

# Studies of Phase Diagram and Glass Transitions of a Liquid Crystal with Ferro- and Antiferroelectric Phases

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Based on the results of the differential scanning calorimetry, of transmitted light intensity measurements and of texture observations the phase diagram of 4-(6-heptafluorobutanoiloxyhexyloxy)biphenyl-4'-carboxylate(S)-4-(methyloheptyloxy-1-carbonyl)-phenyl (4H6) was obtained. The following phases were identified on cooling: isotropic, smectic A, smectic C\*, smectic C<sub>A</sub>\* phases and a highly ordered phase called SmX and its glass. During heating transformation from glass of SmX to SmX phase and then transition to a metastable Cr2 phase, evolving to the more stable Cr1 phase, were observed. On further heating SmC<sub>A</sub>\*, SmC\* and Sm phases were identified. When Cr2 was cooled, a glass transition was also observed.

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## 1. Introduction

Liquid crystals are substances built of anisotropic, mostly rod-shape molecules. For liquid-crystalline phases of some dipolar molecules tilted in smectic layers, the phenomenon of ferroelectricity was predicted in 1974 by Mayer et al. [1], basing on symmetry reasoning, and shortly after that observed. At 1989, features of the anti-ferroelectricity of MHPOBC compound were reported by Chandani et al. [2]. The properties of ferro- and antiferroelectricity of new synthesized chiral smectics as well as of the ferrielectricity in subphases occurring between them, are extensively explored to get better understanding of these phenomena. It is interesting from the fundamental point of view and important due to their potential applicability, especially in construction of ultrafast tri-stable liquid crystal displays of new generation [3–6].

The aim of this paper is to study thermal properties of 4-(6-heptafluorobutanoiloxyhexyloxy)biphenyl-4'-carboxylate(S)-4-(methyloheptyloxy-1-carbonyl)-phenyl, abbreviated as 4H6 and to establish details of the phase diagram. The chiral carbon atom in molecular chain and non-zero electric moment perpendicular to the long axis of the molecule are the factors necessary for ferroelectric ordering.

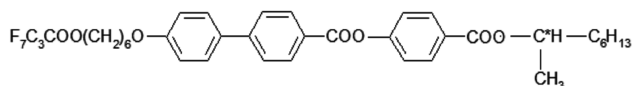


Fig. 1. Molecular structure of 4H6.

Figure 1 shows the molecular structure of the compound. We have chosen for our studies a substance where seven fluorine atoms are substituted for hydrogen atoms in one of the terminal chain. Studies of phase polymorphism were carried out using three complementary

experimental methods: differential scanning calorimetry (DSC), texture observations using the polarizing microscope (POM) and the transmitted light intensity (TLI) measurements. Our goal was to check if the highly ordered liquid crystalline phases of 4H6 reveal a glass transition recently observed in SmI<sub>A</sub>\* of 1F7 with the same chiral terminal group in the molecule [7].

## 2. Experimental

All measurements of 4H6 were performed with a substance synthesized at the laboratory of Prof. R. Dąbrowski group, Department of Chemistry, Military University of Technology, Warsaw. Calorimetric experiments (DSC) were carried out using a Mettler Toledo 822e differential scanning calorimeter. The heat flow signal ( $dQ/dt$ ), proportional to the difference between the power input to the sample and that of the reference, is registered as a function of time and of the sample temperature. The sample was closed in the aluminum vessel of 40  $\mu$ l capacity. The mass of the sample in DSC measurements was 17.35 mg. Molar mass of 4H6 is 742 g/mol.

Texture observations (POM) were performed using Biolar PI polarized microscope (PZO Warsaw) equipped with Linkam heating stage and the temperature controller and the Nikon objective. The sample put between the cover glasses was placed directly on a silver block heating stage in order to eliminate temperature gradients. The observed area was about  $0.5 \times 0.4$  mm<sup>2</sup>. The polarizing microscope was equipped also with camera connected with computer.

Complementary TLI method is a modification of the POM method, where the observer eye is replaced by the photodetector of very high sensitivity and of low “dark current”, allowing to convert the light intensity into the current signal which can be precisely measured and collected in function of temperature. The magnitude of the

recorded signal depends on the wavelength, which allows for detecting the subtle changes of a texture color [8, 9].

All the measurements were performed during both heating and cooling of the samples. The temperature values are given in degrees of Celsius for the convenience. Temperature range and the rate of temperature change were the following:

- (i) from  $-140^{\circ}\text{C}$  to  $150^{\circ}\text{C}$  and  $2^{\circ}\text{C}/\text{min}$ ,  $5^{\circ}\text{C}/\text{min}$ ,  $10^{\circ}\text{C}/\text{min}$ ,  $20^{\circ}\text{C}/\text{min}$  in DSC measurements,
- (ii) from  $-25^{\circ}\text{C}$  to  $150^{\circ}\text{C}$  and  $1^{\circ}\text{C}/\text{min}$ ,  $2^{\circ}\text{C}/\text{min}$ ,  $5^{\circ}\text{C}/\text{min}$  in TLI measurements,
- (iii) from  $-170^{\circ}\text{C}$  to  $150^{\circ}\text{C}$  and  $0.5^{\circ}\text{C}/\text{min}$ ,  $1^{\circ}\text{C}/\text{min}$ ,  $2^{\circ}\text{C}/\text{min}$ ,  $5^{\circ}\text{C}/\text{min}$ ,  $10^{\circ}\text{C}/\text{min}$ ,  $20^{\circ}\text{C}/\text{min}$ ,  $50^{\circ}\text{C}/\text{min}$ ,  $100^{\circ}\text{C}/\text{min}$  in POM measurements (in the vicinity of phase transitions smaller rates of  $0.1^{\circ}\text{C}/\text{min}$  and  $0.2^{\circ}\text{C}/\text{min}$  were applied).

### 3. Results and discussion

In Fig. 2 the textures of eight phases observed by polarizing microscope during cooling and subsequent heating of 4H6 are shown. The sample was first heated to the isotropic phase and then cooled with a rate of  $2^{\circ}\text{C}/\text{min}$ . On cooling the isotropic phase transforms at  $129^{\circ}\text{C}$  to paraelectric Sm phase. Then, the ferroelectric  $\text{SmC}^*$  and the antiferroelectric  $\text{SmC}_A^*$  liquid crystalline phases were identified. During further cooling at  $10^{\circ}\text{C}$  small change in texture of the sample allowed us to discover a new phase, which we called SmX. On further cooling at about  $-115^{\circ}\text{C}$  cracks appeared in the image of the SmX phase texture. During heating cracks were gradually disappearing. At  $T_g$  the substance returns to the SmX phase with no cracks [10]. Then the substance proceeds to the metastable Cr2 phase and next to the more stable Cr1 phase. Further heating leads to the smectic phases;  $\text{SmC}_A^*$ ,  $\text{SmC}^*$ , and Sm, respectively, and finally to the isotropic phase. When the Cr2 phase was cooled, intensive cracking process appeared in the image of its texture (and then on heating, decrease of number of cracks was detected) meaning that also the Cr2 phase was vitrified, presumably being a conformationally disordered crystal (CONDIS). No crystallization was detected on cooling a 4H6 compound.

DSC thermogram of 4H6 substance measured in the whole temperature range is presented in Fig. 3. The measurements were performed on cooling the substance from isotropic phase and then on heating. The monotropic system of thermodynamic phases observed using polarizing microscopy was confirmed. The exothermic process at about  $10^{\circ}\text{C}$  is a non-equilibrium phase transition as one can see from the parameters collected in Table. It can be interpreted as spontaneous ordering of the metastable Cr2 phase to a more stable Cr1 phase as was evidenced by change between two microscopic textures (compare Fig. 2c and g — between Cr2 and Cr1 no extra texture was observed). A similar process was observed by Kolek

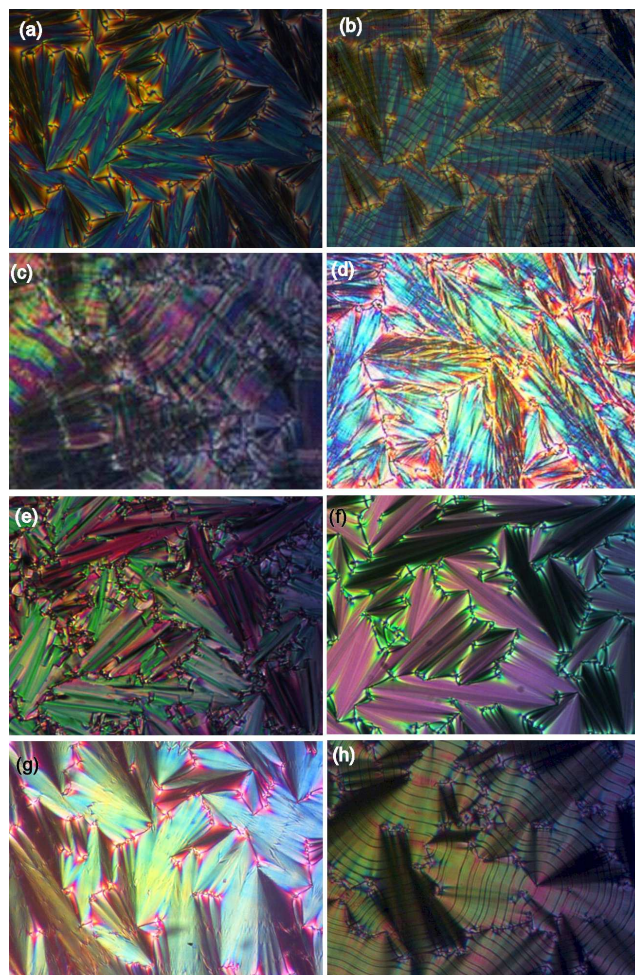
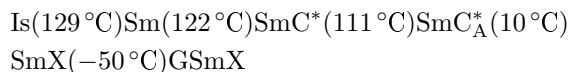


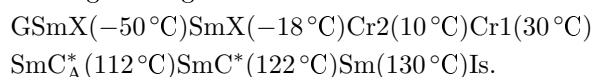
Fig. 2. Textures observed in the eyepiece of the polarizing microscope on cooling and heating the 4H6 sample with the rate of  $2^{\circ}\text{C}/\text{min}$  for: (a) SmX, (b) glass of SmX, (c) Cr1, (d)  $\text{SmC}_A^*$ , (e)  $\text{SmC}^*$ , (f) Sm, (g) Cr2 and (h) glass of Cr2.

et al. for a substance 1F7 with similar chiral molecular chain [7].

Based on the above thermogram (and more detailed checking in the vicinity of phase transitions) the following phase diagram was established during cooling



and during heating



The estimated values of the enthalpy and entropy changes at the phase transitions are collected in Table. The largest thermal effect during cooling was identified at the Is–Sm transition and is associated with appearance of a layered structure of molecules having tendency to be parallel. On heating the largest thermal effect was identified at the Cr1– $\text{SmC}_A^*$  transition, i.e., at the transfor-

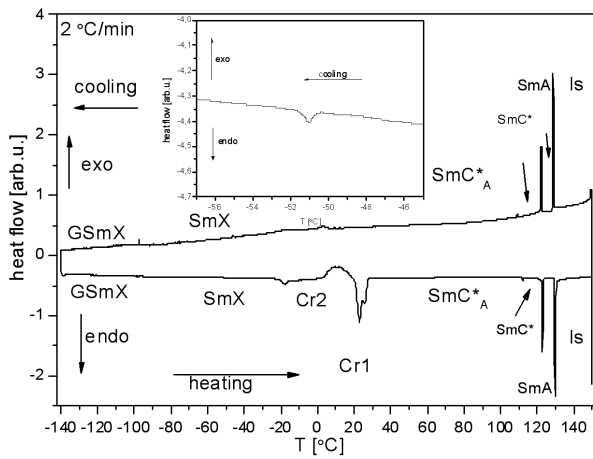


Fig. 3. DSC thermogram of 4H6 in the temperature range from  $-140^{\circ}\text{C}$  to  $150^{\circ}\text{C}$  for heating and cooling with a rate of  $2^{\circ}\text{C}/\text{min}$ . Inset graph shows anomaly near at  $T_g$  observed with a rate of  $5^{\circ}\text{C}/\text{min}$ .

mation between crystalline phase and a liquid-like phase with spiral antiferroelectric ordering. It is accompanied by activation of molecular and collective dynamics evidenced by dielectric spectroscopy [11].

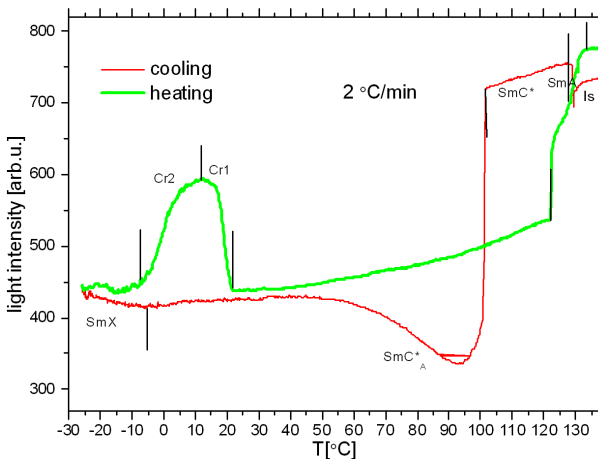


Fig. 4. Transmitted light intensity of 4H6 as a function of temperature in the range from  $-25^{\circ}\text{C}$  to  $135^{\circ}\text{C}$  for cooling and heating with the  $2^{\circ}\text{C}/\text{min}$  rate.

The results obtained for 4H6 in TLI measurements, performed in the temperature range from  $-25^{\circ}\text{C}$  to  $135^{\circ}\text{C}$ , are presented in Fig. 4. Phase transition temperatures obtained from DSC thermogram are confirmed by TLI measurements.

Observations of textures under the polarizing microscope revealed a rich and complex phase polymorphism of the tested substance. It concerns especially a solid state, where two glassy phases (glass of SmX and glass of Cr2) were identified. On cooling of SmX, appearance of cracks at about  $-115^{\circ}\text{C}$  followed each cooling run with rates applied from  $1^{\circ}\text{C}/\text{min}$  up to  $50^{\circ}\text{C}/\text{min}$ . Tempera-

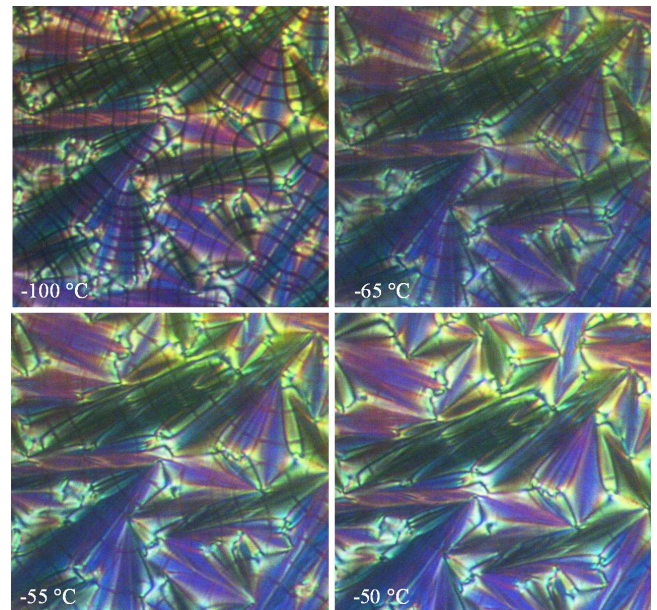


Fig. 5. Textures of glass of SmX phase observed in the eyepiece of the polarizing microscope on heating of 4H6 with the rate of  $2^{\circ}\text{C}/\text{min}$  at four temperatures.

ture of appearance of cracks was practically independent of the rate of cooling.

In Fig. 5 the sequence of textures of glass of SmX phase, showing diminishing of the cracks during heating of the sample with the pace of  $2^{\circ}\text{C}/\text{min}$ , is presented. The last crack disappears at about  $-50^{\circ}\text{C}$ , which we proposed in [10] as signature of glass transition on heating. In case of cooling the Cr2 cracks were observed at about  $-112^{\circ}\text{C}$ . During heating cracks gradually disappear until a temperature of about  $-55^{\circ}\text{C}$ , regarded as the temperature of transformation of glass of Cr2 phase (texture presented in Fig. 2h) to a metastable Cr2 crystal.

#### 4. Conclusions

For 4H6 monotropic system of phases was found. Four enantiotropic liquid crystalline phases, i.e., the Sm, the ferroelectric SmC\*, the antiferroelectric SmC\*\_A, and the SmX phases have been observed. On heating SmX phase crystallizes to metastable crystal Cr2 which evolves slowly to stable crystal Cr1 melting to SmC\*\_A. The sequence of phases was established using three methods, i.e., light transmission intensity measurements, differential scanning calorimetry and polarizing microscope observations. Basing on the temperature of disappearance of cracks in textures observed on heating the heating the vitrified SmX and the vitrified Cr2 phases,  $T_g = -50^{\circ}\text{C}$  and  $T_{g1} = -55^{\circ}\text{C}$ , respectively, were found.

TABLE

Values of the enthalpy and entropy changes at phase transitions observed during heating and cooling.

Process	Phase transition	$T$ [°C]	$\Delta H$ [J/g]	$\Delta H$ [kJ/mol]	$\Delta S$ [mJ/(K g)]	$\Delta S$ [J/(K mol)]
heating	SmX–Cr2	–18	–0.79	0.58	–3.09	–2.29
	Cr2–Cr1	10	7.57	5.62	26.74	19.84
	Cr1–SmC <sub>A</sub> *	30	–13.18	–9.78	–43.50	–32.27
	SmC <sub>A</sub> *–SmC*	112	–0.07	–0.05	–0.18	–0.13
	SmC*–Sm	122	–1.97	–1.46	–4.99	–3.70
	Sm–Is	130	–4.48	–3.32	–11.12	–8.25
cooling	Is–Sm	129	6.02	4.47	14.97	11.10
	Sm–SmC*	122	2.13	1.58	5.39	4.00
	SmC*–SmC <sub>A</sub> *	111	0.08	0.06	0.21	0.15
	SmC <sub>A</sub> *–SmX	10	0.59	0.44	2.08	1.55

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