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A bent-shape liquid crystal compound with antiferroelectric triclinic–monoclinic phase transition

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Electro-optical and polarization current measurements on 1,3-phenylene-bis[4-(3-fluoro-4-decyloxyphenyliminomethyl)benzoate] (3F-10-O-PIMB) revealed a second order phase transition between two antiferroelectric 'smectic banana' phases. The observations show that the switching between the ferroelectric states in the higher temperature (HT) phase requires higher thresholds than in the lower temperature (LT) phase. It is hypothesized that the HT phase has a lower (triclinic, C_1) symmetry, than that of the LT phase (monoclinic, C_2). It is also shown that electric fields can induce transitions between different 'smectic banana' phases.

1. Introduction

Smectic layers of achiral bent-shape ('banana-like' or 'bow-shaped') molecules [1, 2] are polar [3] and biaxial. Theoretically [4] bent-shape molecules can assume four types of biaxial fluid smectic layer structures (see figure 1).

(i) Both the plane of the molecules and the 'director' (average direction of the line connecting the ends of the molecules) are perpendicular to the layer normal, and the structure is a biaxial smectic A type. The layers are polar with polarization along the smectic layers and the kink of the average molecules. Experimental evidence of this phase was found recently [5].

(ii) Only the molecular plane is tilted with respect to the layer normal. In this case the smectic layers have monoclinic chiral symmetry C_2. They used to be called B_2†, or SmCP [6] phase (P stands for 'polar'). Similar to SmAP the layer polarization is along the layers. Most of the switchable smectic phases seem to have this structure. Depending on the relative orientations of the two-fold symmetry axis and the tilt direction, the layers can be right- or left-handed.

(iii) The long axis is tilted with respect to the layer normal but the molecular plane is not tilted. The phase has an achiral monoclinic symmetry C_s. By symmetry the layers can have a polarization component both along the layers (tangential component P_t) or normal to it (normal component P_n). Such a structure has not yet been observed.

(iv) The most general, double tilted phase has a triclinic configuration with chiral C_1 symmetry corresponding to the SmC_G phase proposed by de Gennes [7] (G denotes 'general'). The layer polarization can have both P_t and P_n components. Experimental evidence of this phase was found recently both in free-standing films [8] and in bulk samples [9].

In the SmC_G phase two angles are needed to describe the director tilt: 'clinic' [6], when the molecular planes tilt with respect to the layer normal, and 'leaning' [9], when the director tilts with respect to the layer normal along the molecular plane. Accordingly 'synclinic', 'anticlinic' [6], 'syn-leaning' and 'anti-leaning' structures can be distinguished. Taking into account that the

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†The $B_1, \ldots, B_7$ type nomenclature was adopted in the 1st Banana workshop held in Berlin (1997), but it is not based on structural observations. For example B_7 denotes materials that form telephone-wire-like textures on cooling from the isotropic phase.

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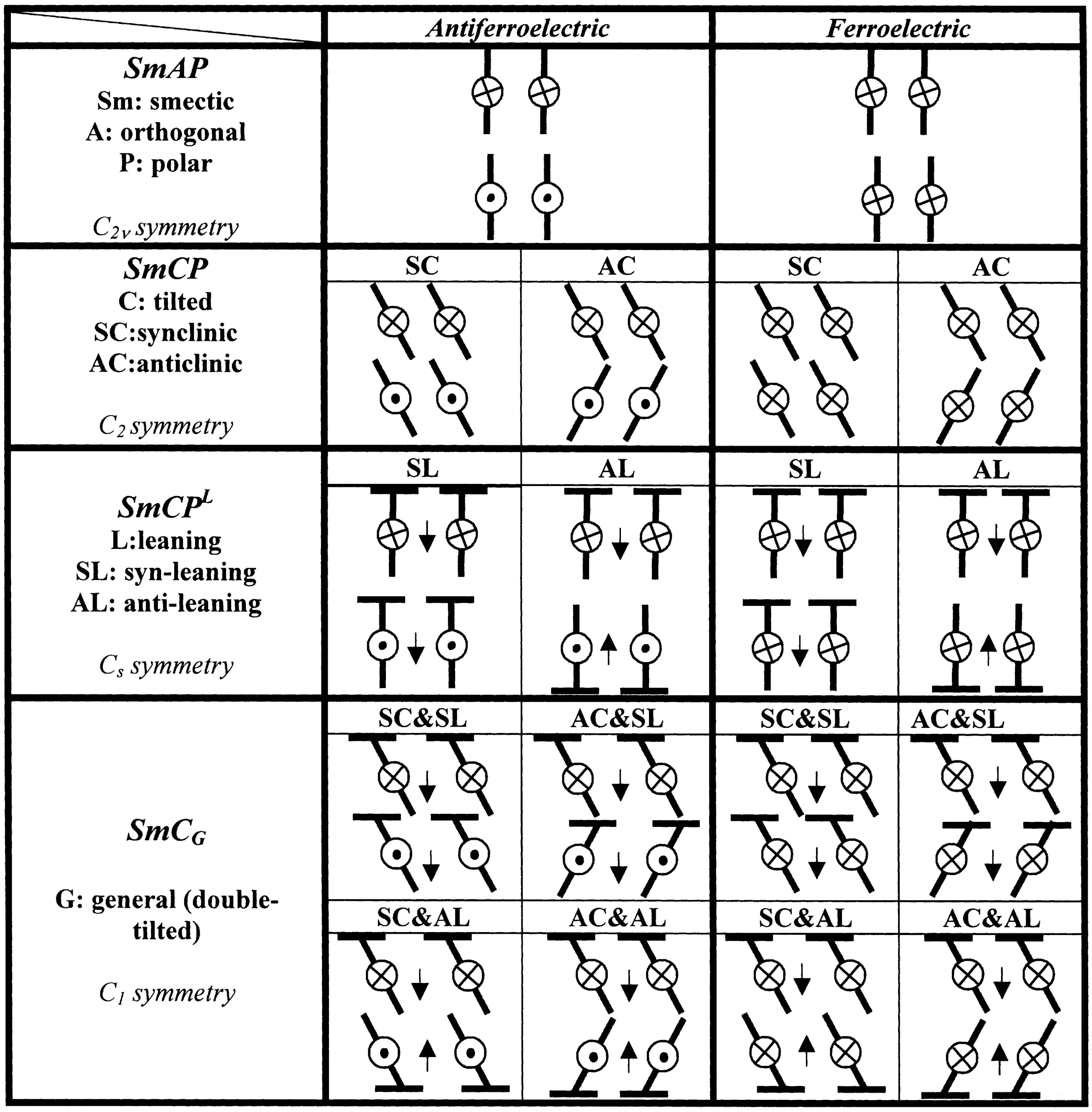

Figure 1. Schematic representation of the structures of polar smectic banana phases. ⊗ (⊙) indicate that the in-plane layer polarization component P_t points outward (inward) from the plane of the drawing. ⊤(⊥): upper (lower) part of the director tilt toward the observer. ↓(↑) indicates that the out-of-plane polarization component P_n points down (up).

double-tilted structure can be constructed by starting either from antiferroelectric (AF) or ferroelectric (FE) orthogonal structures, one finds eight different possible sub-phases (see figure 1) [4, 9].

So far two types of SmC_G sub-phases have been observed experimentally in bulk samples [9, 10]. In the first example, a mixture of 1,3-phenylene-bis[4-(4-dodecyloxyphenyliminomethyl)benzoate (12-O-PIMB) and 1,3-phenylene-bis[4-(3-fluoro-4-decyloxyphenyliminomethyl)benzoate] (3F-10-O-PIMB) formed a bilayer structure, where the resulting polarization was normal to the smectic layers, so that electric fields applied across the film stabilized the layers parallel to the plates (AC and SL of figure 1) [9]. Recently an asymmetric fluoro-substituted material (1,3-biphenylene-bis[4-(3-fluoro-4-octyloxyphenyliminomethyl)benzoate]) was found to have a chiral ferroelectric triclinic phase above an antiferroelectric racemic monoclinic phase [10]. In this case a monolayer-type ferroelectric structure formed, where the polarization has both in-plane and out-of-plane components (SC and SL of figure 1).

In this paper we describe detailed textural and polarization current measurements on 3F-10-O-PIMB in which Heppke *et al.* [11] have reported that the threshold of polarization switching decreases, whereas the value of the polarization increases, with decreasing temperature. We show that these, and our new, observations can be explained by a second order phase transition between two antiferroelectric 'banana smectic' phases, where the polarization of the higher temperature phase has a component (P_n) normal to the smectic layers. In addition we describe novel field-induced transitions between different polar 'banana smectic' phases.

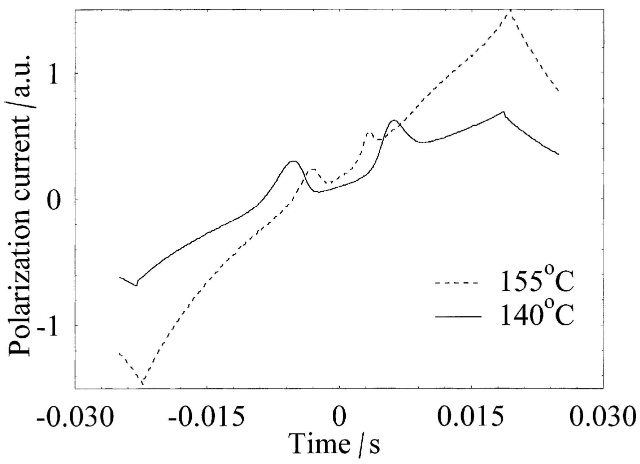

Figure 2. Time dependences of the polarization currents under triangular fields ($E_{peak} = 18$ V μm^{-1}, $f = 25$ Hz) in the HT and LT phases. The peaks at negative and positive fields indicate the antiferroelectric nature of the phases.

2. Experimental results

2.1. *Polarization current measurements*

In accordance with Heppke *et al.* [11] it is observed that the threshold E_o for the appearance of the polarization peak (i.e. for the AF → FE transition) decreases from $E_o = 22$ to 7 V μm^{-1} as the material is cooled from the isotropic–smectic transition (160°C) to 147°C. Below 147°C E_o becomes basically temperature–independent down to the crystallization temperature (110°C). This indicates a phase transition at $T = 147$°C, although this transition is not observable by DSC measurements. Until we confirm the nature of these phases we denote them as lower temperature (LT) and higher temperature (HT) phases.

Time dependences of the polarization currents under triangular fields reveal that both the HT and LT phases are antiferroelectric (see in figure 2).

Measurements under square-wave fields (figure 3) showed a complicated electric field-induced behaviour. Above E_o first a single polarization peak appears, corresponding to the AF–FE transitions. The switching time τ_1 of the polarization can be determined by the current peak position, since this indicates the time when most of the polarization is switching. It was found that τ_1 is inversely proportional to the electric field in the LT phase and almost field-independent in the HT phase. Above a basically temperature–independent threshold field $E_1 \sim 22$ V μm^{-1} a second peak appears. In a narrow range above E_1 the first and second peak coexist, but then the second peak becomes dominant at further increasing fields. The switching time τ_2 determined from the position of the second peak is about twice as large as τ_1 (see figure 3). The switching times at constant fields are temperature-dependent: for example τ_1/E_1 increases from 4 to 8 μs when changing the temperature from the top to the bottom of the LT phase range. The switching times τ_2 of the HT phase are comparable to τ_1 of the LT phase.

2.2. *Textural observations*

The field-induced ferroelectric states were studied simultaneously by polarizing microscope. Typical textures, corresponding to the states distinguished by polarization current measurements are shown in figure 4. Below 147°C the texture contains narrow stripes in the AF range ($E < E_0$), see figure 4 (*a*). In the range where only a single polarization peak is observed by current measurements ($E_0 < E < E_1$), the stripes disappear and a racemic-type switching is observed (i.e. there is no rotation of the optic axis under rectangular fields). The birefringence is $\Delta n \sim 0.1$, which corresponds to the anticlinic arrangement of the field-induced ferroelectric state, see figure 4 (*b*). In the double polarization peak region ($E > E_1$) domains rearrange and the birefringence increases slightly, see figure 4 (*c*). At zero fields the HT phase has a grainy texture, see figure 4 (*a′*), then it breaks up into small needle-like domains when switched between ferroelectric states, figure 4 (*b′*). Near the clearing point these domains are separated by isotropic regions and at low frequencies a rotation along the long axes of the needle-like domains is observed. At increasing fields the switching is accompanied by a vivid domain flow. This usually indicates ionic effects, however in the present case the flow effects disappear at even higher fields ($E > E_1$) and a steady texture forms with a birefringence similar to that of the FE states in the LT phase, figure 4 (*c′*).

The texture transformations were also monitored on 10 μm thick films aligned by mechanical shearing (by shifting the top plate by about 0.1 mm at 130°C). In the

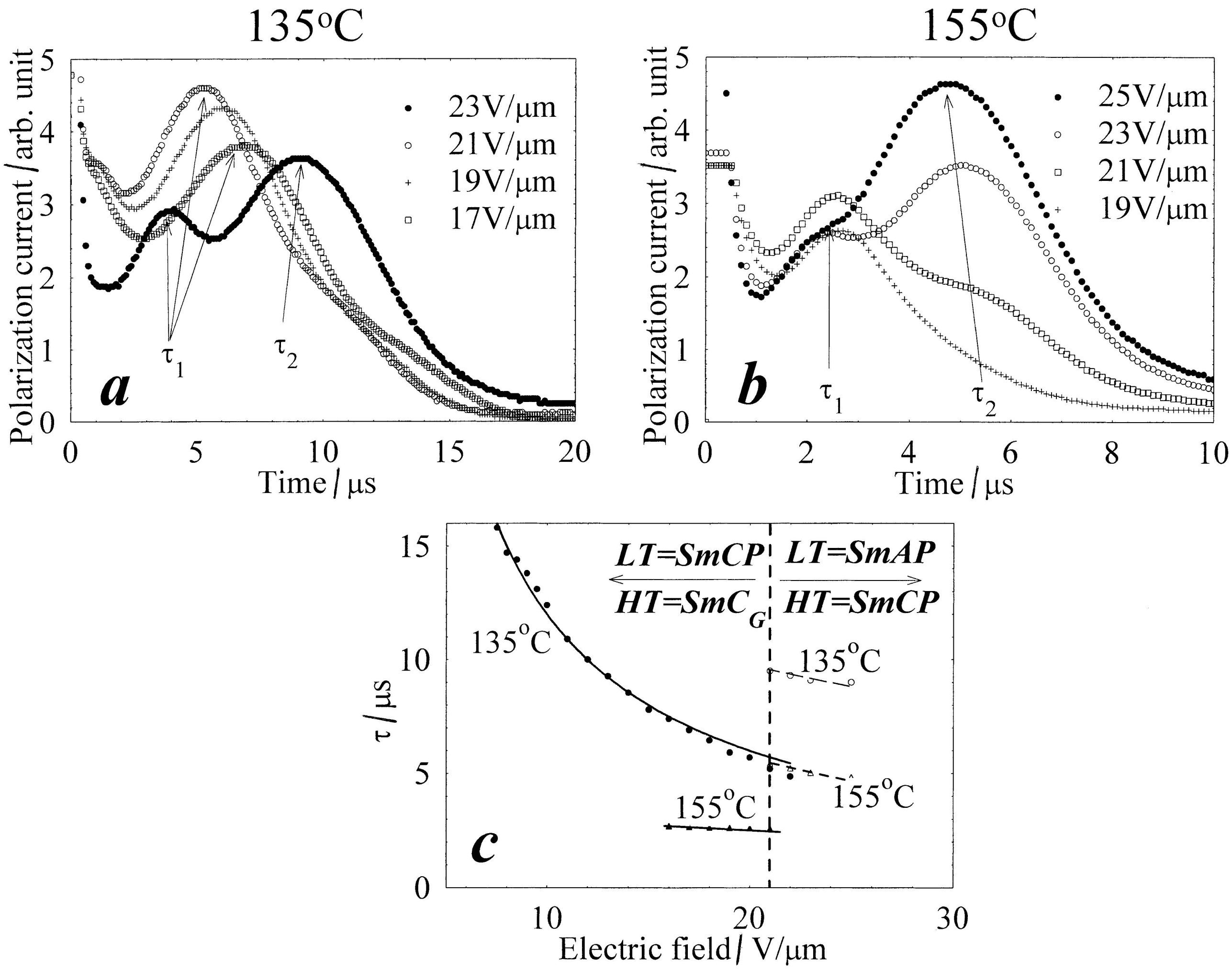

Figure 3. Time dependences of the polarization current after step-wise field reversal in the lower temperature phase (*a*), and higher temperature phase (*b*). Switching times, as determined from the positions of the polarization current peaks (*c*). Solid and open circles: $T = 135°C$; solid and open triangles: $T = 155°C$. Data with solid and open labels correspond to τ_1 and τ_2, respectively.

LT phase the shear-aligned texture is completely black when one of the crossed polarizers is parallel to the shear direction, but becomes inhomogeneous when rotated away from the extinction. At zero field the birefringence is estimated to be smaller than 0.05, but on applying strong electric fields ($E > 8\ \mathrm{V\ \mu m^{-1}}$) the birefringence increases to $\Delta n \sim 0.1$. The absence of stripes of the shear-induced textures at zero fields, and the field-induced birefringence increase, are attributed to a field-induced realignment from the tilted layer structure to the so-called bookshelf geometry (the layers stand normal to the substrates). This indicates that the LT phase is identical with the SmCP phase, since in the SmCP phase strong fields turn the polarization (which is along the layers) parallel to the field. On turning off the field in the bookshelf structure the texture becomes inhomogeneous, containing distinct small homogeneous domains with extinction directions varying between about $+30°$ and $-30°$ with respect to the layer normal, figure 4 (*a*). The various extinction directions correspond to differently oriented synclinic domains. We note that the diffraction pattern of normally incident He-Ne laser light is a continuous line along the layer normal, showing that the domain sizes are randomly distributed. This texture is typical for the antiferroelectric racemic SmCP phase in bookshelf geometry, thus further assuring that the LT phase corresponds to the antiferroelectric racemic SmC_sP_A phase.

On heating the material to the HT phase the domains break up into smaller units. On applying d.c. fields larger than about $10\ \mathrm{V\ \mu m^{-1}}$ a uniform texture forms in which the extinction is parallel to the original shear direction. This texture remains unchanged, and no stripe formation is observed, after field removal and even when cooling

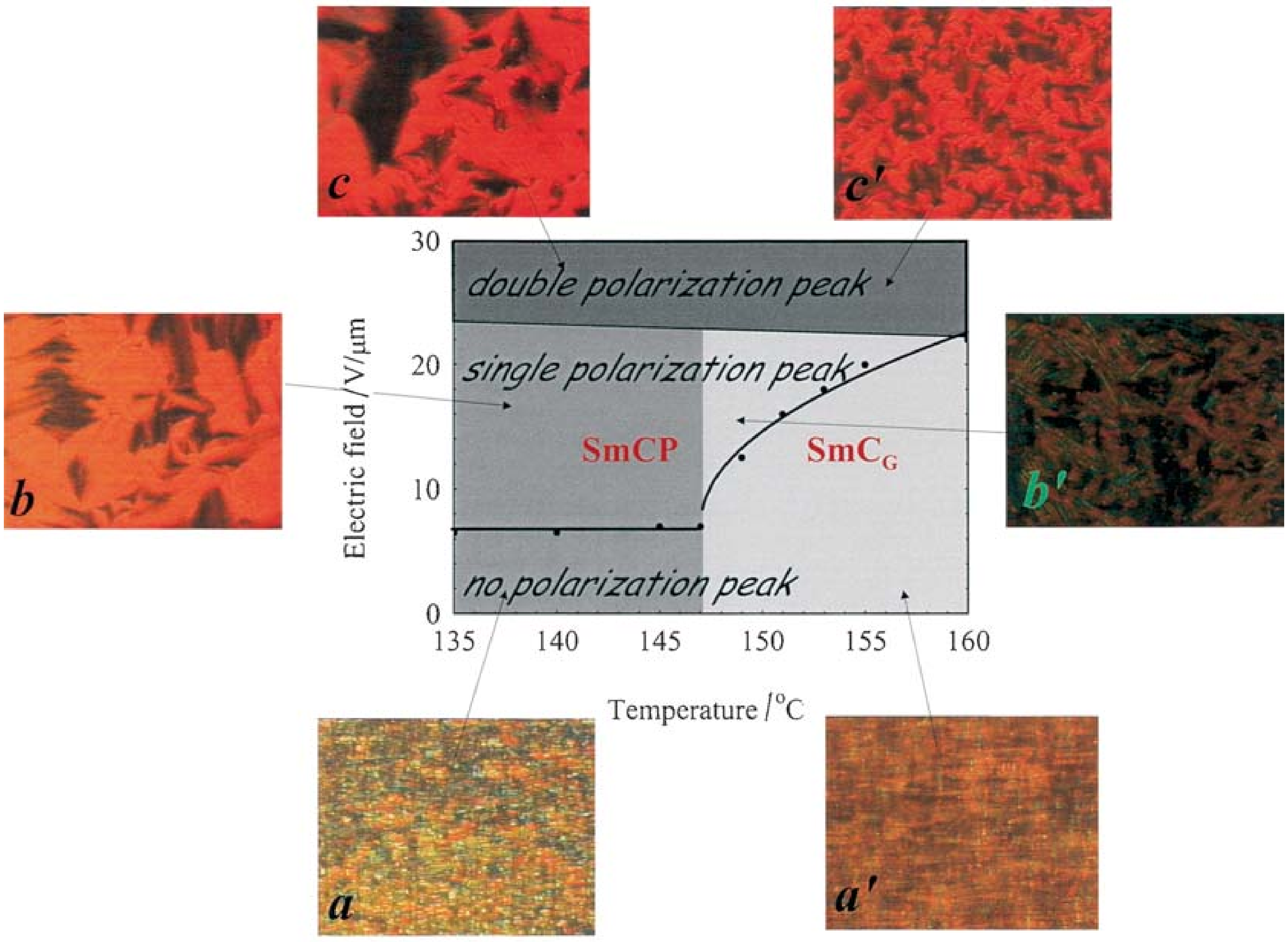

Figure 4. Textures and the phase diagram of 3F-10-O-PIMB. The polarization peaks refer to measurements under rectangular fields. In the phase diagram the curve with solid line corresponds to the temperature dependence of the switching threshold field $E_o(T)$. Light grey regions indicate the HT phase, which is identified as SmC_G; the medium grey area corresponds to the LT phase, which is identified as SmCP, and the dark gray area shows the field-induced phases above $E_1 \sim 22$ V μm^{-1}, which probably correspond to SmAP in the LT phase range and to SmCP in the HT phase range. (*a* and *a′*) are shear-aligned bookshelf textures of a 10 μm film in the antiferroelectric (AF) state at the LT (130°C) and HT (150°C) phases, respectively; (*b* and *b′*) are textures of 4 μm films with unidirectionally rubbed polyimide inner surfaces (cells from Displaytech Inc.) in the ferroelectric single polarization peak range ($E_0 < E < E_1$) at $T = 130$°C and at $T = 150$°C, respectively; (*c* and *c′*) are textures of 4 μm thick films at the same area and temperatures as of textures (*b* and *b′*), but in the double polarization peak range ($E > E_1$). Each picture represents 0.3×0.5 mm^2 areas. The crossed polarizers are along the edges of the pictures.

the sample to the LT phase. The lack of stripe formation in the SmCP phase is a sign of tilted layers [12], so this observation shows that the layers become tilted after switching in between ferroelectric states in the HT phase.

3. Discussion

Observations in the lower temperature (LT) phase are consistent with our picture of the racemic antiferroelectric SmC_sP_A phase. The 'only' unusual feature is the appearance of the double-polarization switching region, which coincides with the appearance of slightly higher birefringence and domain rearrangements. Similar behaviour was observed previously on a material with the same fluorinated bent-core, but with shorter alkyloxy chain (3F-8-O-PIMB) [13], where it was attributed to a field-induced SmCP–SmAP transition due to field-induced suppression of fluctuations. We believe that a similar transition takes place here, also. The appearance and growth of the second polarization peak above E_1 indicates that the switching time, and consequently the rotational viscosity, is larger in the high field state. The coexistence of the two peaks shows that the transition is incomplete (probably due to surfaces effects).

In the HT phase we observe that the switching between two ferroelectric states leads to a structure where the layers are tilted with respect to the electric field. This indicates that the polarization is not along the layers, corresponding to a double-tilted layer structure (SmC_G phase). As can be seen on figure 1, four types of SmC_G sub-phases can be formed starting out from antiferroelectric SmAP structures. Two of them—synclinic & anti-leaning (SC&AL), and anticlinic & anti-leaning (AC&AL)—have compensated out-of-plane polarizations ($\langle P_n \rangle = 0$), so electric fields applied parallel to the planes would not lead to a layer tilt. The remaining two possible configurations (AC&SL) and (SC&SL) shown in figure 1 are represented in 3D style in figure 5 without and with applied electric fields. In the first case, figure 5 (*a*), the ferroelectric states are synclinic, i.e. the optical axes rotate at field reversals, which does not correspond to the observations. The only SmC_G sub-phase that is consistent with our observations is the *antiferroelectric-synclinic-synleaning* configuration—see SC&SL in figures 1 and 5 (*b*). In this case the optic axis is not sensitive to the sign of the electric fields, and under field reversal the layers are tilted in opposite directions. Tilting of the layers requires additional energy, i.e. higher electric fields. If the leaning angle had a jump at the transition, the switching threshold field would also have a jump. The observation that the threshold field increases continuously on heating from the SmCP phase, therefore shows that the leaning angle increases continuously from zero. This explains the second order nature of the transition as observed with calorimetric measurements. We have to note that 3F-10-O-PIMB forms telephone wire-like structures [11] under cooling from the isotropic phase, which is characteristic of the so-called B_7 phase. Recently it was shown by Clark [14] that the B_7 phase, including 3F-10-O-PIMB, has a modulated layer structure. Our observations that 3F-10-O-PIMB has an out-of-plane polarization component, may indicate therefore that the layer modulation (at least in the present material) is due to this component. The physical mechanism that leads to this layer modulation is beyond the scope of the present study.

The other important observation in the HT phase is the transition between the mechanically disturbed switching to a steady texture at fields above $E_1(T)$. At

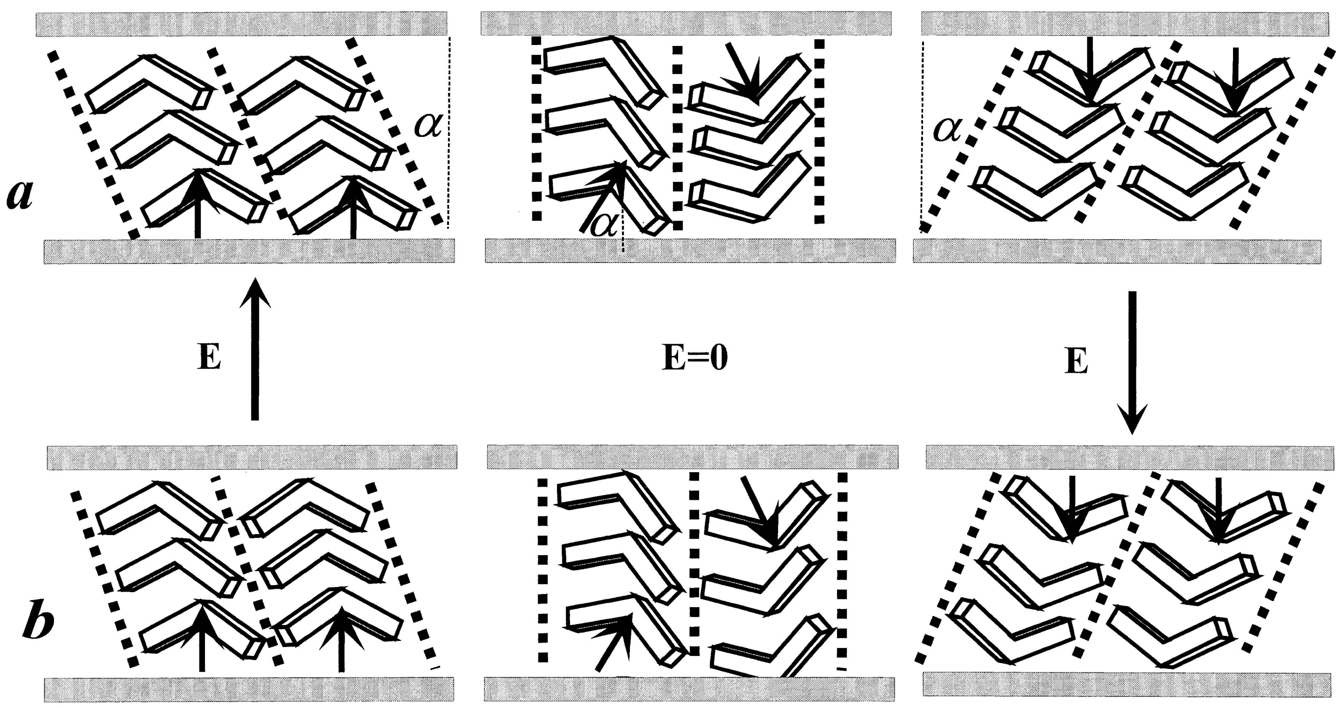

Figure 5. Three-dimensional representation of those antiferroelectric SmC_G structures which have non-zero net polarization component P_n normal to the layers, and therefore would lead to tilted layer structures under high fields. (*a*) Anticlinic, syn-leaning structure. At zero fields the optic axis is parallel to the layer normal, but in the ferroelectric state the optic axis is different for negative and positive fields, which does not correspond to the observations. (*b*) Synclinic, syn-leaning structures. At zero fields the optic axis is tilted with respect to the layer normal. In the ferroelectric states the optic axis is not sensitive to the sign of the fields, similar to the experimental observations. α is the tilt angle of the long axis of the molecule with respect to the layer normal. This also corresponds to the tilt angle of the layers with respect to the substrate normal in the ferroelectric states.

first glance this could indicate that the dielectric interaction ($1/2\varepsilon_a E^2$) overcomes the ferroelectric one ($P_o \cdot E$). In this case the ferroelectric switching would be suppressed, so that no polarization current peaks were present under triangular fields. However we observe the same antiferroelectric-type polarization peaks, which exclude the role of the dielectric interaction. Since this transition takes place simultaneously with the appearance of the second polarization peak observed under rectangular fields, we propose that both in the LT and HT phase regions field-induced phase transitions take place above E_1. In the HT phase region the observations cannot distinguish between transitions to SmAP, SmCP or to one of the anti-leaning SmC_G phases. The observation that τ_2 of the HT phase is comparable to the τ_1 of the LT phase might indicate the SmC_G–SmCP transition. Detailed experimental and theoretical descriptions of the field-induced transitions between banana smectics should be the subject of future study.

4. Summary

We have shown that the banana-shaped material 3F-10-O-PIMB has two distinct antiferroelectric smectic phases [15], in which the higher temperature phase has a layer polarization with both in-plane and out of plane components (SmC_G phase), and the lower temperature phase has only an in-plane polarization component (SmCP phase). Thus the higher temperature phase has a lower C_1 symmetry than the lower temperature phase, which has a C_2 symmetry. We have also observed field-induced phase transitions in both the LT and HT phases, which probably correspond to SmCP–SmAP and SmC_G–SmCP transitions, respectively. It remains to understand the physical mechanism of the field-induced transitions, and the mechanism that leads to an undulated layer structure in the ground state of the HT phase.

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[15] After submission of this manuscript we learned that the existence of two distinct phases was also observed recently by the Halle group. See lecture by G. Pelzl at 2nd Banana workshop, Boulder, USA, August 23, 2002, http://anini.colorado.edu/bananas/pelzl.pdf