Ferroelectric-chiral−antiferroelectric-racemic liquid crystal phase transition of bent-shape molecules

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Detailed dielectric, polarization current, electro-optical, and textural observations are reported on an asymmetric banana-shaped compound 1,3-biphenylene-bis[4-(3-fluoro-4-octyloxyphenyliminomethyl)benzoate]. The material possesses a chiral-ferroelectric–racemic-antiferroelectric phase transition. Our studies reveal that the higher temperature ferroelectric phase has a polar double-tilted smectic structure, where both the molecular plane and the long axis are tilted with respect to the layer normal. Accordingly, it has a chiral triclinic structure with an out-of-plane polarization component. The lower temperature phase has a monoclinic symmetry, which is higher than that of the higher temperature phase. To our knowledge, among liquid crystals such situations were previously observed only in reentrant phases.

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I. INTRODUCTION

Recently, tilted smectic phases of bent-shaped ("banana-like" or bow-shaped) molecules [1,2] have attracted considerable interest as they have ferroelectric properties [3] and represent an example in liquid crystals of the formation of chiral superstructures without chiral structures on the molecular level [4]. Most of the molecules published up to now have a C_{2v} symmetry, but some examples with reduced symmetry are also known [5]. Since the molecules have no cylindrical symmetries two vectors are needed to describe them: the molecular plane normal $\vec{m}$, and the direction of the long axis $\vec{l}$ (the line connecting the two ends of the average molecule). In addition to the orthogonal arrangement, where both $\vec{m}$ and $\vec{l}$ are perpendicular to the layer normal $\vec{n}$, there are three possible arrangements corresponding to tilting of either $\vec{m}$ or $\vec{l}$ or both with respect to $\vec{n}$ [6]. When only the molecular plane is tilted the smectic layers have monoclinic chiral symmetry C_2. They are denoted as Sm CP [4] phases (P stands for "polar") and associated with the B_2 texture [7]. When only the long axis is tilted the smectic layers have achiral monoclinic symmetry C_s. The double-tilted structure has a triclinic structure with chiral C_1 symmetry corresponding to the Sm C_G phase proposed by de Gennes [8] (G stands for "general"). Experimental evidence for this phase was found recently both in free-standing films [9] and in bulk samples [10].

The monoclinic Sm CP and the triclinic Sm C_G phases have chiral layers and, depending on the relative orientations of the twofold symmetry axis and the tilt direction, the layers can be either right, or left handed. In the adjacent layers the sign of the chirality can alternate or can remain unchanged over micrometer ranges. Accordingly, two types of domain are possible: racemic, if the chirality in the adjacent layers alternates, and chiral, if the adjacent layers have the same handedness. Macroscopic domains can be either antiferroelectric (AFE) or ferroelectric (FE) if the layer polarizations

of the subsequent layers are alternating or uniform, respectively. The racemic AFE state is synclinic and is denoted by Sm $C_s P_A$. In bulk the tilt directions are equivalent and domains of opposite director tilt directions form. This results in the appearance of striped texture in films provided that surface interactions do not distinguish between tilt directions. The racemic FE state is anticlinic (Sm $C_a P_F$) and the optical axis is parallel to the layer normal independent of the sign of the external a.c. field, so no electro-optical switching can be observed for square wave fields. The chiral AFE state is anticlinic (Sm $C_a P_A$), whereas the FE state is synclinic (Sm $C_s P_F$) and the optical axis rotates by 2θ (θ is the director tilt angle) under square wave fields. These differences make it possible to distinguish between racemic and chiral domains by electro-optical and textural observations.

Recently, an asymmetric banana-shaped compound 1,3-biphenylene-bis[4-(3-fluoro-4-octyloxy-phenyliminomethyl) benzoate (mBPB8q3F) was reported [11], which shows a transition between ferroelectric and antiferroelectric phases. The molecular structure and the phase sequence of the material were determined as presented in Fig. 1. The lower temperature phase possesses the usual electro-optical and dielectric properties of the racemic antiferroelectric Sm $C_s P_A$ phase. The higher temperature phase

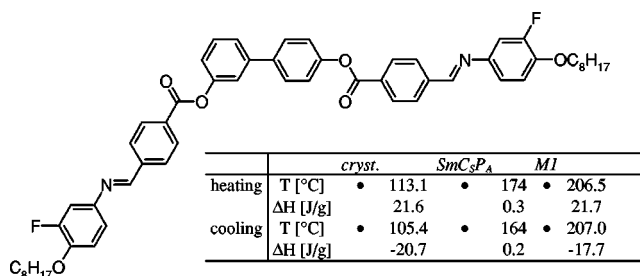|		cryst.		SmC_sP_A		M1	
heating	T [°C]	•	113.1	•	174	•	206.5
	ΔH [J/g]		21.6		0.3		21.7
cooling	T [°C]	•	105.4	•	164	•	207.0
	ΔH [J/g]		-20.7		0.2		-17.7

FIG. 1. Molecular structure and phase sequence with differential scanning calorimetric data of 1,3-biphenylene-bis[4-(3-fluoro-4-octyloxyphenyliminomethyl)] benzoate [11].
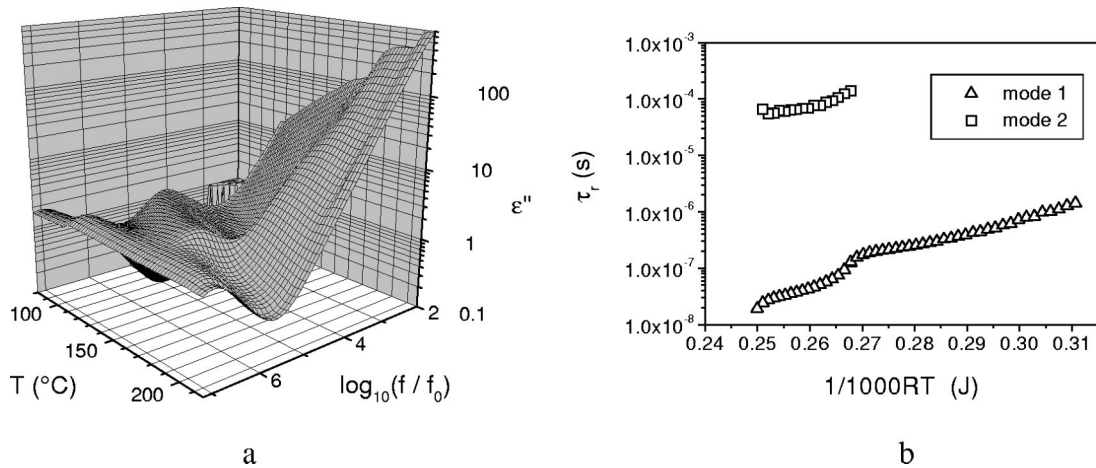
FIG. 2. (a) Temperature dependence of the dielectric loss ϵ'' as measured in heating in a $d = 10$ μm cell and (b) Arrhenius plot of corresponding relaxation times.

was denoted by $M1$ and it appears below the isotropic phase by the formation of telephone-wire-like structures similar to B_7 textures [12,13]. Preliminary dielectric spectra, polarization reversal current, and second harmonic generation signals indicated that the $M1$ phase is ferroelectric. To verify this suggestion and to determine the director and layer structure of the $M1$ phase we carried out detailed dielectric, polarization current, electro-optical, and textural observations. Our studies reveal that the $M1$ phase has a double-tilted structure, i.e., both the molecular plane and the long axis are tilted with respect to the layer normal. Accordingly, it has a chiral triclinic structure with an out-of-plane polarization component.

II. EXPERIMENTAL RESULTS

A. Dielectric investigations

Dielectric measurements were performed with a Hewlett-Packard 4194A impedance analyzer. The substance in the isotropic phase was put into 10 μm and 2 μm thick cells coated with indium tin oxide layers (E.H.C. Co., Japan) with a parallel rubbed polyimide alignment layer. The temperature dependences of the dielectric spectra were measured by placing the cell in a Linkam hot stage (TMS90) under 0.5 K/min heating and cooling rates. Figure 2 shows the dielectric loss of a 10 μm sample on heating. In Sm $C_s P_A$ only one relaxation process (mode 1) is observed in the megahertz range. In the $M1$ phase, in addition to mode 1 a second relaxation (mode 2) appeared at around 1–10 kHz. The relaxation mode 1 is known from previous investigations of other compounds and is assigned to a hindered rotation of the bent molecules around the long molecular axis [14]. The low frequency mode 2 corresponds to the Goldstone mode and is present only in ferroelectric structures. Mode 2 in the $M1$ phase is hardly separable from the ionic contributions, but under bias fields the effect of the ions can be suppressed in fields above $1 V/\mu$m. Figure 3 shows the bias field dependence of mode 2 in a 2 μm cell at 195 °C. The dielectric strength of mode 1 increases with bias voltages until $E_{th} \approx 2.5$ V/μm; then it decreases sharply [11]. In the case of mode 2 $\Delta\varepsilon_2$ is basically constant up to 3 V/μm and decreases only slowly above that [see Fig. 3(b) at $T = 195$ °C]. The dielectric data were analyzed assuming a symmetric distribution of Debye relaxation processes:
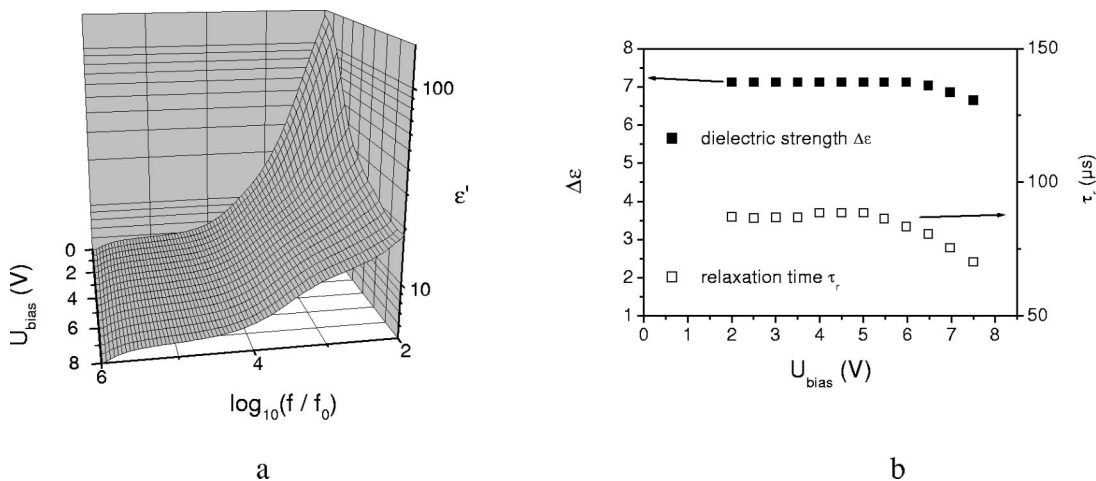

FIG. 3. (a) Real part of the dielectric permittivity of a 2 μm test cell measured under application of a bias voltage. (b) Relaxation times and dielectric strengths of mode-2 as a function of applied voltage. $T = 195$ °C ($M1$ phase).
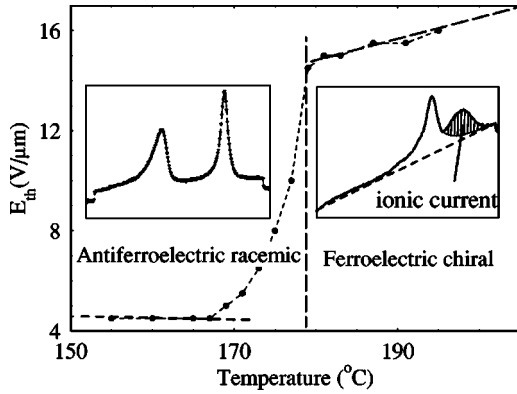
FIG. 4. Temperature dependence of the switching threshold. Below $T = 170\,°C$ the material has an antiferroelectric racemic structure (Sm $C_s P_A$ phase); above it shows a chiral ferroelectric switching (this corresponds to the $M1$ phase).

$$\varepsilon^*(\omega) - \varepsilon'(\infty) = \sum_i \frac{\Delta\varepsilon_i}{1 + (i\omega\tau)^{1-\alpha_i}}.$$

From the Cole-Cole plots we obtained that in the Sm $C_s P_A$ phase $\alpha_1 = 0.95$, $\Delta\varepsilon_1 \approx 8$, $\tau_1 \sim 10^{-7}$–10^{-6} s; in the $M1$ phase $\alpha_1 = 0.99$, $\Delta\varepsilon_1 \approx 1$, $\tau_1 \sim 10^{-8}$–10^{-7} s, and $\alpha_2 = 0.8$, $\Delta\varepsilon_2 \approx 7$, $\tau_2 \sim 10^{-4}$ s.

We see therefore that in the M1 phase the dielectric strength of mode 2 is comparable to that of mode 1 of the Sm $C_s P_A$ phase. However, the relaxation frequency of mode 2 is about three orders of magnitude lower than that of mode 1. The temperature dependences follow Arrhenius-type behaviors with activation energies of about 55 kJ/mol in the Sm $C_s P_A$ phase and about 70 kJ/mol in the $M1$ phase. This indicates a more hindered rotation of the molecules in the high temperature $M1$ phase.

B. Polarization current measurements

The temperature dependence of the switching threshold (i.e., where the polarization peak(s) appear), and the value of the polarization involved in the switching are shown in Figs. 4 and 5, respectively. In the $M1$ phase the threshold field
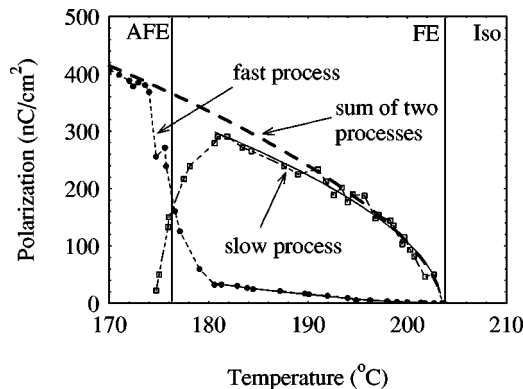

FIG. 5. Temperature dependence of the polarizations associated with the slow and fast switching. Dashed line is the sum of the polarization contributions of the slow and fast processes.
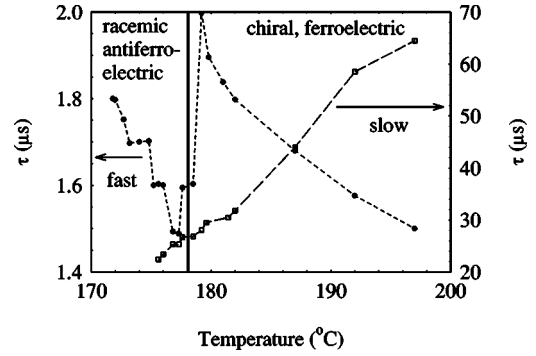

FIG. 6. Temperature dependences of the switching times of slow and fast switching processes.

$E_{th} > 15$ V/μm, i.e., about three times larger than in the lower temperature phase. The current peaks under rectangular fields show that in the Sm $C_s P_A$ phase there is only one switching process with about 2 μs switching time, whereas in the $M1$ phase the polarization switches in two steps: the fast switching takes only 2–3 μs, whereas the slow process is in the 50–100 μs range (see Fig. 6). We note that in the transition region (170–180 °C) there is a coexistence of the two phases. In the $M1$ phase the slow process has the major contribution to the polarization. Interestingly, the sum of the slow and fast polarizations shows a monotonic increase with decreasing temperatures without any jump at the transition to the lower temperature Sm $C_s P_A$ phase (see Fig. 5). This indicates that the polar packing order does not differ significantly in the $M1$ and Sm $C_s P_A$ phases.The features of the fast and slow processes seem to correlate with mode 2 and mode 1 of the dielectric relaxation processes, indicating that they have a common origin. However, there are differences also. For example, the switching time of the slow process decreases at lower temperatures, whereas τ_2 of mode 2 increases; furthermore, the fast switching time decreases whereas τ_1 of mode 1 increases upon the transition to the Sm $C_s P_A$ phase.

C. Electro-optical studies

In order to characterize the director structure we shear-aligned the samples by shifting the cover plates parallel to each other by about 100 μm.

In the Sm $C_s P_A$ phase a weakly birefringent ($\Delta n < 0.07$) smooth texture forms with an extinction direction along the shear (see upper row of Fig. 7). Strong electric fields ($E \sim 15$ V/μm) induce a texture with much larger birefringence ($\Delta n \simeq 0.14$). During the transformation the extinction direction remains parallel to the previous shear direction and it is not sensitive to the sign of the electric field. On switching off the field the texture has an orange color ($\Delta n \simeq 0.18$) and stripes appear.

In the $M1$ phase the optical axis is also along the shear direction although the alignment is less uniform and the birefringence ($\Delta n < 0.05$) is even smaller than in the Sm $C_s P_A$ phase (see lower row of Fig. 7). Above a threshold electric field ($E_{th} \sim 15$ V/μm) a highly birefringent ($\Delta n \simeq 0.18$) texture appears. It possesses chiral switching, i.e., the extinction directions rotate under field reversal. Unlike chiral do-
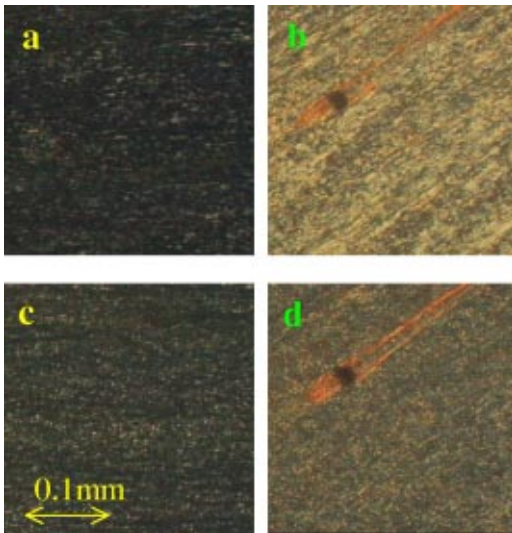
FIG. 7. Textures obtained under shear in the Sm C_sP_A phase (upper row) and in the $M1$ phase (lower row) with the shear direction parallel to the analyzer (left-hand side) and at 45 ° to it (right column). Sample thickness 10 μm.

mains of the Sm CP phase, now the texture breaks up into small domains (see Fig. 8) with typical domain sizes decreasing at higher temperatures. Very near the isotropic phase the electro-optical response is disturbed by random mechanical motions, probably due to ionic contributions. With decreasing temperatures in the $M1$ phase the switching angle is increasing up to about 40 °. After field removal the birefringence decreases slightly ($\Delta n \simeq 0.15$) but otherwise the texture is the same as under the field and no stripe formation is observed [see Fig. 8(c)]. These observations are consistent with the ferroelectric nature of the $M1$ phase. On cooling the material back to the Sm C_sP_A phase a uniform orange texture appears, which does not contain stripes, and the extinction direction is essentially parallel to the layer normal. On applying fields in the Sm C_sP_A phase the birefringence decreases to $\Delta n \simeq 0.14$ without changing the extinction direction. On switching off the field, stripes form again indicating that a sufficiently strong electric field induces a bookshelf texture in the Sm C_sP_A phase.

III. DISCUSSION

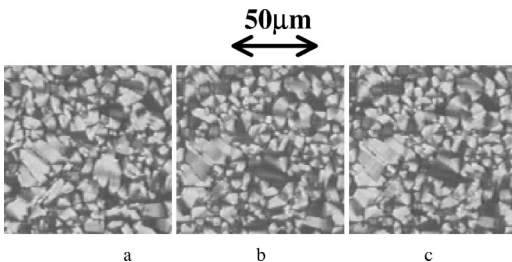The absence of stripe formation in the Sm C_sP_A phase after shear alignment and after full switching in the $M1$

FIG. 8. Chiral switching in the $M1$ phase. (a) $E = +15$ V/μm; (b) $E = -15$ V/μm; (c) $E = 0$. Sample thickness 4 μm; $T = 195$ °C.
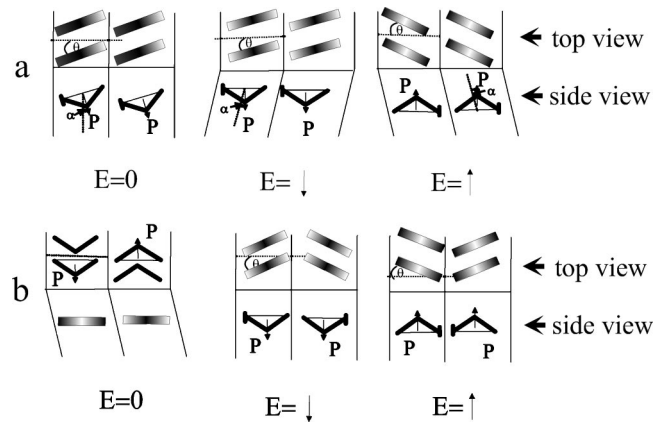

FIG. 9. (a) Proposed structure of the $M1$ phase at zero field and under high electric fields. The structure can be described by two tilt angles: θ is the tilt angle of the molecular plane and α is the angle of the polarization with respect to the smectic layer normal. (b) Structures of the Sm C_sP_A phase at different electric fields after cooling from the $M1$ phase where the polarization was switched between up and down directions. Shadowing indicates the bent shape of the molecules when viewed along the plane of the molecules. The bars indicate that the molecular plane is tilted toward the observer.

phase indicates a tilted layer structure. The layer tilt with respect to the substrate discriminates one of the director tilt directions, since the excluded volume at the substrate will be asymmetric with respect to the differently tilted molecules [15]. As a result only that tilt direction will be realized where the molecular planes and the layer polarizations are almost parallel to the substrates [see Fig. 9(b) at $E = 0$]. The observation that the switching threshold in the $M1$ phase is comparable to the field needed to turn the layers to the upright position in the Sm CP phase confirms that the full switching of the polarization in the $M1$ phase involves layer tilting. Since we can assume that sufficiently high fields turn the polarization parallel to the field, the observed field-induced layer tilt means that the polarization has an out-of-plane component. Keeping in mind that the switching is chiral, we conclude that the $M1$ phase has a C_1 symmetry corresponding to the double-tilted Sm C_G phase. The bistability and ferroelectric-type switching of the $M1$ phase show that the subsequent layers have the same in-plane and out-of-plane polarization directions corresponding to the structure illustrated in Fig. 9(a). This configuration is different from that recently observed on another material [10], where a bilayer structure with compensated in-plane polarization component formed.

It is an interesting observation that the switching of the polarization is very fast (it takes only a few microseconds) in the racemic antiferroelectric Sm C_sP_A phase, whereas in the chiral ferroelectric $M1$ state the majority of the polarization switches are about two orders of magnitude slower. We think that the fast and slow processes are related to the racemic and chiral structures, respectively. A difference in the switching times of the chiral and racemic structures was already noted for another material with antiferroelectric Sm CP phases, where both states could be induced by suitable elec-

tric field treatments [16]. There the switching times in the chiral state were about two times larger than in the racemic state. In the present case the difference is much larger, probably due to the out-of-layer polarization component which involves layer tilting during switching in the $M1$ phase. The small contribution to the polarization of the fast switching indicates that it is related to surface effects. The surface typically prefers anticlinic director structure [17], which means a racemic configuration in the ferroelectric state. The increase of the switching time of the fast process at the transition to the $M1$ phase could also be connected to the $Sm C_G$ structure of the $M1$ phase. The observation that in the chiral state the switching time and the threshold field decrease with decreasing temperature implies that the out-of layer polarization component, i.e., the ''leaning'' angle [10], decreases at lower temperatures until it drops to zero upon the transition to the $Sm C_s P_A$ phase.

As a summary, we showed that the chiral ferroelectric phase of 1,3-biphenylene-bis[4-(3-fluoro-4-octyloxyphenyliminomethyl)] benzoate has triclinic C_1 symmetry. Interestingly, this symmetry is lower than that of the lower temperature $Sm C_s P_A$ phase, which has monoclinic symmetry. So far among liquid crystals this situation was observed only in reentrant phases to our knowledge [18]. The phenomenological theory of this kind of phase transition will be described separately [19].

ACKNOWLEDGMENTS

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