisso Co. Ltd., $\Delta n = 0.142$, $\Delta\varepsilon = 5.7$ at 298 K) and 4-cyano-4′-pentylbiphenyl (5CB, Aldrich, $\Delta n = 0.19$, $\Delta\varepsilon = 11$ at 298 K). A chiral dopant, ZLI-4572 (Merck), was used to induce blue phases and a chiral nematic phase (N*). The monomers used in this study to form a polymer-network in the composite systems were composed of 43.5 wt% of trimethylolpropane triacrylate (TMPTA, Aldrich) and 56.5 wt% of RM257 (Merck). 2,2-dimethoxy-2-phenylacetophenone (DMPA, Aldrich) was used as a photoinitiator. The constituent fractions of the samples reported here are shown in Tables 1 and 2. The precursors heated up to be an isotropic state were filled into glass cells with $12 \sim 13\,\mu$m gap of which inner surfaces were coated with indium tin oxide (ITO) transparent electrodes, followed by

TABLE 1 Constitutions (wt%) and Phase Transition Temperature of Liquid Crystals

	JC-1041	5CB	ZLI-4572	Phase transition temperature/K
LC-A	56.5	43.5	0	I-336.2-N
LC-B	50.0	38.5	11.5	I-326.4-BPII-325.7-BPI-324.9-N*

TABLE 2 Constitutions (wt%) and Phase Transition Temperature of Precursors

LC-A	LC-B	Monomer	DMPA	Phase transition temperature/K
Precursor-A	87.1	12.5	0.4	I-323.6-N
Precursor-B	87.1	12.5	0.4	I-314.0-BPI-306.2-N*

irradiation with ultra violet (UV) light of 1 mW/cm^2 for 20 min. The irradiation temperature was selected from the Conditions-a $\sim$ c shown in Table 3. The precursor-A was irradiated at 325.6 K (Condition-b), and the precursor-B was irradiated at 311.2 K (Condition-a), 316.2 K (Condition-b) and 329.7 K (Condition-c), which afforded Comp.-A, PSBP, Comp.-Bb and Comp.-Bc respectively. The PSBP was obtained from the Condition-a because a precursor-B exhibits BP I at 311.2 K, and optically isotropic composites (Comp.-Bb and -Bc) were obtained from the Condition-b and -c because a precursor-B exhibits an isotropic phase at 316.2 K and 329.7 K. The difference between Condition-b and c is that the liquid crystal phases appear or not during irradiation. The reflection spectra of the cells were measured with a spectrophotometer (JASCO MSV-350). The light-scattering profiles were measured using a light-scattering analyzer with a two-dimentional charge-coupled device (2D-CCD)(DYNA-3000, Othuka Electronics), using a He-Ne lazer (632.8 nm, 5 mW). The method to measure electric birefringence was reported elsewhere [13,14].

3. RESULTS AND DISCUSSION

3.1. Optical Properties

Figure 1 shows temperature dependence of the extinction ratio of the Comp.-A, PSBP, Comp.-Bb and -Bc without electric field. In the temperature range where LC-A and -B were in the isotropic state, the extinction ratio of all composites were nearly zero, respectively, like pure liquid crystals in an isotropic state. As temperature decreased, the Comp.-A showed a rapid increase in the extinction ratio in the

TABLE 3 Irradiation Temperatures for Precursors

Condition-a	Temperature where blue phase I appears.
Condition-b	$T_{c(precursor)}{}^{*} + 2\,\mathrm{K}$ and below $T_{c(LC)}{}^{*}$ of LC-A or -B.
Condition-c	Above $T_{c(LC)}{}^{*}$ of LC-A or -B.

$T_{c(precursor)}$ and $T_{c(LC)}$ are the I-BP or I-N transition temperature of LCs and precursors respectively.

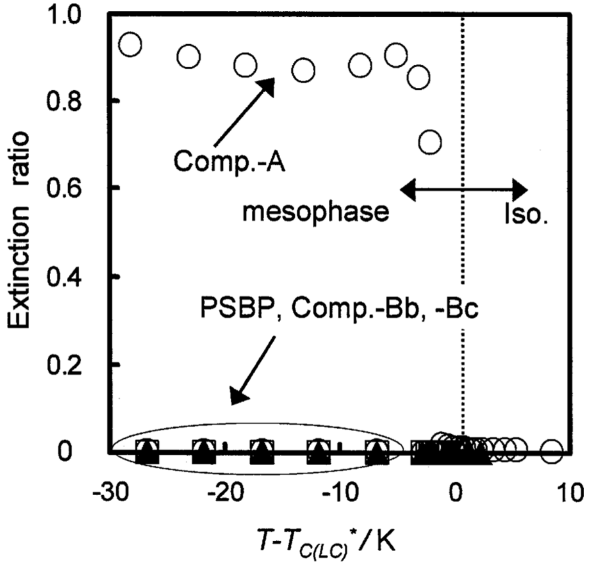

FIGURE 1 Variation of extinction ratio with temperature: $^*T_{C(LC)}$ is the I-BP or I-N transition temperature of bulk liquid crystal (LC-A, LC-B).

neighborhood of T_{NI} of LC-A, indicating that Comp.-A became birefringent due to the emergence of nematic domains through I-N phase transition. On the other hands, as for the PSBP, Comp.-Bb and -Bc, the extinction ratios were almost constant and nearly zero in the temperature range measured, hence these were optically isotropic even in the temperature range in which LC-B exhibited a liquid crystal phase. The composites prepared from LC-A by the way of the condition-c more or less optically anisotropic, and details will be reported elsewhere. LC-B used in the optically isotropic composites differs from LC-A only in the presence of the chirality. Therefore, the chilarity of liquid crystal plays an important role in inducing optically isotropic state. Of course the polymer is necessary for obtaining such a state, because the LC-B without polymer shows large birefringence below $T_{N^*\text{-}BP}$. Therefore, the results shown in Figure 1 reveal that optically isotropic state of the PSBP and Comp.-Bb and Bc could be induced through the incorporative effects of the polymer network and the chirality of the liquid crystal. As for the PSBP, the mechanism to stabilize blue phases is proposed elsewhere [10].

Figure 2 shows polarized microphotographs (a), reflection profiles (b) and H_V scattering profiles (c) of PSBP, Comp.-Bb and Bc at 304.2 K which is 22 K lower than the isotropic-blue phase transition

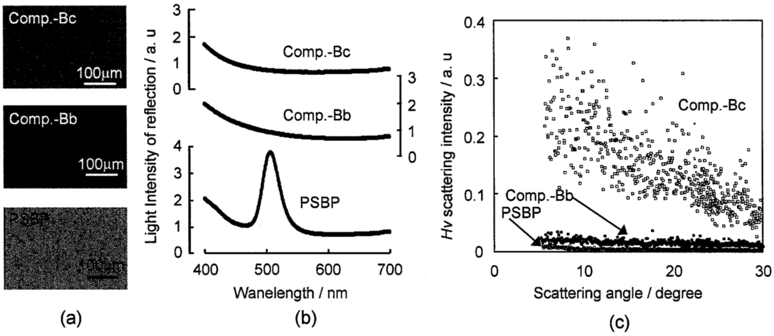

FIGURE 2 Polarized microphotographs (a), and wavelength of reflection (b) and H_V scattering profiles (c) of PSBP, Comp.-Bb and Comp.-Bc measured at 304.2 K.

temperature, $T_{\text{BP-I}}$ of LC-B. The blue phase exhibits light reflection based on Bragg diffraction of the cubic lattice. According to microphotographs, a typical platelet texture for blue phase was observed in that of PSBP, and no platelet textures were observed in those of Comp.-Bb and Bc. Additionally the reflection profile of PSBP was different from those of the other composites in the wavelength of reflection peak. No peaks were seen around the wavelength of 500 nm in Comp.-Bb and Bc, despite the strong reflection was observed in PSBP. The mesophase of PSBP shown in Figure 2(a) is clealy blue phase, but the mesomorphism of Comp.-Bb and Bc is still ambiguous. The H_V scattering intensity followed the order Comp.-Bc > Comp.-Bb > PSBP. The range of H_V light scattering angle measured corresponds to the scattering from anisotropic medium having spatial fluctuations of which the size are $1.5 \sim 0.4\,\mu\text{m}$. The results of Figure 2(c) can be understood that the number of the corresponding fluctuations in Comp.-Bc is much larger than the others. The difference of scattering intensity between them should be due to the structure of polymer-network, because the kind of a liquid crystal used was same, that is LC-B.

3.2. Electro-Optical Properties

The temperature dependence of Kerr constant of composites is shown in Figure 3. On cooling below $T_{\text{BP-I}}$ of LC-B, all the composites exhibited the remarkable Kerr effect, while the Kerr effect usually disappears behind the spontaneous large birefringence in the case of pure liquid crystals. The Kerr constant of the composites below $T_{\text{BP-I}}$ was anomalously large, about $1 \sim 3 \times 10^{-9}\ \text{mV}^{-2}$ which is several hundreds times

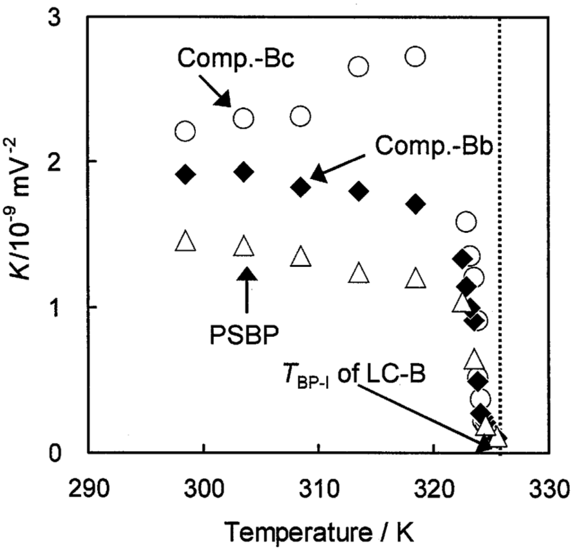

FIGURE 3 Temperature dependence of Kerr constant.

larger than that of nitrobenzene. The temperature dependence of the Kerr constant was relatively insensitive to temperature below $T_{\mathrm{BP\text{-}I}}$ to room temperature. This result implies that a coherence length of ξ of the ordered regions was persisted without divergence in the temperature range which LC-B exhibited a liquid crystal phase. The magnitude of Kerr constant of composites followed the order Comp.-Bc > Comp.-Bb > PSBP. This result might be due to that the coherence length of composites followed the order Comp.-Bc > Comp.-Bb > PSBP, depending on the polymer-network structure.

The electro-optical switching response curves of the transmitted light intensity of Comp.-Bb under the crossed polarizers were fitted by Eq. (4).

$$I = I_o + a \cdot \exp\left[-\left(\frac{t - t_o}{\tau}\right)^{\beta}\right], \quad (0 < \beta \leq 1) \tag{4}$$

where I is the intensity of the transmitted light, a is the magnitude of the modulation of light intensity induced by an electric field, t is time, τ is the response time and β is the distribution factor of the response time τ. The temperature dependence of τ in the rise and decay processes of Comp.-Bb is shown in Figure 4. The magnitudes of β ranged 0.5–0.7 in most cases. Over a broad temperature range, the response times of electro-optical events were the order of microseconds, which

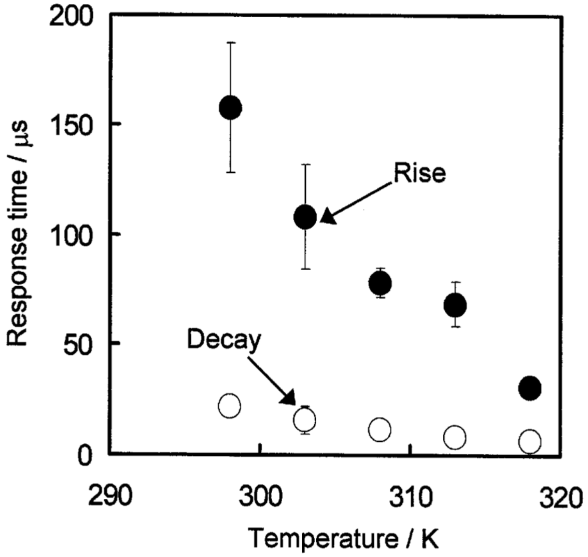

FIGURE 4 Temperature dependence of response time of Comp.-Bb.

were much shorter than those of conventional nematic liquid crystals (5 ~ 100 ms). This fast response might be due to the relatively short coherence length of composites than that of nematic liquid crystals.

4. CONCLUSIONS

We can conclude that the optically isotropic phase of the composite prepared by in-situ photo-polymerization of cross-linking monomers in the blue phase or isotropic phase of chiral liquid crystals showed large electric birefringence with insensitive to the temperature. The response time of Kerr effect was several tens times shorter than that of nematic liquid crystals. These materials could be useful for applications in electro-optics for LCD-TV.

REFERENCES

[1] Oh-e, M. & Kondo, K. (1995). *Appl. Phys. Lett.*, *67*, 3895.

[2] Oh-e, M. & Kondo K. (1996). *Appl. Phys. Lett.*, *69*, 623.

[3] Yoshida, H., Takeda, A., Taniguchi, Y., Tasaka, Y., Kataoka, S., Nakanishi, Y., Koike, Y., & Okamoto, K. (2004). *Mol. Cryst. Liq. Cryst.*, *410*, 255.

[4] Miyashita, T., Yamaguchi Y., & Uchida, T. (1995). *Jpn. J. Appl. Phys.*, *34*, 177.

[5] Kerr. J. (1875). *Phil. Mag.*, *50*, 337.

[6] de genes, P. G. & Prost, J. (1993). *The Physics of Liquid Crystals*, Clarendon Press: Oxford.

[7] Filippini, J. C. (1975). *J. Phys. D: Appl. Phys.*, *8*, 201.
[8] Schneider, L. & Wendorff, J. H. (1997). *Liq. Cryst.*, *22*, 29.
[9] Crooker, P. P. (2001). *Chirality in Liquid Crystals*, Springer: New York.
[10] Kikuchi, H., Yokota, M., Hisakado, Y., Yang, H., & Kajiyama, T. (2002). *Nature Materials*, *1*, 64.
[11] Coles, H. J. & Pivnenko M. N. (2005). *Nature*, *436*, 997.
[12] Hisakado, Y., Kikuchi, H., Nagamura, T., & Kajiyama, T. (2005). *Adv. Mater.*, *17*, 96.
[13] Haseba, Y., Kikuchi, H., Nagamura, T., & Kajiyama, T. (2005). *Adv. Mater.*, *17*, 2311.
[14] Haseba, Y. & Kikuchi, H. (2006). *Journal of the SID*, *14*, 551.