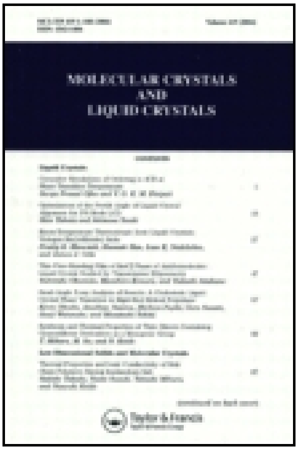

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Molecular Dynamics in the Vicinity of the Transition into the Hexatic Phase in Chiral Smectics

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Molecular Dynamics in the Vicinity of the Transition into the Hexatic Phase in Chiral Smectics

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A single relaxation process has been observed in both SmC* and hexatic SmI*phases by dielectric and electroptic methods, which was attributed to fluctuations of the bond orientation order (BOO). This mode exhibits a softening when approaching the SmI* phase on cooling. The coupling between the BOO and polarization results in an anomalous increase of P_S value at the transition to the hexatic phase.

Keywords: chiral smectics; tilted hexatic phase; bond orientational order

INTRODUCTION

Hexatic phases either orthogonal or tilted may appear below the SmA or SmC phases. While the latter phases are 2D-liquids, in hexatic phases long range three dimensional bond orientational order (BOO) appears[1]. The tilt-bond coupling constrains the local tilt to point either along the local bond directions (SmI*) or between them (SmF*) and orients the molecular tilt parallel in the neighboring smectic layers[2].

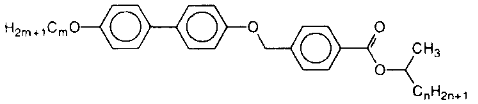
As the symmetry of both SmC* and tilted hexatic (SmI* or SmF*) phases is the same (C_2) the phase transition between them could be only of the first order with a discontinuous change of the BOO. A continuous evolution from one phase to the other cannot be also excluded[3,4].

We have worked out a phenomenological theory to describe both the static and dynamic dielectric behavior in the vicinity of the transition from the SmC* to the hexatic phase[5]. The theory that describes the phase sequence SmA-SmC*-SmI* (or SmF*) involves coupling of the tilt and bond orientation, (similarly as in Ref. 6), and besides, the coupling with the polarization is taken into account for description of dielectric properties.

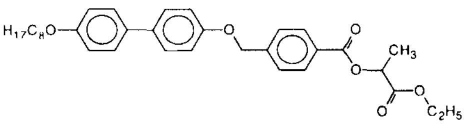
Here we report results of the experimental dielectric and electrooptic studies of three materials which exhibit SmC*-SmI* phase transition. The discussion of the results is based on the above mentioned theory[5].

EXPERIMENT

A general chemical formula of the studied compounds denoted as CmOCOOCn is



where m=13, n=6 for C13OCOOC6 and m=14, n=6 for C14OCOOC6. The third compound C8OdCOOC2 has the same mesogenic core but a different chiral group



Their synthesis has been described in Ref. 7. The phase sequences of the studied compounds[7] are shown in table 1. All compounds exhibit SmC*, SmI*, and a low temperature ordered smectic phase, which is not identified more in details. In compound C8OdCOOC2 the SmC* phase is preceded by the SmA phase.

TABLE I The phase transition temperatures detected from the DSC study. The phase SmX is a low temperature crystal smectic phase. • the phase exists, – the phase does not exist.

Comp.	SmX	°C	SmI*	°C	SmC*	°C	SmA	°C	Iso
C13OCOOC6	•	88.5	•	101.3	•		–	121.5	•
C14OCOOC6	•	86.6	•	99.2	•		–	120.0	•
C8OdCOOC2	•	103.8	•	116.5	•	141.4	•	144.6	•

Frequency dispersion of the complex permittivity $\varepsilon^*(f)=\varepsilon'-i\varepsilon''$ and of the complex electrooptic response has been measured in the range of 1 Hz÷10 MHz as a function of temperature on 25 μm thick samples in book-shelf geometry and on free suspended films. The spontaneous polarization has been determined by integrating the current during the sample switching. The spontaneous tilt angle has been determined from the rotation of the optical axis of sample under the switching electric field. A good sample alignment necessary for optical studies was obtained by applying a low frequency electric field of about 40 kV/cm for about 30 minutes in SmC* phase. In all measurements temperature stability was better than 0.1K.

RESULTS

In the studied frequency range both the dielectric and electrooptic response show a single relaxation process. The dielectric spectra were analyzed using the Cole-Cole formula for the complex permittivity, which yielded the relaxation frequency f_r and the dielectric strength $\Delta\varepsilon$ of that process. From the maximum of the imaginary part of the electrooptic response its relaxation frequency was determined.

Typical temperature dependences of f_r and $\Delta\varepsilon$ in the vicinity of the SmC*-SmI* phase transition T_l are shown in Figs. 1, and 2. All studied compounds exhibit a remarkable decrease of f_r and increase of $\Delta\varepsilon$ when approaching the phase transition from the SmC* to the SmI* phase. The steep decrease in f_r around T_l corresponds to a coexistence of phases, which occurs within 2 to 3 K for all studied compounds. In the SmI* phase f_r is one order lower than in the SmC* phase, and further slightly decreases on cooling. The behavior of $f_r(T)$ is qualitatively the same for all studied compounds and for both planar (book-shelf) geometry and free standing films. The dielectric and electrooptic responses give qualitatively the same results. As for $\Delta\varepsilon(T)$, it exhibits either a continuous increase on cooling (for C13OCOOC6 and C14OCOOC6) or a maximum (for C8OdCOOC2) in the SmI* phase.

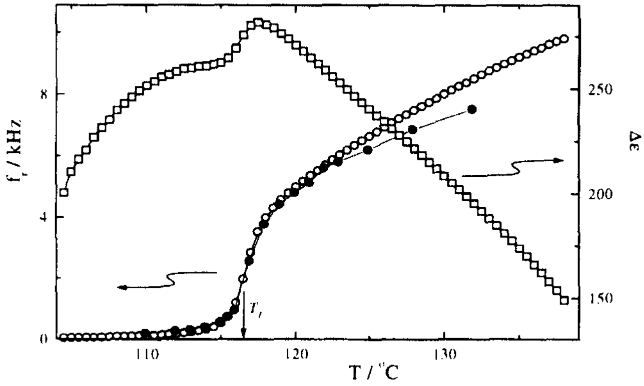


FIGURE 1 Temperature dependence of the dielectric strength (squares) and the relaxation frequency determined from dielectric (open circles) and electrooptic (full circles) response for C8OdCOOC2. T_l is the SmC* - SmI* phase transition.

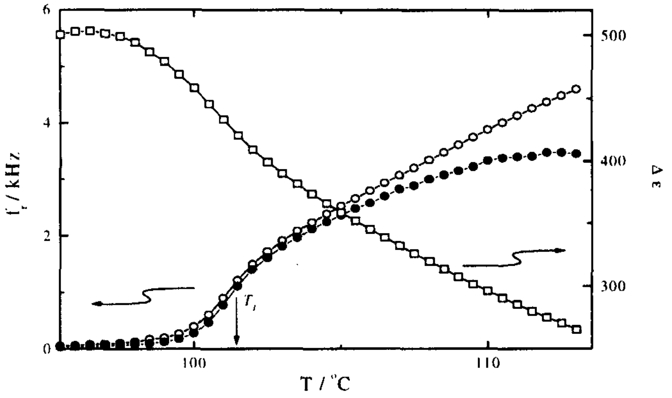


FIGURE 2 Temperature dependence of the dielectric strength and the relaxation frequency determined from dielectric response (open circles) for planar sample of C13OCOOC6. The full circles denote the relaxation frequency of free suspended film. T_t is the SmC* - SmI* phase transition temperature.

The spontaneous polarization, P_S, and spontaneous tilt angle, θ_S, are shown in Fig. 3 for C14OCOOC6. These quantities behave by the same way in all three compounds, namely P_S exhibits a steep increase in the phase transition region, while θ_S only slightly linearly increases on cooling. It is also worth mentioning that in all studied compounds the values of P_S are rather high.

DISCUSSION

According to the theory[5] two main modes are responsible for the low frequency response in the SmC* and SmI* phases, which are phason and amplitudon bond-like modes. These modes represent fluctuations of the phase and amplitude of the bond order, which are modified due to the tilt-BOO coupling. The temperature dependence of relaxation frequencies of these modes following from the theory are shown in Fig. 4. Above T_l the relaxation frequencies of phason and amplitudon are nearly equal and linearly decrease with temperature when approaching T_l. Below T_l the frequency of the amplitudon jumps up and strongly increases on cooling, but phason frequency jumps down and then only slightly decreases.

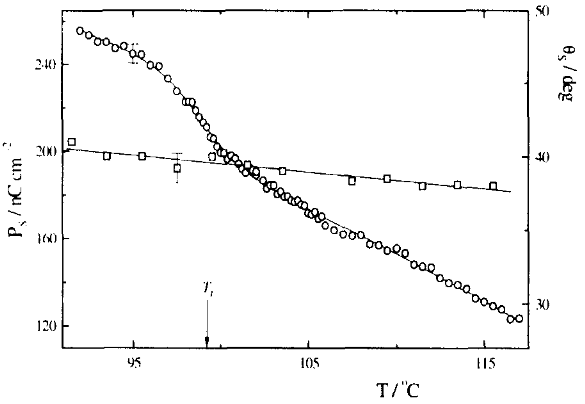


FIGURE 3 Temperature dependences of spontaneous tilt angle (squares) and spontaneous polarization (circles) for C14OCOOC6. T_l indicates the SmC* - SmI* phase transition.

The temperature dependence of f_r found in experiment is compatible with the behavior of the bond - like mode. Above T_l it exhibits a linear softening, below T_l only phason is observed, because amplitudon is shifted to high frequencies and becomes weak. A fitting of the experimental linear dependence to the theory yields a value of the bond mode susceptibility α_0 and of an extrapolated temperature $T_E<T_l$. From the drop of the relaxation frequency at T_l a ratio of the amplitudes of the bond order at T_l extrapolated

from both phases can be calculated[5]. This ratio characterizes a jump of the amplitude of the BOO at the SmC*-SmI* phase transition. The values calculated from the dielectric results on planar samples are summarized in Table 2 for the studied compounds.

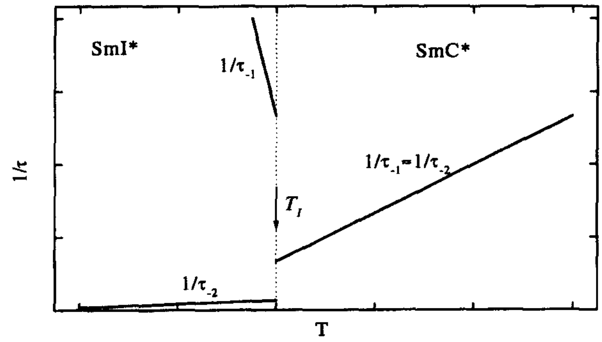


FIGURE 4 Theoretical temperature dependence[5] of the relaxation frequencies of amplitudon $1/\tau_{-1}$ and phason $1/\tau_{-2}$ near T_I.

Table 2 Values of the bond mode susceptibility α_0, extrapolated temperature $T_E < T_I$, and ratio of the amplitudes of the bond order at T_I.

Comp.	$\alpha_0/(\mathrm{Ks})^{-1}$	$T_E/^\circ\mathrm{C}$	$A_0(T_I^{-0})/A_0(T_I^{+0})$
C13OCOOC8	1671	95.3	8.0
C14OCOOC6	837	91.0	16.5
C8OdCOOC2	1754	99.7	20.6

It is worth noticing that values obtained from measurements in planar cells are influenced by boundary conditions. The relaxation frequencies measured in free suspended films are shifted to lower values and the slope of the linear temperature dependence in both SmC* and SmI* phases is also affected. This effect might influence thermodynamic parameters describing SmI* - SmC* phase transition.

The temperature dependence of the spontaneous polarization and tilt angle reflects the strength of their coupling to BOO (see Fig. 3). The sudden increase of *Ps* at the SmC*-SmI* phase transition is connected with the jump of the amplitude of BOO. Non-anomalous behavior of the tilt reflects its weak coupling to BOO.

Acknowledgments

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