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Dielectric spectroscopy of T-shaped blue-phase-III liquid crystal

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Dielectric relaxation spectra of a liquid crystalline (LC) material showing blue-phase-III (BPIII) for a considerably large temperature regime consisting of T-shaped molecules are investigated. A low frequency relaxation mode is observed in the isotropic phase (I) as well as in BPIII of the investigating material which is attributed to the short axis rotation of the T-shaped molecules. The outcome of the temperature and dc bias field variation of dielectric strength ($\Delta\varepsilon$) and relaxation frequency (ν_c) in the vicinity of the I-BPIII transition is also discussed. The temperature dependence of ν_c in BPIII with a minor deviation from Arrhenius activities in the fluctuation-dominated nonlinear region (FDNLR) is found to follow the unusual thermal behavior of the activation energy (E_A). The growth of pretransitional fluctuations is found to be nonlinear in the vicinity of the I-BPIII transition. A moderate growth of transition fluctuation commences from the value of the exponent $\alpha_{\text{eff}} = 0.38/^\circ\text{C}$, which is obtained by an exponential variation of ν_c with respect to temperature in BPIII. Observed dynamic phenomenon in the vicinity of the I-BPIII transition regions is explained on the basis of the Landau–de Gennes and Maier-Saupe Theories.

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I. INTRODUCTION

When an achiral nematic liquid crystalline (LC) material is heated, a direct nematic (N)-isotropic phase (I) transition is observed. In contrast to that, in many cholesteric LC materials, the changeover from the isotropic phase to a very short pitch chiral nematic phase (N^*) occurs through some transitions to intermediate structures collectively known as blue phases (BPs) [1,2]. Depending upon the imposed chirality within a cholesteric LC material, different BPs arise consecutively with increasing temperature in a very small temperature range of ~1 K between N^* and I. Usually the temperature range of stable BPs increases with the decrease of the cholesteric pitch of N^* [3]. BPs are believed to consist of double-twisted cylinders and are classifiable into three categories according to their symmetries: blue-phase-I (BPI) with body-centered-cubic symmetry, blue-phase-II (BPII) with simple cubic symmetry, and blue-phase-III (BPIII), which possesses the same symmetry as an isotropic liquid [4–9]. BPI and BPII are highly ordered: Their disclination networks form a regular cubic lattice, and their physics is well understood. In contrast, the BPIII structure has remained unresolved. Theorists have proposed that BPIII consists of double-twisted cylinders with arbitrary orientation [5,6]. Recently, Henrich *et al.* proposed that BPIII is an amorphous network of disclination lines, which is thermodynamically and kinetically stabilized over crystalline blue phases at intermediate chiralities [10]. Interestingly, BPIII exhibits amorphous behavior, whereas BPI and BPII have lattice periods of several hundred nanometers [11]. Their exotic structures and special properties such as optical activity, nonbirefringence, and selective visible range Bragg reflections forced them to lead in optoelectronic industries. But their narrow temperature range limits their practical applicability [8]. Therefore, stabilizing the BPs has recently attracted a great deal of consideration. Kikuchi *et al.* reported polymer stabilized BPs for which the temperature range of BPs is extended to more than 60 K in which switching with a speed of 10^{-4} s is attributed to the local reorientation of molecules by an electro-optic Kerr effect [12]. Coles and Pivenko have also widened the BP range, where BPI shows a wide color range of reflected color with switching in 10^{-2} s by applied electric fields because of electrostriction [13]. Yoshizawa *et al.* [14] extended the BPIII range of the order of 10 K in a pure T-shaped LC material by coupling between the molecular biaxialiy and chirality to stabilize the double-twisted structure. In these samples the applied field amplifies the nm-scale order of the twisted nematic organization in the BPIII to the μm-scale order of the nematic organization with a response time of the order of 10^{-2} s, with a markedly changed birefringence. Also these samples offer fast switching between a well black state of the BPIII and a homogeneous bright state of the induced N^* phase without surface treatment, which make them important from the viewpoint of their use in novel photonic applications [11,14–16].

The T-shaped molecular topology is expected to produce a characteristic effect since two different nonsymmetric molecular configurations coexist in a single molecule. This molecular architecture can be important for critical applications as they have the ability to form mesophases with a wider temperature range of functionality. LC physicists, chemists, and also technologists always desire to study the dynamics of LC molecular dipoles in the vicinity of isotropic to different mesophasic transitions. The isotropic to BPIII transition is one of the most

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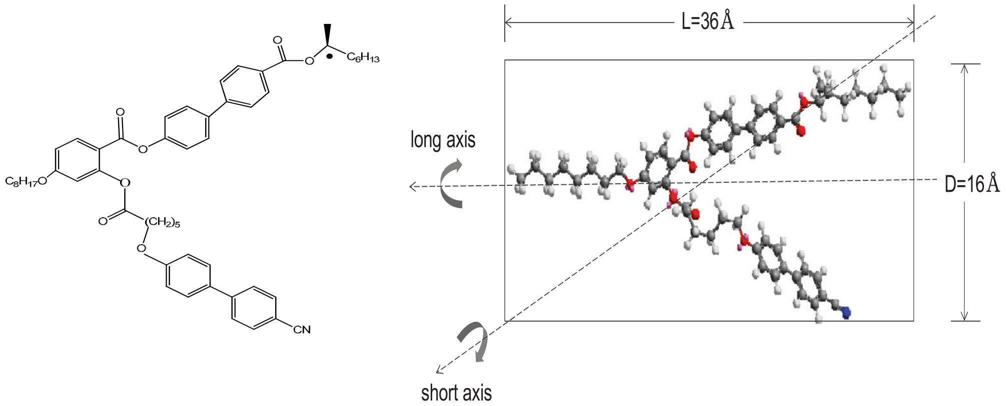

(a) (b)

FIG. 1. (Color online) (a) Molecular structure. (b) Different axes of the T-shaped board molecule with an L/D ratio of 2.25.

complex phase transitions to account for theoretically and as well experimentally. Chirality plays a somewhat fascinating role in terminating this peculiar transition to a critical point [17–19]. A high resolution calorimetric study manifests that the I-BPIII transition is of a first-order nature [20–23]. A detailed dielectric investigation in the vicinity of this first-order I-BPIII transition will eventually provide valuable information in relation to the molecular reorientational motion, relaxation frequencies (ν_c), activation energy (E_A), dielectric strength ($\Delta\varepsilon$), and distribution parameters. It is generally known that the dielectric parameters of the LC compound play an important role in the development of electro-optical devices. Frequency- and temperature-dependent dielectric investigations of BPs will give significant information about bulk properties, molecular parameters, their mutual association, and reorientational movements of dipolar groups, or a whole molecule under an externally applied electric field [24].

In this article we have reported the temperature, dc bias field, and frequency-dependent dielectric relaxation behavior involved in a typical BPIII compound having high chirality. For our study we have chosen the T-shaped LC material synthesized by Yoshizawa *et al.* which shows a stable BPIII for a considerably wide temperature range [14] .In our previous publication on the same sample we had already reported dielectric pretransitional behavior in the vicinity of the I-BPIII transition regime, which showed analogous behavior to that at the I-N transition regime [25]. In this article we discuss the fluctuation-dominated nonlinear regime (FDNLR) near the I-BP-III transition [26]. The results of dielectric relaxation studies are also presented here.

II. EXPERIMENT

The compound was prepared by introducing a polar group in a T-shaped pure LC material in order to couple the molecule with the external electric field. The fluidlike blue colored phase did not exhibit any platelets, indicating BPIII. The compound of our present investigation, viz., (S)-1-methylheptyl-4′-{4-octyloxy-2-{6-4-cyanobiphenyl-4′-yloxy]hexanoyloxy}benzoyloxy}biphenyl-4-carboxylate, has the chemical structure and minimum energy configuration as shown in Fig. 1. It shows the phase sequence (on cooling) as I 49 °C (0.4 kJ mol^{-1}) BPIII 41 °C (0.4 kJ mol^{-1}) N^*-10 °C glass phase; the melting temperature was 61 °C, which is well studied with differential scanning calorimetry (DSC) and optical microscopy measurements [14]. The main outcome of the above-mentioned phase progression is that BPIII exists for a temperature range of ~8 K, which is comparatively wider compared to other reported blue phases in different pure LC systems [7]. The sandwiched type cell of thickness 4.5 μm and active area ~12(4 × 3) mm^2 was prepared by indium-tin-oxide (ITO) coated glass plates (resistance ~50 $\Omega\,\mathrm{cm}^{-2}$) following the process discussed in our previous work [25,27]. Polyvinyl alcohol (PVA) was spin coated on the two glass substrates and baked at 140 °C for 2 h. Homogeneously aligned cells were obtained by rubbing two substrates with a soft cloth in one direction. Mica spacers were used to maintain a uniform cell gap. First the empty cell was calibrated by using air and toluene as standard references. The cells were filled with the investigating compound in its isotropic phase by capillary action. To get better alignment of the molecules, the cell was subjected to a slow cooling process. The temperature of the measuring sample cell was controlled by using a Mettler FP82 hot stage along with a Mettler FP90 controller with an accuracy of ±0.1 °C. A computer controlled HP4192A impedance analyzer (frequency range 10 Hz–13 MHz) was used for dielectric measurements. The capacitance of the empty cell was found to be constant with increasing temperature. The loss exhibited by the empty cell was found to exhibit no peak in the above-mentioned frequency range. This firmly indicates that neither the conductive coating of the cell plates nor any trace level impurities in the cell exhibit any relaxation in this frequency range.

III. RESULT AND DISCUSSIONS

Frequency-dependent complex dielectric permittivity $\varepsilon(\omega,T)$ is given by

$$\varepsilon(\omega,T) = \varepsilon'(\omega,T) - i\varepsilon''(\omega,T), \tag{1}$$

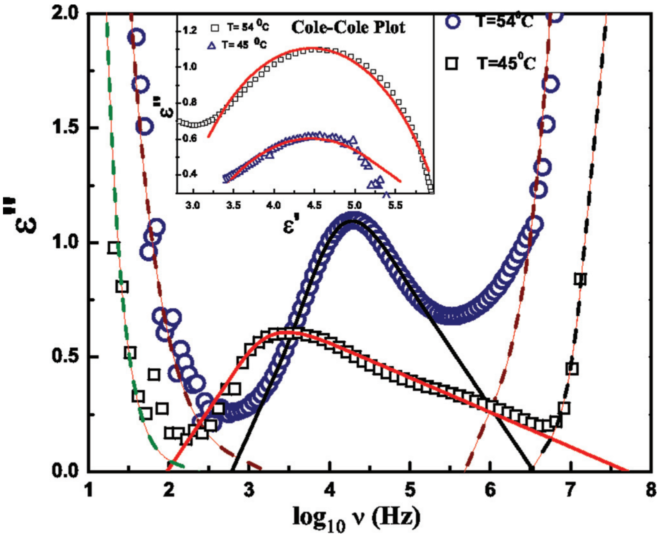

FIG. 2. (Color online) Frequency dependence of the real (ε') and imaginary (ε'') parts of the complex dielectric permittivity in BPIII at $T = 45\,^{\circ}\mathrm{C}$ and in the isotropic phase at $T = 54\,^{\circ}\mathrm{C}$. The frequency is measured in Hz units. The dotted lines show the conductivity contribution of free charges and ITO contributions, with the fitting parameters $\sigma_0 = 4.06 \times 10^{-8}\ \Omega^{-1}\,\mathrm{cm}^{-1}$, $n = 2.12$ (for BPIII), $\sigma_0 = 6.29 \times 10^{-9}\ \Omega^{-1}\,\mathrm{cm}^{-1}$, $n = 1.14$ (for isotropic), and $A = 2.29 \times 10^{-15}$, $m = 2.05$ (for BPIII), $A = 2.88 \times 10^{-8}$, $m = 1.16$ (for isotropic). The solid line shows the Havriliak-Negami fits. The inset shows the Cole-Cole plot with one relaxation phenomenon.

where $\varepsilon'(\omega,T)$ and $\varepsilon''(\omega,T)$ are the real and imaginary parts of the dielectric constant, respectively, ω is the angular frequency, and T is the absolute temperature of the medium. The dielectric spectra of this T-shaped LC material at $45\,^{\circ}\mathrm{C}$ (in BPIII) and at 54°C (in the isotropic phase) are shown in Fig. 2, which has been taken during slow cooling from the isotropic phase. The materials show clearly a single molecular relaxation process in BPIII and an isotropic phase for the probing field applied parallel to the director, as shown in Fig. 2. The ultralow frequency regime of the dielectric spectra is found to be dominated by the ionic charges, whereas in the high frequency part, contribution from the cell relaxation process has been detected. To define the relaxation mechanism present in BPIII of a T-shaped LC material, the experimentally observed pronounced relaxation spectra are conformed to the Havriliak and Negami equation, given by [28]

$$\varepsilon(\omega,T) - \varepsilon_\infty = \sum_k \frac{\Delta\varepsilon_k}{[1 + (i\omega\tau_k)^{\beta_k}]^{\alpha_k}} - i\frac{\sigma_0}{2\pi\varepsilon_0 f^n} - iAf^m, \tag{2}$$

where ε_∞ is the high frequency limit of dielectric permittivity, $\Delta\varepsilon_k$ is the dielectric strength, and τ_k is the relaxation time of the kth absorption process. The characteristic relaxation frequency of the corresponding mode is defined as $\nu_c = 1/2\pi\tau_k$. The exponents α_k and β_k are the symmetric and asymmetric broadening parameters, respectively.

Depending on the values of these broadening parameters, Eq. (2) reduces to a Debye equation (for $\alpha_k = \beta_k = 1$), a Cole-Cole equation (for $\alpha_k = 1,\ 0 < \beta_k \leqslant 1$) [29], and a Cole-Davidson equation (for $0 < \alpha_k \leqslant 1;\ \beta_k = 1$) [30]. The second term of Eq. (2) represents the contribution from the ionic impurity present in the cell. The origin of the ion charges of different polarities lies within the cell manufacturing process as well as in the mesogenic material used intrinsically. σ_0 is the ohmic conductivity, ε_0 is the dielectric constant of the vacuum, and n is a fitting parameter. It is well known that in cells made of ITO coated glass plates a spurious signal appears in the MHz range with a frequency significantly dependent on sample thickness and resistance of the ITO layers. The unwanted signal overlaps with the real relaxation process present in the investigating material, but can be eliminated from the dielectric spectrum during a fitting procedure with the third term appearing in Eq. (2), where A and m are fitting parameters.

The left hand side dotted lines in Fig. 2 are the Havriliak-Negami fitting curves for the very low frequency spectra with the fitting parameters $\sigma_0 = 4.06 \times 10^{-8}\ \Omega^{-1}\,\mathrm{cm}^{-1}$, $n = 2.12$ (for BPIII), and $\sigma_0 = 6.29 \times 10^{-9}\ \Omega^{-1}\,\mathrm{cm}^{-1}$, $n = 1.14$ (for the isotropic phase), suggesting a significant presence of conducting ions inside the cell. A sharp relaxation mode has been observed at frequency 2.2 kHz in BPIII and 19.9 kHz in the isotropic phase. The prominent BPIII relaxation mode with $\Delta\varepsilon = 5.6$, $\alpha_k = 1$, and $\beta_k = 0.16$ suggests a Cole-Cole type relaxation for BPIII of the T-shaped LC material. The Cole-Cole plot for a single relaxation is shown in the inset of Fig. 2. The higher frequency spectra have been found to be dominated by the contribution from the ITO layer as well as the alignment layer on it. The right hand side solid line is the theoretical Havriliak-Negami fitting curve with parameters $A = 2.29 \times 10^{-15}$, $m = 2.05$ (for BPIII), $A = 2.88 \times 10^{-8}$, $m = 1.16$ (for the isotropic phase). The dynamics of the I-BPIII transition is one of the most complex phenomena to consider theoretically as well experimentally. Interestingly, earlier we have observed a dielectric pretransitional behavior in the vicinity of the I-BPIII transition [25].

To understand the origin of the relaxation mode and the dynamics of order parameter fluctuation in the vicinity of the I-BPIII transition, it is important to study in detail the temperature and also the bias field dependence of ν_c and $\Delta\varepsilon$. These parameters have been obtained by fitting the experimental spectra with Eq. (2). Here Fig. 3 depicts the temperature-dependent behavior of ν_c and $\Delta\varepsilon$ both in the isotropic phase and BPIII for a temperature range of 42–60 °C. The observed BPIII relaxation frequencies increase with an increase in temperature and they reach their maximum value at the I-BPIII transition temperature ($T_{I\text{-BPIII}}$), suggesting the first-order nature of the I-BPIII transition [27]. Earlier Thoen *et al.* had shown that BPIII transformed into an ordinary isotropic liquid phase by a first-order transition with a transition enthalpy $\Delta H \approx 0.17\ \mathrm{kJ/mol}$ for cholesteryl nonanoate [21]. This value is of the same order of magnitude as those obtained for normal nematic isotropic transitions. From DSC data for the present I-BPIII transition with a transition enthalpy $\Delta H \approx 0.4\ \mathrm{kJ/mol}$, it is reminiscent of a first-order nature, setting aside other possibilities for continuous transitions [17–19]. From Fig. 3 it is clear that the relaxation time of the BPIII dipoles starts to decay with increasing temperature towards $T_{I\text{-BPIII.}}$ These decaying relaxation times converge to a finite value at $T_{I\text{-BPIII}}$ and indicate a fluctuation region before the isotropic phase. An intense observation of Fig. 3 depicts a strong

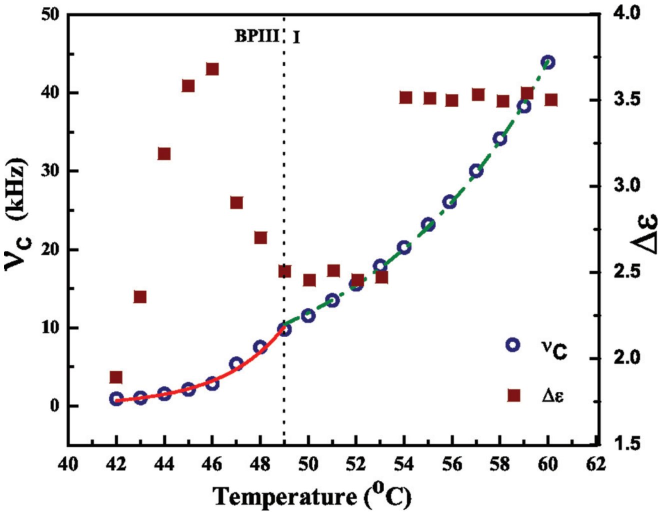

FIG. 3. (Color online) Temperature dependence of the dielectric strength ($\Delta\varepsilon$) and the relaxation frequency (ν_c) in the vicinity of the I-BPIII transition. Solid lines show the fitting to Eq. (3) separately in two phases. The fitted values of α_{eff} are 0.13/°C (for isotropic) and 0.38/°C (for BPIII).

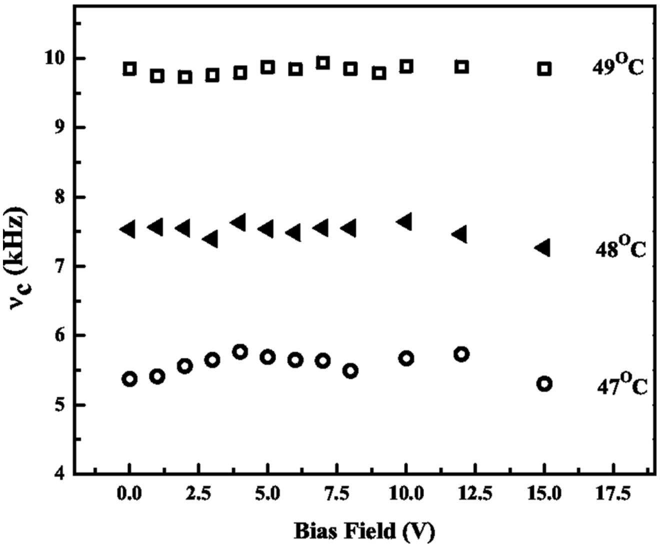

FIG. 4. Bias field dependence of the relaxation frequency (ν_c) in BPIII at different temperatures.

nonlinear decreasing behavior of the relaxation frequency with decreasing temperature, which becomes almost linear in the stable BPIII phase (42–46 °C).The BPIII ordering starts to decay near $T_{I\text{-BPIII}}$ and fluctuation dominates in the nonlinear region The strength of this nonlinear growth of translational fluctuations observed in the fluctuation-dominated nonlinear regime (FDNLR) is estimated by fitting the observed data of the relaxation frequency to the relation [26]

$$\nu_c(T) = A\exp(\alpha_{\text{eff}}T), \tag{3}$$

where $\nu_c(T)$ is the observed relaxation frequency (in kHz) at any arbitrary temperature within BPIII. It is noticed that the thermal span (∼3 K) of the present FDNLR near the I-BPIII transition is rather large in comparison to the other nematic LC of the I-N transition. Apart from exhibiting pretransitional activities, the existence of a large FDNLR in the investigated compound is attributed to the present commencement of pretransitional fluctuations and the existence of a cyano group at the tail of the T-shaped molecule of the LC material [26]. Fitting the experimental data in the BPIII with Eq. (3) gives $\alpha_{\text{eff}} = 0.38/°\text{C}$. This is a distinctive value with which the pretransitional fluctuations exponentially grow and converge to a finite value to implement a first-order I-BPIII transition. This value of α_{eff} reflects the rather moderate nature of growth of pretransitional fluctuations before the I-BPIII transition is reached. In BPIII, with decreasing temperature in the FDNLR, $\Delta\varepsilon$ increases sharply and reaches its maximum value at $T = 46$ °C. With a further reduction of temperature, the value of $\Delta\varepsilon$ falls from its peak value at $T = 46$ °C. For LC materials, if one neglects the librational movements, the molecular dynamics can be described in terms of the following three modes: (i) the rotation of the molecules around its short axis (ω_1), (ii) the molecular precessional motion about the director n (ω_2), and (iii) the rotation around the long molecular axis (ω_3) [31]. The experimental observations are in good agreement with the following relation: $\omega_1 < \omega_2 < \omega_3$. In the present investigation, however, we discard the molecular mode due to the rotation of molecules about the long axis under a planar alignment, as in that case the corresponding relaxation frequency would be in the MHz order. Usually the nematic potential causes the long range orientational order and hinders the rotation of the molecules around the molecular short axis [32]. To understand the behavior of this relaxation mode, we have further investigated the bias field dependence of ν_c in Fig. 4, at three different temperatures in BPIII. It has been found that the relaxation frequencies remain invariant with the applied dc bias. To become more elemental about this mode, we have performed a similar bias dependence of $\Delta\varepsilon$ also in Fig. 5 in BPIII at the same temperatures to find any relevant consistency with ν_c. From these two figures, it is comprehensible that both

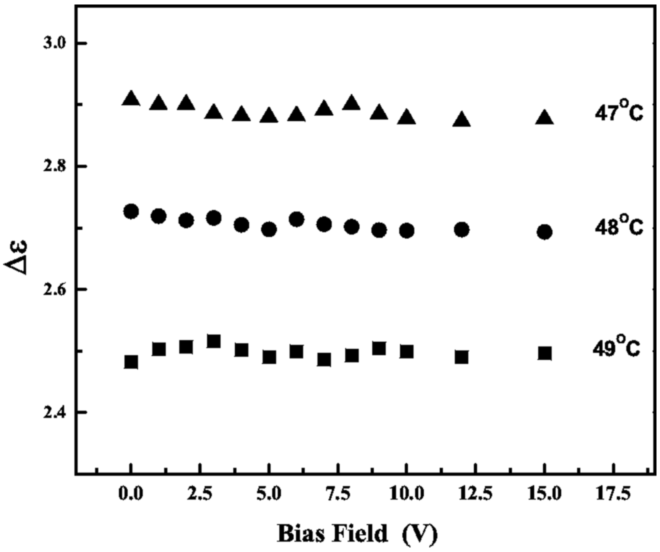

FIG. 5. Bias field dependence of the dielectric strength ($\Delta\varepsilon$) in BPIII at different temperatures.

ν_c and $\Delta\varepsilon$ are independent of applied bias. As $\Delta\varepsilon$ of molecular processes should be bias field independent, so the origin of this mode here is confirmed to originate due to the rotation of the T-shaped molecules about their molecular short axis [33,34]. In order to identify the short axis, the molecular structure was obtained by semiempirical calculations using MOPAC-6/PM3 [Fig. 1(b)]. The T-shaped molecule is thought to have an L/D ratio of 2.25, which is smaller than that of a conventional rodlike liquid crystal. Both realistic long and short axes are inserted in the figure.

The temperature $T_{I\text{-BPIII}}$ obtained from the dielectric spectra coincides almost perfectly to that found from the previous calorimetric studies [14,25]. The characteristic loss peak with ν_c varying in the range 1.12–48.9 kHz has been observed in this comparatively wide BPIII and in the isotropic phase. The presence of a moderate FDNLR composes this interesting result in a large scale and motivates us to explore the temperature dependence of the activation energy (E_A) near $T_{I\text{-BPIII}}$. In LC devices the relaxation time (τ) is of extreme importance, which further depends on the cell gap, the degree of molecular alignment, and many other parameters. Also, the application of high voltage can effectively change τ and all these properties depend on E_A. Note that E_A plays a crucial role in many device applications. Therefore, E_A can be calculated using the following Arrhenius relation [35],

$$\ln\tau(T) = \ln\tau_A + \frac{E_A}{RT}, \tag{4}$$

where the dependence of $\ln\tau(T)$ on T^{-1} is linear, τ is the relaxation time, τ_A is the preexponential factor, R is the universal gas constant, and T is the absolute temperature. Figure 6 represents the temperature dependence (in the form of an Arrhenius plot) of τ corresponding to the molecular rotation around the molecular short axis in the isotropic phase of the T-shaped molecule. For rotating molecules with the dipole moment directed, more or less, along their long axis, as in the case of the compound studied, the dielectric absorption band corresponding to the above-mentioned mode of rotation dominates in the spectrum and the evolution of τ is quite reliable. This plot is satisfactorily fitted to Eq. (4) and the value of E_A obtained from fitted parameters in the isotropic phase is 118.89 kJ/mol. Figure 7 shows the variation of ln(τ) with the inverse temperature in the isotropic phase as well as in BPIII separately. This plot clearly manifests the ever expected proper linear thermal variation of ln(τ) in the isotropic phase. Interestingly, the natural logarithm of the relaxation time for a short axis rotation of T-shaped BPIII molecules slightly deviates from linearity, especially in the FDNLR, and a curved line follows in this FDNLR by going through all the points. So this FDNLR surely carries salient features. Both in the isotropic phase and BPIII, the experimental data points are fitted to Eq. (4) to extract the value of E_A separately by using Arrhenius' law. We obtain E_A in the isotropic phase as 119.63 kJ/mol, which is almost the same as the previously obtained value from our earlier fitting. Similarly in BPIII we find $E_A = 302.02$ kJ/mol. Yoshizawa *et al.* had measured $E_A = 483$ kJ/mol in BPIII of this sample using the Arrhenius formula by the rotational viscosity measurement technique [14]. From the Arrhenius formula, the derivative $\partial \ln\tau(T)/\partial T^{-1}$ gives directly a value of E_A, at a given temperature. Thus, one can analyze the temperature behavior of E_A [36]. Generally, it is assumed that E_A should be temperature independent. However, there is no physical reason to assume a constant E_A for the LC material, as the basic physical properties, the number density, etc., are all temperature dependent. So with a decrease of temperature one should expect an increase of E_A rather than a constant value.

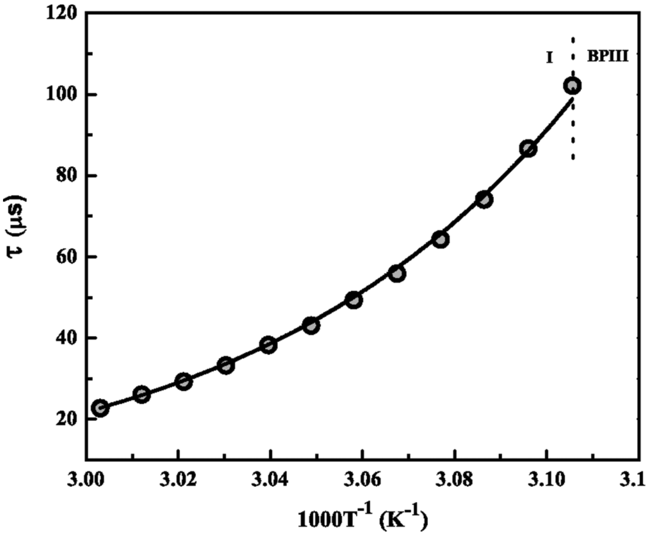

FIG. 6. Arrhenius plot for the dielectric relaxation time (τ) corresponding to the molecular rotation around the short axis measured in the isotropic phase. The solid line shows the fitting to the relaxation time data to Eq. (4) in the isotropic phase. The fitting parameters gives $E_A = 118.89$ kJ/mol for the isotropic phase.

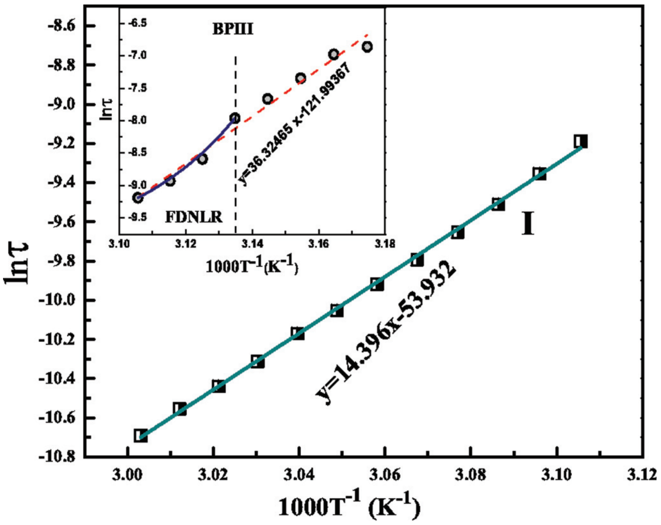

FIG. 7. (Color online) Fitting of the $\ln\tau$ vs $1000/T$ graph according to Eq. (4) of the Arrhenius formula. Fitting parameters in the isotropic phase give $E_A = 119.63$ kJ/mol. The inset shows the Arrhenius fitting in BPIII also, though a slight nonlinearity is there in FDNLR. A curved line follows through the data points in the FDNLR. The fitted parameters give $E_A = 302.02$ kJ/mol in BPIII.

Figure 8 manifests an unusual thermal behavior of the activation energy in the vicinity of the I-BPIII transition

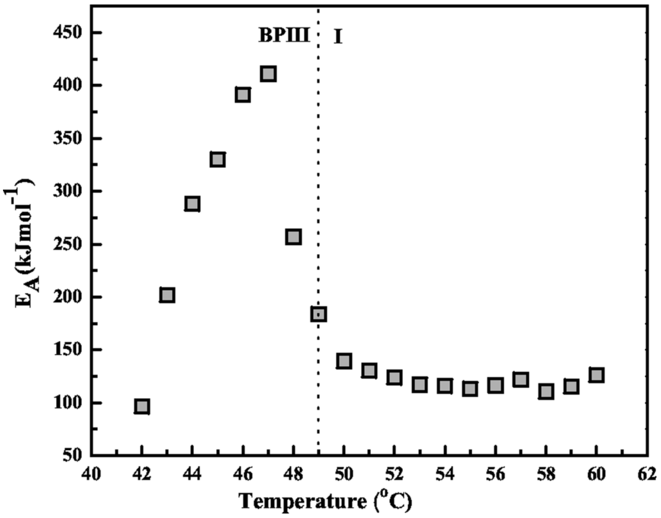

FIG. 8. Temperature dependence of the activation energy (E_A) for the rotation of molecules around the molecular short axis in BPIII and the isotropic phase.

region. When the temperature increases to the transition point ($T_{I\text{-BPIII}}$), E_A of the rotating molecules around the molecular short axis shows a significant change. Most interestingly, this behavior of E_A is remarkable in the FDNLR of width 46–49 °C, and it is analogous to the temperature dependence of the critical dielectric permittivity behavior due to the presence of the dielectric pretransitional anomaly [25,37,38]. Here also E_A increases sharply to avail the peak and falls gradually in the FDNLR. A similar decaying nature is attributed from Fig. 3, where the dielectric strength falls off in the same fashion. But the most frequent situation appears near the chiral nematic phase, where E_A decreases with a decrease of temperature though the relaxation time shows Arrhenius activities. This conflicting thermal analysis draws unique attention. The unusual temperature dependence of E_A in Fig. 8 suggests that different modes of rotation around the short axis can exist in BPIII. Generally a rodlike molecule has the highest symmetry long axis around which the molecule rotates freely. One distinguishable short axis lies perpendicular to the long axis. With the introduction of chirality to a nematic rodlike molecule, the helical axis forms along the short axis in the chiral nematic phase. In contrast, a board molecule might have two distinguishable axes, as shown in Fig. 9. Coupling between chirality and the two short axes might induce a biaxial helix that can stabilize double-twisted structures. The T-shaped molecule is thought to be a board molecule, as shown in Fig. 1(b). The T-shaped compound with a molecular biaxiality can have two short axes. Therefore, the T-shaped compound shows the stable BP. The present results support the hypothesis that the T-shaped compound has two different short axes, which might induce a biaxial helix. So we have wait for future investigations to explain these curiosities.

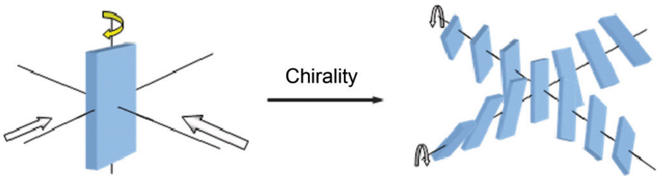

FIG. 9. (Color online) Double-twisted structures of a T-shaped board molecule.

IV. CONCLUSIONS

The temperature- and electric-field-dependent dielectric relaxation behavior of a comparatively wide range T-shaped BPIII LC material, viz., (S)-1-methylheptyl-4′-{4-octyloxy-2-{6-4-cyanobiphenyl-4′-yloxy]hexanoyloxy}benzoyloxy}biphenyl-4-carboxylate, has been investigated. The characteristic changes in ν_c and $\Delta\varepsilon$ of the short axis rotation mode in BPIII have been observed. The dielectric spectroscopic analysis reveals the presence of a characteristically significant FDNLR, and the value of the fitting parameter $\alpha_{\text{eff}} = 0.38/°\text{C}$ in BPIII indicates a moderate growth of the transition fluctuation across the I-BPIII transition region. The thermal variation of the characteristic frequency (ν_c) of the relaxation process in BPIII is found to be slightly off centered from Arrhenius activities in the FDNLR. The obtained value of the activation energy is found to be in good agreement with the previously given value by Yoshizawa *et al.* However, the temperature dependence of E_A shows an interesting critical behavior in the whole BPIII region, especially in the prenematic region, where it falls down strangely with decreases of temperature. However, further detailed investigations in BPIII are necessary for understanding the results obtained so far and to find other relaxation modes, if any.

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