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Electric-field-induced switchable dark conglomerate phases in a bent-core liquid crystal exhibiting reverse columnar phases

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Electric-field-induced transitions into switchable dark conglomerate (DC) phases from two types of reverse columnar mesophases have been observed in the bent-core (BC) compound 2,7-naphthylene bis[4-(3-methyl-4-*n*-tetradecyloxybenzoyloxy)] benzoate. Optical and x-ray studies show that the higher temperature columnar phase corresponds to the orthogonal $B_{1\text{rev}}$ phase, whereas the lower temperature columnar phase is a variant of the $B_{1\text{revtilt}}$ phase. As the layer fragments in this phase are modulated in order to relieve the steric hindrance caused by an anticlinic tilting in adjacent blocks, it has been named $B_{1\text{revtiltM}}$. The shape of the chiral domains are different in the DC phases viz. DC-$B_{1\text{rev}}$ and DC-$B_{1\text{revtiltM}}$ obtained by applying the electric field in the $B_{1\text{rev}}$ and $B_{1\text{revtiltM}}$ phases, respectively. While the chiral domains in the DC-$B_{1\text{rev}}$ phase appear similar to those observed in other DC phases, the shape of the domains in the DC-$B_{1\text{revtiltM}}$ phase appear to have some similarity to the domains in the banana leaf texture in the $B_{1\text{revtiltM}}$ phase implying that the detailed structure in this DC phase may be different. Optical observations, electro-optics, and dielectric studies show that the DC-$B_{1\text{rev}}$ and DC-$B_{1\text{revtiltM}}$ phases are both switchable and possess a local $\text{SmC}_\text{S}\text{P}_\text{F}$ type of structure. As the temperature is decreased the switching behavior changes from ferroelectric to antiferroelectric. The temperature at which this changeover starts occurring coincides with the temperature at which the layer modulation occurs to overcome anticlinic tilt and the $B_{1\text{rev}}$ to $B_{1\text{revtiltM}}$ phase transition takes place without the application of the electric field. The change in switching behavior is attributed to a transformation into flat layers with the $\text{SmC}_\text{A}\text{P}_\text{A}$ type of structure as also evidenced by the nucleation of bright regions alongside the chiral domains.

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I. INTRODUCTION

Bent-core liquid crystals are ideal systems for understanding the interplay of chirality and polarity in generating novel phase structures and interesting physical properties. These liquid crystals are known to exhibit a rich variety of both lamellar and columnar phases in which the polarization vectors, tilt directions, and the chiral sense from layer to layer combine in several different ways [1,2]. The B_2 (SmCP) phase, which is one of the earliest well-characterized phases formed from BC molecules, has a lamellar structure with polar ordering in each layer and molecular tilt about the arrow axis resulting in layer chirality and exhibits electro-optic switching behavior. The interlayer ordering can be ferro- or antiferroelectric and the orientation of the molecules can be either synclinic or anticlinic between the adjacent layers. Variants of the SmCP phase are designated by the general formula $\text{SmC}_{\text{S,A}}\text{P}_{\text{F,A}}$ where the subscripts S and A of C stand for synclinic and anticlinic orientations and subscripts F and A of P for ferroelectric and antiferroelectric forms. In the $\text{SmC}_\text{S}\text{P}_\text{A}$ and $\text{SmC}_\text{A}\text{P}_\text{F}$ types the layer chirality alternates from layer to layer and the structure is racemic, whereas in the $\text{SmC}_\text{A}\text{P}_\text{A}$ and $\text{SmC}_\text{S}\text{P}_\text{F}$ types the structure is homochiral. BC molecules can also arrange themselves in columns and give rise to two-dimensionally periodic structures. In the most common type of columnar phase called the B_1 phase, the density modulation is in the plane parallel to the polarization vector and the phase is nonswitchable. When the density modulation is in a plane orthogonal to the polarization vector, reverse columnar phases are obtained. These phases are switchable and can consist of either nontilted or tilted layers and are designated as $B_{1\text{rev}}(\text{col}_\text{r})$ and $B_{1\text{revtilt}}(\text{col}_\text{ob})$ [3], respectively. Bent-core molecules are also known to form mesophases like the dark conglomerate phase with macroscopic chirality [4]. Detailed freeze fracture TEM studies by Hough *et al.* have shown that in this mesophase the layer spacing of the lamellar structure is preserved but there is disorder on a longer length scale and saddle splay layer deformation. This leads to an optically isotropic texture that appears dark between crossed polarizers. Two types of chiral domains are revealed only on rotation of the analyzer by a few degrees from the crossed position, with one type appearing slightly brighter than the other. Usually in a typical homologous series of symmetric bent-core molecules the SmCP types of phases are exhibited by compounds with longer alkyl chain lengths, whereas the columnar B_1 types of phases are exhibited by compounds with shorter alkyl chain lengths. However, there have been few reports of lamellar phases like the $\text{SmC}_\text{S}\text{P}_\text{F}$ occurring in the middle members of certain fluorine substituted compounds [5]. We have recently reported detailed studies on vitrified states formed from the lamellar dark conglomerate (DC) phase in middle members of a homologous series made of bent-core molecules derived from 2,7-dihydroxynaphthalene and having alkyl chain lengths $n = 11$ to 13 [6]. Usually the compounds with BC molecules exhibit either the columnar or lamellar phases in the same compound and a phase transition from a columnar phase into a lamellar type of phase with variation of temperature is very rare [7,8]. An electric-field-induced transition from the B_1 phase to a SmCP type of phase exhibiting an antiferroelectric switching behavior has been observed at sufficiently high applied fields $\sim 30\ \text{V}/\mu\text{m}$ [9]. However, on removal of the field,

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the B_1 structure is recovered. Field-induced lamellar phases SmC_SP_F and M_x have been observed to be formed from ferro- (col_{rF}) and antiferroelectric (col_{rAF}) columnar phases [10]. An electric-field-induced change from the B_1 phase into a texture with small randomly oriented domains that switch between dark and bright states, has been attributed to a possible transition into a SmCP phase [11].

The effect of an electric field in producing chiral segregation has been reported earlier in liquid crystals made of both rod-shaped and bent-core molecules. For example, electric-field-induced chiral separation into homochiral and racemic states has been reported in a compound made of achiral bent-core molecules [12]. Macroscopic conglomerate domain formation under applied electric fields has been demonstrated using a ferroelectric liquid crystal made of rod-like molecules [13]. Transformation of a fan-shaped texture exhibited by a tilted smectic phase made of achiral bent-core molecules into a texture composed of chiral domains which switch between states of opposite chirality has been observed [14].

We now report on electric-field-induced transitions into DC phases from reverse columnar phases in a bent-core compound. Before the application of the electric field the columnar phases were first studied in detail. Optical and x-ray studies show that the higher temperature columnar phase is nontilted and corresponds to the orthogonal B_{1rev} phase with a *cmm* rectangular lattice. As the temperature is decreased the layer fragments become modulated in order to relieve the steric hindrance caused by an anticlinic tilting in neighboring blocks and a phase transition into another type of columnar phase occurs. The structure conforms with a noncentered rectangular *pmm* lattice. In further discussion the lower temperature columnar phase is designated as $B_{1revtiltM}$ where the subscript revtiltM indicates that this phase with a modulated structure is different from the $B_{1revtilt}$ phase which also has tilted molecules, but with an oblique lattice. Depending on whether the field is applied in the B_{1rev} phase or $B_{1revtiltM}$ phase, two types of DC phases viz. DC-B_{1rev} and DC-$B_{1revtiltM}$ are obtained. The shape of the field-induced chiral domains is different in the two DC phases, however, the sample appears completely dark between crossed polarizers in both cases. While the shape of the chiral domains in the DC-B_{1rev} phase appears similar to what is usually observed, the shape of domains in the DC-$B_{1revtiltM}$ phase has some similarity to the domains of the banana leaf texture in the $B_{1revtiltM}$ phase. This suggests that the detailed structure in this phase may be different from other DC phases. To the best of our knowledge this is the first observation of such a DC phase. Optical observations, electro-optic, and dielectric studies show that both the DC phases are switchable and possess a local SmC_SP_F type of structure in the higher temperature range. The switching behavior changes from ferroelectric to antiferroelectric type as the temperature is decreased in both the DC phases. The temperature at which this changeover starts occurring, coincides with the temperature at which the B_{1rev} to $B_{1revtiltM}$ phase transition takes place in the absence of an applied field. This shows that the change in the switching behavior is therefore related with the tendency for anticlinic tilting which was not feasible in the columnar phase but is possible in the field-induced lamellar DC phases. A corresponding transformation into flat layers with a SmC_AP_A type of structure can be observed in the form of bright regions that nucleate in the DC texture.

II. EXPERIMENTAL

The compound used in the present study belongs to a series of symmetric bent-core compounds consisting of a central naphthylene core derived from 2,7- dihydroxynaphthalene with methyl groups present in the terminal rings at the *ortho* position with respect to the alkyl chains [15]. In this series, compounds with alkyl chain length $n < 11$ exhibit the nonswitchable B_1 columnar phase and compounds with $n > 12$ exhibit reverse columnar phases. The middle homologs with $n = 11$ and 12 exhibit DC lamellar phases. We recently reported the occurrence of a special type of vitrified state obtained on cooling the lamellar DC phase of the 11th ($n = 11$) homolog of the same series [6]. The compound used in the present study is the 14th homolog ($n = 14$) of the series and is 2,7-naphthylene bis[4-(3-methyl-4-*n*-tetradecyloxybenzoyloxy)] benzoate (NMTBB). The molecular structure of NMTBB is shown in Fig. 1.

The sequence of phase transitions exhibited by NMTBB, were initially characterized by optical microscopy. The optical texture exhibited by the compound was studied in cells with different boundary conditions under a polarizing microscope (Leitz Ortholux Pol BK) by placing the sample in a hot stage (Mettler FP 82). A polyimide coated cell (Cell A) with patterned electrodes and thickness of 9 μm (Instec) was used for studies under planar boundary conditions. A locally constructed cell made of patterned glass plates treated with octadecyltriethoxy silane (ODSE) was used to obtain the circular domain texture (Cell B). The phase transitions were also studied by differential scanning calorimetry (Perkin Elmer Pyris ID). X-ray diffraction studies were carried out using Cu K_α radiation from a rotating anode generator (Rigaku Ultrax 18) and an image plate (Marresearch). The ac square and triangular-wave electric fields were generated using an arbitrary waveform generator (Agilent 33220A) along with a high voltage amplifier (Trek Model 601 C). The current response was monitored using an oscilloscope (Agilent 54621). The dielectric parameters were studied both as functions of temperature and frequency, using an Alpha A high performance dielectric analyzer (Novocontrol Technologies) coupled with a temperature controller (Eurotherm, series 2000). Electric fields required to induce the DC-B_{1rev} and DC-$B_{1revtiltM}$ phases from the reverse columnar phases before carrying out the dielectric studies, were generated by using a high voltage booster HVB-300 (Novocontrol Technologies) along with the Alpha A unit.

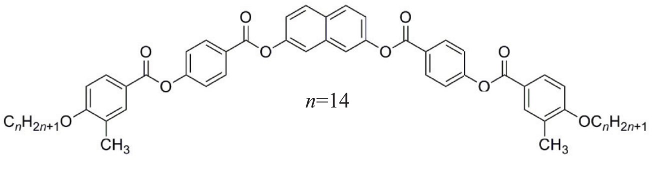


FIG. 1. Molecular structure of the compound NMTBB.

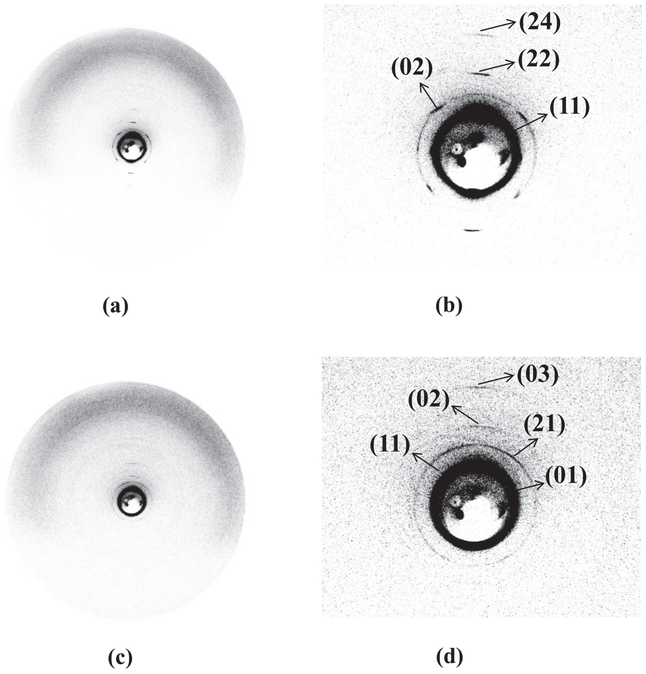
III. RESULTS AND DISCUSSION

A. Optical observations

When the sample taken in the polyimide coated cell (Cell A) was observed between crossed polarizers as it is cooled from the isotropic phase, a bright colorful smooth banana leaflike texture which is often obtained for reverse columnar phases, appears at 132 °C [Fig. 2(a)]. On decreasing the temperature, at 118 °C the banana leaflike domains start appearing broken [Fig. 2(b)], though the overall features of the columnar texture remain. Some domains appear to have a patchy dark appearance but complete extinction cannot be obtained within these domains by rotation of the sample between crossed polarizers. In some other domains the patchy dark appearance can be obtained by rotation of the sample by ∼7 deg. This indicates that the molecules tilt at 118 °C. On decreasing the temperature further the texture remains without any further significant changes down to crystallization. In the cell whose plates have been treated with ODSE (Cell B), circular domains with extinction brushes along and perpendicular to the polarizers can be observed [Fig. 2(c)]. At 118 °C, corresponding to the temperature at which the banana leaf texture develops a broken appearance, very fine concentric fringes form within the circular domains. However, no change in the orientation of the dark brushes could be observed and they remain parallel and perpendicular to the polarizers [Fig. 2(d)].

B. X-ray diffraction studies

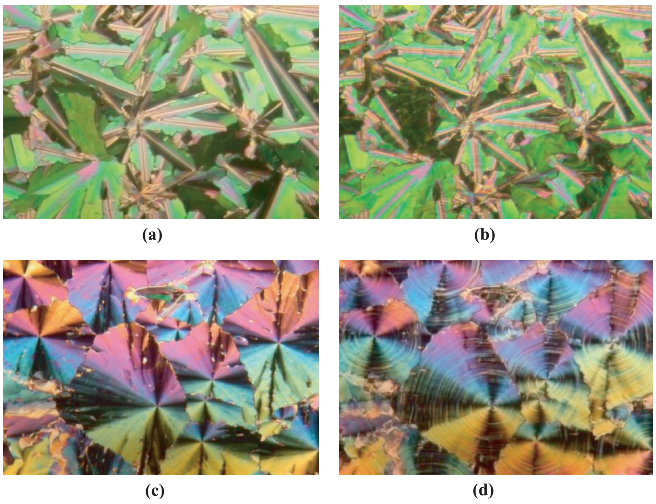
X-ray diffraction studies were carried out on a surface aligned sample mounted as an open drop on a glass plate, with the x-ray beam incident at grazing angle. The diffraction patterns were obtained at 125 °C and 116 °C corresponding to the temperatures at which textural differences could be clearly observed by optical studies. The diffraction patterns are shown in Fig. 3. At 125 °C the diffraction pattern shows that the sample is reasonably well aligned. The observed spacings from the diffraction pattern could be indexed as reflections from a two-dimensional centered rectangular lattice (*cmm*) with lattice parameters **a** = 55.5 Å and **b** = 47.4 Å. In the wide angle region a diffuse scattering ∼4.6 Å corresponding to the liquidlike in-plane ordering could be observed. The spacings obtained from reflections lying orthogonal to the equatorial plane could be indexed as (11) and (22) whereas the reflection at an angle could be indexed as (02). This indexing scheme shows that the rectangular blocks in the surface aligned sample may be tilted with respect to the substrate similar to what was proposed in [16]. The lattice parameters **a** and **b** are orthogonal and parallel to the bow axis of the molecules, respectively. X-ray diffraction shows that the scattering pattern or intensity in the wide angle region is symmetric with respect to the line perpendicular to the equatorial plane which could indicate either absence of tilting or poor sample alignment. But as the small angle reflections show that the sample is reasonably aligned we can expect that if a tilt is present it would have shown up in the intensity distribution in the wide angle region. Also in the higher temperature range, optical studies show that the orientation of the dark brushes in the circular domain texture are present along and perpendicular to the polarizers which can be expected if the 2D phase is orthogonal. The observed value of **b** can be accounted for if the bow axes in the adjacent ribbons of the 2D structure are shifted such that there is a partial overlap of the aromatic parts of the molecules in adjacent ribbons. In fact it has been shown that a partial segregation of the aromatic and alkyl chain lengths leads to better stabilization of the columnar phase [17]. We therefore propose that the structure in the higher temperature phase is similar to that in the $B_{1\text{rev}}$ phase and is as shown in Fig. 4(a). As the temperature of the sample is decreased below 118 °C there is a change in the diffraction pattern suggesting



(a) (b)

(c) (d)

FIG. 3. X-ray diffraction patterns obtained from a sample mounted on a glass plate in which x-rays are incident at grazing angle: (a), (b) at 125°C and (c), (d) at 116°C.



(a) (b)

(c) (d)

FIG. 2. (Color online) Optical textures of NMTBB viewed between crossed polarizers taken in: (a), (b) Cell A made of polyimide coated plates and (c), (d) Cell B made of ODSE coated plates. (a), (c) are at 125°C and (b), (d) are at 115°C.

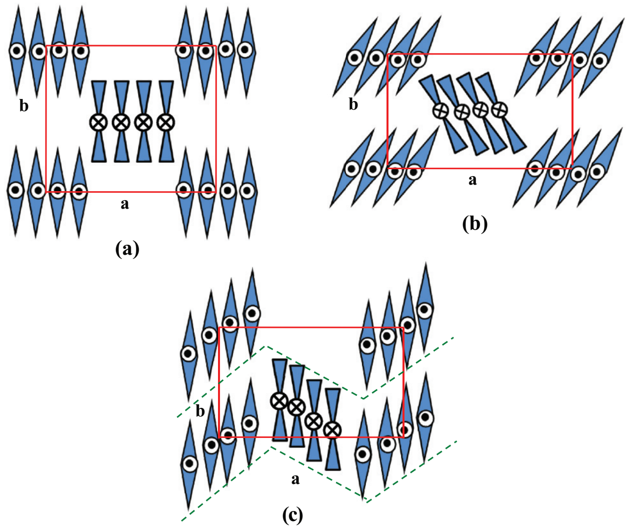


FIG. 4. (Color online) (a) Structure in the $B_{1\text{rev}}$ phase, (b) unfavorable structure in lower temperature reverse columnar phase with anticlinic tilt orientation in adjacent blocks, and (c) proposed structure with modulated layer fragments in the $B_{1\text{revtiltM}}$ phase.

a change in structure. The obtained x-ray spacings can be indexed to a noncentered rectangular *pmm* lattice. The lattice parameters obtained at 116 °C are $\mathbf{a} = 61.11$ Å, $\mathbf{b} = 35.66$ Å. As textural studies show that changes are observed both on heating and cooling of the sample ∼118 °C it can be envisaged that a phase transition occurs at this temperature. A thermal analysis using differential scanning calorimetry reveals the transition at 118 °C only at slow rates of cooling (1 °C) and the corresponding enthalpy is very small ($\Delta H = 0.1\text{J/g}$). The overall textural features, both above and below this temperature, have features typical of reverse columnar phases and suggest that the structure is two-dimensionally periodic in both the phases which is also supported by x-ray diffraction studies. In samples exhibiting the circular domain texture concentric fringes appear as the temperature is decreased suggesting that there is some structural change. At the same temperature in samples exhibiting the banana leaf texture evidence for tilting of the molecules can be observed. If this tilting is synclinic in nature, the structure in the lower temperature columnar phase should conform to an oblique lattice and the structure should be similar to the $B_{1\text{revtilt}}$ phase. However x-ray studies show that the reflections can be indexed to a noncentered rectangular lattice. This shows that the lower temperature columnar phase is most likely different from the $B_{1\text{revtilt}}$ phase. On the other hand if an anticlinic tilting does take place without change in the position of the molecular blocks, the expected 2D structure would be that of a centered oblique lattice or a pseudorectangular lattice. But such a structure is not favorable as this will have an opposing orientation of the aromatic cores at the interfaces of the ribbons [Fig. 4(b)]. The sterically unfavorable anticlinic orientation between the ribbons of the columnar structure can be avoided by increasing the ribbon width which minimizes the incompatibility at the boundaries. In the extreme case the ribbon size can increase and the molecules can undergo a displacement in a direction parallel to the long axis of the bent-core molecules leading to a lamellar SmC_AP_A phase. Such an anticlinic tilt orientation has been observed at a transition from the $B_{1\text{revtilt}}$ phase to an undulated smectic phase [18] in which case the x-ray diffraction studies show that cross reflections vanish and only reflections that can account for a layer structure remain. But as mentioned above, with the NMTBB sample, x-ray diffraction studies show evidence for a rectangular lattice in the lower temperature phase. One way in which the rectangular lattice can be accounted for and the incompatibility in the structure caused by the anticlinic orientation also overcome, is by having a modulation of the layer fragments, as proposed in the case of a modulated smectic phase with staggered zig-zag layer modulation [19]. In this case the modulated smectic phase with a rectangular *p*2*gg* lattice appears from a smectic phase with randomized tilt orientation. But in NMTBB as the modulation of the layer fragments appears on decreasing the temperature from the columnar $B_{1\text{rev}}$ phase, the columnar structure is also retained. Based on the optical observations and the x-ray diffraction studies, the mesophase above 118 °C is identified as the rectangular $B_{1\text{rev}}$ phase and that below 118 °C as a reverse columnar phase with modulated layer fragments and designated as $B_{1\text{revtiltM}}$. The proposed structure in this phase is shown in Fig. 4(c).

C. Optical observations under applied electric fields

An ac electric field was applied to the sample taken in cell A under two different conditions: (Case 1) The sample was cooled into the $B_{1\text{rev}}$ phase from the isotropic phase and a square-wave electric field (1 KHz) applied. (Case 2) The sample was heated back to the isotropic phase and cooled into the $B_{1\text{revtiltM}}$ phase after passing through the $B_{1\text{rev}}$ phase and then subjected to the square-wave electric field (1 KHz). Both these methods result in field-induced transitions from the columnar phase to DC phases though there are some striking differences.

Case 1. As the applied voltage (in V_{rms}) was increased to ∼4 V/μm the birefringence starts decreasing [Figs. 5(a)–5(c)] and at ∼9 V/μm the texture changes over to a completely dark state when viewed between crossed polarizers [Fig. 5(d)]. On rotating the analyzer by a few degrees from the crossed position, two types of domains can be observed. The brightness within the domains can be interchanged on rotating the analyzer in the opposite direction [Figs. 5(e) and 5(f)]. The domains could not be observed between crossed polarizers and there is no change in brightness within the domains when the sample is rotated between slightly uncrossed polarizers. This shows that the domains are conglomerate domains as usually observed in the DC phase [4]. Once formed the domains persist even if the field is switched off. The birefringent texture of the columnar phase can be recovered only if the sample is heated back into the isotropic phase and cooled again in the absence of an electric field. As this DC phase is obtained on applying the electric field in the $B_{1\text{rev}}$ phase it is named as the DC-$B_{1\text{rev}}$ phase.

Case 2. The sample is cooled down into the $B_{1\text{revtiltM}}$ phase from the isotropic phase and a similar electric field as used in case 1 applied at ∼116 °C. The columnar texture again starts undergoing a transformation ∼4 V/μm and appears completely dark between crossed polarizers ∼9 V/μm. On

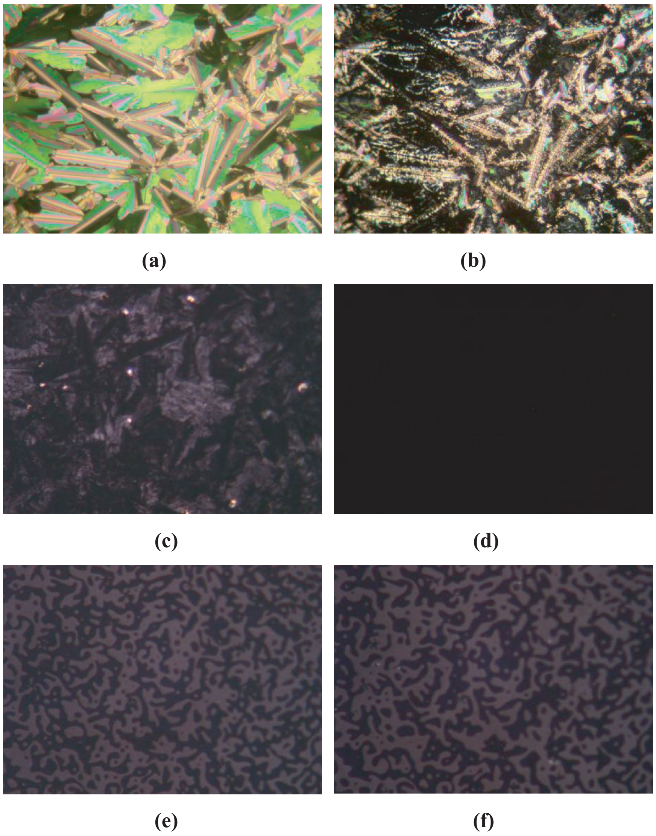


FIG. 5. (Color online) Transformation into the DC-$B_{1\mathrm{rev}}$ phase on application of an ac electric field (1 KHz) (a)–(d) 123 °C. (a) No field, (b) 4V/μm, (c) 4.5 V/μm, (d) 9 V/μm, crossed polarizers. (e) and (f) Well-formed chiral domains, 122 °C, analyzer rotated by 4° on either side from crossed position.

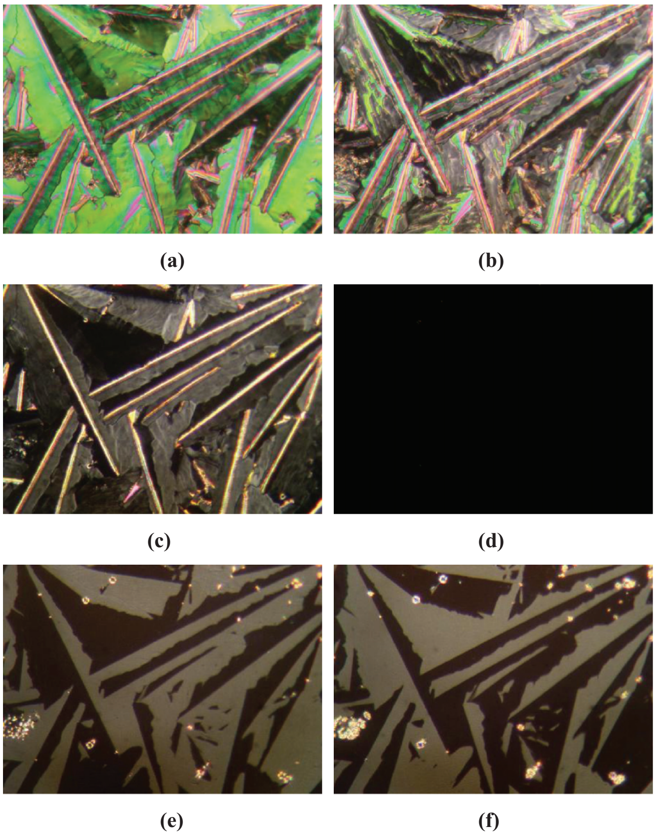


FIG. 6. (Color online) Transformation into the DC-$B_{1\mathrm{revtiltM}}$ phase on application of an ac electric field (1 KHz), (a)–(d) 116 °C. (a) No field, (b) 4 V/μm, (c) 4.5 V/μm, (d) 9 V/μm, crossed polarizers. (e) and (f) Well-formed chiral domains, 115 °C, analyzer rotated by 4° on either side from crossed position.

rotating the analyzer by a few degrees from the crossed position two types of chiral domains can be observed, but the shape of the domains appear somewhat similar to the domains in the banana leaf texture in the $B_{1\mathrm{revtiltM}}$ phase (Fig. 6). The field-induced DC phase in this case is identified as DC-$B_{1\mathrm{revtiltM}}$.

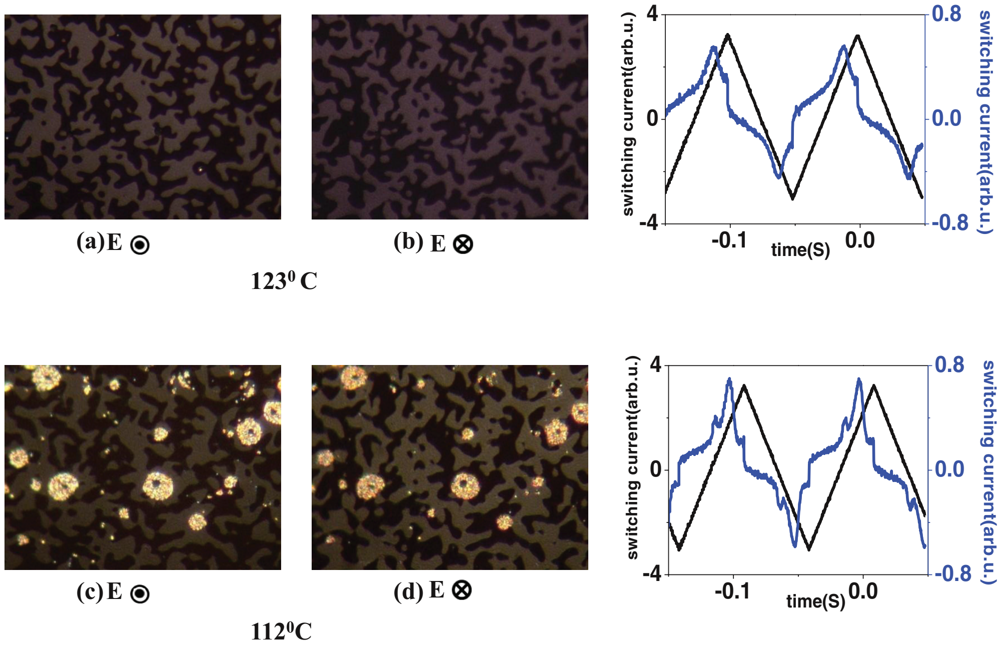
In case of the reverse columnar phases a reorientation of the spontaneous polarization is possible under the electric field. In the $B_{1\mathrm{rev}}$ phase, the switching mechanism involves only a rotation around the long axis, whereas in the $B_{1\mathrm{revtilt}}$ phase with tilted molecules, the mechanism can also involve a collective rotation of the molecular long axis on the tilt cone around the layer normal [20]. While rotation around the long axis reverses the polarization direction and hence the chirality, rotation on the tilt cone retains the chiral sense. Usually in the orthogonal $B_{1\mathrm{rev}}$ phase, application of an electric field does not cause any optical changes. Even in the case of NMTBB below ~4 V/μm there is no change in the optical texture but as the field is increased further the birefringence within the bright banana leaflike domains starts decreasing and at ~9 V/μm the sample appears totally dark. Rotation around the long axis results in a reversing of the polarity and the antiferroelectric structure present in the layer fragments of the $B_{1\mathrm{rev}}$ phase changes over to a ferroelectric structure. Further segregation of the aromatic and aliphatic parts in the columnar structure is promoted by the applied field and a transition into a lamellar SmCP phase takes place. However, instead of a $\mathrm{SmC_SP_F}$ phase with flat layers, conglomerate domains with opposite chirality are seen to develop. It has been proposed that in the DC phase the difference in the in-plane area of the alkyl chains and the aromatic cores gives rise to a mismatch between the tilt planes of the two half-arms of the BC molecule, making their projections on the layer plane nearly orthogonal to each other, as a consequence of which layer frustration results [4]. Focal conic domains with negative Gaussian curvature, along with saddle splay layer deformation are characteristic of the DC phase which locally consists of homochiral $\mathrm{SmC_AP_A}$ or $\mathrm{SmC_SP_F}$ structures. In this homologous series the formation of the DC phase may be related to the particular combination of the bulky naphthylene core in the aromatic part of the molecules and the alkyl chain lengths of the middle homologs of the series, which makes the mismatch between the tilt planes of the two half-arms of the BC molecule more pronounced resulting in the formation of a distorted DC phase instead of a lamellar phase with flat layers. In fact in this homologous series even without the application of an electric field the formation of the DC phase seems to be preferred for the homologs with $n = 11$ and 12 [6,15]. In NMTBB with $n = 14$ the application of the electric field initially favors a segregation of the aromatic core and alkyl chains in the columnar structures, which easily transforms into the distorted structure of the DC phases instead of the birefringent flat $\mathrm{SmC_SP_F}$ structure. As the temperature is reduced, the conglomerate domains which start forming as tiny domains, slightly grow in size for 2–3 °C and then remain without significant change down to crystallization. As the temperature is decreased further, at 118 °C small bright regions start appearing in the DC texture. It is around this temperature that modulation of the layer fragments occur in order to avoid the sterically unfavorable anticlinic tilt orientation in the $B_{1\mathrm{revtiltM}}$ phase. The bright regions may correspond to flat layers but before they grow bigger and extend throughout the sample, crystallization sets in.

When the square-wave electric field is applied after cooling the sample into the $B_{1\mathrm{revtiltM}}$ phase the modulation amplitude of the layer fragments decreases and the molecules shift in a direction parallel to the bow axis and as in the $B_{1\mathrm{rev}}$ phase, rotation around the long axis and subsequent changeover to a DC phase takes place. As the layer modulation may not be entirely removed the structure may be similar to an undulated smectic structure which can have a 2D periodicity [21]. The local structure can then be $\mathrm{SmC_SP_F}$ type which is consistent with the observed ferroelectric switching. However, x-ray studies under applied fields are necessary to establish this further and will be taken up in future.

The DC phase itself has often been found to transform into a chiral SmCP phase with flat layers on the application of a high electric field and electro-optic switching behavior has been observed in some cases [22–28]. The optical texture of the field-induced lamellar phase is usually highly birefringent. Compounds incorporating siloxane units or nonsilylated molecules containing fluorine substituents exhibiting DC textures have been reported to exhibit ferroelectric switching [29]. Previous reports on field-induced columnar to SmCP phase transitions have usually shown that the change is accompanied by an increase in birefringence and that the columnar phase is recovered on field removal. In contrast the well formed chiral domains with local $\mathrm{SmC_SP_F}$ structure as seen in case of the field-induced DC-$B_{1\mathrm{rev}}$ and DC-$B_{1\mathrm{revtiltM}}$ phases of NMTBB are stable even after the removal of the electric field.

D. Electro-optic studies

In order to investigate the switching behavior of the field-induced dark phases, a triangular-wave electric field was applied to the sample taken in Cell A after the transformation into the DC-$B_{1\mathrm{rev}}$ and DC-$B_{1\mathrm{revtiltM}}$ phases. On rotation of the analyzer by ∼2°–3° from the crossed position it can be observed that the contrast between the two types of chiral domains increases with application of field. The brightness within the two types of domains is also seen to interchange with reversal of field. A single polarization current peak is recorded for each half-cycle indicating a ferroelectric switching behavior for the DC-$B_{1\mathrm{rev}}$ phase (Fig. 7). During the switching process if the field is switched off when the chiral state of a domain is different from the initial field free state, the field-induced state is retained even after 2 h if the sample is maintained in the temperature range in which a single polarization peak is observed. This confirms bistability and shows that the ground state corresponds to $\mathrm{SmC_SP_F}$. On the other hand if the ground state had corresponded to an antiferroelectric structure the chiral state present before the application of the field should have been restored. However, between crossed polarizers the dark texture is retained which shows that the deformation of the layers is not totally removed. The switching mechanism in this case corresponds to a collective rotation around the long axis resulting in an inversion of both the chiral sense and polarization which results in a single peak in the electro-optic signal and switching of the


(a)E ⊙ (b) E ⊗

123^0 C

(c)E ⊙ (d) E ⊗

112^0C

FIG. 7. (Color online) Optical textures corresponding to the electro-optic switching in the DC-$B_{1\mathrm{rev}}$ phase at 121 °C and 112 °C, 9 V/μm (10 Hz), analyzer rotated by 3° from the crossed position. Corresponding switching current responses at these temperatures are shown on the right-hand side.

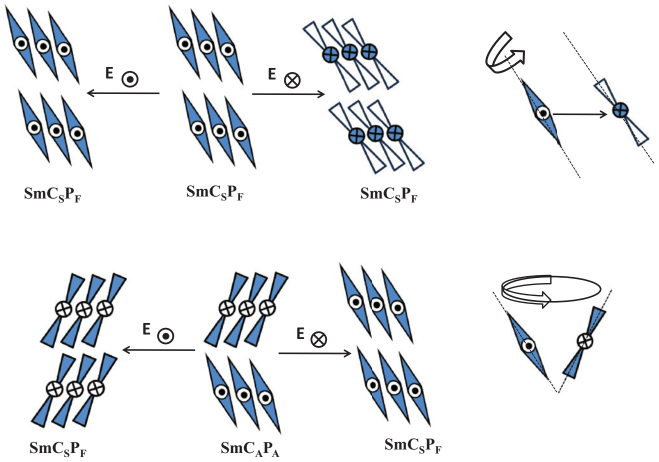
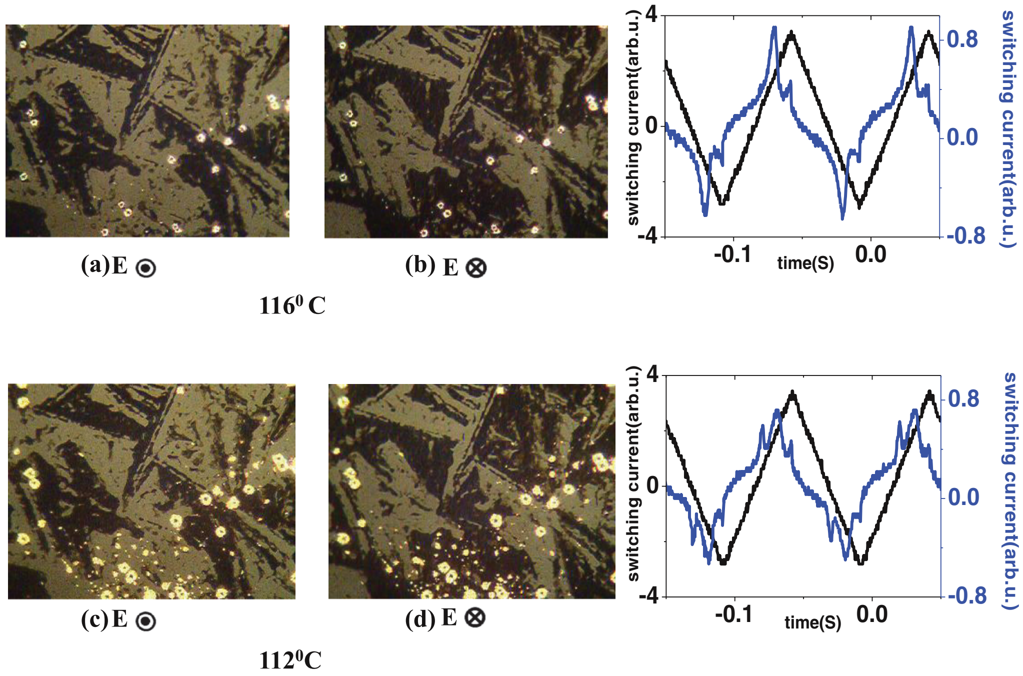


FIG. 8. (Color online) Illustration of polar switching mechanism in the (a) chiral domains with local $\mathrm{SmC_SP_F}$ structure and (b) bright regions with $\mathrm{SmC_AP_A}$ structure; filled and open molecules represent layers with different chirality.

chiral domains into states of opposite handedness on reversing the sense of the field.

When the temperature is decreased below 114 °C, a small second peak can be clearly observed in the current response indicating an antiferroelectric type of switching (Fig. 7). Around this temperature the bright regions which exist alongside the chiral domains also become more prominent. However, there is no significant change in the optical appearance of the two types of chiral domains. The bright or dark state of the chiral domains remains similar to what is observed in the higher temperature ferroelectric state for the same sense of the applied field. The antiferroelectric switching behavior can be accounted for, if the bright regions that start forming at the 118 °C have a racemic $\mathrm{SmC_SP_A}$ or homochiral $\mathrm{SmC_AP_A}$ structure. It is possible that the $\mathrm{SmC_SP_A}$ structure can give rise to two $\mathrm{SmC_SP_F}$ structures with opposite chirality by a switching mechanism involving rotation around the long axis which can account for the antiferroelectric switching behavior. But, interestingly, the bright regions start forming around the temperature (118 °C) at which the $\mathrm{B_{1rev}}$ to $\mathrm{B_{1revtiltM}}$ phase transition occurs where there is tendency for anticlinic tilting and the layer fragments modulate to avoid this as explained earlier. It is therefore more likely that the formation of the bright regions is related with this and that they correspond to flat layers with the homochiral $\mathrm{SmC_AP_A}$ structure as the field-induced phase is now lamellar and anticlinic tilting is possible. In that case the switching mechanism is related with a rotation around the tilt cone. The polar switching mechanisms corresponding to the chiral domains with local $\mathrm{SmC_SP_F}$ structure and the bright regions with $\mathrm{SmC_AP_A}$ structure are shown in Fig. 8.

It can also be noticed that the peak observed at higher temperatures and related with the ferroelectric switching in the electro-optic signal appears sharper whereas the second peak which appears at lower temperatures is much smaller. This may indicate that the electro-optic signal may be arising from a combined effect of the two types of homochiral domains. The optical textures and switching current responses in the DC-$\mathrm{B_{1revtiltM}}$ phase are shown in Fig. 9. As the DC-$\mathrm{B_{1revtiltM}}$ phase has been obtained by applying the field after cooling the sample into the $\mathrm{B_{1revtiltM}}$ at 116 °C which is below the temperature at which the layer modulation occurs in the absence of the field, some tiny bright regions can already be observed. However, if the sample is now heated above 118 °C the bright regions disappear and the switching is clearly



(a) E ⊙ (b) E ⊗

116⁰ C

(c) E ⊙ (d) E ⊗

112⁰C

FIG. 9. (Color online) Optical textures corresponding to the electro-optic switching in the DC-$\mathrm{B_{1revtiltM}}$ phase at 116 °C and 112 °C, 9 V/μm (10 Hz), analyzer rotated by 3° from the crossed position. Corresponding switching current responses at these temperatures are shown on the right-hand side.

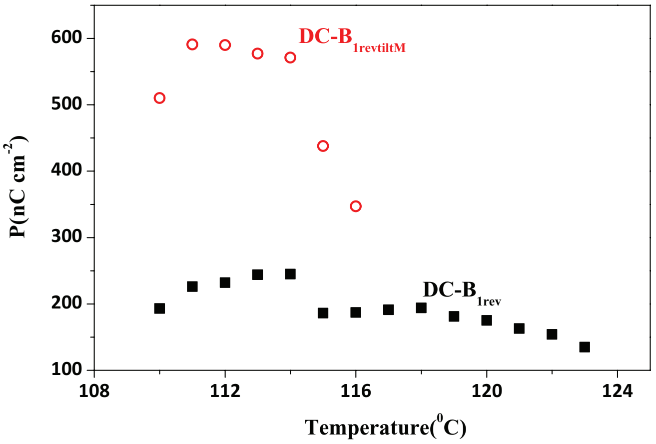


FIG. 10. (Color online) Temperature variation of the switching polarization P in the field-induced DC-$\mathrm{B}_{\mathrm{1rev}}$ (closed squares) and DC-$\mathrm{B}_{\mathrm{1revtiltM}}$ (open circles) phases.

ferroelectric. As in the case of the DC-$\mathrm{B}_{\mathrm{1rev}}$ phase the change in switching behavior from ferroelectric to antiferroelectric can be observed only when the bright regions with $\mathrm{SmC_AP_A}$ structure become prominent below 114 °C. The switching mechanism in this case is again similar to what has been shown in Fig. 8. The temperature variation of the switching polarization (P) in both the DC-$\mathrm{B}_{\mathrm{1rev}}$ and DC-$\mathrm{B}_{\mathrm{1revtiltM}}$ phases are shown in Fig. 10. In the DC-$\mathrm{B}_{\mathrm{1rev}}$ phase there is an increase in P at the temperature corresponding to the formation of bright domains and antiferroelectric switching behavior. The DC-$\mathrm{B}_{\mathrm{1revtiltM}}$ phase is formed by applying the electric field in the $\mathrm{B}_{\mathrm{1revtiltM}}$ phase. An anticlinic tilting is possible in the lamellar DC phase and the effect is more pronounced and a sharp increase in P is noted at the temperature when antiferroelectric switching behavior is clearly observed in the current response. Hence the value of P is also higher in the DC-$\mathrm{B}_{\mathrm{1revtiltM}}$ phase. The decrease at lower temperatures in both cases is due to the onset of crystallization.

E. Dielectric studies

The temperature and frequency variation of the real (ϵ') and imaginary (ϵ'') parts of the dielectric permittivity in the $\mathrm{B}_{\mathrm{1rev}}$ and $\mathrm{B}_{\mathrm{1revtiltM}}$ phases was initially measured using Cell A by applying a square-wave electric field of 0.5V (1 KHz) before the transformation into the DC phases. The phase transition into the $\mathrm{B}_{\mathrm{1revtiltM}}$ phase is revealed by a sharp decrease in ϵ' at 118 °C. The sample was then transformed into the field-induced DC phases by application of a square-wave electric field of 9 V/μm (1 KHz) as described earlier. The field was then slowly reduced and the dielectric permittivity measured in the field-induced DC phases by applying a small voltage of 0.5 V (1 KHz). Figure 11 shows the temperature variation of ϵ' in the $\mathrm{B}_{\mathrm{1rev}}$, $\mathrm{B}_{\mathrm{1revtiltM}}$, and DC-$\mathrm{B}_{\mathrm{1rev}}$ phases. In the DC-$\mathrm{B}_{\mathrm{1rev}}$ phase, the decrease in ϵ' occurs around the same temperature at which the $\mathrm{B}_{\mathrm{1rev}}$ to $\mathrm{B}_{\mathrm{1revtiltM}}$ phase transition occurs in the absence of an applied field and the sudden change in P and nucleation of flat layers with $\mathrm{SmC_AP_A}$ structure occur. The value of ϵ' is also not very high in all the three phases.

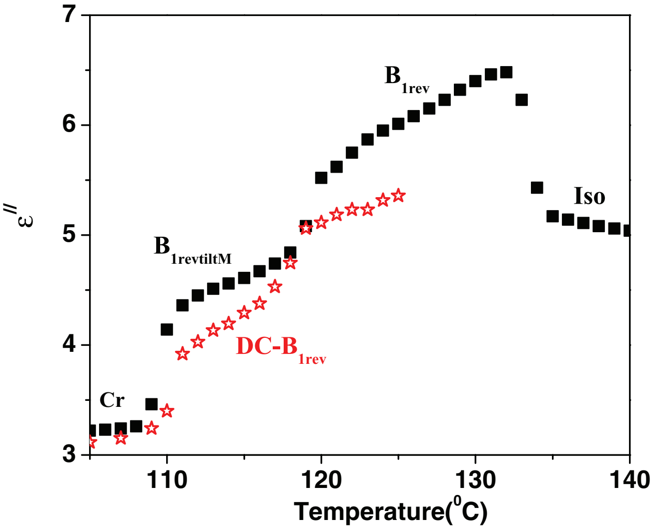


FIG. 11. (Color online) Temperature variation of the real part of the dielectric permittivity (ϵ') in the $\mathrm{B}_{\mathrm{1rev}}$, $\mathrm{B}_{\mathrm{1revtiltM}}$, and field-induced DC-$\mathrm{B}_{\mathrm{1rev}}$ phases.

The frequency response was studied in the range 100 Hz to 1 MHz. The imaginary part of the permittivity in the $\mathrm{B}_{\mathrm{1rev}}$ and field-induced DC-$\mathrm{B}_{\mathrm{1rev}}$ phases is shown for comparison in Fig. 12. In the $\mathrm{B}_{\mathrm{1rev}}$ phase a single mode which can be attributed to molecular reorientation around the short axes is observed whereas in the field-induced DC-$\mathrm{B}_{\mathrm{1rev}}$ phase, two modes can be observed. The high frequency mode (mode1) can be attributed to molecular reorientation and the lower frequency mode (mode2) to a collective process as in the SmCP phase. The dielectric modes in columnar phases are usually weaker than in SmCP phases. But the two modes in the DC-$\mathrm{B}_{\mathrm{1rev}}$ phase are much weaker and have dielectric strength comparable to that in the $\mathrm{B}_{\mathrm{1rev}}$ phase although it has a local SmCP structure probably because of the highly distorted structure. A similar trend is noted in the $\mathrm{B}_{\mathrm{1revtiltM}}$ and DC-$\mathrm{B}_{\mathrm{1revtiltM}}$ phases. The detailed dielectric response in the reverse columnar phases and field-induced DC phases occurring in NMTBB will be reported elsewhere [30].

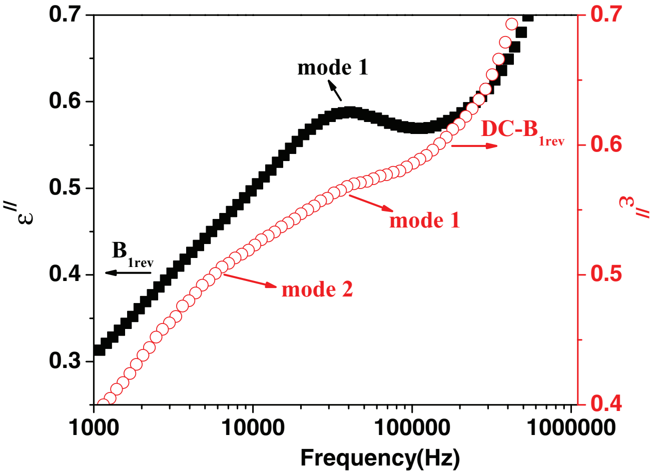


FIG. 12. (Color online) (a) Frequency variation of the imaginary part of the dielectric permittivity (ϵ'') in the $\mathrm{B}_{\mathrm{1rev}}$ phase and field-induced DC-$\mathrm{B}_{\mathrm{1rev}}$ phase at 124 °C.

IV. CONCLUSION

DC phases induced by the application of an ac electric field have been observed in the bent-core compound 2,7-naphthylene bis[4-(3-methyl-4-*n*-tetradecyloxybenzoyloxy)] benzoate exhibiting two reverse columnar phases. Detailed textural studies in the absence of the electric field indicate that the columnar phases show no drastic changes in the overall features of the columnar texture. In samples exhibiting the banana leaf texture, evidence for a tilting of the molecules is observed at the transition into the lower temperature columnar phase. X-ray studies show that the higher temperature columnar phase is nontilted and corresponds to the orthogonal B_{1rev} phase with a *cmm* rectangular lattice and the lower temperature columnar phase has a noncentered *pmm* rectangular lattice and is therefore different from the $B_{1revtilt}$ phase. The rectangular lattice has been accounted for by considering that the layer fragments in the lower temperature columnar phase get modulated in order to reduce the steric hindrance caused by the anticlinic tilting and this phase has therefore been designated as $B_{1revtiltM}$. The columnar phases undergo transitions into the DC-B_{1rev} and DC-$B_{1revtiltM}$ phases depending on whether the field is applied in the B_{1rev} phase or after cooling into the $B_{1revtiltM}$ phase. The shape of the field-induced chiral domains is different in the two cases. Electro-optic studies show that both the DC phases are switchable with a local SmC_SP_F type of structure and exhibit ferroelectric switching behavior in the higher temperature region. At the temperature at which a phase transition from the B_{1rev} to $B_{1revtiltM}$ phase takes place in the absence of the field, flat layers with SmC_AP_A structure start nucleating in the DC texture and antiferroelectric switching is observed. The temperature and frequency variation of the dielectric permittivity reflects the nature of the phase transitions observed both in the absence and presence of the electric field.

The columnar phase exhibited by bent-core molecules does not usually respond to electric fields. There are only few examples of field-induced transitions from columnar to lamellar phases. As observed in this work the transformation of columnar phases into highly distorted DC phases under the application of an electric field is even more interesting. Such studies would be helpful in further understanding of chiral segregation and macroscopic conglomerate domain formation in liquid crystals made of achiral molecules. High resolution x-ray diffraction studies will be carried out in the future to further probe the detailed phase structures both before and after application of the electric field.

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