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Dielectric Investigation of a Bent-Core Liquid-Crystalline Material and Its Mixture with a Rod-Like Compound

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The dielectric relaxation behavior of a bent-core liquid-crystalline (BC) material showing B_2 phase and its 17% mixture with another rod-like material (R-BC) has been investigated. The appearance of a newly induced B_1 phase has been detected in the R-BC system. We found comparatively lower value of dielectric permittivity of the R-BC system than that of BC material. Moreover, a lower value of relaxation frequency of the long axis rotation mode in BC material compared to that of the R-BC material has been observed. These results have been discussed on the basis of molecular origin for the formation of B phases in the materials.

Keywords Bent-core molecules; dielectric relaxation; induced phase; mixture of bent-core and rod-like molecules

Introduction

Long after the discovery of bent-shaped liquid crystals (LC) by Vorlander and Apel [1], Niori and his coworkers [2] showed that achiral compounds composed of banana-shaped or bow-shaped molecules exhibit a smectic phase with polarized layers. Subsequently, Natale and Link [3] demonstrated that chirality arising in these smectic layers is due to the tilting of the molecules about the arrow direction of the bows, thus breaking the achiral symmetry of the layers. Since then several banana-shaped LCs have been designed and synthesized to understand the relationship between the molecular structure and mesophase observed by this type of compound. These LC properties of bent-core molecules such as the observation of ferroelectricity and spontaneous breaking of chiral symmetry in the smectic phases composed of achiral molecules [4] have broad implications for the general field of soft condensed matter. Because every ordering proved a restriction to the dynamics

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of molecular reorientation process, it is possible to classify various B phases of LC based on dynamical point of view using the impedance spectroscopic technique. Typically, in a homologous series of symmetrically substituted bent core materials, a B_2 phase with a lamellar structure, a B_1 phase with a rectangular columnar structure, and a B_6 phase having an intercalated lamellar structure are known to occur with decreasing chain length.

To meet the demands of the display market, the required LC properties can be reached by mixing compounds with various molecular shapes rather than by looking for pure compounds with definite properties. Hence, many efforts have been made in order to understand the mechanisms of molecular interactions using various mixtures of LC systems because LC mixtures often yielded new phases that are not present in either of the mixing compounds. Goc *et al.* [5] reported the occurrences of an orthoconic antiferroelectric SmC^*_A phase by mixing the calamatic molecules possessing the SmC^* phase with high tilt angle and a bent compound. Schröder *et al.* [6] reported two types of binary mixtures in which bent-core molecules possess a lamellar B_2 phase and rod-like molecules having a nematic phase exhibit B_2-SmA transition in a relatively wide concentration interval (20–62 mol% BC) instead of a B_2-N transition. On the other hand, a bent-core molecule mixed with a rod-like molecule having an SmC phase exhibit a B_2-SmC phase transition at higher concentrations (78–80 mol%) of rod-like molecules, B_2-SmC-SmA at 78 mol% and B_2-SmC-SmA-N at a concentration in between 45 and 63 mol%.

In the present article, we have made a detailed dielectric spectroscopic study of a bent-core liquid crystal material, viz. (*E*)-4-((3-(4-(4-(dodecyloxy)benzoyloxy)-2-hydroxybenzylidene-amino)phenoxy)carbonyl)phenyl 4-(dodecyloxy)benzoate (designated as BC) possessing a B_2 phase and also the 17% mixture of the mentioned BC material with a chiral rod-like compound, viz. (8S,9S,10R,14S,17R)-10,13-dimethyl-17-((*R*)-6-methylheptan-2-yl)-2,3,4,7,8,9,10,11,12,13,14,15,16,17-tetradecahydro-1H-cyclopenta[a]phenanthren-3-yl6-4-((*E*)-1-methyl-2-oxo-1,2-dihydroquinolin-6-ylimino)-methyl)phenoxy) hexanoate (designated as R). The mixture (designated as R-BC) shows a newly induced B_1 phase that is not present in either BC or R compound [7]. This rich phase sequence of the pure material and the mixture has been characterized from their dielectric relaxation behavior and have been analyzed on the basis of molecular origin for the formation of B phases in the pure material and mixture.

Experimental

The phase sequence of BC, R, and mixture (R-BC) during the cooling cycle are shown below [7].

BC: Iso.-134.1°C-B_2-76.0°C-Cr
R: Iso-211.1°C-N^*-198.7°C-TGBA-198.0°C-SmA-153.3°C-Cr
R-BC: Iso-207.5°C-Chol-183.0°C-SmA_d-135.0°C-B_1-87.0°C-Cr

Figure 1 illustrates the structure of BC and R material.

For dielectric studies, indium tin oxide (ITO)-coated transparent glass substrates were used as electrodes. Substrates were prepared by coating the glass plates with polyvinyl alcohol and baking at 140°C for 2 h. Because the R-BC sample possesses a higher transition temperature, another pair of substrates was prepared by coating the glass plates with nylon 6/66 and baking at 210°C for 1 h. Homogeneously aligned samples were obtained by rubbing the substrate in one direction. Each cell

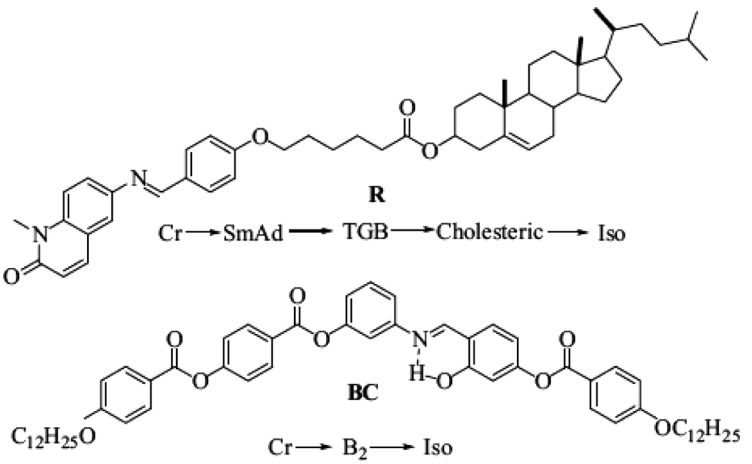

Figure 1. Molecular structures and phase sequences exhibited by the bent-core (BC) and rod-shaped (R) compounds.

was previously calibrated by using air and toluene as the standard references. A 6 μm thick cell with active area 16 mm^2 was filled with the samples by means of capillary action technique in the isotropic phase of the liquid crystal similar to our earlier works [8,9]. The samples under investigations were subjected to slow cooling for better alignment. The measuring temperature was controlled by a Mettler FP82 hot stage along with a Mettler FP90 temperature controller with an accuracy of ±0.1°C. A computer-controlled HP 4192A impedance analyzer was used for dielectric measurements.

Results and Discussion

Temperature-dependent dielectric permittivity (ε') has been studied in different phases of BC samples during the cooling cycle. Figure 2 shows the temperature dependence of ε' of the sample measured at various frequencies (viz. 500 Hz and 1, 5, 10 kHz) for a 6-μm-thick cell. The observed phase sequence, viz. Iso-B_2-Cryst, during cooling is presented in the same figure. However, minor deviations as observed in the transition temperatures from those reported earlier [7] might be attributed to the influence of different cell thickness. As shown in the figure, at low frequency, the high dielectric permittivity value (∼74) might originate due to the contribution of an electric double layer formed by the free charges. However, for higher frequency, the permittivity value was found to be low. When the chain length is sufficiently long, the molecules have strong biphilicity and there is segregation of the aromatic cores and the aliphatic chains, resulting in a layering order of the B_2 phase [2,10]. In most BC molecules, the bend angle (between each arm and the bow axis) is greater than 60 degrees. The BC molecules cannot rotate freely about the long (bow) axes and pack with an in-layer polar order. The aromatic cores are associated with several dipolar groups having components in the molecular plane, which can give rise to a tilting about the arrow axis. This dipolar mechanism is similar to the case of the smectic C liquid crystal formed by rod-shaped molecules, where the off-axis components of the dipoles can produce tilting of the molecules

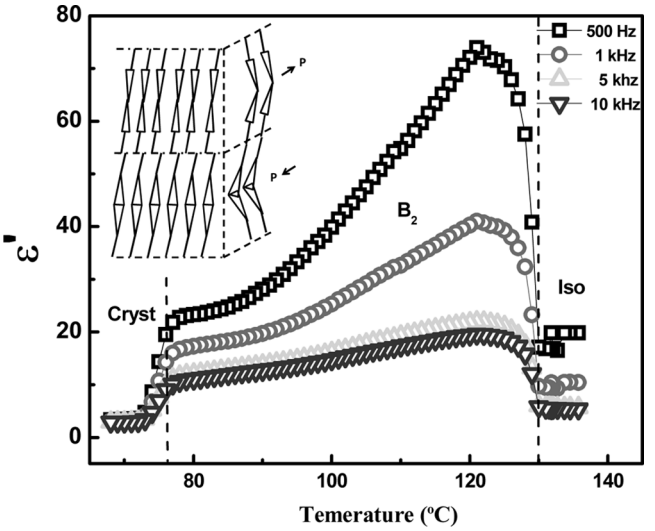

Figure 2. Temperature dependence of the real part of dielectric constant (ε') at different fixed frequencies for a 9.5-μm-thick cell for the BC sample. Inset shows the schematic representation of the structure in the B_2 phase exhibited by BC compound.

[10,11]. On the other hand, a larger molecular cross section of chains compared to the cores in these types of molecules can also produce tilt [10]. Though the individual molecules are achiral, as a result of the polar ordering of the molecules and the tilt, the layer becomes chiral [3,10]. The B_2 phase usually has an antiferroelectric interlayer order due to entropic reasons and the medium has no net polarization. However, due to the deformation in the domain structure we should expect a low value of spontaneous polarization as well as dielectric permittivity in the B_2 phase. The schematic representation of the structure in the B_2 phase is shown in the inset of Fig. 2.

Figure 3 shows the temperature dependent dielectric permittivity at different frequency of the R-BC material. It is assumed that the aromatic group of bent molecules in 17% BC approximately matches and sits on the aromatic group of rod molecules and may give rise to an induced B_1 phase [12]. As shown in the figure, the permittivity value of the R-BC sample showing a B_1 phase is lower than that of the BC material showing a B_2 phase. This may be described on the basis of the proposed model of mixtures of bent-core and rod-like molecules. With the addition of rod-like material within the bent-core materials, the effective chain length of the bent-core compound decreases and this type of deformed structure formation induces the B_1 phase. The aromatic moieties of the rods are attracted to the aromatic parts of the BC molecules and this is exploited by the medium to reduce the electrostatic energy of the polarized layers of the B_2 phase. In the proposed model of the induced B_1 phase, the rods lie at the interfaces between neighboring domains (inset of Fig. 3). The aromatic parts of the rods partly overlap with the aromatic cores of the BC molecules at the interface of both domains, enhancing the attractive interaction between the domains. The rods aid in holding the domain structure together, thus acting like glue [10]. This type of structure formation keeps the successive polarization direction to be opposite and a more perfect cancellation of polarization occurs in the B_1 phase, resulting in a lower value of dielectric permittivity in the

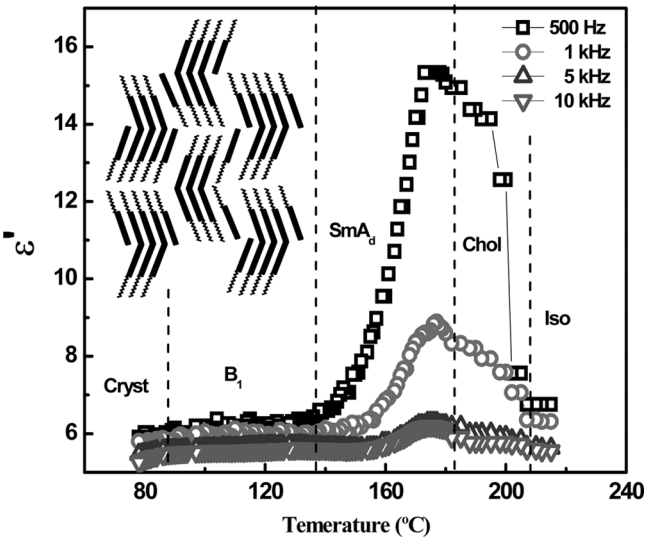

Figure 3. Temperature dependence of the real part of dielectric constant (ε') at different fixed frequencies for a 9.5-μm-thick cell for the R-BC sample. Inset shows the schematic representation of the structure in the induced B_1 phase exhibited by R-BC compound.

R-BC sample than that of BC. Moreover, the low-frequency ionic contribution is found to be lower in the R-BC sample than that of the BC sample. We may predict, due to the strong interaction of rod-shaped and bent-core molecules; the free charges are trapped between the layers and contribute less in the dielectric permittivity value.

From the earlier literature survey it was found that in a mixture of bent-core and rod-like sample as the concentration of rod-like molecule exceeds 15%, the B_1 phase is induced [13] and the phase exists until 63% of rod-like molecule. Beyond this composition, the B_6 phase is induced, which is stable up to 87% of rod-like compound. This is because as the concentration of rods is increased, they are no longer confined to the interfaces between the domains and the 2D lattice structure gets disrupted resulting a B_6 phase. Similar effect occurs in the case of short homolog of bent-core material. But, interestingly, in the present case, in the mixtures with 10–50% of BC, an induced B_1 phase appears [7]. This is because the induced B_1 phase appears at lower temperature where the pure R is in a solid form. So it may be predicted that the aromatic group of bent molecules in 17% BC mixture approximately matches and sits on the aromatic group of rod-like molecules and may give rise to an induced B_1 phase. Because the induced B_1 phase appears at lower temperature where the pure R is in a solid form, the intermolecular interaction might be large enough to stabilize the induced phase.

Figures 4 and 5 show the frequency dependence of the imaginary (ε'') part of complex dielectric permittivity $\varepsilon^*(\omega, T)$ for the BC and R-BC systems, respectively, at 100°C. In general, in bent-core materials, one can expect two relaxation modes due to the rotation along the short and the long axes. Another low-frequency relaxation process is expected originating from a collective process connected with the formation of anitiferroelectric ordering [14]. From the structure of the BC material it is evident that the rotation around the short axis is accompanied by a very small change of dipole moment. Thus, the intensity of the corresponding dielectric absorption process should be very small and hard to detect. In our case, for the

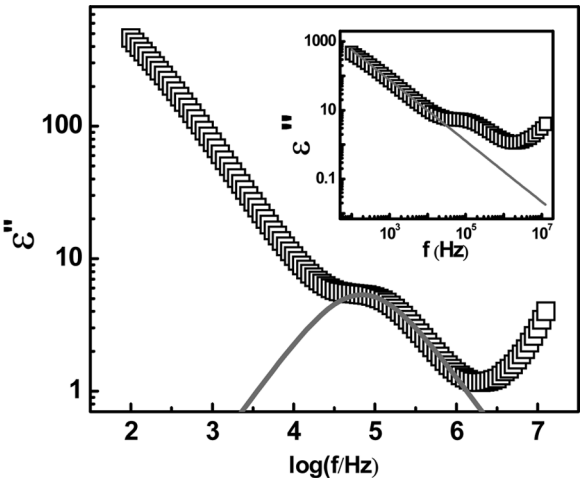

Figure 4. Frequency dependence of the real (ε') and imaginary (ε'') parts of dielectric permittivity in the B_2 phase at 100°C of BC sample. The solid line shows the Cole-Cole fitting. Inset shows the conductivity contribution of the free charges.

BC sample we cannot detect any low-frequency mode as shown in Fig. 4 due to the large ionic contribution in low frequency.

The experimental dielectric data were analyzed using Cole-Cole modified Debye theory [15]. According to this model, the angular frequency ω ($=2\pi$f; f is linear frequency), dielectric strength $\Delta\varepsilon = \varepsilon_S - \varepsilon_\infty$, ($\varepsilon_S$ is the static dielectric permittivity and ε_∞ is the high-frequency dielectric constant), and the relaxation time $\tau = 1/2\pi f_r$ (where f_r is the relaxation peak frequency) follow the dispersion equation, viz.

$$\varepsilon^* - \varepsilon_\infty = \frac{\Delta\varepsilon}{1 + (i\omega\tau)^{(1-\alpha)}} \tag{1}$$

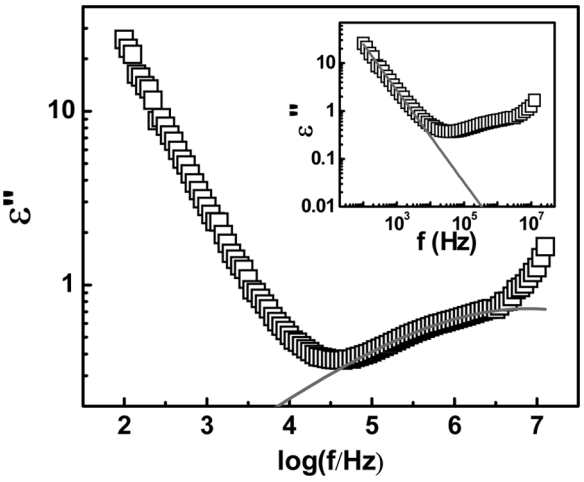

Figure 5. Frequency dependence of the real (ε') and imaginary (ε'') parts of dielectric permittivity in the induced B_1 phase at 100°C of R-BC sample. The solid line shows the Cole-Cole fitting. Inset shows the conductivity contribution of the free charges.

where the complex dielectric permittivity (ε^*) can be expressed as

$$\varepsilon^* = \varepsilon'(\omega, T) - i\varepsilon''(\omega, T) \tag{2}$$

T is the temperature and the parameter α measures the distribution of relaxation times ($0 \leq \alpha \leq 1$). $\alpha = 0$ represents a single relaxation time, whereas its higher values measure the extent of distribution of relaxation times. It is well known that the contribution of ionic conduction is higher at lower frequencies. Its frequency dependence can be expressed by the relation [8,16]

$$\varepsilon''(\omega) = \frac{\delta_0}{\varepsilon_0 \omega^{(1-S)}} \tag{3}$$

where δ_0 and S are fitting parameters. The power law exponent S is generally less than one, indicating a polaron hopping-type of conduction mechanism. It appears that the conductivity contribution covers all the processes. However, by considering conduction, a qualitative explanation of the relaxation mechanism is possible.

The spectra (Figs. 4 and 5) reveal ion dominance instead of Goldstone mode in the low-frequency ($\sim$100 Hz) regime and it is followed by a high-frequency absorption process. In both the figures, the symbols show the experimental data points and the solid line represents the respective Cole-Cole fitting in accordance with Eq. (1). The origin of the high-frequency absorption processes, observed in both the samples, has been explored in our subsequent discussion. As seen from the figures, the BC sample shows dielectric strength ($\Delta\varepsilon$) $\sim$ 12.92 and relaxation frequency (f_r) $\sim$ 73.59 kHz and $\alpha \sim 0.12$, whereas R-BC shows $\Delta\varepsilon \sim 5.08$ and relaxation frequency $\sim$7.66 MHz with $\alpha \sim 0.42$. Significant suppression of $\Delta\varepsilon$ and increment in f_r and α have been observed in R-BC in the induced B_1 phase in comparison with BC in the B_2 phase. However, the high value of α for R-BC indicates that there might be an overlapping of another low-frequency mode originating from strong antiferroelectric coupling in the mixed R-BC sample. The ionic conduction for both the samples has been estimated by fitting the ε''-f plot with Eq. (3) as shown at the inset of Figs. 4 and 5. The BC sample shows $\delta_0 \sim 1.53 \times 10^{-6}\,\Omega^{-1}\,\mathrm{cm}^{-1}$ and $S = 0.11$ and for R-BC $\delta_0 \sim 1.07 \times 10^{-7}\,\Omega^{-1}\,\mathrm{cm}^{-1}$ and $S = 0.04$. The earlier prediction of low ionic contribution in the R-BC sample compared to the BC sample is also evident from the fitting parameters.

Figures 6 and 7 show the temperature dependent dielectric strength ($\Delta\varepsilon$) and relaxation frequency (f_r) for the BC and R-BC sample, respectively. The notable reduction in $\Delta\varepsilon$ and significant increment in ν is found in the R-BC than that of the BC system. As discussed earlier, in R-BC, the effective chain length of the bent-core molecule decreases due to the addition of rod-like material, so the rotation around the long axis is somehow hindered in the B_2 phase of BC material. Due to more structurally favorable condition, in the B_1 phase the long axis rotation occurs in a higher frequency than in the B_2 phase of BC. The insets of Figs. 6 and 7 show ln $f_r - (1/T)$ plots of the corresponding samples. For the B_2 phase of pure BC, there is clear evidence from the figure (inset of Fig. 6) that the long axis rotation is influenced by a glass transition [17]. To verify the molecular dynamics, we fitted the experimental data with the Vogel-Fulcher-Tamman (VFT) equation [18]

$$\ln f_r = \ln f_0 + C/(T - T_0) \tag{4}$$

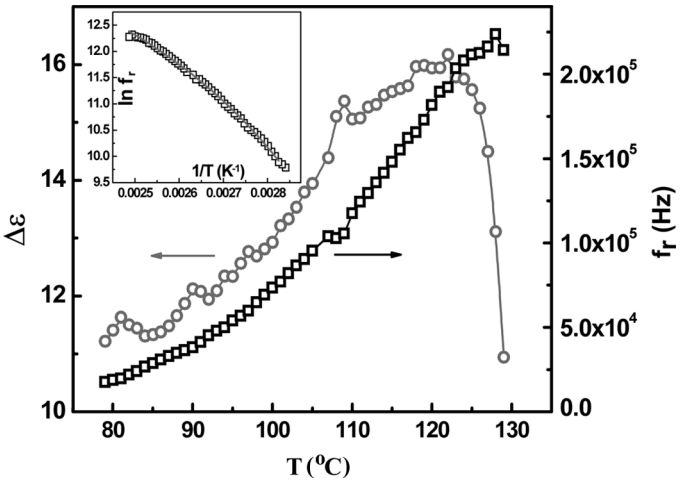

Figure 6. Temperature-dependent relaxation frequency (f_r) and dielectric strength of the relaxation processes observed in the B_2 phase of BC sample. Inset shows $\ln f_r - 1/T$ plot and the fitting according to VFT formula, indicating that the molecular motion is influenced by the glass transition process.

where $\ln f_0$ and C are constants and T_0 is the so-called Vogel temperature, which is characteristic for the molecular dynamics of glass-forming systems. However, for the observed induced B_1 phase of the mixed R-BC sample, the relaxation mode is found to be a noncollective type showing Arrhenius behavior with an activation energy $22.27\,\mathrm{kJK^{-1}mol^{-1}}$ (inset of Fig. 7), which is in accordance with other compounds having a B_1 phase [19].

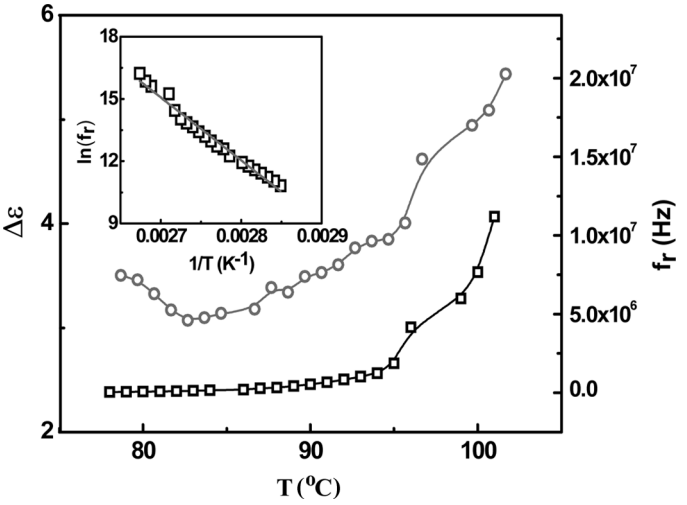

Figure 7. Temperature-dependent relaxation frequency (f_r) and dielectric strength of the relaxation processes observed in the induced B_1 phase of the R-BC sample. Inset shows $\ln f_r - 1/T$ plot and the fitting according to an Arrhenius formula, indicating that the molecular motion is influenced by the noncollective-type molecular process.

Conclusion

To conclude, we have performed a detailed dielectric study (10 Hz–13 MHz) of a bent-core liquid-crystalline material having a B_2 phase and its 17% mixture with a rod-like compound having a B_1 phase. We found a comparatively lower value of dielectric permittivity in R-BC than that of the BC material. This is attributed to the strong interaction of the rod-shaped and bent-core molecules in the mixture, which produces a more arranged antiparallel polarization direction. Also, the lower value of relaxation frequency of the long axis rotation mode in BC compared to that of R-BC has been ascribed to the lowering of effective molecular chain length in the mixture. The molecular dynamics of the process observed in the B_2 phase of the BC compound was found to be influenced by its glass behavior, whereas the corresponding process in the induced B_1 phase of the R-BC mixed compound was found to follow noncollective-type behavior.

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