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Ferroelectricity of Hexatic Phases

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Two fluorinated compounds: 3-(2-fluoroctyloxy)-6-(4octyl-phenyl) pyridine (FOOPP) and 3-(fluornonyl)-6-(4-heptyloxy-phenyl)pyridine (FNHPP), synthesized by E. Merck Company in earlier 1990s, which show a pronounced increase of spontaneous polarization at the SmC-hexatic SmI* transition have been reinvestigated. In this contribution we shall present calorimetric, dielectric and electrooptic behavior of two perfluorinated compounds which display enhanced high spontaneous polarization in enantiotropic hexatic phases. Phase transitions have been studied by DSC, polarizing microscopy, X-ray diffraction, and reversal current method, and molecular and collective dynamics – by dielectric spectroscopy. Spontaneous polarization measurements vs. temperature show that the SmI* phase of FOOPP exhibits almost 3 times larger spontaneous polarization than the high temperature ferroelectric SmC* phase.*

Keywords: de Vries phase; hexatic phase; hysteresis loop; spontaneous polarization; X-ray diffraction

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INTRODUCTION

Ferroelectric liquid crystals discovered in 1974 by Meyer *et al.* show rather small spontaneous polarization in comparison with classical ferroelectrics. Hexatic phases composed of chiral molecules show interesting ferroelectric and linear dielectric properties [1–3]. However, due to some disadvantages in their practical applications the number of papers devoted to this subject is rather small as yet. Recently a few papers devoted to ferroelectricity of hexatic phases have been published. Hexatic phases display one-dimensional positional order along the layer normal and bond-orientational order (BOO) within the layers. One of the disadvantages of hexatic phases consists in multi-defect alignment. However, in many cases hexatic phases show up on cooling only and their study is cumbersome. In our previous papers some enantiotropic and monotropic hexatic phases have been investigated [1]. It has been shown that some of them show enhanced spontaneous polarization in highly ordered hexatic phases. In this paper two compounds showing enantiotropic SmI* phase are discussed. Their molecular weight is the same but the structures of the side chains are different and that's why both materials exhibit much different ferroelectric properties of hexatic phases. As found before the soft mode observed in the paraelectric SmA* is much stronger than the Goldstone mode in the ferroelectric SmC* phase what is typical for the de Vries-type SmA*-SmC* transition. In addition X-ray diffraction studies substantiate this idea.

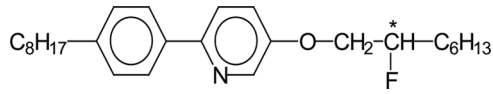
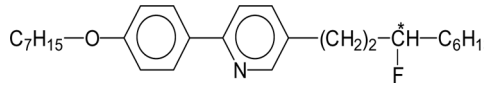
EXPERIMENTAL

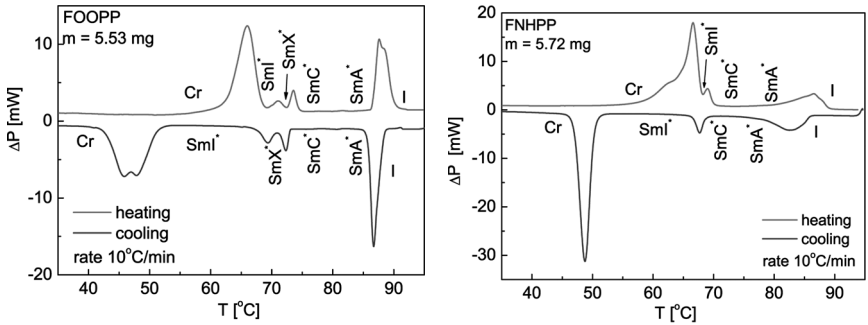
DSC calorimetry, dielectric spectroscopy and electro-optic methods have been applied to study phase transitions and ferroelectric properties of hexatic phases of two perfluorinated compounds. Two substances investigated are presented in Table 1.

Additionally, the dielectric and DSC data substantiate the existence of an intermediate sub-phase (SmX*) for FOOPP between the SmC* and SmI* phases (Figs. 1(a)). The SmX* phase exhibits a characteristic doublet in reversal current spectrum [2], which is typical for antiferroelectric phases.

Spontaneous polarization has been measured using different ITO cells (AWAT-trade mark of electro-optic cells made at AWAT Company, LINCAM, and EHC) and gold coated cells (5 μm-AWAT). Exemplary data obtained recently using ITO and the gold–coated cells are presented in Figure 2. It was found that the hexatic phases display much higher threshold voltages for switching (Fig. 3(a)).

TABLE 1 Substances Studied

No.	Full name and acronym	Chemical structure and phase sequence
1.	3-(2-fluoroctyloxy)-6-(4octyl-phenyl) pyridine **FOOPP**	 Heating: Cr. 64.3°C SmI* 69.3°C SmX* 73.3°C SmC* 80.8°C SmA* 87.2°C I Cooling: I 87.7°C SmA* 82.1°C SmC* 73.6°C SmX* 70.0°C SmI* 53.5°C Cr.
2.	3-(fluornonyl)-6-(4-heptyloxy-phenyl) pyridine **FNHPP**	 Heating: Cr. 64.4°C SmI* 67.7°C SmC* 80.2°C SmA* 83.1°C I Cooling: I 85.9°C SmA* 79.8°C SmC* 68.6°C SmI* 51.2°C Cr.



(a) (b)

FIGURE 1 DSC heating and cooling curves obtained for FOOPP (a) and FNHPP (b).

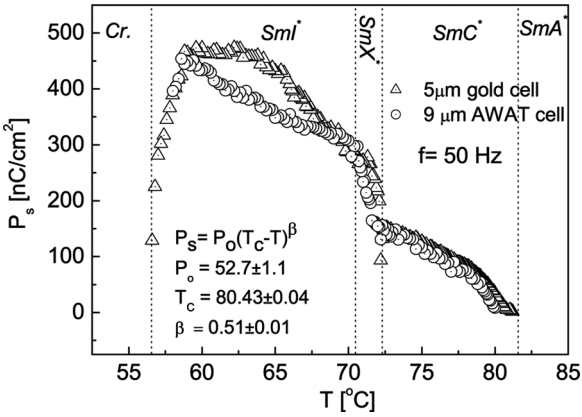


FIGURE 2 Spontaneous polarization of FOOPP vs. temperature acquired for two different cells.

RESULTS AND DISCUSSION

Ferroelectricity of hexatic phases composed of chiral molecules is not well understood as yet [3–5,7]. One of the reasons is that some of them are unstable monotropic phases lacking experimentally reproducible data. It has been shown that FOOPP and another similar compound studied by us exhibit enantiotropic ferroelectric hexatic phases. Their static and dynamic parameters are governed by the BOO fluctuations [4,5,7]. The results obtained for two fluorinated compounds will be compared with the literature data and confronted with the theory [4,5].

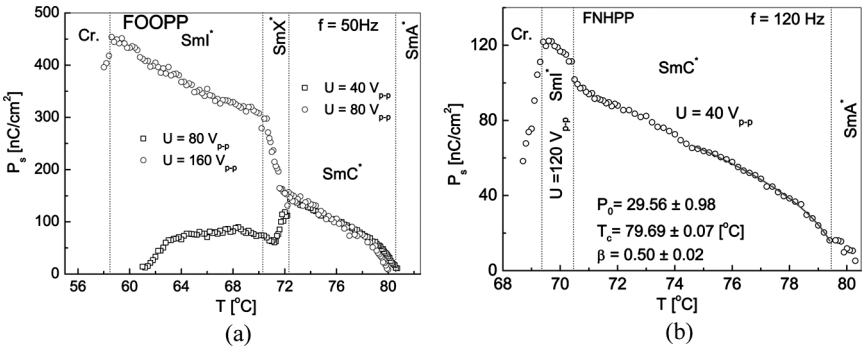


FIGURE 3 Spontaneous polarization vs. temperature for FOOPP obtained by using two driving voltages (a) and for FNHPP (9-μm ITO cell) (b).

Spontaneous Polarization Measurements

Spontaneous polarization measurements were done using reversal current as well as hysteresis loop methods. The measurements were done on planar aligned samples using AWAT with ITO or gold-coated electrodes.

For FOOPP one can observe a pronounced jump of the spontaneous polarization in the vicinity of the SmC*-SmX*-SmI* transition (Fig. 3). In the SmI* phase the value of spontaneous polarization is large (ca. 530 nC/cm^2). In the case of FNHPP the transition from the SmC* to SmI* phase is also discontinuous, however, the jump as well as the value of spontaneous polarization in SmI* (ca. 120 nC/cm2) is distinctly smaller than for FOOPP. It was found that the hexatic phases display much higher threshold voltages for switching [8]. To prove that ferroelectricity of the hexatic phase does not depend on surface treatment and the cell thickness different types of cells were used. In Figure 2 one can see the results obtained for gold-coated ITO AWAT cells.

Other examples of $P_s(T)$ measurements are presented in Figs. 3(a) and (b). As seen in Figure 3(a) a high voltage is needed to measure the value of spontaneous polarization in the heaxatic phase. Spontaneous polarization measurements have been done by hysteresis loop method (Figs. 4(a), (b) and (c)) to better understand ferroelectric properties of hexatic phases.

The Layer Spacing Studies of FOOPP

The question arises whether the SmA* phase is the so-called de Vries phase or not. As it was mentioned before, X-ray measurements were done by small angle X-ray scatering (SAXS) method to find the layer thickness versus temperature for smectic phases (Fig. 5). The SAXS measurements revealed the layer shrinkage of about 3% for FOOPP throughout the SmA* to the SmC* phase transition what suggests that SmA* phase for both substances may be the de Vries type.

Dielectric Studies

Dielectric measurements were done using the Agilent 4294A impedance analyzer in the frequency range from 40 Hz to 15 MHz. The sample was introduced into the gold-coated cell by means of capillary action. In our previous paper [6] the dielectric studies performed by using ITO cells were reported. There are some differences in the low frequency dielectric spectra. In ITO cells one observes a low frequency

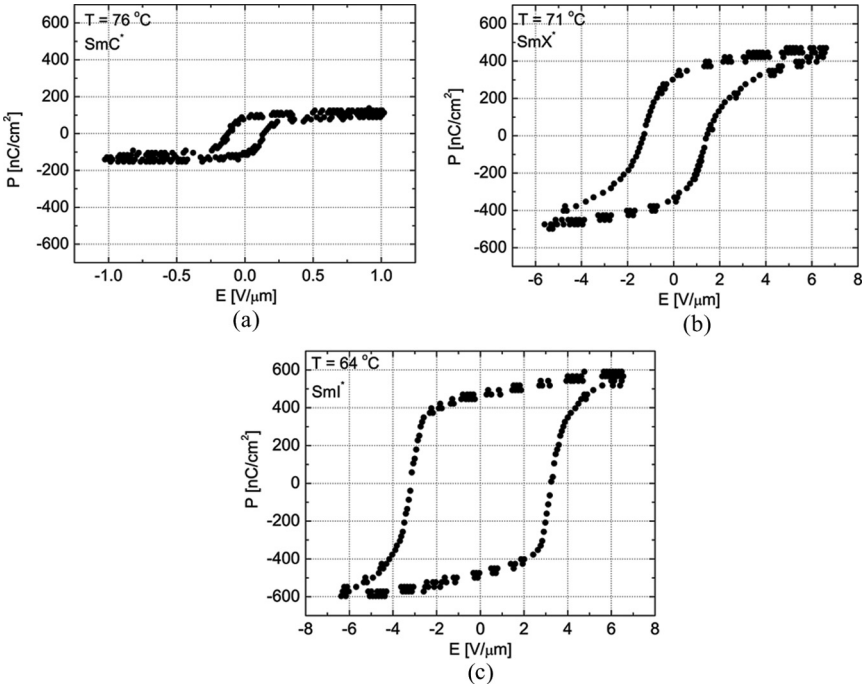


FIGURE 4 Hysteresis loops obtained for FOOPP in the SmC* (a), SmX* (b) and SmI* (c) phase.

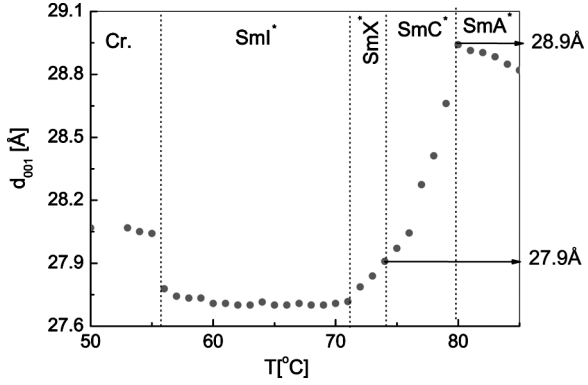


FIGURE 5 Temperature dependence of layer spacing for FOOPP.

relaxation process which may be due to surface interaction. As far as the bulk relaxation processes are concerned there is a good agreement between both experiments.

Figures 6(a) and (b) present, respectively, the dielectric dispersion and absorption vs. frequency and temperature. As one can see the soft mode overwhelms the dielectric spectrum even below the SmA*-SmC*

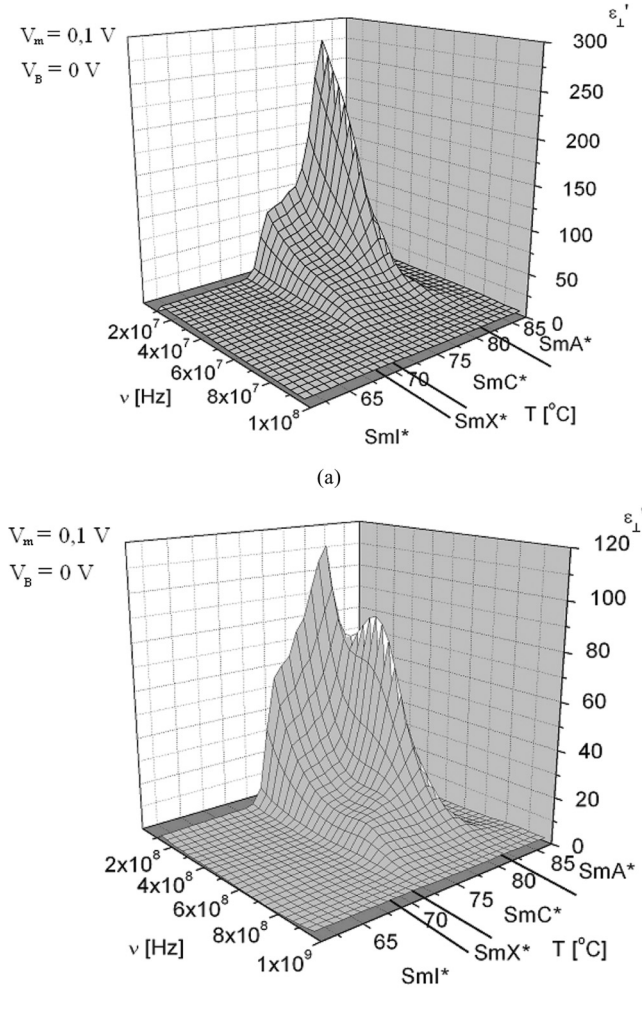


FIGURE 6 Dielectric dispersion (a) and absorption (b) spectra vs. frequency of FOOPP in the whole temperature range.

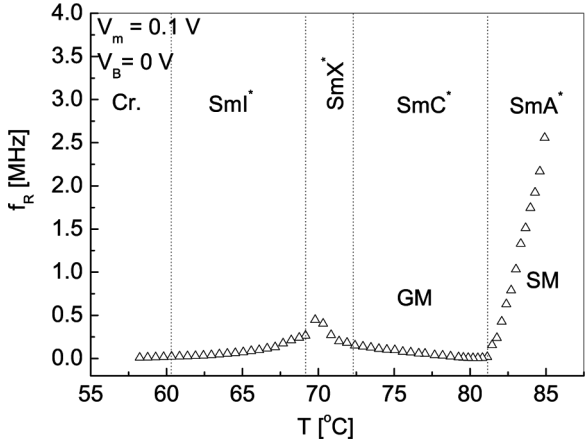


FIGURE 7 Relaxation frequencies versus temperature obtained for FOOPP.

transition. It means that the fluctuations of the tilt angle (amplitudon) are very strong in the pretransition region.

Figure 7 shows relaxation frequencies obtained without bias field. As one can see the characteristic soft mode (SM) is observed in the SmA* phase, Goldstone mode (GM) – in the SmC* phase. There is a slight step at the transition between the SmX* and SmI* phases. The dielectric spectra show that only one dielectric process is observed in the SmX* and in the hexatic phase. The process observed in the SmX* phase is hard to identify because of narrow temperature range of this phase. The dielectric process in the SmI* phase is probably connected with the fluctuations of the bond-orientational order (BOO).

CONCLUSIONS AND PERSPECTIVES

In scope of this work two substances (FOOPP and FNHPP) exhibiting hexatic phases have been studied. DSC results show that both substances studied display enantiotropic ferroelectric SmI* phase. There is a jump of the spontaneous polarization observed for FOOPP and FNHPP substances at the SmC*-SmX*-SmI* and the SmC*-SmI* phase transitions, respectively. Additionally, only for FOOPP very high value of P_s (ca. 530 nC/cm^2) is observed in the SmI* phase. Based on the results of SAXS measurements the SmA* phase was recognized as the de Vries-type for FOOPP compound.

Influence of molecular structure on ferroelectric properties of hexatic phases is demonstrated. A flexible spacer separating the molecular

body from the chiral centre diminishes the spontaneous polarization in the SmI* hexatic phase. It means that increase of intermolecular order is not sufficient for enhancing spontaneous polarization.

Dielectric studies revealed a step at the SmC*-SmX*-SmI* transition for FOOPP. One dielectric process shows up in the SmI* phase for FOOPP, which is probably related to bond-orienational order (BOO) fluctuations.

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