Chirality Switching

Field-Induced Switching of Chirality in Undulated Ferroelectric and Antiferroelectric SmCP Phases Formed by Bent-Core Mesogens[**]

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Chirality is a fundamental property of matter. In most cases chirality is an inherent molecular property, but it can also occur in solid crystals even though the constituent moieties are nonchiral, for example, as a consequence of a spontaneous discrimination during the crystallization process. Chirality in liquid systems formed by nonchiral molecules seems to be impossible because of the mobility of the particles. However, there are new kinds of mesophases formed by nonchiral bent-core molecules which are also able to exhibit phase chirality. The molecules can be packed in a polar fashion because of their bent shape and give rise to a long-range correlation of the lateral dipoles and therefore to a macroscopic polarization in the smectic (SmC) layers.[1] In the most widely studied SmCP phase (P = polar), the polar packed molecules are tilted with respect to the normal of the layer. As first shown by Link et al.[2] four structures can be distinguished depending on the stacking of the molecules in adjacent smectic layers (Figure 1). The molecules can have either a synclinic or an anticlinic interlayer correlation which is indicated in the phase symbol SmCP by the subscripts S and A after C. The polar order is specified by the suubscripts A and F, where A corresponds to an antiferroelectric structure and F designates a ferroelectric structure (the possible phase symbols are thus SmC_AP_A, SmC_SP_A, SmC_AP_F, and SmC_SP_F).[2] The polar packing as well as the tilt of the molecules in the SmCP phases are two steps of symmetry breaking which create a layer chirality without any molecular chirality. As seen in Figure 1, two equivalent layer structures with antiparallel polar axes exist for a given tilt direction which are mirror images of each other. The opposite handedness is depicted by filled (black) or open (white) molecule symbols. All layers of a macroscopic domain in the SmC_AP_A and SmC_SP_F structures have the same layer chirality (homochiral state) whereas the chirality alternates from layer to layer in the SmC_SP_A and SmC_AP_F structures (racemic state).

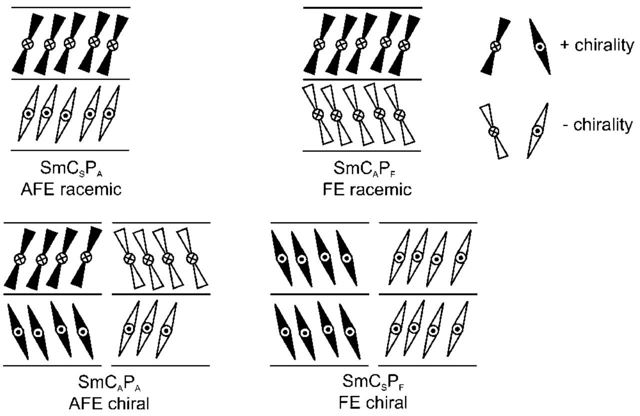

Figure 1. Possible orientations of the tilt and polar axes of bent-core molecules in adjacent layers that lead to chiral or racemic ferroelectric and antiferroelectric SmCP phases. Filled and open molecule symbols designate layers of opposite chirality.

To avoid bulk polarization an antiferroelectric ground state exists in most cases where the polarization alternates in adjacent layers.[3] The antiferroelectric states can be switched to the corresponding ferroelectric states (Figure 1). This field-induced reorientation takes place through rotation of the director around the normal to the layer on the tilt cone such as occurs in ferro- and antiferroelectric phases of calamitic compounds. The chirality of the layers is preserved during this switching process and is also the case for a switch between two ferroelectric states. Recently, it was found that the polar switching in "banana phases" can also take place by another mechanism, which is based on the collective rotation of the molecules around their long axes (Figure 2a). In polar smectic A (SmAP) phases[4,5] and in B_{1rev} phases formed by SmAP-like layer fragments[6] this mechanism is the only possibility for polar switching. There are a few examples that this switching mechanism can also occur in tilted $SmCP_A$ phases[7–9] as well as in B_{1rev} phases with SmCP-like layer fragments,[6] mostly under special experimental conditions. Nakata et al.[8] and Bedel et al.[9] were able to detect this switching mechanism above a critical electric field. Schröder et al.[7] observed this kind of polar switching only on very slow increase or decrease of the electric field. It should be emphasized that the field-induced switching in tilted

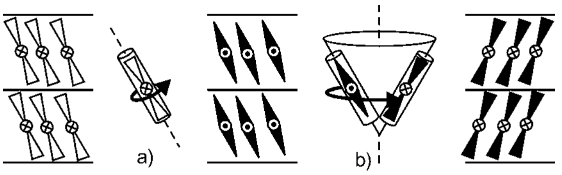

Figure 2. Mechanisms of polar switching a) by collective rotation of the molecules around their long axes and b) by rotation of the director around the tilt cone. Filled and open molecule symbols designate layers of opposite chirality.

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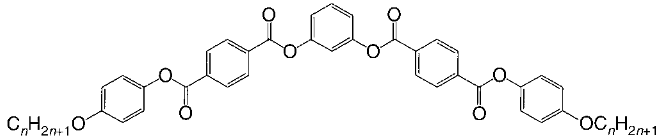
"banana phases" by rotation around the long axes is accompanied by an inversion of the layer chirality.

Herein we focus mainly on the switching of chirality by external electric fields. We investigated eight homologues of a new series of bent-core mesogens in which the outer linking groups are reversed compared to isomeric compounds reported in the literature.[10] We found that all the homologues form a polar tilted smectic C (SmCP) phase with undulated smectic layers. From electrooptical experiments it follows that the short-chain members possess an antiferroelectric ground state while the long-chain members are ferroelectric. It is the first example where the switching process is changed from an antiferroelectric to a ferroelectric one with increasing chain length. Furthermore, for the first time, we found a clear dependence of the switching mechanism on the experimental conditions, that is, on the frequency and the temperature. At higher frequencies or lower temperatures, the polar switching of the ferroelectric phase takes place in the usual way, that is, by the rotation of the director around the tilt cone. This switching process retains the chirality of the layer and reverses only the polarity of the layer (see Figure 2b). The other type of polar switching takes place through collective rotation of the molecules around their long axes at sufficiently low frequencies or high temperatures. This process, which was first observed for the ferroelectric tilted "banana phases", reverses the polarity of the layer and is now accompanied by an inversion of the macroscopic chirality (see Figure 2a). Interestingly, both switching mechanisms compete at intermediate frequencies. By using polarizing microscopy an irreversible field-induced inversion of chirality could be clearly visualized in a texture which exhibits circular domains of opposite handedness. It should be noted that rotation around the long axes is probably the only mechanism of polar switching in the antiferroelectric phase of the short-chain homologues.

All members **5**–**10**, **12**, and **16** of the series have been prepared by esterification of resorcinol with the corresponding 4-(4-*n*-alkyloxyphenoxycarbonyl)benzoic acids in the presence of *N*,*N*'-dicyclohexylcarbodiimide (DCC) and 4-(*N*,*N*-dimethylamino)pyridine (DMAP) as the catalyst in dichloromethane (for the reaction pathway and analytical data for compound **12**, see the Supporting Information). The transition temperatures together with the enthalpy values are recorded in Table 1. Compounds **5**–**9** show similar optical textures, thus indicating they have the same phase. Cooling the isotropic liquid of any of these compounds results in the mesophase growing with ribbonlike textures together with the helical filaments (Figure 3a). However, the textural features observed for the higher homologues, namely, compounds **10**–**16**, are completely different to that of the first group, thus indicating a different mesophase. The mesophases of these longer chain compounds only show a spherulytic texture as shown in Figure 3b.

Table 1: Transition temperatures and corresponding enthalpies of compounds **5**–**10**, **12**, and **16**.[a]



Compound	*n*	Transition (T [°C]) [δH [kJ mol^{-1}]]	Transition (T [°C]) [δH [kJ mol^{-1}]]
5	5	$\mathrm{Cr\rightarrow Sm\tilde{C}P_A}$ (168.5) [92.2]	$\mathrm{Sm\tilde{C}P_A\rightarrow I}$ (163.5) [18.8]
6	6	$\mathrm{Cr\rightarrow Sm\tilde{C}P_A}$ (166.5) [70.9]	$\mathrm{Sm\tilde{C}P_A\rightarrow I}$ (168.0) [20.6]
7	7	$\mathrm{Cr\rightarrow Sm\tilde{C}P_A}$ (161.5) [79.3]	$\mathrm{Sm\tilde{C}P_A\rightarrow I}$ (165.0) [11.6]
8	8	$\mathrm{Cr\rightarrow Sm\tilde{C}P_A}$ (160.0) [68.7]	$\mathrm{Sm\tilde{C}P_A\rightarrow I}$ (168.0) [21.5]
9	9	$\mathrm{Cr\rightarrow Sm\tilde{C}P_A}$ (157.5) [83.9]	$\mathrm{Sm\tilde{C}P_A\rightarrow I}$ (165.5) [20.7]
10	10	$\mathrm{Cr\rightarrow Sm\tilde{C}P_F}$ (154.5) [86.7]	$\mathrm{Sm\tilde{C}P_F\rightarrow I}$ (164.0) [21.7]
12	12	$\mathrm{Cr\rightarrow Sm\tilde{C}P_F}$ (152.0) [79.7]	$\mathrm{Sm\tilde{C}P_F\rightarrow I}$ (162.0) [23.6]
16	16	$\mathrm{Cr\rightarrow Sm\tilde{C}P_F}$ (151.0) [110.4]	$\mathrm{Sm\tilde{C}P_F\rightarrow I}$ (160.5) [24.3]

[a] Abbreviations: Cr = crystalline solid, $\mathrm{Sm\tilde{C}P_A}$ = antiferroelectrically switchable undulated tilted smectic phase, $\mathrm{Sm\tilde{C}P_F}$ = ferroelectrically switchable undulated tilted smectic phase, I = isotropic liquid.

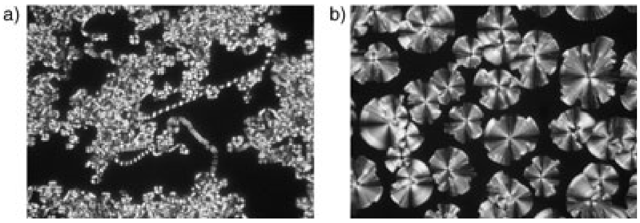


Figure 3. Optical photomicrographs of a) the $\mathrm{Sm\tilde{C}P_A}$ phase of compound **8** at 167 °C and b) the $\mathrm{Sm\tilde{C}P_F}$ phase of compound **12** at 161 °C.

The compounds under discussion are interesting from a structural point of view. X-ray powder diffraction patterns recorded with a Guinier film camera show strong layer reflections indicating that the basic structure is smectic. In addition, satellites of weak intensity could be clearly seen behind the layer reflections which suggests the presence of an undulated layer structure. The XRD powder pattern obtained for the mesophase of compound **6** is shown as an example in the Supporting Information. Satellites of weak intensity are obtained for the complete homologous series (see the Supporting Information). The undulation period increases from 100 to 150 Å with increasing chain length. The X-ray diffraction pattern of a partially aligned sample of the mesophase (see the Supporting Information) allows a tilt angle of about 20° to be estimated for compound **12** (designated as $\mathrm{Sm\tilde{C}P}$, where the symbol ~ indicates the periodic in-plane density wave according to the recommendation in ref. [11]). This value is relatively small compared with the tilt angle of smectic phases of other bent-core compounds. A wide-angle diffuse maximum obtained at 4.7 Å indicates the absence of any long-range positional order. As shown by Coleman et al.,[12] the modulated layer structure formed by bent-core molecules is generated by splayed polarization with domains of alternate tilt and polarization periodically arranged. This is another way to avoid bulk polarization.

In addition to the structural features, the electrooptical behavior is also particularly interesting. On applying a triangular-wave electric field[13] to the mesophase of compound **7**, two polarization current peaks per half period were recorded which indicates an antiferroelectric ground state (see the Supporting Information). The calculated polarization value is about 520 nC cm^{-2}. However, the field-induced circular domains in which the extinction crosses are aligned along the directions of the crossed polarizers do not change on reversal of the field. At first sight, these observations could indicate a racemic ground state for the mesophase. However, no relaxation of the extinction crosses could be seen on terminating the applied field, apart from a small change in the birefringence. If the effect arose from a racemic nature of the domains, the texture should have shown a striped pattern parallel to the smectic layers as a result of an alternating chirality.[2] Instead we only observe a smooth fan-shaped texture (see the Supporting Information). Therefore, these observations suggest that the chirality of the layer switches by collective rotation of molecules around their long axes on reversing the applied field. A similar switching behavior could be observed for the homologues (**5**, **6**, **8**, and **9**) exhibiting antiferroelectric switching. On the basis of these experimental observations, mesophases of these compounds have been designated as the $\mathrm{Sm}\tilde{\mathrm{C}}\mathrm{P}_\mathrm{A}$ phase.

The mesophase of compounds with longer aliphatic chains (**10**, **12**, and **16**) shows a different and interesting electro-optical switching behavior. A ferroelectric switching current response could be observed in the mesophase of compound **12** (see the Supporting Information); this result was also confirmed by applying a modified triangular wave (the plateau is introduced at zero voltage), which shows only a single polarization peak per half period. Therefore, we designated this phase as $\mathrm{Sm}\tilde{\mathrm{C}}\mathrm{P}_\mathrm{F}$. A texture with spherulytic patterns appeared on cooling the mesophase of compound **12** under a polarizing microscope, and application of an electric field afforded a texture with bright and dark domains which depends on the polarity of the applied field. The texture remains unchanged on terminating the field, thus indicating bistable switching. Circular domains with extinction crosses could be obtained on increasing the voltage above a threshold value ($E > E_\mathrm{th}$). These domains show bistable (ferroelectric) switching and the extinction crosses remain unchanged after removing the applied field. These bistable states are stable for several hours (Figures 4 and 5 a), thus confirming the ferroelectric ground state of this mesophase. We strongly believe that the appearance of switching chiral domains at higher electric fields (triangular wave) is the consequence of the suppression of the undulated structure of the ground state, as observed for several other compounds.[12] The field-induced $\mathrm{SmC_sP_F}$ phase is stable on sudden removal of the field. However, the switching circular domains disappear slowly when the applied field is slowly reduced, which indicates a transition back to the undulated ground state. The switching mechanism of the ferroelectric $\mathrm{Sm}\tilde{\mathrm{C}}\mathrm{P}$ phase clearly depends on the frequency and on the temperature, which contrasts the behavior of the antiferroelectric $\mathrm{Sm}\tilde{\mathrm{C}}\mathrm{P}$ phase of the short-chain members.

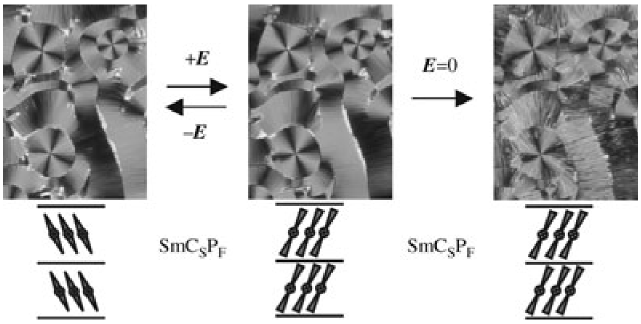


Figure 4. Bistable (ferroelectric) switching states obtained for the mesophase of compound **12** (±40 V µm^{-1}, 30 Hz at 149 °C), which are stable for several hours.

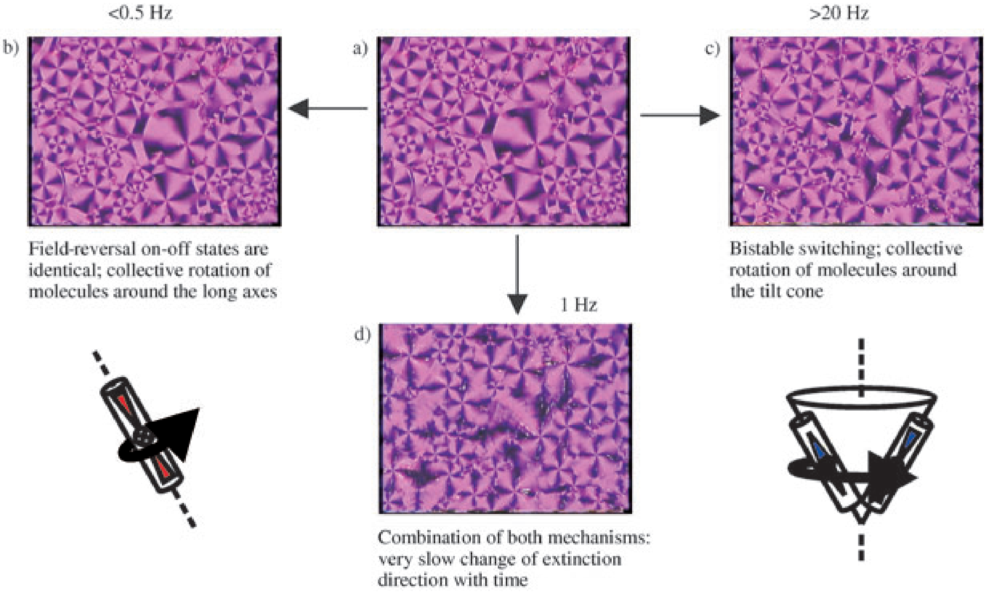


Figure 5. Frequency-dependent switching mechanism under a triangular-wave field for the $\mathrm{Sm}\tilde{\mathrm{C}}\mathrm{P}_\mathrm{F}$ phase of compound **12** at 148 °C and ±40 V µm^{-1}. Red and blue molecule symbols designate layers of opposite chirality.

No change in the position of the extinction crosses and no change of the birefringence could be seen by reversing the polarity of the applied field at lower frequencies (< 0.2 Hz), although the optical effect and a current response could be clearly detected. These findings indicate that a reversal of the polarization takes place through the collective rotation around the long molecular axes. This kind of switching not only reverses the polarity but also the chirality of the layer. This result means that the chirality of the whole domain is inverted in the case of ferroelectric phases (Figure 5b).

At higher frequencies (≥ 20 Hz) a fast bistable switching is observed where the extinction crosses rotate clockwise or anticlockwise depending on the handedness of the circular domains (Figure 5c). This observation indicates that reversal of the polarization occurs by rotation of the director around the tilt cone. In this case, the chirality of the layer is retained and only the direction of polarization is reversed, as in SmC* phases.

Interestingly, at intermediate frequencies (> 0.5 Hz) a switching process could be clearly seen which takes place in the frequency of the applied a.c. field (Figure 5d), and simultaneously a very slow rotation of the extinction crosses (clockwise or anticlockwise) could be observed. These two results indicate a combination of both switching mechanisms.

No optical switching could be seen in the temperature interval 5 °C below the clearing temperature irrespective of the frequency, which suggests switching by a rotation around the molecular long axes. Bistable switching domains slowly appeared on further cooling the sample, which indicates switching around the tilt cone. The temperature dependence could be explained if we assume that the viscosity χ_α (related to the rotation around the long axes) is lower than the viscosity χ_φ (related to the rotation around a tilt cone) for a given field $\boldsymbol{E}$ and a given polarization $\boldsymbol{P}$ at higher temperature, whereas at lower temperatures the situation is opposite.

We also observed the inversion of the macroscopic chirality under the influence of an a.c. field over time. As seen from Figure 6, the texture consists of circular domains of opposite handedness; there are domains which have both an outer and inner part (indicated by arrows) with opposite handedness. If a sufficiently high voltage (a.c. field) is applied for some time (see snapshots after 30, 60, and 95 seconds) it can be seen that the inner domain with opposite chirality grows at the cost of the outer one. After about 60 s, the nucleation of a new domain begins in the center of the growing inner domain, again with opposite handedness. In this way, the field-induced change of chirality can be directly visualized. In this context it should be noted that an irreversible changeover of a homochiral into a racemic structure was reported in a $\mathrm{SmCP_A}$ phase [14] by application of a triangular electric field.

In conclusion, we have presented a new homologous series of bent-core mesogens where all members form a polar tilted smectic C phase with an undulated layer structure. We have found for the first time that the polar structure is changed from antiferroelectric to ferroelectric with increasing

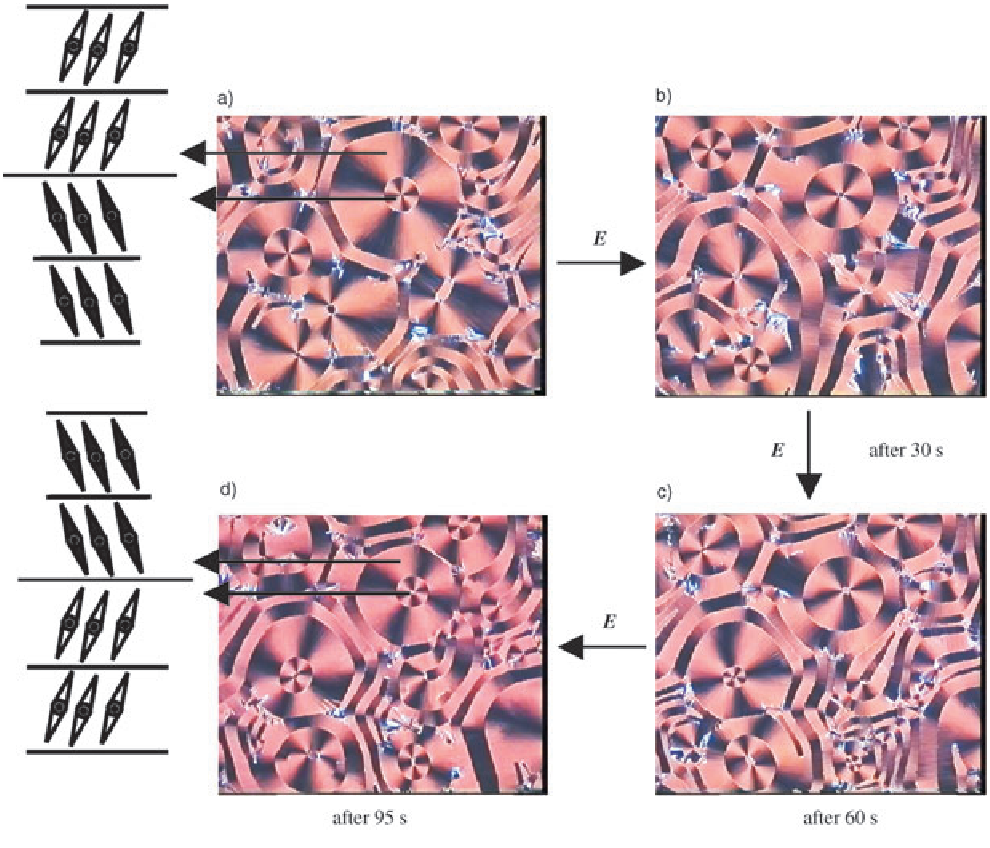


Figure 6. Visualization of the inversion of macroscopic chirality with time under a triangular-wave field in the $\mathrm{Sm\tilde{C}P_F}$ phase of compound **12**; ± 40 V μm^{-1}, 30 Hz at 148 °C. Filled and open molecule symbols designate layers of opposite chirality.

chain length. This observation can be explained in terms of interlayer interactions: they could be stronger for short-chain members which would clearly favor the formation of an antiferroelectric polar structure. Another remarkable feature is the occurrence of two different mechanisms of polar switching. In the case of ferroelectric phase, the switching mechanism clearly depends on the experimental conditions. At low temperatures and high frequencies the polar switching is based on the rotation of the director around the tilt cone. At a high temperature and a low frequency the polar switching takes place through rotation of the long molecular axes. Furthermore, we were able to change the chirality of circular domains irreversibly by application of an a.c. field.

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