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Optically isotropic liquid-crystal phase of bent-core molecules with polar nanostructure

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We found that the optically isotropic (I_M) mesophase observed recently below the nematic phase of the bent-core liquid crystal 4-chlororesorcinol bis[4-(4-n-dodecylxybenzoyloxy)benzoate] shows ferroelectric-type switching. Polarizing microscopic, electric current, dielectric, and dynamic light scattering studies lead us to propose that the I_M phase is composed of interconnected orthorhombic racemic smectic (Sm-C_P1) nanodomains with random layer orientations. Near the nematic phase, where the polarization can be saturated by electric fields, the system responds in a fashion analogous to the granular structure of a magnetic spin glass—in particular, we observed that the relaxation back to the nonpoled structure follows a similar, inverse logarithmic rule.

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I. INTRODUCTION

The discovery of the mesogenic properties of bent-core molecules has opened up a major new and exciting direction in the science of thermotropic liquid crystals (LC’s). Seminal findings—with broad implications for the general field of soft condensed matter—include the observation of (anti)ferroelectricity and spontaneous chiral symmetry breaking in phases that are solid like in one dimension (smectic phases) but are composed of molecules that are not intrinsically chiral themselves [1–4]. To date, most of the research effort has focused on bent-core smectics [5], mainly since nematic phases are rather uncommon in bent-core compounds. This is because the translational freedom required for a nematic phase is typically favored when the molecules can rotate relatively freely around their long axis, a property that is not readily compatible with bent-shaped molecules. Indeed, the viscosities associated with both director rotations and flow in the optically uniaxial nematic phase of bent-shaped molecules [6–9] are unusually high, a feature that has led to the suggestion of a structure consisting of smectic “cybotactic” groups even far away from a smectic phase [10,11]. Since the cybotactic groups are uncorrelated and perpetually changing, we do not expect macroscopic polarization in the nematic phase, but only in a polar smectic phase below the nematic. A few examples found recently include N−Sm-A−Sm-C−Sm-CP [7,12] and N−Sm-CP [8,13,14] polymorphisms. In these cases the Sm-CP phases were antiferroelectric and birefringent.

Recently Pelzl et al. [15] and Weissflog et al. [16] have reported a material, 4-chlororesorcinol bis[4-(4-n-dodecylxybenzoyloxy)benzoate] (4-CBDB), with an unusual transition from a nematic phase to an optically isotropic (I_M) mesophase with local smectic structure. Both the nematic and I_M phases are monotropic with the following phase sequence in cooling: I 95 °C N 80 °C I_M 64 °C Cr. In heating the melting point is 98 °C. By x-ray measurements the presence of cybotactic smectic groups was observed over the entire nematic range with correlation length in the range of 4–5 nm. Upon the transition to the I_M phase the smectic layer correlation length was increased 22 nm [17]. Simultaneously, the diffuse spots disappeared and formed a closed ring, indicating an isotropic distribution of the smectic layers. The director tilt angle was found to be about 45° both in the smectic phase and in the cybotactic groups of the nematic phase. This value was derived from the relative position of the small-angle scattering with respect to that of the wide-angle scattering.

From the measured layer periodicity and tilt angle, furthermore using the structural model of the molecule, the opening angle (the angle between the molecular arms) was estimated to be 140°. It was also pointed out that in several aspects (weak birefringence, short layer correlation length) the I_M phase is similar to the so-called smectic blue phases [18], although there are also a number of profound differences. First of all, the Sm blue phases appear below the isotropic and above a TGB phase, whereas the I_M lies below the nematic and above a crystal phase. Second, the x-ray profiles of Sm blue phases show definite peaks, whereas in the I_M phase of 4-CBDB only a uniform ring was observed, which points to random layer orientations similar, for example, to the sponge phase of lyotropic systems.

The aim of the present study is to determine more completely the properties of the I_M phase through a range of experimental techniques and to thereby offer a more definite model for its structure. Our measurements lead us to propose that the I_M phase consists of randomly aligned, antiferroelectric smectic (SmC_P1) nanodomains.

II. EXPERIMENTAL RESULTS

We conducted polarizing microscopic, electric current, dielectric, and dynamic light scattering measurements on samples of 4-CBDB.
> 10 V/μm for a few seconds [see the electrode area of Fig. 1(c)] or on further cooling without electric field [Fig. 1(d)], the texture becomes completely black between crossed polarizers.

**B. Polarization measurements**

Electric current measurements were performed on the samples described above first by the triangular voltage method. For applied electric fields above ~10 V/μm, we observed the appearance of single peaks in the current in each half period, which is a clear indication for ferroelectric-type polarization switching. The temperature and electric field dependences of the electric currents are shown in Figs. 2(a) and 2(b), respectively. The peaks completely disappear in the nematic phase, which rules out the influence of ionic effects and assures the ferroelectric origin of the observations. We note that in some cases one can observe only one peak even in antiferroelectric materials if the period of the applied triangular voltage is short compared to the ferroelectric-antiferroelectric relaxation time. To clarify this, we also have measured the polarization by the Diamant-Bridge method [19] [see the inset of Fig. 2(c)] and observed only single hysteresis loop down to the lowest frequency (1 Hz) available in the measurement, again indicating ferroelectric-type switching.

The electric field dependence of the magnitude of the polarization at 77 °C is plotted in Fig. 2(c). The apparent polarization increases up to about 500 nC/cm² at 40 V/μm, which is the highest field we could reach without electric fields.

**FIG. 2.** (Color online) Summary of the electric current measurements on a 4-μm-thick sample in the I_M phase. (a) Time-dependent response under triangular voltages ($E=25$ V/μm) at different temperatures. (b) Time-dependent response at $T=77$ °C under triangular voltages of different amplitudes. (c) The field dependence of the polarization at 77 °C (inset shows the hysteresis loop measured by Diamant-Bridge method). (d) The field dependence of the switching time as determined by the current peak position under square wave fields at 77 °C.
breakdown. At lower temperatures the polarization, measured at a fixed 40 V/μm field decreases, but is still measurable down to 64 °C. The apparent decrease is attributable to a continuous shift to higher switching threshold with decreasing temperatures.

C. Dielectric measurements

We measured the dielectric properties of a 5-μm film in the same type of electro-optical cell (with antiparallel rubbed polyimide alignment layers) over a frequency range of from 20 Hz to 1 MHz by a precision LCR meter (Quadtech, model 1920). Figure 3 displays the temperature dependence of the dielectric constants at two fixed frequencies (2 kHz and 100 kHz). The data reveal the existence of a low-frequency mode that relaxes above 2 kHz. At 100 kHz the dielectric constant is smaller in the \( I_M \) than in the homogeneously aligned nematic phase, indicating that the rotation around the average molecular long axis is much more suppressed in the \( I_M \) phase.

The frequency dependences of the real and imaginary parts of the dielectric constants before and after 5 and 30 min applications of the field (Fig. 3). The different curves correspond to the same sample right after it was cooled from the nematic phase and with no prior exposure to an electric field (“virgin” sample). The other two curves were measured after a 16.5-V/μm 27-Hz triangular field was applied for 5 and 30 min, respectively. In all samples there is a higher-frequency relaxation mode at around 450 kHz, which does not depend much on the field treatment applied prior to the dielectric measurement. There is another mode at around 7 kHz, which is weak in the virgin (or relaxed) sample, but strengthened substantially after field treatment. Its amplitude saturates after about 15 min of field treatment (or faster if higher fields are applied). At the saturated stage the strength of the susceptibility related to this mode is about 5. This low-frequency mode decays slowly in time following an inverse logarithmic law [see inset of Fig. 3(a)], implying a continuously slowing relaxation process at increasing time scales. This situation is very similar to the nature of the magnetization relaxation in spin glasses [20] with a polydisperse size distribution of the magnetic granules [21]. The stress relaxation from the randomly oriented state toward uniformly aligned liquid crystalline elastomers follows this behavior, too [22], as does the relaxation of granular materials from their lower-density structure to the higher-density final steady state [23].

D. Light scattering measurements

Light scattering studies were also performed in order to test for optical anisotropy with greater sensitivity. The optical anisotropy \( \Delta n \), detected either through the depolarized forward transmission of normally incident laser light [Fig. 4(a)] or the time correlation function of depolarized intensity fluctuations [Fig. 4(b)], can be estimated to be at least two orders of magnitude smaller in the \( I_M \) than in the nematic phase. During cooling through the \( N \)-to-\( I_M \) transition in zero field, we observed a continuous decrease in the amplitude-to-background ratio of the correlation function for director fluctuations, which is consistent with the coexistence of nematic and randomly aligned, microscopic \( I_M \) domains [as detected in the texture in Fig. 1(c)]. The fully developed \( I_M \) phase produced practically no observable dynamic scattering in zero field. In isolated spots (probed by a focused laser beam), however, a low-frequency sinusoidal electric field with \( E \sim 2–3 \) V/μm amplitude induces a weak optical anisotropy, and an oscillatory correlation function [Fig. 4(b)] was observed with the same frequency as the applied field. This is consistent with a linear (i.e., polar) response to the field. In the nematic phase, the relaxation rate of director fluctuations is nearly two orders of magnitude smaller than for ordinary calamitics. This is similar to other bent-core nematic materials [10] and can be explained by enhanced rotational viscosities that would arise due to cybotactic groups. The overall uniaxial nematic behavior implies that the morphology of the cybotactic groups fluctuates rapidly such that the in-layer orientational order (and polarization) associated with close-packed bent cores is averaged out over short lengths.

III. DISCUSSION

One could explain the optical isotropy characteristic of the \( I_M \) phase by assuming large single smectic domains with anticalinic tilt order, a 45° tilt angle [24], and a nearly 109.5° opening angle of the bent cores [25,26]. This situation indeed
has been observed experimentally for an antiferroelectric anticonclic bent-core smectic with long-range layer correlations [27]. However, in the presently studied 4-CBDB, the opening angle, at least in the nematic phase, is far from the tetrahedral (109.5°) angle, and the layer correlation length is short (~22 nm) [17]. In this case, one can produce an optically isotropic structure by assuming that the short-range smectic order arises due to a collection of nanoscopic smectic domains, with an uncorrelated layer orientation among the different domains. Although the individual nanodomains may be birefringent, the material would still appear optically isotropic, because the optical axis is randomly oriented on a length scale much smaller than the wavelength of visible light. A similar model was suggested recently by Huang et al. [28] and Ortega et al. [29] without, however, any observation of ferroelectric switching. We note that the optical isotropy would be true for either anticonclic or synclinic director structure in the granules, although the anticlinic structure, especially for the 45° tilt angle, in every other layer the director would need to be perpendicular to the rubbing direction, which would depress the transition at the surface regions. This is consistent with the observed texture at the phase transition, which reveals a 1–2 °C coexistence region characterized by a weakly birefringent pattern reflecting the rubbing direction, therefore indicating that it is coming from the surface region. We note that the phase sequences in anticonclic antiferroelectric materials of chiral rod-shaped molecules are known to be also very sensitive to the surface effects [30]. An anticlinic structure can also explain the observations that a strong electric field, which can break the surface anchoring (and thus switch the synclinic surface structure to anticlinic), can induce complete optical isotropy in this coexistence region.

In principle, the optical properties of the \( I_M \) phase, observed during switching, could also be explained by a different model proposed by Focia et al. [31], wherein a racemic structure is produced by a mixture of anticonclic antiferroelectric nanodomains of opposite chiralities. Due to the antiferroelectric nature of this model, we would need to assume that the slow decay of the low-frequency dielectric mode is related to the ferroelectric-antiferroelectric relaxation. However, it is hard to imagine that such a relaxation would follow the observed inverse logarithmic rule characterized by exponentially increasing time scales. A broad spread in relaxation rates could arise when there is a distribution in the size and shape of structural units and when units that have relaxed to an equilibrium orientational distribution hinder other units from finding it. This is very different from the ferroelectric-to-antiferroelectric relaxation process, which is determined by local next-layer interactions that should give rise to a single well-defined relaxation time.

The observed polarization current curves shown in Figs. 2(a) and 2(b) and the one-loop hysteresis curve [Fig. 2(c)] all indicate local ferroelectric order. Similarly, the observed low-frequency dielectric mode, which becomes stronger after poling the film by strong electric fields [see Fig. 3(a)], also points to local ferroelectric order. The optical isotropy and short smectic coherence length suggest a nanodomain structure in the \( I_M \) phase with a random smectic layer orientation. In this case, an external electric field would exert a ferroelectric torque on the layers in the nanodomains and (at sufficiently high field) eventually would reorient the layers parallel to the field direction. We found this poling to be more effective when the field was applied just below the nematic phase and where we observed a saturation of the polarization [Fig. 2(c)]. It is important to note that in the plane normal to the field the orientation of the layer normal would be still arbitrary, thus maintaining the optical isotropy for normal light incidence. The nanodomain structure, corresponding to the above considerations of the \( I_M \) phase, is sketched in Fig. 5.

The dramatically reduced dynamic light scattering [Fig. 4(b)] found in the fully developed \( I_M \) phase suggests
FIG. 5. Sketch of the model of the optically isotropic ferroelectric phase. Lines within the smectic granules indicate the layer planes. Enlarged we show the local director structure and molecular polarization direction within the smectic layers. At high fields \( E \) \( >30 \) V/\( \mu m \) and close to the nematic phase, the grains may rotate so that the majority of the layers turn parallel to the field, but the layers between granules remain randomly oriented in the plane of the cell.

that at low temperature the nanodomains are not free to rotate, but are locked in their random orientations (e.g., by a network of defects). At higher temperatures, however, rotation would be possible if the interfaces between smectic nano-domains are melted.

Two qualitative tests of the self-consistency of our results can be made from the polarization and dielectric data. First we estimate the dielectric relaxation time—i.e., the decay time of the induced polarization—which averages out soon after field removal due to polarization self-interaction. Just as for helical smectic-C liquid crystals, where the relaxation time is determined by the wave numbers \( q=2\pi/p \) (\( p \) is the pitch of the helix), in our proposed model for the \( I_M \) phase, the analogous wave number would be \( q \sim 2\pi/\xi \), where \( \xi \) is the orientational correlation length. For the purposes of a rough calculation, we can then use an expression [32] for the static dielectric susceptibility, \( \chi=P_{in}/E=(P/\xi\theta)^2/2\varepsilon_0K \), where \( E \) is the applied electric field that induces a polarization \( P_{in} \), \( K \sim 10^{-11} \) N is the Frank elastic constant for azimuthal rotation of the tilted director, \( P \) is the saturated ferroelectric polarization, and \( \theta \) is the director tilt angle. Our data for the \( I_M \) phase (Figs. 2 and 3) gave \( \chi \sim 5 \) and \( P \sim 500 \) nC/cm\(^2\). Then, using \( \theta \sim \pi/4 \) rad (45\(^\circ\)), we find \( q \sim 2 \times 10^9 \) m\(^{-1}\), providing an estimate of \( \xi \sim 30 \) nm, which is indeed of the same order as the smectic coherence length. As a second check on consistency, we estimate the rotational viscosity both from the dielectric relaxation frequency and from the flipping time of the polarization. The dielectric relaxation frequency associated with a director rotation within the nanodomains can be related to a rotational viscosity \( \gamma \) via \( \gamma = Kq^2/\gamma \) [32]. Taking into account that the measured relaxation frequency is 7 kHz, we find \( \gamma \sim 60 \) Pa s. On the other hand the rotational viscosity can also be estimated from the switching time in an applied field through the well-known formula \( \tau \sim \gamma/PE \) [33]. From Fig. 2(d) we see, for example, that at \( E=2 \times 10^7 \) V/\( \mu m \), \( \tau \sim 0.55 \) ms, which gives \( \gamma \approx 55 \) Pa s, a value in good agreement with the estimate from dielectric relaxation measurements. This rotational viscosity value is about two orders of magnitude higher than typical values for calamitic FLC’s. This mirrors the large difference in relaxation times found for director fluctuations in bent-core nematics relative to their calamitic counterparts [10].

In summary, we described an optically isotropic liquid-crystal phase (\( I_M \)) showing ferroelectric-type electric current switching. We analyzed the possible structural models and proposed a model that may account for all the experimental observations. According to this model the \( I_M \) phase consists of randomly oriented ferroelectric nanodomains with antclinic director orientation. Ferroelectricity in optically isotropic liquid crystals is not only a unique phenomenon, which has academic interest, but also may present new practical applications, when it is desired that the electronic information set by the polarization can be decoupled from optical information.

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[17] The correlation length in the \( I_M \) phase was given in Ref. 16 as 11 nm, but after recalculating the full width at half maximum and the instrumental line width values, it is corrected to 22 nm [S. Diele (private communication)].