Reentrant Ferroelectricity in Liquid Crystals

D. Pociecha,[1] E. Gorecka,[1] M. Čepič,[2] N. Vaupotič,[3] B. Žekš,[2] D. Kardas,[1] and J. Mieczkowski[1]

[1]*Chemistry Department, Warsaw University, Zwirki i Wigury 101, 02-089 Warsaw, Poland*
[2]*J. Stefan Institute, Jamova 39, 1000 Ljubljana, Slovenia*
[3]*Faculty of Education, Koroška 160, 2000 Maribor, Slovenia*
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The ferroelectric (Sm C^*)–antiferroelectric (Sm C_A^*)–reentrant ferroelectric (re Sm C^*) phase temperature sequence was observed for systems with competing synclinic-anticlinic interactions. The basic properties of this system are as follows: (i) the Sm C^* phase is metastable in the temperature range of the Sm C_A^*; (ii) the helix handedness inverts at both Sm C^*-Sm C_A^* and Sm C_A^*–re-Sm C^* phase transitions; (iii) the threshold electric field that is necessary to induce synclinic ordering in the Sm C_A^* phase decreases near both Sm C_A^*-Sm C^* and Sm C_A^*–re-Sm C^* phase boundaries. All these properties are properly described by a simple Landau model that accounts for nearest neighboring layer steric interactions and quadrupolar ordering only.

There are two types of tilted smectic phases with a liquid-like in-layer order: the synclinic (Sm C) phase in which molecules are tilted in all layers in the same direction and the anticlinic (Sm C_A) phase in which the tilt direction alternates when going from one smectic layer to another. For the chiral tilted systems the spontaneous electric polarization in the smectic layers along the $c \times n$ direction is allowed, where c is projection of the tilt onto the smectic layer and n is the layer normal. As a result the synclinic Sm C phase acquires ferroelectric (Sm C^*) properties. The anticlinic Sm C_A phase becomes the antiferroelectric phase (Sm C_A^*) since the P_s is canceled out in two consecutive layers as the c vector direction alternates [1]. For some liquid crystals the free energy of the synclinic and the anticlinic structure is very similar and the type of the tilted phase formed can be tuned by very slight modifications in molecular structure. It could be observed that within the same homolog series, when the length of the terminal alkyl chain is changed, some homologs exhibit synclinic (ferroelectric) Sm C^*, while others exhibit the anticlinic (antiferroelectric) Sm C_A^* phase, and usually more complicated behavior than the simple odd-even function of alkyl chain length takes place [2]. When competing interactions of comparable strength are present, one can also expect a more complex temperature sequence of polar phases. In chiral materials, between synclinic and anticlinic phases the number of intermediate phases with ferrielectric order are sometimes detected [3]. The competing synclinic-anticlinic interactions might also lead to the reentrancy of the ferroelectric order. We show that when the temperature is lowered, instead of the simple Sm C^*-Sm C_A^* phase sequence, the Sm C^* phase reappears below the Sm C_A^* phase.

In the phase diagram of the *mPIRn* [4], with the chemical formula given in Fig. 1, m is the number of carbon atoms in the achiral tail and n is the number of carbon atoms in a chain attached to the chiral center homolog series, in which m is fixed to 8 and n is changed (Fig. 2); the phase sequence Sm C^*–Sm C_A^*–re-Sm C^*–Sm I

is observed for compounds with $n = 2, 3$, and Sm C^*–Sm C_A^*–re-Sm C^*–Sm B_{cry} for $n = 4$. In materials with a longer chiral tail, $n = 5, 6$, the Sm C_A^* phase disappears and only one tilted phase, ferroelectric Sm C^*, is present. When the chiral end is fixed to $n = 4$ and the nonchiral end is changed (Fig. 2 inset) we observed an increase of the Sm C_A^* phase temperature range with increasing m; homolog $m = 9$ exhibits the sequence Sm C^*-Sm C_A^*-Sm I_A-Sm I, which means that the ferroelectric properties are restored in the hexatic phase. The phase diagram for the *mPIRn* series was constructed based on measurements performed at slow temperature scans (up to 5 K min^{-1}). However, it should be noticed that under sufficiently fast cooling or heating, sometimes the antiferroelectric phase was missing, and only ferroelectric phases were observed. For chosen homologs, it has been checked that enantiomeric and racemic samples have the same sequence of the synclinic Sm C and the anticlinic Sm C_A phases and that the phase transition temperatures coincide.

The enthalpy changes detected in calorimetric measurements (Perkin Elmer DSC 7) at Sm C^*-Sm C_A^* and Sm C_A^*–re-Sm C^* (e.g., for *8PIR4*) phase transitions were comparable, which suggests that the reconstructing of the azimuthal angle structure does not involve the changes of the other order parameters.

The ferroelectric and antiferroelectric properties of the phase could be distinguished by electric switching and dielectric and optical methods. In the Sm C^* phase bistable switching is detected, while in the Sm C_A^* phase tristable switching with a threshold field is observed. The threshold field in the Sm C_A^* phase critically decreases near both
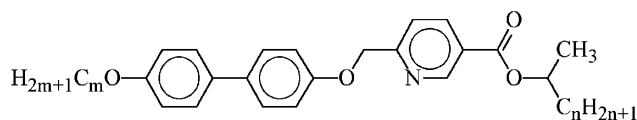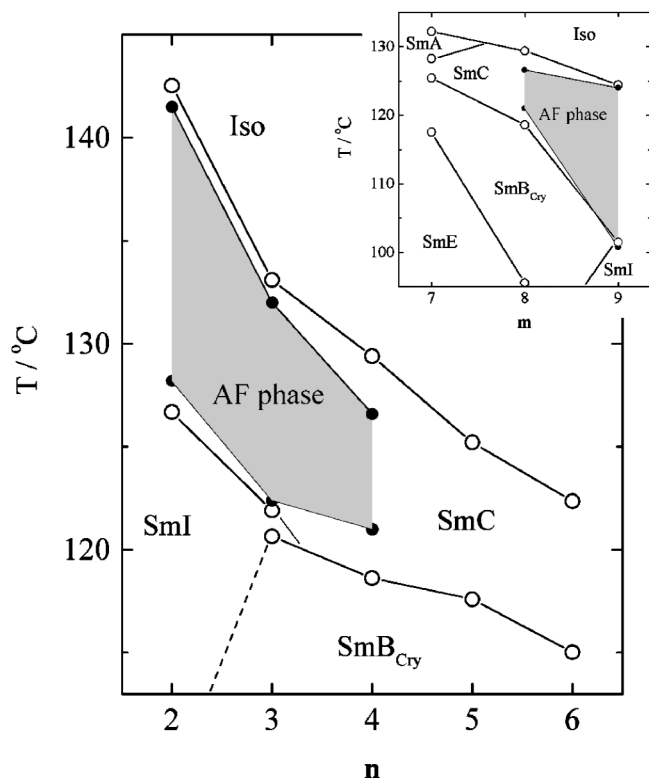

FIG. 1.   Chemical formula of the material *mPIRn*.

FIG. 2. Phase diagram for the homolog series *8PIRn* in which the length of the alkyl chain attached to the chiral carbon atom is changed. Inset: phase diagram for *mPIR4* in which the length of the achiral alkoxy chain is changed.

Sm C^*-Sm C_A^* and Sm C_A^*-re-Sm C^* phase transitions, which shows that the strength of the anticlinic interactions decreases. The type of electro-optic switching is consistent with the detected current signal; the single or double current peak was found upon reversing the spontaneous polarization (P_s) by electric field of low frequency (~ 1 Hz) in Sm C^* and Sm C_A^* phases, respectively. Moreover, both Sm C^*-Sm C_A^* and Sm C_A^*-re-Sm C^* phase transitions are marked by notable changes in the texture, related to the changes of the birefringence and the helical structure. Except for the shortest homolog, in the *8PIRn* series in synclinic phases the helical structure gives selective reflection in a visible light range (e.g., ~ 650 nm for *8PIR4*), while in the anticlinic phase the helical pitch is of a micron length. For the shortest homolog *8PIR2* in both Sm C^* and re-Sm C^* phases, as well as in the Sm C_A^* phase, the pitch is longer than the visible light wavelength ($>1.7 \mu$m), and significant optical activity is detected. The optical activity changes sign when going from the Sm C^* phase to the Sm C_A^* phase, having the same sign in both Sm C^* and re-Sm C^* phases. This indicates that the sense of the helical structure alternates when going from the synclinic to the anticlinic phase.

No tilt anomaly was detected at Sm C^*-Sm C_A^*-re-Sm C^* phase transitions. The tilt angle slightly increases on cooling over all temperature ranges of tilted phases (e.g., from 24° to 28° and from 22° to 25° for

8PIR2 and *8PIR4*, respectively), without any pretransitional anomaly either at phase transition to the hexatic smectic *I* or to the crystalline smectic *B* phase. Also the P_s value does not exhibit anomaly at the Sm C^*-Sm C_A^* phase transitions.

Dielectric measurements were carried out with a Wayne Kerr impedance analyzer for glass cells of various thicknesses ($2-100 \mu$m) covered with indium-tin-oxide transparent electrodes and a parallel rubbed polyimide layer. In thick, 25 and 100 μm cells the Goldstone (phason) mode with the relaxation frequency in the kHz regime was detected in both ferroelectric Sm C^* and re-Sm C^* phases (Fig. 3a). The transition to the antiferroelectric Sm C_A^* phase is marked by sudden suppression of the phason mode, where no dielectric mode was found within the studied frequency range (20 Hz–300 kHz).
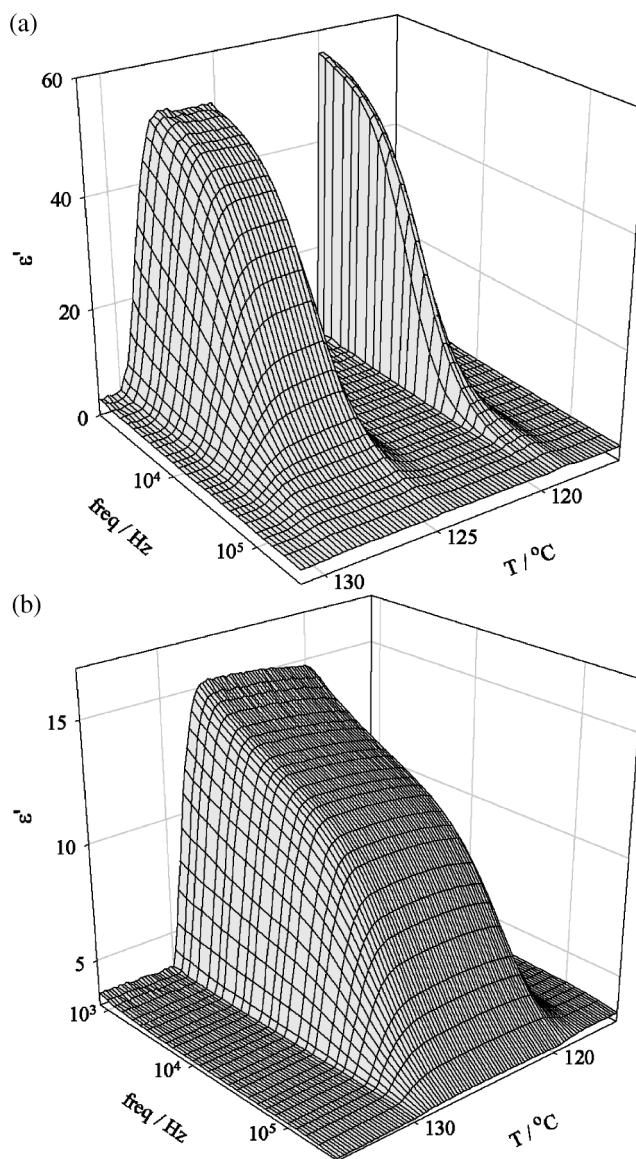
(a)

(b)

FIG. 3. 3D temperature-frequency plot of the real part of the dielectric constant ε^* for compound *8PIR4* measured in 100 μm (a) and 2 μm (b) thick cells.

In thin, 2 μm cells in which interactions from the surfaces favoring ferroelectric order become more significant, we observed suppression of the antiferroelectric order (Fig. 3b). In such cells in the whole range of tilted smectic phases the Goldstone mode was detected, with significantly higher relaxation frequency than observed in thicker cells [5]. In cells with intermediate thickness, in the temperature range of the Sm C_A phase stability, the clusters of both Sm C^* and Sm C_A^* phases are observed, and the number of Sm C^* clusters increases when the thickness decreases [6].

The proper order parameter to describe the transition between tilted smectic phases is the vector given by $\boldsymbol{\xi}_j = \theta(\cos\varphi_j, \sin\varphi_j)$, where θ is the magnitude of the tilt and the azimuthal angle φ_j describes the tilt direction in the jth layer. Since the synclinic-anticlinic-synclinic phase sequence is observed in enantiomers and their racemate mixture, we can assume that for the studied system the chiral interactions as well as polar interactions between layers are negligible. Thus the Landau free energy density expansion can be written as

$$
\begin{aligned}
G = \sum\Bigg(&\frac{1}{2}a_0\boldsymbol{\xi}_j^2 + \frac{1}{4}b_0\boldsymbol{\xi}_j^4 + \frac{1}{6}c_0\boldsymbol{\xi}_j^6 \\
&+ \frac{1}{2}a_1(\boldsymbol{\xi}_j \cdot \boldsymbol{\xi}_{j+1}) + \frac{1}{2}a_1'\boldsymbol{\xi}_j^2(\boldsymbol{\xi}_j \cdot \boldsymbol{\xi}_{j+1}) \\
&+ \frac{1}{2}a_1''\boldsymbol{\xi}_j^4(\boldsymbol{\xi}_j \cdot \boldsymbol{\xi}_{j+1}) + \frac{1}{4}b_1(\boldsymbol{\xi}_j \cdot \boldsymbol{\xi}_{j+1})^2\Bigg), \quad (1)
\end{aligned}
$$

where the only temperature dependent parameter is $a_0 = a(T - T_0)$, T_0 being the transition temperature from orthogonal to the tilted smectic phase in the absence of interlayer correlations. The first three terms with the parameters a_0, b_0, and c_0 model intralayer interactions and resume the fact that the transition to the tilted phase is of the strong first order and that the tilt over the whole stability region of the Sm C^* and the Sm C_A^* phase does not change significantly. Interlayer interactions are given by the terms a_1, a_1', a_1''. Quadrupolar interlayer interactions are given by the b_1 term. Introducing the new parameter $\alpha_j = \alpha = \varphi_{j+1} - \varphi_j$ which is 0 for the Sm C^* phase and π for the Sm C_A^* phase, the free energy (1) can be rewritten as

$$
\begin{aligned}
G = &\frac{1}{2}a_0\theta^2 + \frac{1}{4}b_0\theta^4 + \frac{1}{6}c_0\theta^6 \\
&+ \frac{1}{2}(a_1 + a_1'\theta^2 + a_1''\theta^4)\theta^2\cos\alpha + \frac{1}{4}b_1\theta^4\cos^2\alpha.
\end{aligned}
$$
$$(2)$$

The effective interlayer interactions are determined by the sign of $a_{1ef} = (a_1 + a_1'\theta^2 + a_1''\theta^4)$; if negative, the interlayer interactions enforce synclinic tilt in the neighboring layers; if positive, anticlinic structure is favored. On the microscopic level, the sign of the a_{1ef} term results from competing interactions, e.g., molecular interpenetration through the layers benefits a negative sign while strong

attractive van der Waals interactions between molecules from neighboring layers benefit a positive sign. A positive sign also favors antiparallel dipolar ordering of neighboring layers and can be significant in systems with strong electrostatic interactions [7].

The observed reappearance of the Sm C^* phase raises the question: "What is the driving force to this phenomenon." From the expression for a_{1ef} it can be deduced that the reentrant phenomenon could be observed in systems where a_{1ef} changes its sign at two different temperatures. This could happen in systems where either the tilt θ or the spontaneous polarization P_s (or both) depends on the temperature nonmonotonically. However, we have to exclude both factors. In the studied system, tilt steadily grows with a lowering of the temperature and the synclinic-anticlinic-resynclinic phase sequence is also observed in racemic compounds forming nonpolar mesophases.

Thus the other interactions have to be explored as a driving mechanism for the reentrancy of the Sm C^* phase. At higher temperatures one can expect a negative sign of a_{1ef} due to the strong diffusion of molecules between layers. At lower temperatures the quadrupolar ordering can change interactions between molecules from a neighboring layer. If the molecules are considered as flat, lathlike species, their quadrupolar ordering means correlations between the directions of short molecular axes. For the tilted phase as the biaxial ordering becomes more important with decreasing temperature, the molecules arrange with their short axes perpendicular to the tilt direction [8]. This type of ordering might promote the interlayer diffusion of molecules and consequently the reappearance of the Sm C^* phase.

It should be stressed that although nonmonotonic dependence of a_{1ef} can also be observed in other tilted phases [9], but only in the systems where the free energy part of synclinic and anticlinic interactions is similar in a broad temperature range, the free energies $G_{\alpha=0}(T)$ and $G_{\alpha=\pi}(T)$ can become equal at two different temperatures; thus the reentrant phenomenon could be observed.

When molecules order quadrupolarly as discussed, also the sign of the b_1 term defining quadrupolar interlayer interactions is negative, since tilts bound to one plane are preferred and therefore the free energy has always two minima as a function of α. The behavior has been observed also in some other materials [10]. Appearance of the local minimum explains why in a temperature range when the anticlinic structure is thermodynamically stable, the metastable synclinic phase can sometimes be observed.

In order to analyze helicoidal modulations, in the chiral system the Lifshitz term which accounts for chiral interlayer interactions should be added to the free energy.

$$G_{\text{chir}} = G + f(\boldsymbol{\xi}_j \times \boldsymbol{\xi}_{j+1})_z = G + f\theta^2\sin\alpha. \quad (3)$$

For weak chiral interactions we can assume that $\alpha \approx 0$ in the Sm C^* phase and $\alpha \approx \pi$ in the Sm C_A^* phase. Minimizing the free energy with respect to α one obtains
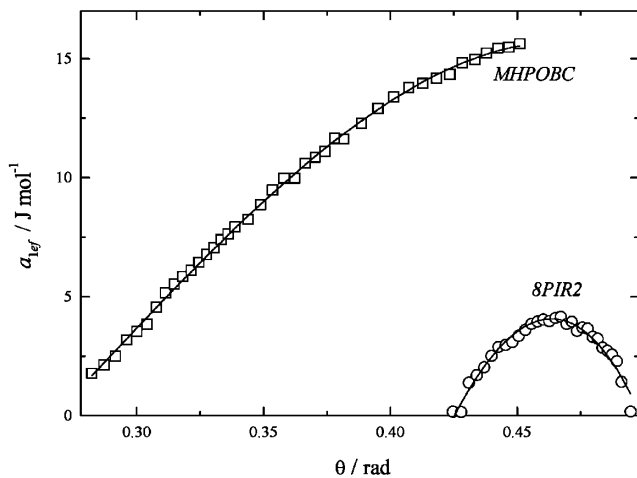
FIG. 4.   Tilt dependence of a_{1ef} effective interlayer interactions for *8PIR2* and *MHPOBC* in the Sm C_A^* phase. At the transitions Sm C^*-Sm C_A^* and Sm C_A^*–re-Sm C^*, the a_{1ef} changes sign.

$\alpha = \frac{f}{a_{1ef}+b_1\theta^2}$ for the Sm C^* phase and $\alpha = \pi - \frac{f}{-a_{1ef}+b_1\theta^2}$ for the Sm C_A^* phase, respectively. The sign of f correlates with enantiomer chirality. If in the Sm C^* phase $\alpha > 0$, then it is slightly less than π (since a_{1ef} reverses sign when going from Sm C^* to Sm C_A^*) in the Sm C_A^* phase; thus opposite handedness of the helices in the Sm C^* phase and the Sm C_A^* phase is expected as experimentally observed.

To account for the system interaction with electric field, the term $-\boldsymbol{E} \cdot \boldsymbol{P}_j$ is added to the free energy G, where $\boldsymbol{P}_j$ is the polarization in the jth layer. The straightforward calculations show that the energies of the untwisted Sm C^* and Sm C_A^* phases become equal when the electric field induced switching is observed at E_{th} given by $E_{th}P_s = a_{1ef}\theta^2$, where P_s is the spontaneous polarization. In the Sm C_A^* phase the threshold field E_{th} therefore follows the a_{1ef} temperature dependence (Fig. 4); it is largest in the middle of the temperature range of the Sm C_A^* phase stability and decreases near both Sm C_A^*-Sm C^* phase transitions. Fitting simultaneously tilt θ vs temperature and $a_{1ef} = \frac{E_{th}P_s}{\theta^2}$ vs θ provided for compound *8PIR2* the following set of parameters describing the strength of molecular interactions, in-layer and nearest neighboring interlayer $a_0 = 1.2$ kJ mol^{-1} K^{-1}, $b_0 + b_1 = -146.0$ kJ mol^{-1}, $c_0 = 1003.5$ kJ mol^{-1}, $a_1 = -0.16$ kJ mol^{-1}, $a_1' = 1.51$ kJ mol^{-1}, $a_1'' = -3.52$ kJ mol^{-1}. The temperature dependence of the tilt $\theta = \sqrt{\frac{-B+\sqrt{B^2-4AC}}{2C}}$ with $A = a(T - T_0) - a_1$, $B = b_0 + b_1 - 2a_1'$, and $C = c_0 - 3a_1''$ was obtained by minimizing free energy (2) in the anticlinic phase with respect to the tilt. The parameters $a_0 = 0.2$ kJ mol^{-1} K^{-1}, $b_0 + b_1 = -11.7$ kJ mol^{-1}, $c_0 = 343.3$ kJ mol^{-1}, $a_1 = -0.02$ kJ mol^{-1}, $a_1' = 0.32$ kJ mol^{-1}, $a_1'' = -0.73$ kJ mol^{-1} were obtained if a similar procedure is applied in the Sm C_A^* phase of the prototype antiferroelectric material *MHPOBC* [1] (Fig. 4).

For the above parameters, it has been estimated that the interlayer interactions contribution to the free energy is less than 0.03% for *8PIR2* and 0.3% for the *MHPOBC* compound, which clearly indicates that the interlayer interactions in the compound *mPIRn* series are much weaker than interlayer interactions in materials without reentrant behavior.

Summarizing, the system with a temperature sequence of synclinic (Sm C^*)-anticlinic (Sm C_A^*)-synclinic (Sm C^*) tilted smectic phases was found. It has been proved that the unusual phase sequence is related to steric interactions since it is observed in enantiomeric as well as in racemic compounds. The Sm C_A^* phase can be easily suppressed by surface interactions in thin cells. The Sm C^* state could be observed as a metastable phase in the temperature range Sm C_A^* thermodynamic stability. The simple Landau model that accounts only interactions with nearest neighboring layers and quadrupolar ordering is able to explain the Sm C^*–Sm C_A^*–re-Sm C^* phase sequence and properties of *mPIRn* compounds. It also explains observed in experiment fact that the helix in Sm C^* and re-Sm C^* phases has the opposite sign from that in the Sm C_A^* phase. It also explains that the threshold field which induces synclinic ordering in the Sm C^* phase decreases near both Sm C_A^*–Sm C^* and Sm C_A^*–re-Sm C^* phase boundaries and has maximum in the middle of the Sm C_A^* region.

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