Optically isotropic ferroelectric liquid crystal phase

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We show that the optically isotropic phase observed recently in a bent core liquid crystal material, 4-chlororesorcinol bis[4-(4-n-dodecyloxybenzoyloxy)benzoate], is ferroelectric. Polarizing microscopic, electric current and dynamic light scattering studies reveal that the structure in the ferroelectric phase consists of weakly interconnected orthoconic racemic smectic (SmC_aP_F) granules with random layer directions.

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 (LCs). 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. [1,2,3,4] 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 shape molecules [6,7,8,9] 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] The entropy loss arising from cybotactic groups can be compensated by an energy reduction associated with the close packing of bent-core molecules achieved by a locally layered structure; the close packing in turn implies a polar molecular arrangement within the individual cybotactic groups. Since the cybotactic groups are uncorrelated and perpetually changing, we do not expect macroscopic polarization in the nematic phase. However, we can expect the formation of a polar smectic phase below the nematic. A few examples found recently include N-SmA-SmC-SmCP [7,12] and N-SmCP [8,13,14] polymorphisms. In these cases the SmCP phases were antiferroelectric and birefringent.

Very recently Pelzl et al. [15] and Weissflog et al. [16] have reported a material 4-chlororesorcinol bis[4-(4-n-dodecyloxybenzoyloxy)benzoate] (4-CBDB) with an unusual transition from a nematic phase to an optically isotropic mesophase (OIM) with local smectic structure. Its phase sequence is the following: (I 95°C N OIM 80°C) Cr 98°C. The presence of cybotactic smectic groups was observed in the entire nematic range. The monotropic, optically isotropic smectic phase that appears below the nematic phase on cooling has a correlation length

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of only about 11 nm. The director tilt angle was found to be about 45° both in the smectic phase and in the cybotactic groups of the nematic phase. The angle between the molecular arms (opening angle) was estimated as 140° in the nematic phase. It was also pointed out that in several aspects OIM is similar to the so-called smectic blue phases.[17] They are weakly birefringent ($\Delta n \sim 10^{-3}$ for Bp Sm1 and $\Delta n \sim 10^{-4}$ for BpSm2). Their smectic correlation length (~20-60nm) is also similar to the correlation lengths (~11nm) observed in the isotropic mesophase of 4-CBDB. However, 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 isotropic mesophase of 4-CBDB lies below the nematic and above a crystal phase. Second, blue phases are strongly related to chirality, whereas in 4-CBDB only weak optical activity is observed in cells thicker than 6-10μm. Finally, the X-ray profiles of Sm blue phases show definite peaks, and not the uniform ring that persists into the isotropic mesophase of 4-CBDB.

In this letter we report additional investigations on 4-CBDB and, in particular, show that the optically isotropic phase, just below the nematic, is ferroelectric, which, to our best knowledge, is the first account of an isotropic ferroelectric liquid crystal mesophase. Electric current, dynamic light scattering and polarizing microscopic measurements lead us to conclude that the ferroelectric phase consists of randomly aligned, roughly 10 nm size orthoconic anticlinic racemic smectic (SmC_aP_F) granules.

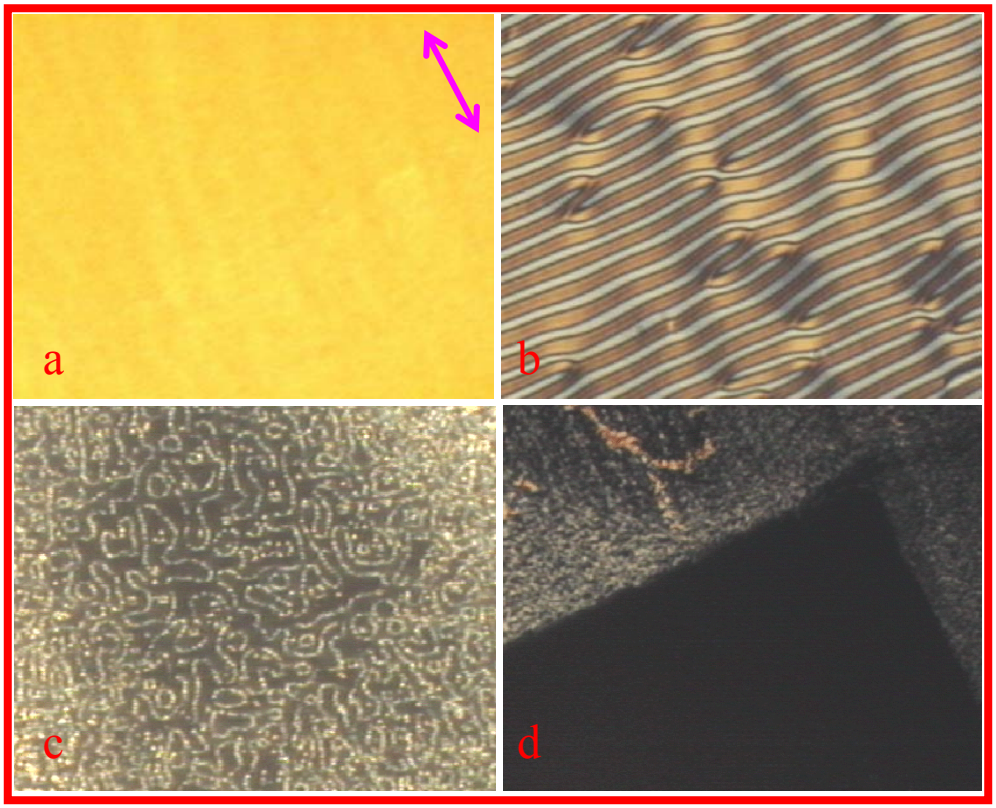

Figure 1: Typical textures of a 4μm thick sample of 4-CBDB contained in an electro-optic cell treated for homogeneous alignment of the nematic director. Pictures show 75μm x 100μm areas imaged through crossed polarizer and analyzer. Upper row: Textures in the nematic phase at zero fields (a), and under ac fields (f= 580Hz E=12.5V/μm) (b). Lower row: Textures just below the nematic phase: E=0, T=80°C (c); T=79°C, electrode and non-electrode area (d), with E=0 but after a E=12.5V/μm, f=12Hz square wave field was applied for 10 seconds. The system has stabilized into an optically isotropic state. Arrow indicates the rubbing direction. The polarizers are set in the horizontal and vertical directions.

Samples of 4-CBDB were loaded into standard electro-optic cells treated with rubbed alignment layers for homogeneous alignment of the nematic director. After cycling through the isotropic liquid, we observed uniform nematic alignment, with the optical axis oriented along the rubbing direction, over the entire nematic range. However, when electric fields are applied, the textures become inhomogeneous. As reported previously [15,16], under DC fields a domain texture, similar to a smectic phase, appears (Figure 1/a). Under AC fields, however, the patterned texture is suggestive of electrohydrodynamic instability (Figure 1/b). On cooling from the nematic phase there is a 1°C range starting at 80°C, when the optically isotropic areas are decorated with birefringent filaments (Figure 1/c). This range indicates a coexistence of the nematic and lower temperature isotropic mesophase. On further cooling, or after applying electric fields of E > 10V/μm for a few seconds, the texture becomes completely black between crossed polarizers (Figure 1/d).

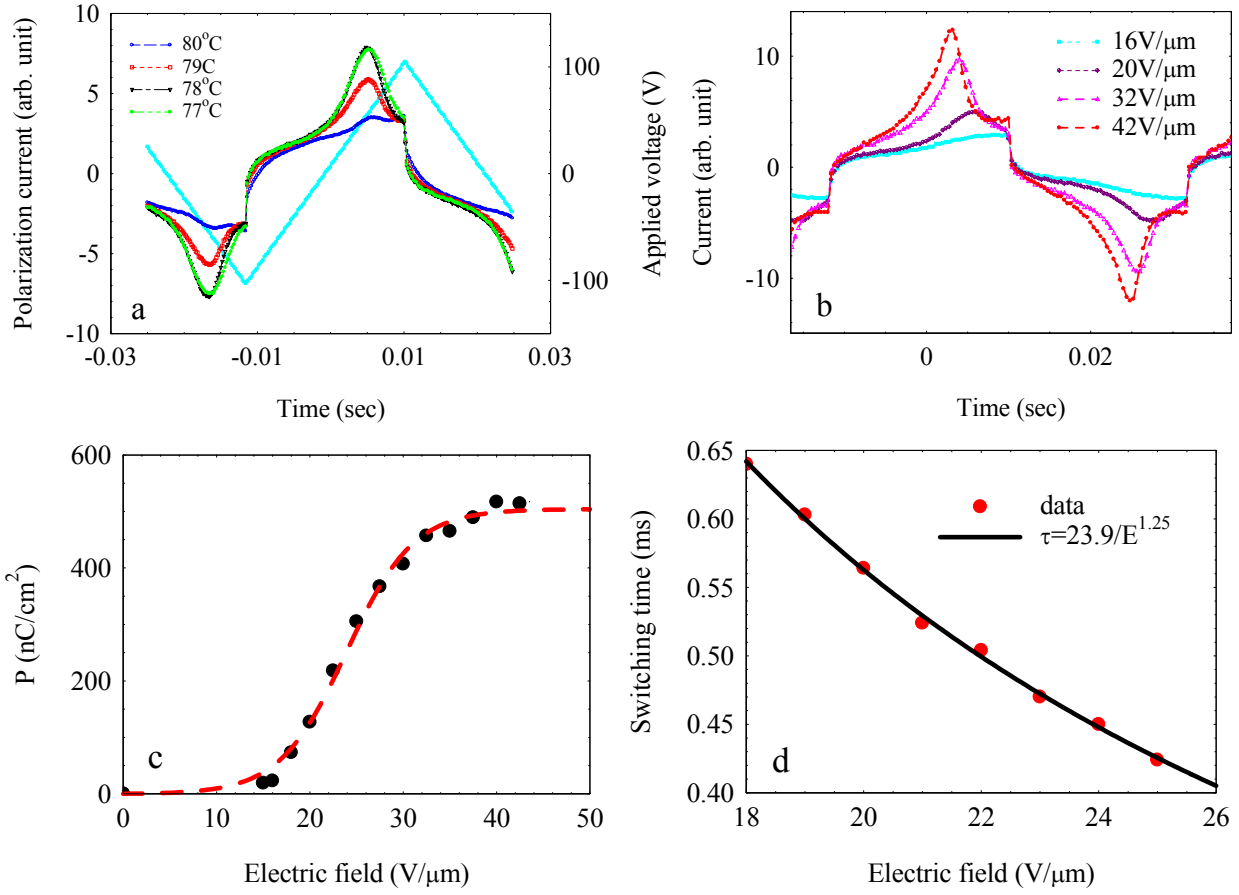

Figure 2: Summary of the electric current measurements made on a 4μm thick sample in the isotropic ferroelectric mesophase of 4-CBDB. (a) Time dependent response at different temperatures under triangular voltages (E= 25V/μm); (b) Time dependent response at T=77°C under triangular voltages of different amplitudes; (c) The field dependence of the polarization at 77°C; (d) The field dependence of the switching time as determined by the current peak position under square wave fields at 77°C.

We next performed electric current measurements using triangular electric fields. Above ~8V/μm, we observe the appearance of single peaks in the current in each half period (Figure 2/a and b), which is a clear indication for ferroelectric type polarization switching. The peaks completely disappear in the nematic phase, which rules out the influence of ionic effects and

assures the ferroelectric origin of the observations. The temperature and electric field dependence of the electric current are shown in Figure 2/a and b, respectively.

The polarization deduced from the current measurements reaches a maximum of about $500nC/cm^2$ (Figure 2/c) at $T=77^oC$ and E just above $40V/\mu m$. At lower temperatures the polarization measured at a fixed $40V/\mu m$ field decreases, but is still measurable down to 64°C. The apparent decrease is due a continuous shift to higher E of the polarization switching threshold and saturation point with decreasing temperatures. At temperatures more than 2°C below the transition from the nematic phase, the switching of the polarization occurred without any electro-optical response that could be detected in the polarizing microscope.

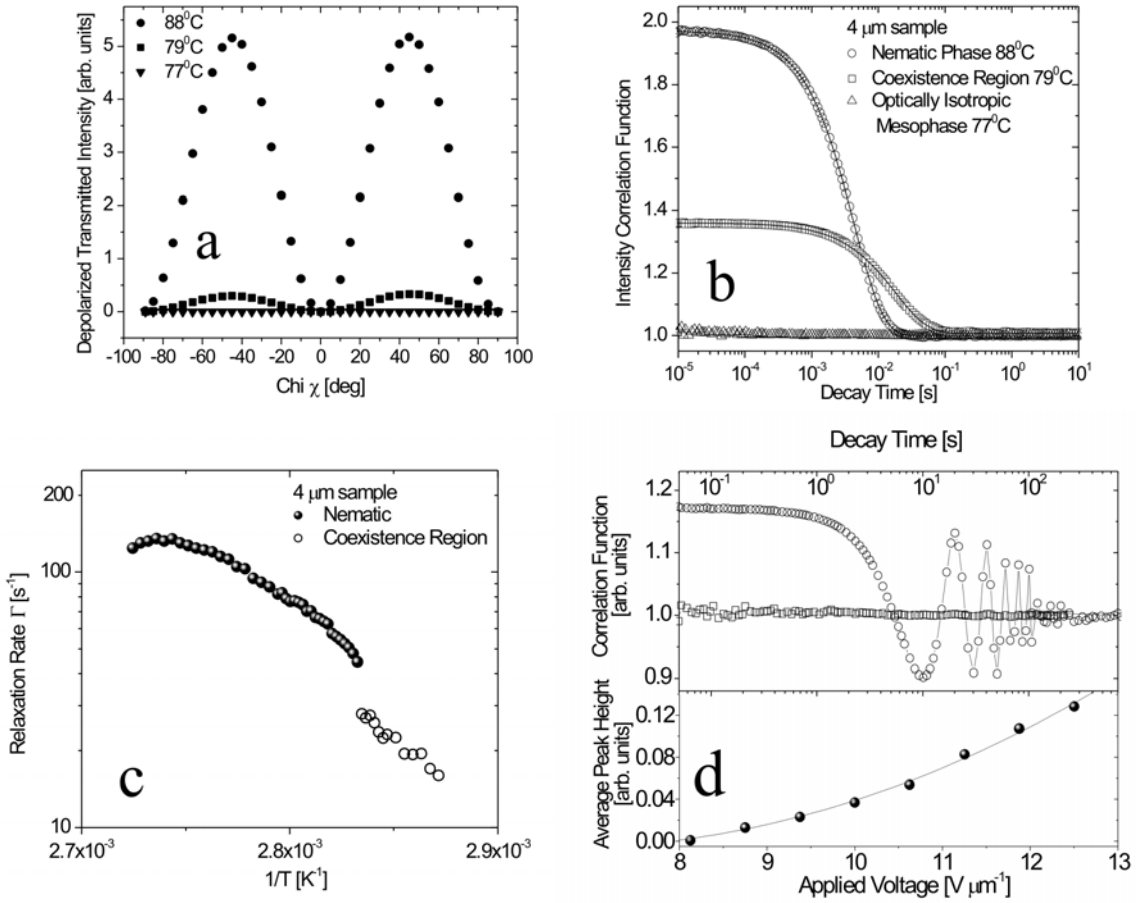

Figure 3: Summary of light scattering measurements. (a) Depolarized transmission of a normally incident HeNe laser beam through 4 μm sample of 4-CBDB as a function of the angle χ between the cell alignment direction and the polarizer axis in the nematic phase (black circles), in the coexistence region (black squares), and in the isotropic mesophase (black triangles). (b) Typical intensity-intensity correlation functions <I(0)I(t)> taken on a 4 μm sample in the nematic phase (open circles) at T=88°C, in the coexistence region (open squares) at 79°C and in the isotropic mesophase (open triangles) at 77°C. The scattering vector is 65,000 cm^{-1} along the optic axis. (c) Temperature dependence of the relaxation rate Γ of nematic director fluctuations in a homogeneously-aligned 4 μm sample without electric field. Open circles represent nematic – isotropic mesophase coexistence while black circles show nematic phase. (d) Top graph: Depolarized <I(0)I(t)> obtained on a 4 μm sample in the optically isotropic mesophase with an applied 0.05 Hz sinusoidal electric field. The scattering vector is 17,000 cm^{-1}. Open circles represent regions where it was possible to detect an electro-optical response, while open squares indicate the lack of any measurable signal in other regions. Bottom graph: Normalized amplitude of the oscillatory component of <I(0)I(t)> as a function of applied voltage, revealing a linear response to applied E with a small quadratic contribution.

Light scattering studies were also performed in order to test for optical anisotropy in the lower temperature mesophase with greater sensitivity. As Figures 3/a and b show, below the coexistence region and in the case of zero applied field, there is no evidence of anisotropy either in the depolarized forward transmission of normally incident laser light or in the time correlation function of depolarized intensity fluctuations measured at a scattering vector 65,000 cm^{-1} along the initial (nematic) optic axis. These measurements were taken on cooling a 4 μm thick, homogeneously aligned sample of 4-CBDB from the nematic phase. From the data in Figure 3/a, we estimate at least a 100-fold reduction in Δn (measured for normal incidence) in the lower temperature mesophase from the value in the nematic phase. Figure 3/c shows that similar to other bent-core nematic materials [10], the relaxation rate Γ of director fluctuations is nearly two orders of magnitudes smaller than for ordinary calamitic nematics. This can be explained by enhanced rotational viscosities that would arise due to cybotactic groups. The temperature dependence of Γ is basically consistent with an activated viscosity, and reveals a first order transition, through a significant coexistence region, to the lower temperature isotropic mesophase.

The experimental results reported above, together with previous *X*-ray, *NMR* and dielectric observations [15,16], enable us to describe the structures of the nematic and isotropic mesophase. The nematic phase can be pictured as a conglomerate of skewed cybotactic groups of limited smectic layer correlation length but with layers orientationally ordered on average. The overall uniaxial nematic behavior implies that the morphology of the cybotactic groups fluctuates rapidly such that in-layer orientational order (and polarization) associated with close-packed bent cores is averaged out over short lengths. Upon cooling, the number of the coherently packed layers increase, and the local morphology stabilizes, resulting in a distribution of stable smectic grains ("granules"). The loss of optical anisotropy, at least for normal incidence of light, can be explained by the observed nearly 45^o tilt angle combined with an anticlinic tilting between layers, similar to anticlinic antiferroelectric calamitic smectic materials.[18] Such an orthoconic antiferroelectric structure was also recently found in bent-core smectics (with long range layer correlations). [19] In that case the smectic material was antiferroelectric and with strong electric fields it could be switched to a birefringent ferroelectric state, furthermore the optical isotropy was due to a nearly 109.5^o opening angle of the bent cores [20,21].

In contrast, the isotropic mesophase of 4-CBDB is ferroelectric, i.e. the anticlinic structure cannot be switched over to a synclinic state. Therefore the orthoconic arrangement remains undistorted upon switching the sign of polarization, explaining the absence of electro-optical signal. The observed switching of the polarization can happen via rotating the molecules around the layer normal, or by rotation around their long axis (in the direction along the end–to–end distance). In the former case the chirality of each layer is conserved. In the second case the chirality of each layer changes sign, but the overall chirality remains racemic.

Note that anticlinic director order is not compatible with the uniform surface alignment (if the director is along the rubbing direction in one layer, it would be almost perpendicular in the neighboring layers). Accordingly, at the transition from nematic to the lower temperature mesophase (where the smectic density wave increases somewhat), the surface will decouple from the bulk, leaving a thin melted surface layer. Within the bulk, the layer orientation in the different smectic granules will be arbitrary. Although the individual granules may be birefringent (the tilt angle is not exactly 45^o and the opening angle can be far from 109.5^o), the optical axes will be randomly oriented in a length scale much smaller than the wavelength of the visible light, so the material will be optically isotropic similar to that observed recently by Ortega et al. [22]

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As Figure 3/b indicates, no dynamic light scattering signal is observed in this state, presumably because the granules are static objects, cannot freely rotate, and perhaps are even weakly bonded into local networks. When we apply a sufficiently strong electric field, these bonds will break, and the granules will be reoriented (due to the torque acting on the polar axes of the granules), so that everywhere the smectic layers are parallel to the electric field (bookshelf orientation). In the plane normal to the field the layers orientation would be still arbitrary, thus maintaining the optical isotropy for normal incidence. After repeated exposure to the field (or "annealing" in the field), the bookshelf orientation will be everywhere established, and subsequent applications of the electric field will not exert a torque on the layers; the switching of the polarization will involve only the rotation of the director within the layers as described above.

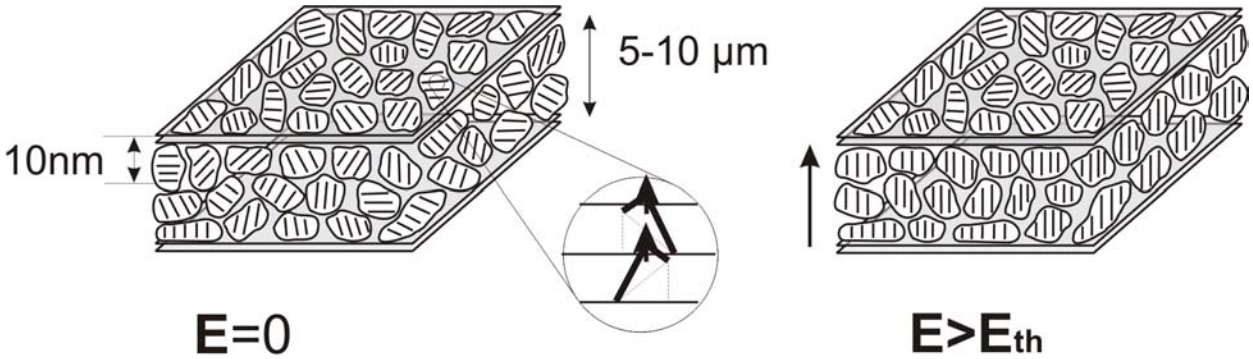

Figure 4: Sketch of the model of the optically isotropic ferroelectric phase. Lines within the smectic granules indicate the layer planes. Enlarged we show the local director structure and molecular polarization direction within the smectic layers. Above a threshold field, the layers assume bookshelf geometry; however, the layer normals between granules remain randomly oriented in the plane of the cell.

Light scattering induced by an applied AC field (Figure 3/d) confirms several aspects of this picture. The scattering is very weak (>100-fold reduction in intensity compared to the nematic), even in a substantial field, and was only observable at particular spots on the sample (which seemed randomly distributed). This result is consistent with only a weak modulation in optical anisotropy when driving the system from 3D-random granular to the bookshelf configuration. The amplitude of the oscillations on the intensity correlation function in Figure 3/d (induced by the oscillatory applied field and measured in the heterodyne regime) has a combined linear and quadratic dependence on E, consistent with polar (ferroelectric) switching and a secondary role played by the molecular dielectric anisotropy, which is negative (~-2). We also find a threshold field for observable light scattering that is consistent with the threshold to achieve the initial transition to bookshelf in the polarization data. Finally, the field-induced scattering confirms the annealing effect: after sufficient time (<1 to several hours, depending on the spot) in fields ~10 V/μm or higher, the signal always began to drop and eventually disappear. This corresponds to fully developed bookshelf domains of the layer orientation, where switching via pure molecular rotation (and no layer motion) takes place with essentially zero accompanying birefringence for normally (or near normally) incident light. Apparently, however, there is some distribution of more and less strongly bound granules in the initial random (i.e., "virgin") structure.

We note that our observations do not exclude the possibility that the OIM has SmC_G – type local structure. In this case the granules may have tilted layers with respect to the electric field, yet we could switch the polarization by rotating the molecules about their long axes. Since

the correlation length of the layer structure is short, in each SmC_G granules the direction of polarization could make a different angle with respect to the tilt plane of the molecules. In this case we may have all kinds of layer orientations with uniform polarization direction field, so the truly optical isotropy would remain even under strong electric fields. In fact there are some X-ray evidences [23] that some of the optically isotropic banana phases have random B_7 type structures.

In summary, our model accounts for the short-range smectic order, optically isotropic texture, field annealing effect, and ferroelectric switching characteristic of the lower temperature mesophase of 4-CBDB. On the other hand, to explain the observed polar switching in the framework of a Bp Sm model, which is also optically isotropic, would be very problematic. The polar switching was observed at fields above 10V/μm, which is usually enough to realign the smectic layers. In a blue phase that is composed of a 3D lattice of orthogonal smectic cylinders, the layer orientation over large areas of the cylinders perpendicular to the field will not lie along the field direction. In these cylinders, the molecular polarization cannot rotate into an orientation parallel to the field without a concomitant layer reorientation, and consequently, there will be a strong torque that should realign the cylinders, completely disrupting the optically isotropic arrangement. This scenario is precisely the opposite of what we observe in our optical measurements (i.e., the sample becomes more isotropic). On the other hand, if for some reason the lattice of cylinders was so strong that the threshold for realignment exceeded practical fields, the majority of polarization would not have been switched in our experimental sample. Then, a macroscopic polarization comparable to the value we measured (>500nC/cm^2), with only a minority of the molecules participating, would imply an unrealistically high local polarization of the system. In our model the smectic layers are all parallel to the field so that all the molecules can contribute to the observed polarization. Finally, we would like to point out that ferroelectricity in optically isotropic liquid crystals is not only a unique phenomenon, which has academic interest, but also may present new practical applications, where it is desired that the electronic information set by the polarization be decoupled from optical information.

Acknowledgements:
Two of us (Stojadinovic and Sprunt) would like to acknowledge support from the NSF under grant DMR99-04321.

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