PHYSICAL REVIEW E **89**, 042504 (2014)

Chiral symmetry breaking dictated by electric-field-driven shape transitions of nucleating conglomerate domains in a bent-core liquid crystal

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(Received 17 January 2014; published 21 April 2014)

Generating and controlling chiral symmetry breaking and enantiomeric excess is not only interesting from a fundamental perspective but can also lead to novel functional materials. In this work, we show how the dark conglomerate (DC) liquid crystalline phase characterized by macroscopic chiral domains offers such a possibility if formed under an electric field. In addition the chiral domains are electro-optically switchable. The chiral segregation in the DC phase can be tuned by using dc or ac fields at different frequencies. Consequently, the enantioselectivity, dielectric parameters and switching polarization in the DC phase become tunable. Another interesting aspect is that the nucleating conglomerate domains formed under ac fields exhibit frequency dependent shape transitions which have a striking resemblance to domain shape changes observed in two-dimensional monolayers. This can therefore be used as a model experimental system to get a physical insight into the effects of chiral and electrostatic interactions, under external fields, on domain growth and interface structures. The domain shape transitions can also be used to investigate the role of growth morphology in coarsening and scaling hypotheses. From a technological point of view this opens up the possibility of obtaining chiral thin films with preferential sense of chirality which can be useful in chiroptical and nonlinear optical applications.

DOI: 10.1103/PhysRevE.89.042504 PACS number(s): 61.30.Gd, 64.60.Q−

I. INTRODUCTION

Chiral symmetry breaking which occurs in a variety of systems, ranging from naturally occurring biomolecules to liquid crystals synthesized in the laboratory, has been a topic of extensive theoretical and experimental research. The emergence of an enantiomeric excess state arising from a racemic mixture can also be attractive technologically. Interestingly, intrinsic molecular chirality is not a prerequisite for deracemization to occur. Conglomerate crystallization has been observed with achiral inorganic molecules such as $NaClO_3$ and 1,1-binaphthyl under certain conditions [1–3]. In the case of fluids, homochiral domains of opposite handedness have been observed in the dark conglomerate (DC) and B4 phases exhibited by certain liquid crystals made of achiral bent-core (BC) or bow shaped molecules [4,5].

Bent-core liquid crystals (BCLCs) exhibit lamellar SmCP phases in which a coupling of the molecular tilt about the arrow axis and polar ordering within the layers leads to layer chirality. Both homochiral (SmC_AP_A and SmC_SP_F) and racemic (SmC_SP_A and SmC_AP_F) versions are observed [6,7]. Here the subscripts A and S of C refer to anticlinic and synclinic tilting and the subscripts A and F of P refer to antiferroelectric and ferroelectric order between adjacent layers. The packing of these BC molecules having a highly polar shape and large bend angle of ∼120° within a layer results in spontaneous transverse polarization. Most often these phases exhibit electro-optic switching.

The DC and B4 phases are special types of lamellar phases made of BC molecules in which macroscopic domains of opposite handedness form spontaneously. The optical texture in these phases appears totally dark between crossed polarizers. Chiral domains are revealed only on rotation of the analyzer by a few degrees from the crossed position with domains of opposite handedness appearing bright and dark. On rotating the analyzer in the opposite direction the brightness within the domains is interchanged. The homochiral domains have a SmC_AP_A or SmC_SP_F structure locally. In spite of the lamellar order being well established, there is disorder on a longer length scale, rendering the system macroscopically isotropic. Based on detailed freeze fracture transmission electron microscope (TEM) studies it has been proposed that the layer frustration in these phases is relieved by saddle splay layer deformation [4,5]. As a consequence, focal conic domains with negative Gaussian curvature characterize the DC phase and helical nanofilaments form in the B4 phase. Most often these phases do not respond to electric fields. Sometimes the DC phase has been found to transform into a highly birefringent chiral SmCP phase with flat layers under high electric fields [8]. Some compounds which form DC type of textures under high electric fields are reported to exhibit electro-optic switching [9–11]. The chiral domains switch into states of opposite handedness and the switching is found to be bistable, but in these cases the switching polarization is not very high and the shape and size of the chiral domains cannot be controlled.

BCLCs also form columnar phases with two-dimensionally periodic structures formed by fragmented ribbons of smectic layers. In the nonswitchable B_1 phase, the density modulation is in a plane parallel to the polarization vector whereas in the switchable reverse columnar phases, viz., $B_{1\mathrm{rev}}$ with nontilted and $B_{1\mathrm{revtilt}}$ with tilted layers, the density modulation is in a plane orthogonal to the polarization vector [12]. Usually phase transitions between lamellar and columnar phases in the same BCLC are rare [13,14]. But under high electric fields, a transition from the B_1 phase into a SmCP type of phase with a birefringent texture and exhibiting an antiferroelectric switching behavior has been observed [15]. However, in this case the B_1 structure is restored on field removal.

We have recently investigated a homologous series made of bent-core molecules derived from 2,7-dihydroxynaphthalene. The middle homologues of this series with alkyl chain lengths

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$n = 11$–13 exhibit a nonswitchable DC phase in which the chiral domains form spontaneously on cooling from the isotropic phase [16]. Textural observations under a polarizing microscope and x-ray diffraction studies showed that the next higher homologue with $n = 14$, viz., 2,7,-naphthylene bis[4-3-methyl-4-*n*-tetradecyloxybenzoyl)]benzoate (NMTBB) forms two reverse columnar phases [17]. In this compound the higher temperature columnar phase was found to correspond to the nontilted orthogonal B_{1rev} phase. In the lower temperature phase, optical observations showed evidence for tilting of the molecules. If the tilting was synclinic, the lower temperature phase should have corresponded to the $B_{1revtilt}$ phase in which case x-ray diffraction should have shown evidence for an oblique lattice. However, our studies showed that the reflections could be indexed to a noncentered rectangular lattice. Though it is possible that an anticlinic tilting without change in the position of the molecular blocks could result in a structure with a centered oblique or a pseudorectangular lattice, this would not have been favored as this would have an opposing orientation of the aromatic cores at the interfaces of the ribbons. We had therefore proposed that there is a tendency for anticlinic tilting with decrease in temperature, but as a steric hindrance is caused by such a tilting, the layer fragments modulate to relieve it. This model could also account for the observed x-ray spacings. The lower temperature columnar phase was therefore designated as $B_{1revtiltM}$ phase. We also found that application of a high frequency ac electric field, either in the B_{1rev} or $B_{1revtiltM}$ phase, results in a transformation into dark phases with chiral domains. While the shape of the chiral domains obtained by applying the field in the B_{1rev} phase appear similar to domains usually observed in DC phases, the shape of domains obtained by applying the field after cooling into the $B_{1revtiltM}$ phase has some similarity to the domains of the banana leaf texture obtained in the $B_{1revtiltM}$ phase. This suggests that the detailed structure in this phase may be different. We therefore named the respective field-induced phases as DC-B_{1rev} and DC-$B_{1revtiltM}$. The chiral domains obtained in both cases are well formed and remain stable even after field removal and are also electro-optically switchable [17].

We now report that if the same compound, NMTBB, is cooled under an ac or dc field from the isotropic phase, the reverse columnar phases are eliminated and a direct transition into a dark mesophase with chiral domains which appear similar to those usually observed in DC phases is obtained. We also find that the morphology of the nucleating chiral domains is different under the ac and dc fields. Further, the shape of the domains obtained under ac fields depends on the frequency of the applied field. Interestingly, these shapes appear very similar to domains observed in two-dimensional (2D) monolayers. We also find that the sustainability of the dark phase, dielectric parameters and switching polarization are influenced by the shape of the nucleating domains. An indication of preferential enantioselectivity is also observed when the chiral domains are formed under the dc field.

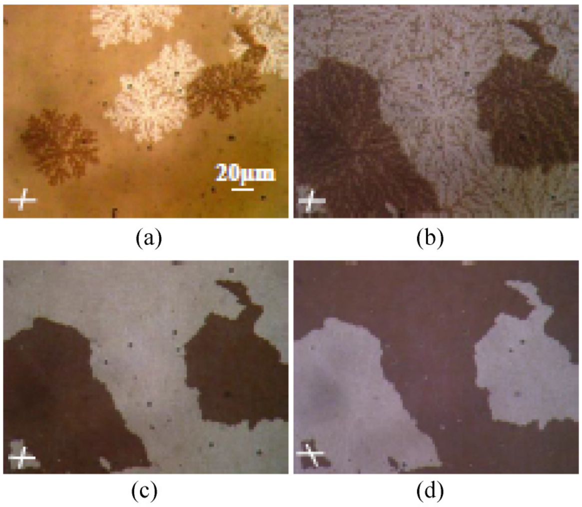
II. EXPERIMENT

All the experimental studies have been carried out on 2,7-naphthylene bis[4-(3-methyl-4-*n*- tetradecyloxybenzoyloxy)] benzoate (NMTBB) exhibiting the phase sequence I 132 B_{1rev} 118 $B_{1revtiltM}$ 110 Cr (°C) [17]. Textural observations were carried out under a polarizing microscope (Leitz, Ortholux Pol BK) on a sample taken in a cell treated for homogeneous alignment (Instec Inc., 9 μm) and placed in a hot stage (Mettlar FP 82). The dc electric field was applied using a constant dc power supply (Aplab, Model No. 7235) while the ac square and triangular-wave fields were generated using an arbitrary wave form 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 form the DC phases from the isotropic phase before carrying out the dielectric studies, were generated by using a high voltage booster HVB-300 (Novocontrol Technologies) along with the Alpha A unit. The software, IMAGEJ 1.32J from National Institutes of Health, USA, was used for obtaining the fractal dimensions and for generating the histograms.

III. RESULTS

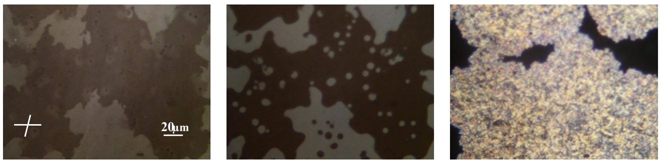
A. Optical observations

Optical observations were carried out on the sample under a polarizing microscope as it was cooled from the isotropic phase in the presence of an electric field. The brightly colored banana leaf texture corresponding to the B_{1rev} phase is absent, indicating that the columnar phase is eliminated under the field. The texture now appears totally dark between crossed polarizers and hence all observations have been made after rotating the analyzer by a few degrees from the crossed position. Initially the sample was cooled at the rate of 1 °C/min under a dc electric field (10 V/μm). At ~127 °C fractal



(a) (b)
(c) (d)

FIG. 1. (Color online) Formation of the DC_{dc} phase from the isotropic phase under a dc field of 10 V/μm in a sample cooled at 1 °C/min. (a) Conglomerate fractal domains (126.6 °C), (b) further growth of fractal domains (126.3 °C), (c) and (d) well formed chiral domains (125 °C). Analyzer rotated by 2° in the clockwise direction from the crossed position in (a)–(c) and anticlockwise direction in (d).

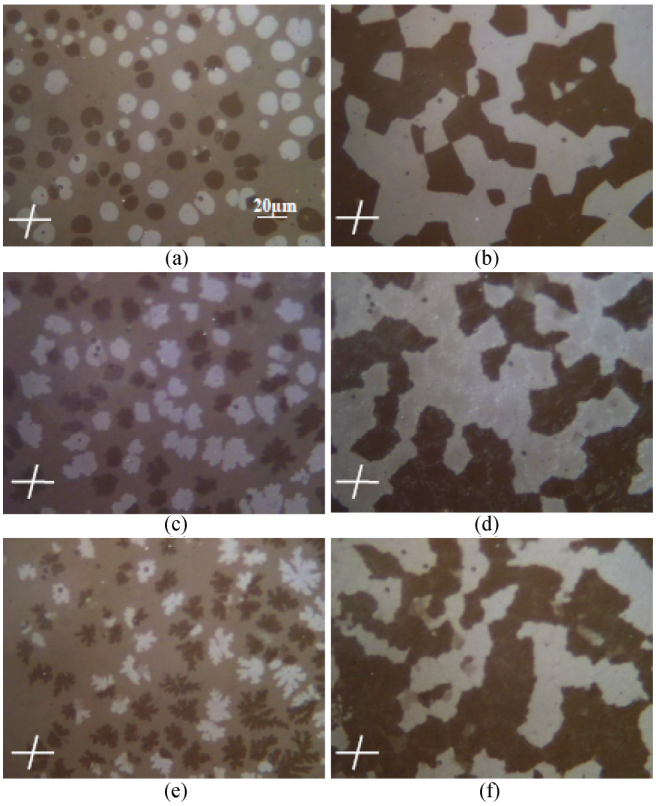


(a) (b) (c)

FIG. 2. (Color online) Formation and racemization of the $\mathrm{DC_{ac}}$ phase under a square wave ac field of 10 V/μm, f = 100 Hz in a sample cooled at 1 °C/min. (a) Chiral domains (128 °C), (b) formation of small domains of opposite chirality within the larger domains on switching off the ac field (124 °C), (c) onset of racemization (120 °C). Analyzer rotated by 2° from the crossed position in the clockwise direction in all cases.

domains which appear either bright or dark begin to nucleate [Fig. 1(a)]. The brightness of the fractal structures can be interchanged on rotating the analyzer in the opposite direction from the crossed position as in the chiral domains of DC phases. The fractals retain the sense of chirality as they enlarge [Fig. 1(b)] and finally coalesce to form a dark mesophase with well segregated large chiral domains with a slight increase in birefringence at ~125 °C [Figs. 1(c) and 1(d)]. These domains remain stable down to crystallization even if the field is switched off. In further discussion this phase is referred to as the $\mathrm{DC_{dc}}$ phase, as the optical appearance resembles the DC phase texture and the subscript is used to indicate that it is formed under the dc field.

In order to investigate the effect of an ac field on the phase behavior of NMTBB, the same sample was heated back into the isotropic phase and cooled again at the rate of 1 °C/min under an ac square wave field (10 V/μm). However, we must mention that all the experimental results would be similar even if a new cell filled with NMTBB is used. Observations were made during different runs by varying the frequency (f) from 100 Hz to 4 kHz. The growth pattern and sustainability of the chiral segregation now depends on the frequency of the applied field. When f = 100 Hz, large chiral domains form without much coexistence with the isotropic phase [Fig. 2(a)]. But on switching off the field, small domains of opposite chirality start nucleating in the larger domains [Fig. 2(b)] and finally highly birefringent racemic regions encompass the sample throughout [Fig. 2(c)]. The same sample was again cooled from the isotropic phase, after increasing the frequency. The temperature range between nucleation and coalescence of the chiral domains increases with increase in frequency. When f = 500 Hz, although some well formed chiral domains form initially, racemization takes place on switching off the field. This trend persists up to about f = 1 kHz, beyond which the chiral domains once formed remain stable even if the field is switched off. Interestingly, the growth morphology of the chiral domains as they nucleate from the isotropic phase changes from being almost circular when formed at frequencies in the range of 1–2 kHz [Fig. 3(a)] to noncircular and branched structures for frequencies >2 kHz [Figs. 3(c) and 3(e)] with the number of modes increasing with increasing frequency. The dark mesophase that is formed by coalescence of the chiral domains formed under the ac field is now referred to as the $\mathrm{DC_{ac}}$ phase. The textural appearance and domain interfaces in the $\mathrm{DC_{ac}}$ phase also depend on the frequency. The domains appear smooth with faceted interfaces in the $\mathrm{DC_{ac}}$ phase formed when f = 1–2 kHz [Fig. 3(b)] and slightly coarse having corrugated interfaces when f = 3 and 4 kHz [Figs. 3(d) and 3(f)]. Beyond 5 kHz the DC phase ceases to form under the field and the $\mathrm{B_{1rev}}$ phase with the typical banana leaf texture is formed, as obtained in samples cooled in the absence of the electric field [17].



(a) (b) (c) (d) (e) (f)

FIG. 3. (Color online) Formation of the $\mathrm{DC_{ac}}$ phase from the isotropic phase under a square wave ac field of 10 V/μm, in a sample cooled at 1 °C/min with the nucleating conglomerate domains undergoing shape transitions as a function of frequency. (a) Circular domains (124 °C) and (b) corresponding $\mathrm{DC_{ac}}$ phase (116 °C) obtained when f = 2 kHz; (c) domains with undulating boundaries (124 °C) and (d) corresponding $\mathrm{DC_{ac}}$ phase (116 °C) obtained when f = 3 kHz; (e) branched domain structures (124 °C) and (f) corresponding $\mathrm{DC_{ac}}$ phase (116 °C) formed when f = 4 kHz, analyzer rotated by 2° from the crossed position in the clockwise direction in all cases.

As our experiments with NMTBB sample show that the appearance and growth of the chiral domains depend on the nature of the electric field, it can be expected that the chiral segregation and hence some of the properties in the DC phase can be controlled by the applied field. In order to investigate this we carried out an analysis of the enantioselectivity, switching polarization, and dielectric parameters in the $\mathrm{DC_{dc}}$ and $\mathrm{DC_{ac}}$ phases.

B. Analysis of enantioselectivity

The extent of enantioselectivity in the field-induced DC phases was investigated by generating histograms using pixel intensity values obtained from the optical textures having the

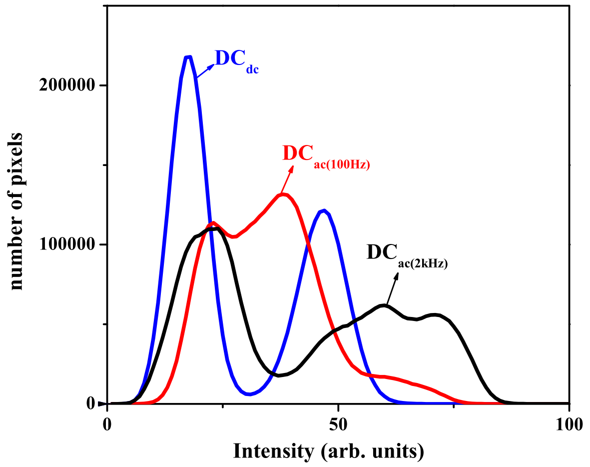


FIG. 4. (Color online) Comparison of the histograms generated from pixel intensity values obtained from the optical textures with chiral domains in the DC_{dc} and DC_{ac} phases.

chiral domains. It was ensured that the analyzer was rotated from the crossed position in the same direction while acquiring all the optical textures used in generating the histograms, so that domains with a specific handedness always appear with a similar hue (dark or bright). The part of the resulting bimodal histogram curve in the region with lower intensity values is related with the dark domains while the part in the region with higher intensity values corresponds to the bright domains [Fig. 4]. The distribution of the modes, therefore, gives an estimate of the distribution of the domains with a specific chirality. In the DC_{ac} phase obtained by applying a low frequency (∼100 Hz) ac field the measurement was carried out before racemization sets in. In this case the two modes are not very well resolved, implying that the chiral segregation is not very good. This is also corroborated by the more rapid racemization observed in this case. In the case of DC_{ac} phase obtained with frequencies >1 kHz the two modes are quite broad and the area under the corresponding curves is also similar showing that the distribution of domains with opposite chirality is not very clear. However, in the case of DC_{dc} phase the modes are well resolved, which shows that the dc field aids in a better chiral segregation leading to well separated chiral domains. Also the curve in the low intensity region corresponding to the dark domains with a specific chirality clearly occupies a larger area which means that they are present to a larger extent. Interestingly the preference for domains with a specific chirality always remains the same, even if the domains are formed under a dc field applied in the opposite direction.

C. Electro-optics

The electro-optic response was investigated by using the triangular wave technique [18] after switching off the square wave electric field used to obtain the DC_{dc} and DC_{ac} phases. An applied voltage of 10 V/μm at a frequency of 10 Hz was used in the experiment. In the DC_{dc} phase, between slightly uncrossed polarizers, a clear interchange between the brightness of the two types of chiral domains could be observed with reversal of field [Figs. 5(a) and 5(b)], (see also Movie.1 in the Supplemental Material [19]). This shows that there is a change in the chiral sense within the domains. A single polarization reversal peak can be observed in the current response [Fig. 5(c)] for each half cycle indicating a ferroelectric type of switching behavior. On switching off the field the chiral sense of a domain is retained showing that the process is bistable and that the ground state structure corresponds to SmC_SP_F. As already mentioned the sample cooled under 500 Hz ac field has a tendency for racemization when the square wave field, used to form the domains, is removed. Therefore, although a switching behavior similar to what is observed in the DC_{dc} phase can be observed initially, the periodically varying triangular wave field drives the sample towards racemization. Even the chiral domains formed in the DC_{ac} phase obtained by cooling under a high frequency square wave field (e.g., 2 kHz), which usually remain stable after switching off the field, are affected by a low frequency triangular wave field. This is evidenced by the formation of small regions of opposite chirality within the bigger chiral domains. In spite of this, the bigger domains as a whole continue to exhibit a ferroelectric switching behavior (see Movie.2 [19]). The switching polarization (P_s) was measured in all the cases and was found to be highest in the DC_{dc} phase and lowest in the DC_{ac} phase obtained when $f = 500$ Hz [Fig. 6]. Further P_s measured in all the DC phases formed by applying the field in the isotropic phase is much higher than what is obtained in a sample where the chiral domains are formed by applying the field in the B_{1rev} phase as reported earlier [17].

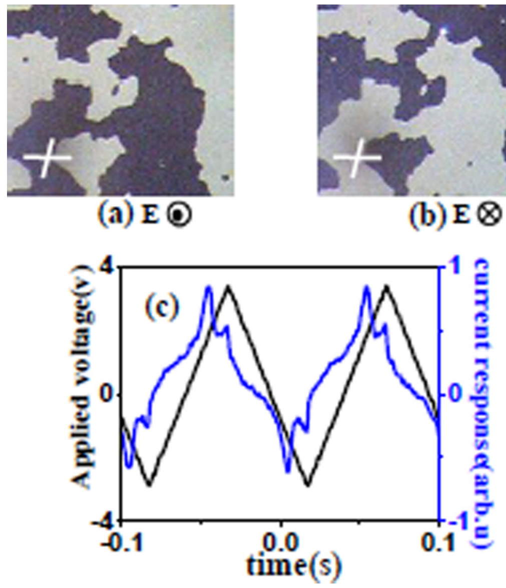


FIG. 5. (Color online) Electro-optic switching in the DC_{dc} phase under a triangular wave field at 121 °C, 10 V/μm at $f = 10$ Hz. (a) and (b) Optical textures showing the interchange of the chiral sense in the domains on reversal of field. Analyzer rotated by 2° from crossed position in the clockwise direction in both cases. (c) Corresponding switching current response.

D. Dielectric studies

Dielectric studies were also found to reflect the trend shown by P_s. The real part of the dielectric permittivity (ε') was found to be slightly higher when measured in the DC_{dc} phase

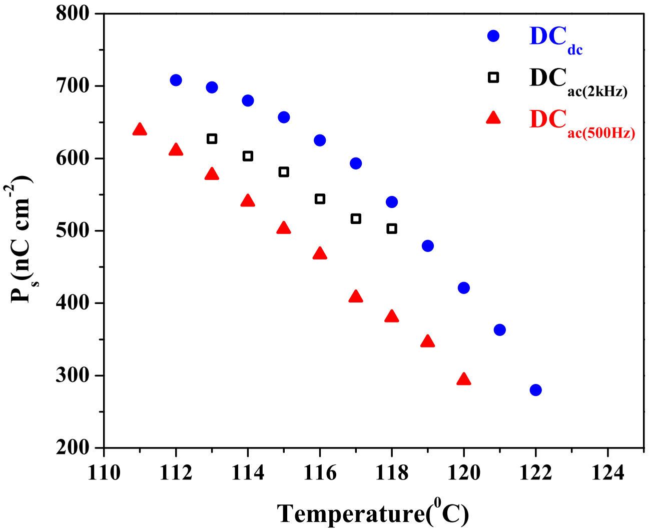


FIG. 6. (Color online) Temperature dependence of the switching polarization in the DC_{dc} and DC_{ac} phases.

[Fig. 7(a)]. The frequency variation of the imaginary part of the permittivity (ε'') shows up one mode in the high frequency range ($mode_H$) which corresponds to molecular reorientation, with the relaxation frequency (f_r^H) in the range of 10^5 Hz in both the DC_{ac} and DC_{dc} phases. The low frequency mode ($mode_L$) is not clear in the DC_{ac} phase but is prominent in the DC_{dc} phase, with the relaxation frequency f_r^L being in the range of 10^3 Hz. [Fig. 7(b)]. The dielectric strengths ($\Delta\varepsilon$) of the high and low frequency modes have been obtained by fitting the data to a generalized Cole-Cole equation [20]. A comparison of the dielectric strengths in the DC phases at a temperature (116 °C) when the chiral domains are well formed shows that $\Delta\varepsilon_H$ corresponding to $mode_H$ is quite low and, respectively, equal to 0.19 and 0.95 in the DC_{ac} and DC_{dc} phases. On the other hand $\Delta\varepsilon_L$ corresponding to $mode_L$ in the DC_{dc} phase is found to be slightly higher and equal to 2.9.

IV. DISCUSSION

Electric-field-induced dark textures with switchable chiral domains reported earlier in BCLCs have been found to form by application of a sufficiently high field in samples in which the texture initially appears birefringent. The chiral domains form above a certain threshold voltage (10–20 V/μm) by a continuous transformation from the birefringent texture [9,10] or after switching off the field [11]. Under a triangular wave field a clear interchange of the handedness of the domains can be observed under the microscope and the switching is bistable in nature with a ferroelectric ground state. Two models have been mainly used to account for the dark texture and switching of chirality in the domains. In one of the models, the dark texture is attributed to smectic layers present parallel to the substrate and a helical superstructure formed by molecules tilted with respect to the layers [10]. The chiral domains are supposed to be composed of opposite handed helices. Further, the switching of chirality within the domains is explained by assuming that the layers have a triclinic symmetry as in the SmC_G phase. Another model is based on the existence of chiral conformers of BC molecules [7]. Existence of chiral conformational states in achiral BC molecules has been indicated in experiments [21]. Computer simulations have also shown evidence for the existence of chiral conformers of some BC molecules [22]. Deracemization can therefore occur by segregation of enantiomeric conformers. Theoretical calculations show that deracemization depends on factors such as packing density, polar order within the layers depending on spontaneous polarization, and tilt angle of the molecules [22]. The coupling between molecular conformational chirality and layer chirality, which depends on the polarization and tilt, finally leads to the formation of chiral domains. The electric field aids in improving the molecular organization within a layer, resulting in a better packing of similar conformers, leading to enhanced chiral segregation. But beyond a certain limit such a packing is not sustained in flat layers and results in layer distortion [7]. It would be appropriate to mention here that the spontaneously formed DC phase exhibited by the lower homologue with alkyl chain length $n = 11$ of the same series

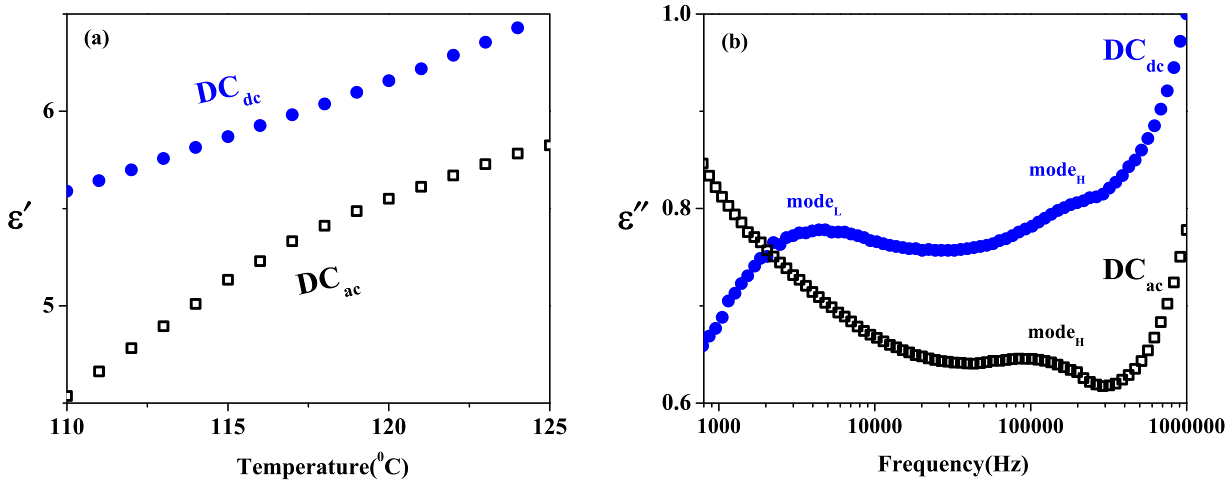


FIG. 7. (Color online) (a) Temperature variation of the real part of the dielectric permittivity (ε') in the DC_{dc} and DC_{ac} phases measured at $f = 1$ kHz. (b) Frequency variation of the imaginary part of the dielectric permittivity (ε'') in the DC_{dc} and DC_{ac} phases at 116 °C.

to which NMTBB belongs [16] has been investigated using TEM [23]. A clear signature for the formation of focal conic domains as observed with a typical DC phase [4] was found for this compound implying that the dark phase exhibited by this compound owes its origin to layer distortion. It is to be noted that the computer simulations which show the existence of chiral conformers have been carried out on a BC molecule with a structure very similar to that of NMTBB [22]. This shows that the tendency to form DC phases with distorted layer structures by compounds belonging to this series is related with the molecular structure and the presence of conformers. We therefore consider that the mechanism for the formation of the field-induced DC phase in the case of NMTBB is related with the chiral segregation strengthened by the applied field.

We will now consider the formation of the nucleating conglomerate domains of different shapes. Starting with the dc field the fractal growth patterns appear very similar to fractals observed in various other soft matter systems. Normally fractals are accounted for by two processes, viz., percolation mechanism and diffusion-limited aggregation (DLA) [24]. In the former case the domains or clusters are said to have an occupational probability with further growth governed by local interactions. In the case of DLA the domains originate and then diffuse randomly and aggregate to form larger domains. The resulting fractal dimensions in these two cases are different. The Sm*CP* phase of bent-core liquid crystals is sometimes found to nucleate from the isotropic phase in the form of fractal domains. Based on an analysis of the fractal dimensions, the percolation mechanism has been used to account for this [25]. It has also been observed that the fractal dimensions in this case are not affected by the rate of cooling and quench depth. In one particular case, conglomerate fractal domains which finally change into chiral domains have been found to form in the Sm*CP* phase [26]. However, these domains are not stable with respect to an electric field and transform into the SmC_AP_A phase with a highly birefringent grainy texture which eventually changes into a fan texture. In this respect, the stable chiral domains obtained from conglomerate fractal structures under a dc field in the present NMTBB sample are quite distinct.

As the NMTBB sample is cooled from the isotropic phase under the dc field chiral segregation starts occurring due to the effect of both molecular conformational chirality and layer chirality. As the polar direction is fixed by the dc field, the layer chirality is mainly decided by the average local tilt of the molecules. In accordance with the percolation mechanism because of local interactions and mainly due to steric reasons, molecules in the close vicinity adopt similar tilt orientations and the fractal domain starts enlarging. The sense of chirality is decided by the type of coupling between the molecular conformational chirality and the layer chirality. Incidentally an analysis of the fractal dimensions (D) of the conglomerate fractal domains based on the fractal box counting method [27] gives a value of $D = 1.8968$ [Fig. 8] which is in the range expected for the percolation mechanism.

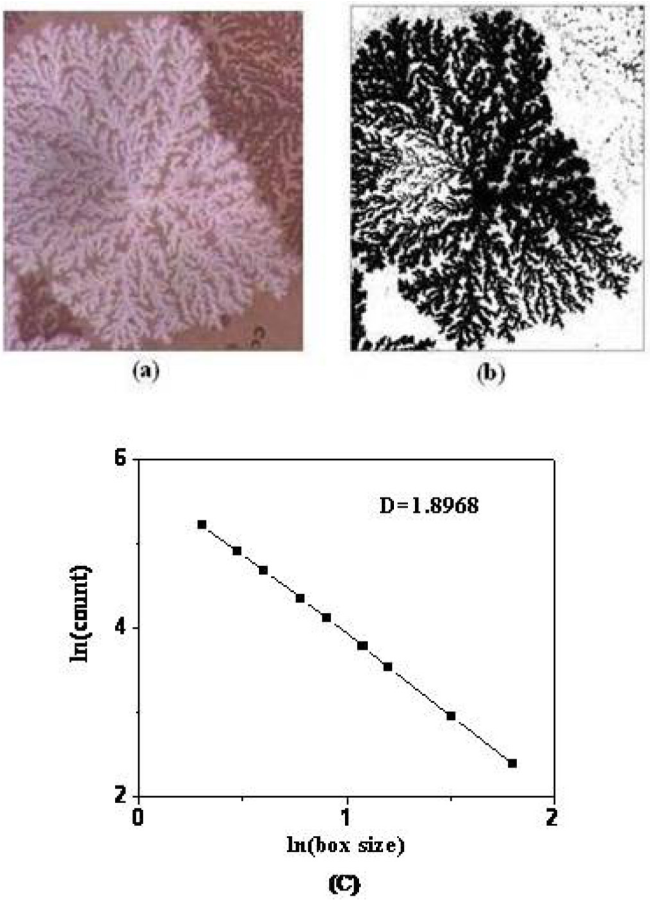


FIG. 8. (Color online) Images used to calculate the fractal dimension of the domains obtained under a dc field of 10 V/μm. (a) Optical texture of the fractal domain, (b) binary image used for the fractal box counting method, (c) plot of number of boxes with increasing size against box size used to obtain the fractal dimension D by IMAGEJ software.

In the absence of the electric field there is no preference and both left-handed and right-handed domains are equally probable as usually observed in the DC phase formed spontaneously from the isotropic phase. But in the presence of the field a specific combination of the molecular conformational chirality and layer chirality would be energetically more favorable. Domains in which this condition is satisfied would be preferable. The specific sense of chirality depends on the type of coupling. The particular choice is related with the molecular twisting power and the magnitude of the tilt angle which may also have some influence from the applied field. As mentioned earlier the layer chirality is decided by the combination of both tilt orientation and polarization. As the polar direction is fixed under the dc field, domains in which the tilt orientation gives rise to a layer chirality that satisfies the minimum energy condition would be more in number. When the field direction is reversed, though the polarization is reversed, domains in which the tilt orientation is opposite would now have the same sense of layer chirality that can couple with the molecular chirality to minimize the energy. These domains, which have the same handedness as in the former case, therefore form in excess. This is the reason that domains with the same sense of chirality are found in excess irrespective of the direction of the applied dc field. A thorough experimental investigation into this aspect is not very easy and would be considered in the future. However, we would like to emphasize that the present experimental results are quite reproducible and clearly indicate a preference for domains with one type of chirality when formed under the dc field.

Let us now consider the domain formation under the ac field. In this case the chiral segregation and domain nucleation are based on similar factors as described above and the handedness of the domains as discussed earlier is decided by the coupling of the molecular conformational chirality and layer chirality. However, the mechanism of further growth appears to be different. When the nucleation process begins, as the field direction is periodically varying, domains with opposite chirality can form in close proximity depending on the local tilt and polarization direction determined by the field at that instance of time. The growth rate of the domains is much slower in this case. The temperature range over which the domains grow and coalesce is found to be larger during the formation of the $\mathrm{DC_{ac}}$ phase than in the case of the $\mathrm{DC_{dc}}$ phase. The exact reason is still not very clear to us, but as the ac field causes a periodic reorientation of the polarization, and hence the layer chirality, it may be difficult for domains of one type to enlarge very fast. In fact the domain size is found to be larger when the frequency is lower and the reorientation slower [see Fig. 2(a)]. The cooling rate does not really affect the shape of the domains. A comparison of the domain shapes obtained by maintaining the frequency of the applied field equal to 2 kHz, but changing the cooling rate from 1 °C/min to 0.1 °C/min, results in domains with circular shape in both cases. This shows that the shape transitions are influenced only by the frequency of the applied field. A detailed analysis of the kinetics of growth under the field is required to understand this behavior.

The shapes of the domains obtained as a function of frequency have a striking resemblance to the domains observed in lipid monolayers where they have been attributed to compositional changes [28], and domains formed at the liquid expanded to liquid condensed phase transition of myristic acid monolayers where they occur due to concentration gradients [29]. Domain shapes occurring in phospholipid monolayers have been explained by McConnell's shape transition theory which is based on a competition between the line tension at the boundary, which prefers compact circular shapes and electrostatic interactions [30,31]. It has also been shown in this case that harmonic domain shape transitions can be induced by external fields where the field can be periodically varying [32]. However in the case of the NMTBB sample the chiral domains obtained under an ac field correspond to a three-dimensional system. As mentioned earlier the generation of layer chirality in the case of achiral BC molecules owes its origin to a special reason which involves a combination of polarization and tilt. While the tilt is determined by electrostatic interactions between the permanent dipoles, the equilibrium direction of the spontaneous polarization is set by a balance between the dispersion and dipole-dipole interactions [33]. The equilibrium shape of the chiral domains that form in the presence of a periodically varying electric field $E = E_0 \sin\omega t$ can therefore be obtained by minimization of a free energy which should also consist of a surface term which can describe the shape changes.

$$F_{\text{Chiral domain}} = F_S + F_{(P,\theta)} + F_E. \tag{1}$$

Understanding scaling hypotheses and curvature-driven coarsening dynamics during domain growth is of interest in both physical and biological systems [34]. An analysis of the formation and coarsening of chiral domains formed by an electric-field-induced deracemization in a liquid crystal made of achiral bent-core molecules has shown that the process is curvature driven [35]. The chiral domains obtained with NMTBB under electric fields can therefore be an interesting experimental system where the relationship between growth morphology and distribution of domain areas, formation of interfaces, and final coarsening can be followed in a very controlled manner on a single sample by forming the domains under different types of electric fields. As seen in Fig. 3 the growth patterns have a direct influence on the fluctuations at the interface which makes it corrugated when formed at higher frequencies. This also affects uniformity within the domains, with those obtained at 1 kHz [Fig. 3(b)] appearing smoother than those obtained at 4 kHz [Fig. 3(f)].

The switching of chirality of the domains under a triangular wave field can also be explained as due to a coupling of the molecular conformational chirality and layer chirality. Based on the strength of this coupling, the change in layer chirality brought about by rotation around the long axis can also induce a change of the conformational chirality which can lead to the optical effect that can be observed under the polarizing microscope [7]. The enhanced low frequency peak shown by dielectric studies indicates the presence of ferroelectric clusters and the high values of switching polarization is related with the increased ferroelectric order caused by the packing of the enantiomeric conformers. However, the low values of the dielectric strength, which is much smaller than what is usually observed in Sm*CP* phases with flat layers, support the idea that there is layer distortion.

From a practical point of view this study is of interest as it demonstrates the possibility of controlling the enantioselectivity which can have interesting technological consequences. Different strategies such as specific molecular design architectures [36] or using incident light to flip chirality [37] have been tried with chiral molecules. But it is not easy to bias chiral segregation or selectively produce macroscopic conglomerates of one type in the case of achiral molecules or in systems where chirality can be influenced by external means. It has been shown that this could even lead to a nonuniform situation where one type of enantiomer can arrange into a supramolecular structure, whereas the other type is not well organized [38]. In the case of achiral inorganic molecules such as $\mathrm{NaClO_3}$ the enantiomeric ratio of the optically active chiral crystals can be biased only by constant stirring during the crystallization process [1], and with 1,1-binaphthyl crystal, chiral symmetry breaking is found to be more efficient only when growth rate is extremely slow. At faster growth rates the solid phase can even become polycrystalline and the racemic phase can be present within the chiral phase [3].

There have also been some reports on chiral segregation in the case of liquid crystals made of achiral BC molecules under an applied field. Homochiral and racemic states have been observed to segregate in the presence of an electric field [39]. In specially prepared mixtures of the bent-core compound NOBOW and 8CB, helical filaments of the B4 phase have been found to preserve the sense of chirality as they grow from the isotropic phase [40]. But usually it is difficult to make detailed observations or control the growth morphology of the chiral domains and chiral segregation or enantiomeric excess in the DC phase formed spontaneously on cooling from the isotropic phase. There have been some attempts to obtain chiral domains with a specific handedness in BCLCs by addition of a chiral dopant [41]. Preferential formation of one type of conglomerate has been observed in a compound that exhibits a phase transition from a calamitic nematic (N) phase into the B_x phase when taken in twisted cells [42]. Bent-core dimers with photochromic groups have been found to form chiral domains of one handedness in the presence of circularly polarized light [43]. But most often these chiral domains do not respond to electric fields. In this regard switchable DC phases obtained with NMTBB are attractive, especially as the properties such as switching polarization can also be tuned on a single sample by just forming the chiral domains under different conditions.

V. CONCLUSIONS

Our studies on electric-field-induced nucleation and formation of chiral domains show that while the dc field promotes deracemization in the form of fractal conglomerate domains, the morphology of the chiral domains nucleating under ac fields depends on the frequency. The chiral domains in the DC phase formed under high frequency fields are sustained even after switching off the field, but domains formed under low frequency fields are unstable and tend towards racemization. We also find that the shape of the growing domains has an influence on the stability of the DC phase and affects the dielectric parameters and switching polarization. The domain shapes observed under the ac field appear similar to those observed in 2D monolayers and can be used as a convenient system for studying the affect of electrostatic interactions in the presence of electric fields on shape transitions and coarsening dynamics. In addition, this study also demonstrates the possibility of obtaining controlled deracemization with selective enantiomeric state and tunable properties in a single sample, by just forming the chiral domains under different types of electric fields. The switching property and field-induced changes in optical contrast of the domains opens up the possibility of using these electro-responsive homochiral thin films to form novel electro-optic devices.

ACKNOWLEDGMENT

The authors thank Professor B. K. Sadashiva for providing the bent-core liquid crystal NMTBB.

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