Re-entrant ferroelectricity in liquid crystals

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Abstract

The ferroelectric (Sm C\textsuperscript{*}) – antiferroelectric (Sm C\textsubscript{A*}) – reentrant ferroelectric (re Sm C\textsuperscript{*}) phase temperature sequence was observed for system with competing synclinic - anticlinic interactions. The basic properties of this system are as follows (1) the Sm C\textsuperscript{*} phase is metastable in temperature range of the Sm C\textsubscript{A*} stability (2) the double inversions of the helix handedness at Sm C\textsuperscript{*} – Sm C\textsubscript{A*} and Sm C\textsubscript{A*} – re-Sm C\textsuperscript{*} phase transitions were found (3) the threshold electric field that is necessary to induce synclinic ordering in the Sm C\textsubscript{A*} phase decreases near both Sm C\textsubscript{A*} – Sm C\textsuperscript{*} and Sm C\textsubscript{A*} – re-Sm C\textsuperscript{*} phase boundaries, and it has maximum in the middle of the Sm C\textsubscript{A*} stability region. All these properties are properly described by simple Landau model that accounts for nearest neighboring layer steric interactions and quadrupolar ordering only.

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There are two types of tilted smectic phases with liquid like in-layer order, synclinic (Sm C) phase in which molecules are tilted in all layers in the same direction, and antclinic (Sm C\textsubscript{A}) phase in which 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 $\mathbf{c} \times \mathbf{n}$ direction is allowed, where $\mathbf{c}$ is projection of the tilt onto the smectic layer and $\mathbf{n}$ is the layer normal. In result the synclinic Sm C phase acquires ferroelectric (Sm C\textsuperscript{\star}) properties. The anticlinic SmC\textsubscript{A} phase becomes antiferroelectric phase (Sm C\textsuperscript{\star\textsubscript{A}}) since the $P_s$ is canceled out in two consecutive layers as the $\mathbf{c}$ vector direction alternates \cite{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 homologue series, when the length of the terminal alkyl chain is changed, some homologues exhibit synclinic (ferroelectric) Sm C\textsuperscript{\star} while the others anticlinic (antiferroelectric) Sm C\textsuperscript{\star\textsubscript{A}} phase, and usually more complicated behavior than simple odd-even function of alkyl chain length takes place \cite{2}. When competing interactions of comparable strength are present, one can also expect more complex temperature sequence of polar phases. In chiral materials, between synclinic and antclinic phases the number of intermediate phases with ferrielectric order are sometimes detected \cite{3}. The competing synclinic – anticlinic interactions might also lead to the re-entrancy of the ferroelectric order. We will show that when the temperature is lowered, instead of simple Sm C\textsuperscript{\star} – Sm C\textsuperscript{\star\textsubscript{A}} phase sequence, the Sm C\textsuperscript{\star} phase re-appears below Sm C\textsuperscript{\star\textsubscript{A}} phase.

On the phase diagram of the $m$PIR\textsubscript{n} \cite{4}, with chemical formula given on Fig. 1, $m$ is number of carbon atoms in achiral tail and $n$ is number of carbon atoms in a chain attached to the chiral center homologue series, in which $m$ is fixed to 8 and $n$ is changed (Fig.2), the phase sequence Sm C\textsuperscript{\star} – Sm C\textsuperscript{\star\textsubscript{A}} – re-Sm C\textsuperscript{\star} –Sm I is observed for compounds with $n = 2, 3$ and Sm C\textsuperscript{\star} – Sm C\textsuperscript{\star\textsubscript{A}} – re-Sm C\textsuperscript{\star} – Sm B\textsubscript{cry} for $n = 4$. In materials with longer chiral tail, $n = 5, 6$ the Sm C\textsuperscript{\star\textsubscript{A}} phase disappears and only one tilted phase, ferroelectric Sm C\textsuperscript{\star} is present. When the chiral end is fixed to $n = 4$ and the non-chiral end is changed
(inset Fig. 2) we observed increase of the Sm C* A phase temperature range with increasing m; homologue 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 mPIRn series were 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 homologues, 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. More detailed studies have been performed on the homologues which do not exhibit the reentrant ferroelectric properties in the hexatic phase.

The enthalpy changes detected in calorimetric measurements (Perkin Elmer DSC 7) at Sm C* – Sm C* A and Sm C* A – re-Sm C* (eg. 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, 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 Sm C* A phase critically decreases near both 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 electrooptic 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 shortest homologue, in 8PIRn series in synclinic phases the helical structure gives selective reflection in visible light range (eg. ~ 610 nm for 8PIR4), while in anticlinic phase the helical pitch is of few microns length. For the shortest homologue
$8PIR2$ in both Sm C$^*$ and re-Sm C$^*$ phases as well as in the Sm C$^*_A$ phase the pitch is longer than visible light wavelength, since 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 synclinic to 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 range of tilted phases (e.g. from 24° to 28° and from 22° to 25° for $8PIR2$ and $8PIR4$, respectively), without any pretransitional anomaly neither at phase transition to hexatic smectic I nor to 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 Wayne Kerr impedance analyzer for glass cells of various thickness (2 - 100 microns) covered with indium-tin-oxide (ITO) transparent electrodes and parallel rubbed polyimide layer. In thick, 25 and 100 micron cells the Goldstone (phason) mode with the relaxation frequency in kHz regime was detected in both ferroelectric Sm C$^*$ and re-Sm C$^*$ phases (Fig.3a). The transition to 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).

In thin, 2 micron, 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 SmC$^*_A$ 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 transition between tilted smectic phases is vector given by $\xi_j = \theta \left( \cos \varphi_j, \sin \varphi_j \right)$, where $\theta$ is the magnitude of the tilt and the azimuthal angle $\varphi_j$ describes the tilt direction in the $j$-th 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

$$\begin{align*}
G &= \sum \left( \frac{1}{2} a_0 \xi_j^2 + \frac{1}{4} b_0 \xi_j^4 + \frac{1}{6} c_0 \xi_j^6 + \\
&\quad \frac{1}{2} a_1 (\xi_j \cdot \xi_{j+1}) + \frac{1}{2} a'_1 \xi_j^2 (\xi_j \cdot \xi_{j+1}) + \\
&\quad \frac{1}{2} a''_1 \xi_j^4 (\xi_j \cdot \xi_{j+1}) + \frac{1}{4} b_1 (\xi_j \cdot \xi_{j+1})^2 \right) \tag{1}
\end{align*}$$

where the only temperature dependent parameter is $a_0 = a(T - T_0)$, $T_0$ being 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 new parameter $\alpha_j = \alpha = \varphi_{j+1} - \varphi_j$ which is 0 for the Sm C* phase and $\pi$ for Sm C*_A phase, the free energy (1) can be re-written as

$$\begin{align*}
G &= \frac{1}{2} a_0 \theta^2 + \frac{1}{4} b_0 \theta^4 + \frac{1}{6} c_0 \theta^6 + \\
&\quad \frac{1}{2} \left( a_1 + a'_1 \theta^2 + a''_1 \theta^4 \right) \theta^2 \cos \alpha + \\
&\quad \frac{1}{4} b_1 \theta^4 \cos^2 \alpha. \tag{2}
\end{align*}$$

The effective interlayer interactions are determined by 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 microscopic level, the sign of $a_{1ef}$ term results from competing interactions e.g. molecular interpenetration through the layers benefits negative sign while strong attractive van der Waals interactions between molecules from neighboring layers benefit positive sign. Positive sign also favour antiparallel dipolar ordering of in neighboring layers and can be significant in systems with strong electrostatic interactions [7].

The observed re-appearance of the Sm C* phase raises the question what is the driving force to this phenomenon. From the expression for $a_{1ef}$ can be deduced that reentrant phe-
nomenon could be observed in systems where $a_{1ef}$ changes its sign at two different temperatures. This could happen in systems where either the tilt $\theta$ or the spontaneous polarization $P_s$ (or both) depend on the temperature nonmonotonically. However, we have to exclude both factors. In studied system tilt steadily grows with lowering the temperature and the synclinic – anticlinic – re-synclinic phase sequence is also observed in racemic compounds forming non-polar mesophases.

Thus the other interactions have to be explored as a driving mechanism for the re-entrancy of the Sm C* phase. At higher temperatures one can expect 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 neighboring layer. If the molecules are considered as flat, lath-like species, their quadrupolar ordering means correlations between direction 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 re-appearance 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 are 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 re-entrant phenomenon, could be observed.

When molecules order quadrupolarly as discussed, also the sign of $b_1$ 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 $\alpha$. The behavior has been observed also in some other materials [10]. Appearance of the local minimum explains why in temperature range when the anticlinic structure is thermodynamically stable, the metastable synclinic phase can be sometimes observed.

In order to analyze hellicoidal modulations, in chiral system the Lifshitz term which account for chiral interlayer interactions should be added to the free energy.
For weak chiral interactions we can assume that $\alpha \approx 0$ in Sm C* phase, and $\alpha \approx \pi$ in the Sm C_A phase. Minimizing the free energy with respect to $\alpha$ one obtains $\alpha = \frac{f}{a_{1ef} + b_1 \theta^2}$ 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 $\pi$ (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 $-E \cdot P_j$ is added to the free energy $G$, where $P_j$ is the polarization in the $j$-th 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 $\theta$ vs. temperature and $a_{1ef} = \frac{E_{th} P_s}{a_{1ef} \theta^2}$ vs. $\theta$ provided for compound 8PIR2 the following set of the parameters describing the strength of molecular interactions, in-layer and nearest neighboring interlayer $a_0 = 1.2 \text{ kJ mol}^{-1} \text{K}^{-1}$, $b_0 + b_1 = -146.0 \text{ kJ mol}^{-1}$, $c_0 = 1003.5 \text{ kJ mol}^{-1}$, $a_1 = -0.16 \text{ kJ mol}^{-1}$, $a'_1 = 1.51 \text{ kJ mol}^{-1}$, $a''_1 = -3.52 \text{ kJ mol}^{-1}$. 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 anticlinic phase with respect to the tilt. The parameters $a_0 = 0.2 \text{ kJ mol}^{-1} \text{K}^{-1}$, $b_0 + b_1 = -11.7 \text{ kJ mol}^{-1}$, $c_0 = 343.3 \text{ kJ mol}^{-1}$, $a_1 = -0.02 \text{ kJ mol}^{-1}$, $a'_1 = 0.32 \text{ kJ mol}^{-1}$, $a''_1 = -0.73 \text{ kJ mol}^{-1}$ were obtained if the similar procedure is applied in the Sm C_A phase of the prototype antiferroelectric material MHPBOBC [1]. For 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 MHPBOBC compound, which clearly indicates that the interlayer
interactions in compounds $mPIRn$ series are much weaker than interlayer interactions in materials without reentrant behavior.

Summarizing, the system with 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 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 resumes observed in experiment fact that the helix in Sm C$^*$ and re-Sm C$^*$ phases has opposite sign than in Sm C$_A^*$ phase. It also explains that the threshold field which induce 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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FIGURES

FIG. 1. Chemical formula of the material \( mPIRn \).

FIG. 2. Phase diagram for homologue series \( 8PIRn \) in which the length of alkyl chain attached to the chiral carbon atom is changes, in the inset phase diagram for \( mPIR4 \) in which the length of the achiral alkoxy chain is changed.

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

FIG. 4. Tilt dependence of \( a_{1ef} \) effective interlayer interactions for \( 8PIR2 \) and \( MHPOBC \), in the Sm \( C_A^* \) phase. At the transition Sm \( C^* \) –Sm \( C_A^* \) and Sm \( C_A^* \) – re-Sm \( C^* \), the \( a_{1ef} \) changes sign, thus stabilizes the synclinic Sm \( C^* \) phase.
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