

Unusual temperature dependence of the splay elastic constant of a rodlike nematic liquid crystal doped with a highly kinked bent-core molecule

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We report an unusual temperature dependence of the elastic constants of a rodlike nematic liquid crystal (RLC) mixed with a highly kinked bent-core liquid crystal (BLC). On cooling through the nematic phase, the splay elastic constant (K_{11}) of the RLC-BLC mixture increased below the nematic-isotropic phase transition temperature, but started to decrease midway through the nematic phase. The decrease of K_{11} was more prominent with a greater concentration of BLC. On the other hand, the bend elastic constant (K_{33}) of the RLC-BLC mixture monotonically increased through the nematic phase with decreasing temperature.

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I. INTRODUCTION

Bent-core liquid crystal (BLC) has drawn much attention for its interesting physicochemical properties. Some achiral BLC molecules were found to form a chiral structure by a molecular conformation [1–3] or a combination of polar packing and spontaneous tilt of the molecules [4–6]. The antiferroelectric state of BLC has been predominantly observed compared to the ferroelectric state, suggesting the ferroelectricity of a liquid crystal (LC) is deeply related to the entropy of the system [7–9]. Some BLC molecules were reported to possess a biaxial ordering in the nematic phase [10–13]. In addition, some BLC materials were found to show a greater flexoelectric effect than the general rodlike liquid crystal (RLC) [14–17].

Recently, binary mixtures of RLC and BLC have been studied, and many interesting physical phenomena were reported. An orientational coupling between RLC and BLC resulted in a drastic change of the electric and the elastic properties. For instance, a small amount of BLC ~ 5 wt % increased the flexoelectric anisotropy of the mixture by a factor of 3 or more [16,17]. The bend elastic constant (K_{33}) of RLC was significantly reduced by doping BLC [18–20]. Kundu *et al.* reported an anomalous decrease of K_{33} of octyloxy cyanobiphenyl (8OCB) and BLC mixture in the nematic phase [20]. As the sample was cooled from the isotropic-nematic phase transition temperature (T_{NI}), K_{33} increased until $\Delta T = T - T_{NI} \sim 8$ °C, but decreased with greater ΔT until approaching nematic-smectic A phase transition temperature (T_{AN}) [20]. Recently, Sathyanarayana and Dhara mentioned a decrease of K_{11} with a greater concentration of highly kinked BLC molecules [21].

In this paper, we investigated the temperature dependence of the dielectric anisotropy ($\Delta\epsilon$), the optical birefringence Δn , the order parameter S , K_{11} , K_{33} , and a rotational viscosity (γ) of RLC doped with highly kinked BLC. The kink angle θ of BLC used in this study was about 130° [Fig. 1], much larger than that of the conventional BLC molecules $\sim 60^\circ$. On cooling the

sample, K_{11} of RLC doped with highly kinked BLC increased just below T_{NI} but started to decrease midway through the nematic phase. The decrease of K_{11} was more prominent with a greater concentration of BLC. Meanwhile, K_{33} of the RLC-BLC mixture monotonically increased through the nematic phase similar to pure RLC. The reversed temperature dependence of K_{11} and K_{33} compared to the paper of Kundu *et al.* [18] seems to be related to the different kink angle of the BLC molecule used.

II. EXPERIMENT

A commercial RLC mixture ZGD5071 (JNC Corporation) was mixed with BLC at 100 °C for 24 h. T_{NI} of pure ZGD5071 is 65 °C. BLC has a phase sequence Cry (116 °C), Sm-A (133 °C), N (138 °C), I [Fig. 1]. T_{NI} of the RLC mixtures doped with 1.0, 2.5, 5.0, and 10.0 wt % BLC was 67 °C, 72 °C, 75 °C, and 81 °C, respectively. The binary mixture was phase separated and the BLC molecules formed crystal domains provided the concentration of BLC was over 10 wt %. The indium-tin-oxide (ITO)-deposited glass substrate was coated with a planar alignment polyimide PIA-X189-KU1 (JNC), and then baked at 230 °C for 1 h. The substrates were rubbed and assembled in an antiparallel fashion. Cell gap d was maintained to be 12 μm using bead spacers. The RLC-BLC mixture was then injected into an empty cell at 100 °C. $\Delta\epsilon$ of the mixtures was measured by checking the capacitance of the samples in the planar and homeotropic aligned state. K_{11} was measured by investigating the Fréedericksz transition voltage $V = \pi(K/\epsilon_o \Delta\epsilon)^{1/2}$ and K_{33} was obtained by fitting phase difference under a higher voltage [22]. Rotational viscosity γ was obtained from the relaxation time $\tau = \gamma d^2 / K_{11} \pi^2$ of the transmittance after removing an electric field. Details of the measurement are same as the methods described in the literature [22,23].

III. RESULTS AND DISCUSSION

Figure 2 shows the polarizing optical microscopy (POM) image of the pure RLC, 5.0, and 10.0 wt % BLC-mixed RLC samples. All samples showed a homogeneous bright state when

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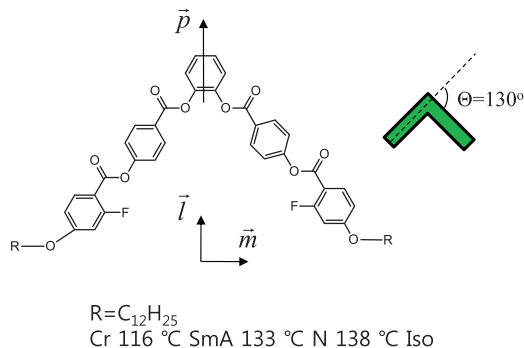


FIG. 1. (Color online) Molecular structure and phase sequence of the BLC molecule used.

the rubbing direction was at 45° to the polarizing axis of an incident light [Figs. 2(a)–2(c)]. The samples also showed a uniform dark state when the rubbing direction was parallel to the polarizer [Figs. 2(d)–2(f)]. In addition, the samples were transparent without a severe light scattering and we could not find any micron or over-micron-sized domains in the POM observation. Thus, the BLC molecules doped less than 10 wt % were well diluted in the RLC host without a phase-separated domain.

Figure 3 shows the dielectric anisotropy $\Delta\epsilon$ of the various RLC-BLC mixtures vs $T - T_{NI}$. The repetition error of $\Delta\epsilon$ was less than 0.1 in all samples. On cooling the sample, $\Delta\epsilon$ was increased in all mixtures. With respect to the BLC concentration, $\Delta\epsilon$ was increased in the 1.0 and 2.5 wt % BLC-mixed samples, but started to decrease with a greater BLC concentration, 5.0 and 10 wt %. $\Delta\epsilon$ of the 0, 1, 2.5, 5, and 10.0 wt % BLC-mixed RLC was 6.5, 7.8, 8.2, 7.3, and 5.6, respectively, at $T - T_{NI} = -40^\circ\text{C}$. On cooling the sample, the relative dielectric constant parallel to the optic axis ϵ_{\parallel} was monotonically increased both in the pure RLC and BLC-RLC mixtures. In addition, the dielectric constant perpendicular to the optic axis ϵ_{\perp} was monotonically decreased as the sample was cooled.

We also measured the optical birefringence Δn using the Soleil-Babinet compensator as described in Ref. [24] [Fig. 4(a)]. Δn of 1.0 and 2.5 wt % BLC mixtures was similar to pure RLC, but decreased with a greater concentration of BLC. We deduced the order parameter S of the RLC-BLC mixtures

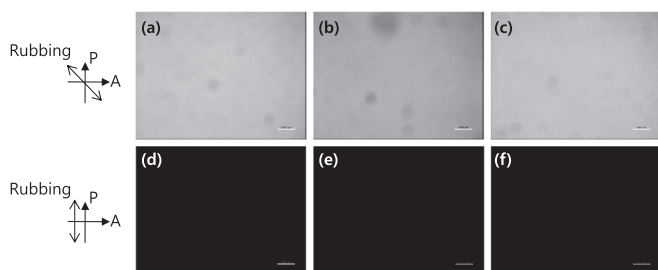


FIG. 2. POM image of the RLC-BLC mixtures with various BLC concentration. (a), (d) 0 wt %, (b), (e) 5 wt %, and (c), (f) 10 wt % BLC were mixed with RLC. Rubbing direction of the cell was at 45° to the polarizer in (a)–(c) and parallel to the polarizer in (d)–(f). Scale bars correspond to $100\ \mu\text{m}$.

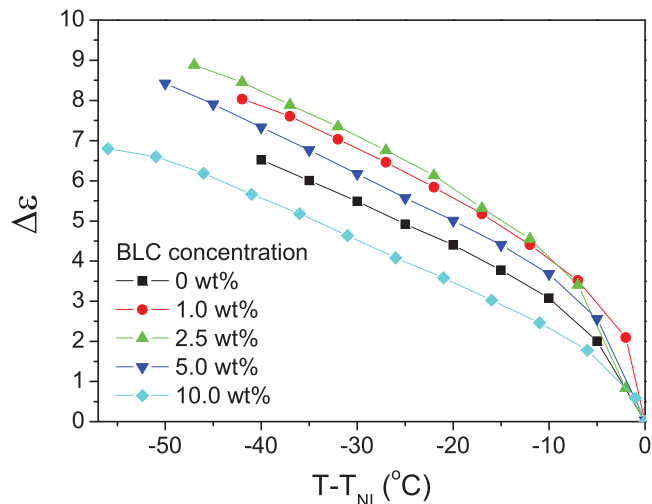


FIG. 3. (Color online) Dielectric anisotropy $\Delta\epsilon$ of the RLC-BLC mixtures with various BLC concentrations vs $T - T_{NI}$. The connected lines were drawn for better readability.

by fitting the measured birefringence with Haller's equation $\Delta n = \delta n(1 - T/T^*)^\beta$, where T is the absolute temperature, and T^* , δn , and β are fitting parameters [25,26] [Fig. 4(b)]. Assuming $S = 1$ at the temperature of absolute zero, order parameter is given by $S(T) = \Delta n(T)/\delta n$. We should mention that a change of pretilt angle was observed adjacent to T_{NI} . The increased pretilt resulted in the reduction of in-plane Δn . To eliminate the pretilt effect on S , we discarded the birefringence data adjacent to T_{NI} [Fig. 4(a)]. On cooling the sample, S was monotonically increased similar to $\Delta\epsilon$ in Fig. 3. Concerning the BLC concentration dependence, S was nearly similar or slightly increased when the BLC concentration was less than 2.5 wt %, but started to decrease with a greater BLC concentration over 5.0 wt %.

Comparing the temperature and concentration dependence of S , we can understand the temperature dependence of $\Delta\epsilon$. In the mean field approximation, $\Delta\epsilon$ is proportional to S . The BLC molecule has a dipole moment \vec{p} to the arrow direction \vec{l} [Fig. 1] due to the pair of fluorine atoms and the large kink angle $\sim 130^\circ$; i.e., BLC has a positive dielectric anisotropy [17]. Therefore, $\Delta\epsilon$ can be increased with greater S . With a small fraction of BLC, BLC is considered to enhance the overall RLC ordering. Meanwhile, the decrease of $\Delta\epsilon$ with a concentration of BLC over 5.0 wt % is thought to be due to the decreased S of the constituent molecules. Perhaps the heavily doped BLC molecules induce deformed orientation of the neighboring RLC molecules. Because we could not find any micron-sized domains by POM observation [Fig. 2], the domains seems to be sufficiently small with a nano-sized diameter at $T - T_{NI} > -40^\circ\text{C}$.

Figure 5(a) represents K_{11} of the various RLC-BLC mixtures vs $T - T_{NI}$. Although pure RLC showed a monotonic increase of K_{11} with decreasing temperature, all RLC-BLC mixtures showed unusual temperature dependence of K_{11} . On cooling the RLC-BLC mixture samples from T_{NI} , K_{11} increased at first, but started to decrease midway through the nematic phase. We refer to the critical temperature showing the local maximum of K_{11} as T_c hereinafter. The decrease of K_{11}

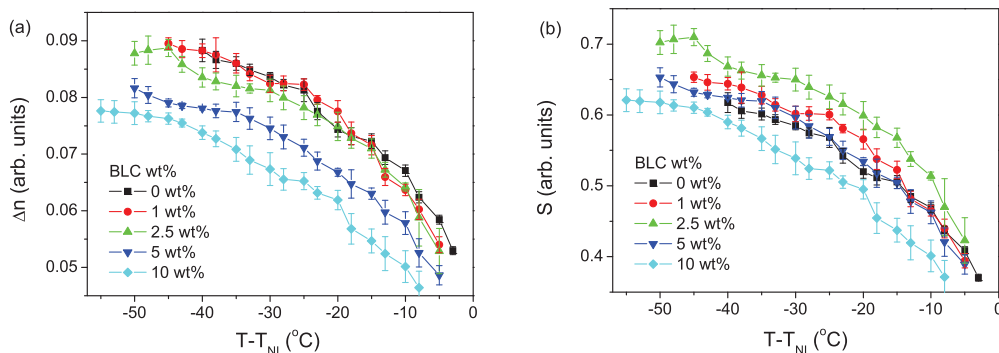


FIG. 4. (Color online) (a) Optical birefringence Δn and (b) order parameter S of the RLC-BLC mixtures with various BLC concentrations vs $T - T_{NI}$. Error bars are the maximum variation of the experimental value from the repeated measurements in three different points of the samples. The connected lines were drawn for better readability.

was more prominent in the sample with a greater fraction of BLC. K_{11} of the 10 wt % BLC-doped cell was 12.9 pN at $T - T_{NI} = -20$ °C, but decreased to 2.2 pN at $T - T_{NI} = -40$ °C. As the sample was further cooled, K_{11} increased again. Thus, K_{11} of the RLC-BLC mixtures increased in the high temperature nematic phase, then decreased in the middle nematic phase, and re-increased in the low temperature range of the nematic phase. Concerning to the BLC concentration dependence at $T - T_{NI} = -40$ °C, K_{11} was 12.3 pN in pure RLC, and gradually decreased with a greater BLC concentration, showing 2.2 pN in 10 wt % BLC-mixed sample.

Meanwhile, K_{33} of the RLC-BLC mixtures monotonically increased with decreasing temperature through the nematic phase [Fig. 5(b)]. K_{33} of the 1 and 2.5 wt % BLC-mixed sample was nearly the same as that of pure RLC, but K_{33} of the 5 and 10.0 wt % BLC-mixed cell was decreased compared to the pure RLC cell. At $T - T_{NI} = -40$ °C, K_{33} was greater than K_{11} in all concentrations. In addition, the decrease of K_{11} after doping BLC was greater than the change of K_{33} at the given temperature and the BLC concentration.

Let us consider a physical model to interpret the unusual temperature dependence of K_{11} in Fig. 5(a). Just below T_{NI} , thermal fluctuation is certainly significant; hence the orientation of the constituent RLC and BLC molecules may be hardly coupled to each other [Fig. 6(a)]. Thus, the RLC-BLC mixture represents normal temperature dependence of K_{11}

similar to pure RLC [Fig. 5(a)]. On cooling the sample $T - T_{NI} < T_c$, the thermal fluctuation is decreasing and the RLC molecules can couple to the neighboring BLC molecules with the splay deformation [Fig. 6(b)]. In our previous paper, we showed that the same BLC molecule could form nano-sized domains with 5CB molecules in the nematic phase from a small angle x-ray scattering experiment [17]. Because the BLC molecule has a large kink angle $\sim 130^\circ$, the splay deformation can be preferred rather than the bend deformation, thus reducing K_{11} midway through the nematic phase.

As the sample was further cooled, K_{11} re-increased in Fig. 5(a). For a plausible interpretation of this re-increase of K_{11} , we conjecture a structural conformation change of the BLC molecules. As described in the previous literature [27,28], the conformational degree of freedom can give a crucial effect on the elasticity and the flexoelectricity of the LC molecules. Recently, Sathyanarayana and Dhara also noted the conformational freedom of BLC possessing alkoxy chains can be reduced with a greater fraction of BLC, thus increasing the longitudinal dipole moment [21]. We conjecture that decreasing temperature in our study might give an analogous effect of increasing BLC concentration [21]. The conformational freedom of BLC at the alkoxy chain might be suppressed in the low temperature. Consequently K_{11} can again increase. In addition, the continuously increasing S

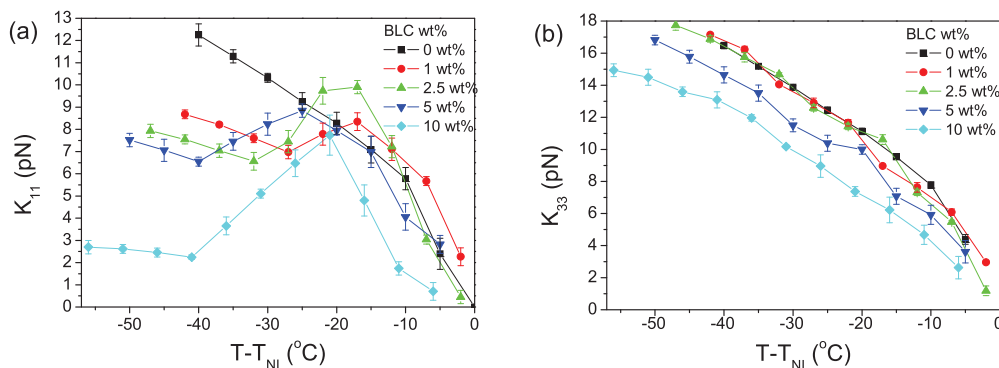


FIG. 5. (Color online) (a) Splay and (b) bend elastic constants of the various mixtures vs $T - T_{NI}$. Error bars are the maximum variation of the experimental value from the repeated measurements in three different points of the samples. The connected lines were drawn for better readability.

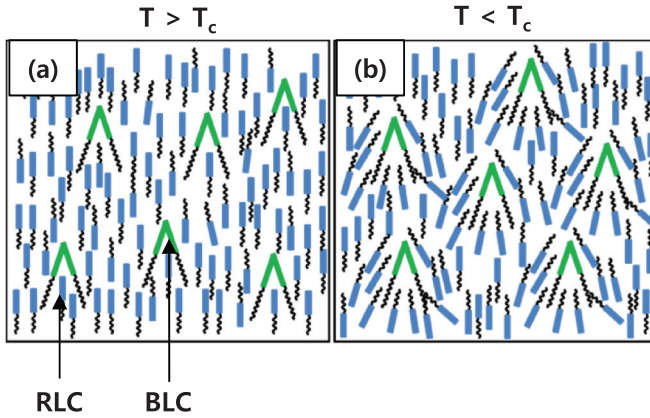


FIG. 6. (Color online) Schematic illustration of the RLC and BLC molecules orientation (a) $T > T_c$ and (b) $T < T_c$. T_c means the critical temperature showing the local maximum of K_{11} midway through the nematic phase in Fig. 5(a).

can also contribute to the re-increase of K_{11} . The normal temperature dependence of K_{33} through the whole nematic phase can be also understood by considering the large kink angle of BLC. K_{33} of the RLC-BLC mixture was greater than K_{11} [Fig. 5]. Thus, the splay deformation can be easily adapted compared to the bend deformation and K_{33} can represent the similar temperature dependence with pure RLC.

We should compare our result with the report of Kundu *et al.* about the anomalous temperature dependence of the elastic constants in the 8OCB-BLC mixture [20]. Kundu *et al.* reported an abnormal decrease of K_{33} midway through the nematic phase and re-increase near T_{NA} [20]. Contrary to our result, K_{11} did not show such an abnormal temperature dependence in the nematic phase, and monotonically decreased with a greater fraction of BLC. Kundu *et al.* used BLC with small $\theta \sim 60^\circ$ and K_{11} was much greater than K_{33} . Recently, Sathyanarayana *et al.* also reported a similar temperature dependence of K_{33} in a RLC-BLC mixture where the BLC used has a small kink angle [29]. On the other hand, Sathyanarayana and Dhara reported a decrease of K_{11} in the mixture of RLC doped with highly kinked BLC [21]. These results strongly imply that the temperature dependence of the elastic constants

of the RLC-BLC binary mixture is deeply related to the shape of the BLC molecules. We think the BLC molecule with large θ can induce splay deformation of neighboring RLC molecules provided the intermolecular interaction between the BLC and the RLC molecules is more predominant than the thermal fluctuation. In the same sense, a BLC molecule with small θ can induce bend orientation of surrounding RLC molecules in a certain temperature range.

Figure 7(a) shows rotational viscosity γ of the various RLC-BLC mixtures vs $T - T_{NI}$. γ increased in the 1 and 2.5 wt % BLC-doped samples and decreased with a greater BLC concentration. In the mean field theory and the modified Arrhenius model, γ is proportional to S and given by $\gamma = b \text{Sexp}(W/kT)$, where b is the proportionality constant, W is the activation energy of the molecular rotation, and k is the Boltzmann constant [30,31]. Thus, the greater γ of 1 and 2.5 wt % BLC mixtures can be interpreted with the effect of greater S in Fig. 4(b). The decrease of γ with a greater BLC concentration over 5.0 wt % is also consistent with S data in Fig. 4(b).

In order to make a more meaningful analysis, we normalized γ to S [Fig. 7(b)]. γ/S showed the similar temperature and BLC concentration dependence and was well fitted to the modified Arrhenius model, $\gamma = b \text{Sexp}(W/kT)$. Thus, the rotational viscosity of the RLC-BLC mixture was well approximated to the mean field theory. Fitted W of the pure RLC was 5.4×10^{-20} J and the magnitude was physically reasonable as reported in the theoretical prediction [32,33]. Although γ was increased by mixing BLC in most of the previous literature [34], our result showed a reduction of γ after doping BLC. Avci *et al.* recently reported that BLC with an asymmetric shape could show relatively low viscosity [35]. Thus, γ is certainly deeply related to the structure of BLC. Probably, the conformational degree of freedom and elastic deformations with low order parameter may be responsible for the reduction of γ .

IV. CONCLUSION

To summarize, we observed an unusual temperature dependence of K_{11} of RLC mixed with a highly kinked BLC molecule. On cooling the sample, K_{11} was increased near

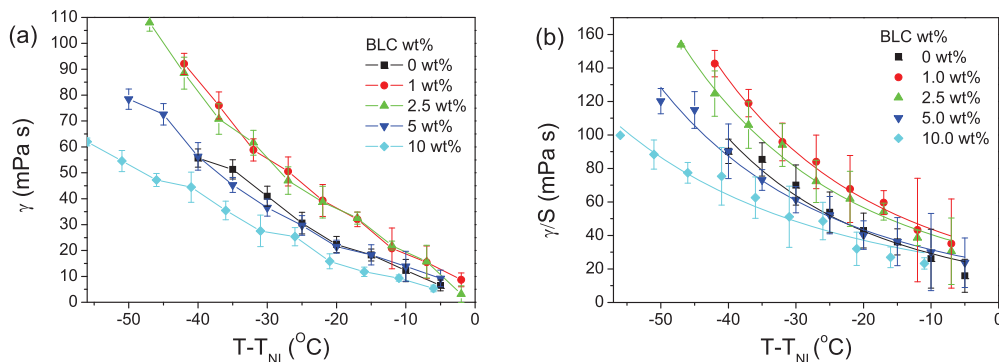


FIG. 7. (Color online) (a) Rotational viscosity γ and (b) γ/S of the various RLC-BLC mixtures vs $T - T_{NI}$. (c) fitted parameter W and b by fitting data (b) using the modified Arrhenius model $\gamma = b \text{Sexp}(W/kT)$. The connected lines in (a) and (c) are drawn for better readability. Error bars are the maximum variation of the experimental value from the repeated measurements in three different points of the samples.

T_{NI} , but decreased midway through the nematic phase. The decrease of K_{11} was more prominent with a greater fraction of BLC. On the other hand, K_{33} monotonically increased with decreasing temperature similar to pure RLC. We think this unusual temperature dependence of K_{11} is related to the large kink angle of BLC inducing the splay deformation of the neighboring RLC molecules. This study also can give a method to optimize the elastic property of the commercialized LC mixture for the various LC display modes by adding a small amount of the BLC molecules.

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