

THERMAL BEHAVIOR OF SELECTED FERROELECTRIC LIQUID CRYSTALS

Małgorzata Godlewska

Institute of Physics, Jagiellonian University, Cracow, Reymonta 4, Poland

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Abstract

Thermal properties of three ferroelectric liquid crystals, namely: 3-octyloxy-6-[2-fluor-4-(fluorocyloxy)phenyl]-pyridine (FFP), 3-(3-fluor-nonyl)-6[4-heptyloxyphenyl]-pyridine (FNHPh-P), 4-[(S,S)-2,3-epoxyhexyloxy]phenyl 4-(decyloxy)benzoate (EHPhDB) were studied using heat flux differential scanning calorimetry method. All the transitions expected in this compounds, except the $\text{SmC}^*-\text{SmA}^*$ and SmC^*-S_3 transitions, were detected in the DSC curves. The temperatures of the phase transitions and the enthalpy changes associated with them were determined. The transition from the liquid crystalline to the crystalline state showed significant hysteresis for all three compounds studied. The following transitions: SmA^*-Is , $\text{SmG}^*-\text{SmC}^*$ for FNHPh-P, N^*-Is for EHPhDB, N^*-Is and SmC^*-N^* for FFP also showed a small hysteresis basing on which first-order character of all the above transitions was implied. All three substances studied in this work are characterized by a complex polymorphism in the solid state.

Keywords: DSC method, ferroelectric liquid crystals, phase transitions

Introduction

Liquid crystals are built of strongly elongated molecules and display an exceptional variety of phase transitions [1]. They melt from the anisotropic solid state to an isotropic liquid in several steps. A variety of mesophases with decreasing order and properties intermediate phases between the crystal and the isotropic liquid can be present. The more common intermediate between those of a crystal and a liquid are the nematic, smectic A and smectic C phases. In the nematic phase the molecular axes are aligned along a unit vector called the director. The centers of mass of the molecules are randomly positioned. Nematics are positionally disordered, but orientationally ordered. At higher temperature they undergo a transition into an isotropic liquid phase. Smectic A phase has a layered structure with layer planes perpendicular to the director. Within the layers there is no long-range order in the position of the center of mass of the molecules. In the smectic C liquid crystal the molecules are also arranged in layers, with the long molecular axes parallel to one another but they are tilted at an angle θ from the layer normal. Both smectics A and C can be viewed as sets of two dimensional liquid layers stacked on each other with a well-defined spacing. Apart from these two types, there are many different types

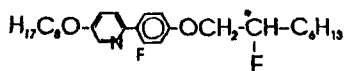
of smectics with varying amount of order and periodicity inside each layer. It has been predicted by symmetry considerations and experimentally verified that smectic C liquid crystals composed of chiral molecules (lacking mirror symmetry) must have a spontaneous polarization [2]. The investigation of these new materials exhibiting ferroelectric liquid crystalline phases has attracted increasing attention in recent years.

In the present paper the results of the investigation of thermal properties of three ferroelectric liquid crystals with potential applications in materials science are presented.

Experimental

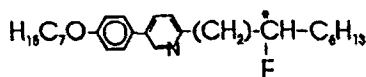
The following substances were studied:

- 1) 3-octyloxy-6-[2-fluor-4-(fluorooctyloxy)phenyl]-pyridine (later on referred to as FFP)



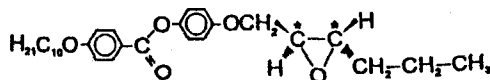
Cr (44.1°C) SmC* (47.6°C) N* (64.5°C) Is

- 2) 3-(3-fluor-nonyl)-6[4-heptyloxyphenyl]-pyridine (is short FNHPh-P)



Cr (67°C) SmG* (70°C) SmC* (80°C) SmA* (86°C) Is

- 3) 4-[(S,S)-2,3-epoxyhexyloxy]phenyl 4-(decyloxy)benzoate (EHPhDB)



Cr (75°C) SmC* (80°C) N* (97°C) Is

Two first samples (FFP and FNHPh-P) were obtained from E. Merck Company due to the courtesy of Prof. W. Haase from TH Darmstadt, Germany. The third sample (EHPhDB) was synthesized in Prof. Dabrowski group from the Military Technical Academy in Warsaw, Poland.

The thermal behaviour of these compounds was studied using the Heat Flux Differential Calorimeter DSC 404 produced by NETZSCH. The measurements were carried out in air atmosphere. Several experimental series were performed with various heating rates and various masses of the samples. The samples were placed in aluminum crucibles. Empty aluminum crucible was used as a reference. The sensitivity curve of the instrument was obtained using synthetic sapphire as a standard material. The peak temperatures of anomalies are given with the accuracy of 0.2 K and the enthalpy changes at the transitions with the accuracy of about 15%.

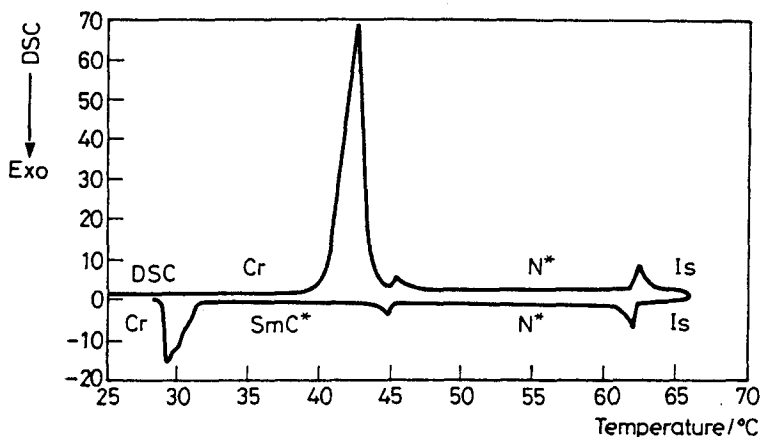


Fig. 1 DSC curves for FFP obtained on heating (upper curve) and cooling (lower curve) of the sample (mass of the sample was 2.15 mg, heating and cooling rates $2^{\circ}\text{C min}^{-1}$)

Results and discussion

Preliminary DSC measurements for the above substances were given in [3–5]. In this paper we present new results concerning more detailed study of their phase behavior. For all the compounds studied in this work the measurements were performed in the following way: fresh samples were heated above the clearing point temperatures (transition liquid crystalline – isotropic), next they were cooled down to room temperature and then the cycle was repeated two times. Figure 1 presents the results obtained for FFP on heating and cooling of the fresh sample. In Fig. 2 a DSC curve registered during second heating of the same sample is shown. As it is seen from Fig. 1 three anomalies are observed on the heating curve. Their temperatures and enthalpy changes at the transitions are given in Table I. It is also seen that the smectic SmC^* phase can be supercooled and that the transition into the crystal phase takes place only at about 30°C . However, the peak area for the recrystallization transition is significantly lower than that for the melting process. Second heating of the sample revealed that the melting from solid into SmC^* phase took place in two steps (Fig. 2). Peak areas in subsequent heating cycles were not reproducible. Such behavior is probably connected with the existence of various metastable modifications of the solid state.

Figures 3 and 4 present the results obtained for the second compound studied i.e. for FNHPH-P. Heating and cooling curves of the fresh sample are presented in Fig. 3 and the second heating is shown in Fig. 4. Next heating gave the result identical with that shown in Fig. 4. For fresh sample instead of the phase sequence: $\text{Cr-SmG}^*-\text{SmC}^*-\text{SmA}^*$ one unresolved anomaly centered around 68°C is observed. On cooling, due to the supercooling of the SmG^* phase the transition $\text{SmC}^*-\text{SmG}^*$ becomes well separated. The $\text{SmC}^*-\text{SmA}^*$ transition is not visible which is not surprising in view of the fact that this transition exhibits extremely

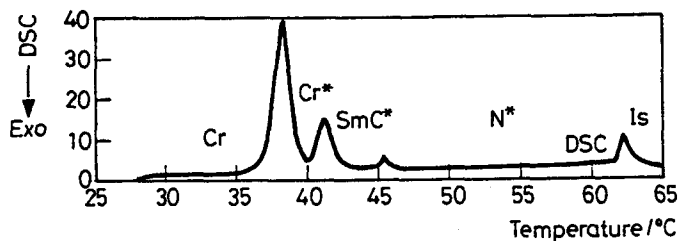


Fig. 2 DSC curve obtained during second heating of the FFP sample (heating rate $2^{\circ}\text{C min}^{-1}$)

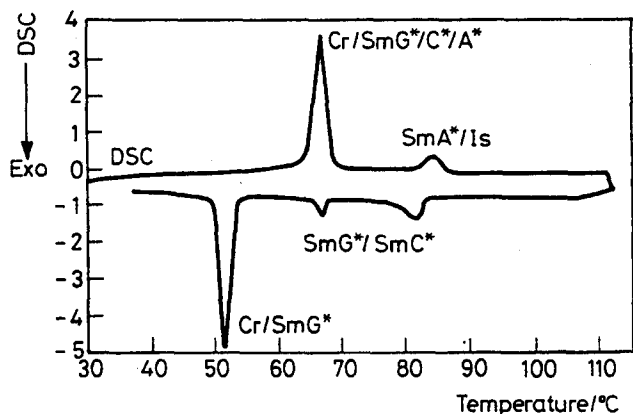


Fig. 3 DSC curves obtained on heating (upper curve) and cooling (lower curve) of FNHPh-P (mass of the sample was 4.22 mg, heating and cooling rates were equal to $2^{\circ}\text{C min}^{-1}$)

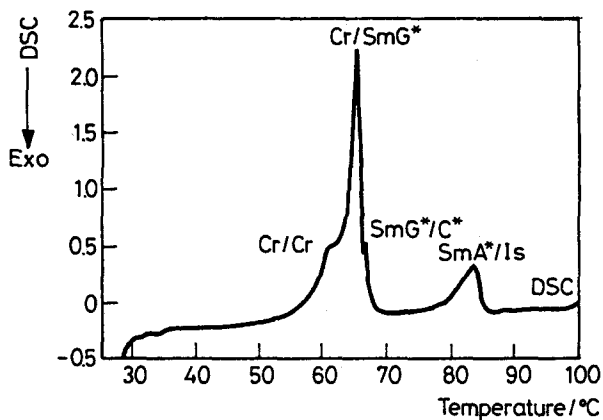


Fig. 4 DSC curve detected during second heating of the FNHPh-P sample (heating rate was equal to $2^{\circ}\text{C min}^{-1}$)

Table 1 Temperatures and enthalpy changes for the transitions detected for FFP, FNHPh-P and EHPPhDB

Substance	Transition	Temperature/ $^{\circ}\text{C}$	Enthalpy/ kJ mol^{-1}
FFP	Cr-SmC*	42.4	40.7
	SmC*-N	45.3	0.6
	N*-Is	62.4	1.9
FNHPh-P	Cr-SmA*	68.4	25.8
	SmA*-Is	86.4	6.5
EHPPhDB	Cr-N*	75.8	38.0
	N*-Is	95.6	2.5

small or even vanishing values of the transition enthalpy [6]. On the second heating curve a more complex structure is visible. Melting into the SmG* phase (at 67.8°C) and the transition SmG*-SmC* (at 69.6°C) can be distinguished. A shoulder at 64°C is probably connected with a solid-solid transition. Unlike in the case of FFP, the total heat of transition is the same in the first and next heating cycles. It means that in the case of FNHPh-P the recrystallization process leads always into a stable crystal. As the transitions Cr-SmG* and SmG*-SmC* are lying very close together it is not possible to obtain separate transition enthalpies and in Table 1 only the total enthalpy change at the Cr-SmA* transition is given.

Figure 5 shows the heating and cooling curves for a fresh sample of EHPPhDB. For that substance subsequent heating and cooling cycles yielded always identical results. As it is seen in Fig. 5 melting anomaly is broad and overlaps the SmC*-N* transition. The latter is only visible in the cooling curve as a weak anomaly at about 77°C . In order to separate it in the heating curve, in one experimental run a sample was cooled down only to about 65°C and next it was heated. The result is shown in Fig. 6. At 78.7°C a weak anomaly corresponding to the SmC*-N* transition is clearly visible. However, it is too small to determine its enthalpy with a reasonable accuracy. In all runs EHPPhDB recrystallized into a stable crystal through two transitions: liquid crystalline-metastable crystal phase at about 56°C and metastable-stable crystal at a lower temperature. The temperature of the latter transition varied in different runs by several degrees. It is interesting to mention here that the dielectric measurements for this compound indicate that between about 61 and 57°C there exists a phase which is both ferroelectric and metastable (S_3 phase). The dielectric response of the sample in that temperature range changed with time. A detailed study of this phenomenon by dielectric and DSC methods will be published soon [7]. The SmC*- S_3 transition is not detected in the present measurements. The temperatures of the transitions and the enthalpy changes which could be determined for EHPPhDB are given in Table 1. From Table 1 it is seen that, as one could expect, the melting enthalpies for all the compounds are significantly higher than those of the other phase transitions. Also, the SmA*-Is transitions shows higher enthalpy change than the N*-Is transition. This can be explained by smaller structural changes between

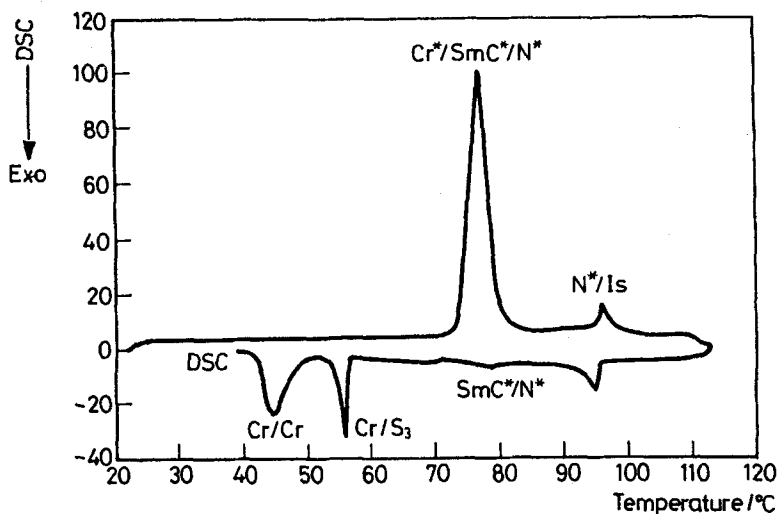


Fig. 5 DSC curves obtained for EHPHDB on heating (upper curve) and cooling (lower curve) of the sample (mass of the sample was 3.17 mg, heating and cooling rates were $5^{\circ}\text{C min}^{-1}$)

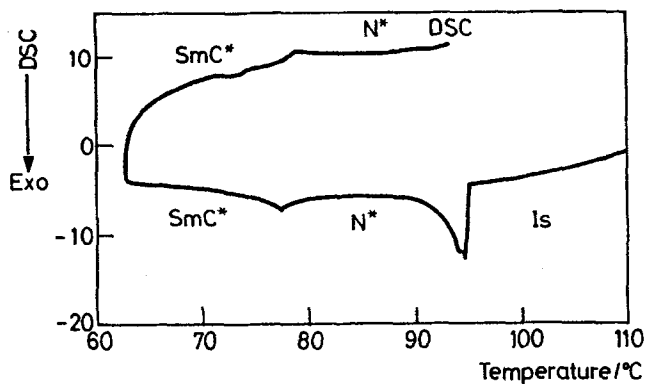


Fig. 6 Lower curve: DSC curve obtained on cooling of the EHPHDB sample (cooling rate $5^{\circ}\text{C min}^{-1}$) down to 65°C . Upper curve: DSC curve recorded on heating of the sample (heating rate $5^{\circ}\text{C min}^{-1}$)

the phases in the latter case. The transition enthalpies are directly connected with the structural changes at the phase transitions. With respect to the large variety of phase transitions seen in liquid crystals the matter of determining their nature (i.e. first or second order) arises. It can be a difficult problem because transition effects are often very small [6]. In addition, for DSC experiments it is not possible to distinguish in the total heat of transition the latent heat alone (if present) from pretransitional effects [8]. However, in the present measurements distinct hysteresis was detected on cooling for several transitions. For all three compounds studied the

transition from the liquid crystalline to the crystalline state shows significant hysteresis (up to about 20 K). Also, the following transitions show marked hysteresis (about 1 to 3 K): SmA^*-Is , $\text{SmG}^*-\text{SmC}^*$ in FNHPh-P and $\text{Is}-\text{N}$ in EHPHDB. One can imply first-order character of these transitions. It seems also that $\text{Is}-\text{N}^*$ and N^*-SmC^* transitions in FFP are first-order. In this case the hysteresis is very small (0.6 K) but always appears in all the experimental runs.

Conclusions

Thermal behavior was studied for three ferroelectric liquid crystals: FFP, FNHPh-P and EHPHDB exhibiting rich polymorphism. All the transitions expected in these compounds, except the $\text{SmC}^*-\text{SmA}^*$ and SmC^*-S_3 transitions, could be detected in the DSC curves. The transition from the liquid crystalline to the crystalline state showed significant hysteresis for all three compounds studied. The following transitions: SmA^*-Is , $\text{SmG}^*-\text{SmC}^*$ for FNHPh-P, N^*-Is for EHPHDB, N^*-Is and SmC^*-N^* for FFP also showed a small hysteresis. One can conclude first-order character of these transitions. All three substances are characterized by complex polymorphism in the crystalline state.

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