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Calorimetric and microscopic investigations of selected members from the thioester homologous series☆

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Abstract

DSC measurements and microscopic observations of three compounds from the thioester series (4-*n*-pentylphenyl-4′-*n*-alkoxythiobenzoates, abbreviated to $\bar{n}$S5) have been performed.

In addition to the nematic and smectic phases known previously from the literature, a new monotropic low-temperature phase has been detected by both methods for $\bar{9}$S5 and $\bar{10}$S5. This new phase exists below a highly ordered smectic J phase and a crystal phase. The nature of this new phase is discussed.

Keywords: DSC; Polymorphism; Textures; Thioester homologous series

1. Introduction

Liquid crystal phases occur between real solids and real liquids. Studies of the properties of liquid crystals are of great interest as they are often regarded as a new state of matter incorporating properties of solids (structure and anisotropy) and liquids (flow, dynamics of molecules). It has been shown that there is a relationship between the mesomorphic properties and molecular structure [1]. For thiol esters, an interesting and complex sequence of mesomorphic phases has been reported [2, 3]. Thiol esters belong to the homologous series of 4-*n*-pentylphenyl-4′-*n*-alkoxythiobenzoate ($\bar{n}$S5). It

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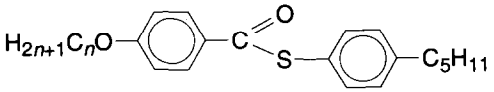
seemed interesting to study the polymorphism of thiol esters in more detail using the complementary methods of DSC and texture observations.

2. Experimental

The substances studied ($\bar{n}$S5, $n = 8, 9, 10$) have the following molecular structure



They were synthetised in the Institute of Chemistry of the Agricultural and Pedagogical University in Siedlce by the method described in Ref. [4].

Textures for the various phases were observed using a Jenapol polarizing microscope equipped with a calibrated heating state. Photographs were taken using a Praktica PLC 3 camera. The same area was maintained within each sequence of photographs. The magnification of the microscope was 50.

DSC measurements were made using a high-temperature differential scanning heat-flux calorimeter (Netzsch 404). Several experimental series were carried out for various masses of samples placed in aluminium crucibles. An empty aluminium crucible was used as a reference. The sensitivity curve of the instrument was obtained using synthetic sapphire as a standard material. The temperatures of the anomalies were obtained with an accuracy of 0.5 K and the enthalpy changes at the transitions

Table 1
Transition temperatures (°C) for three members of the $\bar{n}$S5 series [2]

	Cr	S_Y	S_C	S_A	N	Is
$\bar{8}$S5	19.4	(31.1–31.3)	(56.0–56.3)	58.0–58.6	62.7–63.5	86.5
$\bar{9}$S5	37.4	(39.0–39.2)	61.5–62.5	62.2–62.4	72.6	84.4–84.6
$\overline{10}$S5	39.3	(47.4–47.9)	59.7–62.3	62.5–62.7	79.5–79.6	85.4–85.6

Table 2
Transition temperatures (°C) observed in the present work for $\bar{8}$, $\bar{9}$ and $\overline{10}$S5

		Cr	C_X	SmJ	SmC	SmA	N	Is
$\bar{8}$S5	Heating	–	–	–	–	58.3	62.2	85.4
	Cooling	23.3	–	29.7	51[a]	61[a]	84.5	
$\bar{9}$S5	Heating	–	–	–	63.6	68[a]	72.0	83.5
	Cooling	29.7	35.3	37.1	57[a]	71.8	82.7	
$\overline{10}$S5	Heating	–	–	–	65.2	69[a]	80.1	85.4
	Cooling	30.2	39.4	46.9	58[a]	79.3	84.9	

[a] From texture observations.

with an accuracy of about 15%. The heating rate was 5 K min^{-1}, the cooling rate was 2 K min^{-1}.

3. Results and discussion

Thiol esters have been the subject of studies by several methods. The properties of a number of thiol esters have been reported in Ref. [2]. Table 1 presents the transition temperatures for $\overline{8}$, $\overline{9}$ and $\overline{10}$S5 obtained in Ref. [2] using a microscopic method. A new S_y phase was later identified in Ref. [5] as a smectic J phase.

Table 3
Thermodynamical parameters for $\overline{10}$S5

	Is/N	N/SmA	SmA/SmC	SmC/SmJ	SmJ/C_X	C_X/Cr
T/°C	85.4	79.3	58	46.9	39.4	30.2
ΔH/kJ mol^{-1}	1.5	1.0	–	3.3	6.1	3.2
ΔS/J K^{-1} mol^{-1} [a]	4.2	2.8	–	10.3	19.5	10.5

[a] Entropy values were calculated using the equation $\Delta S = \Delta H/T$.

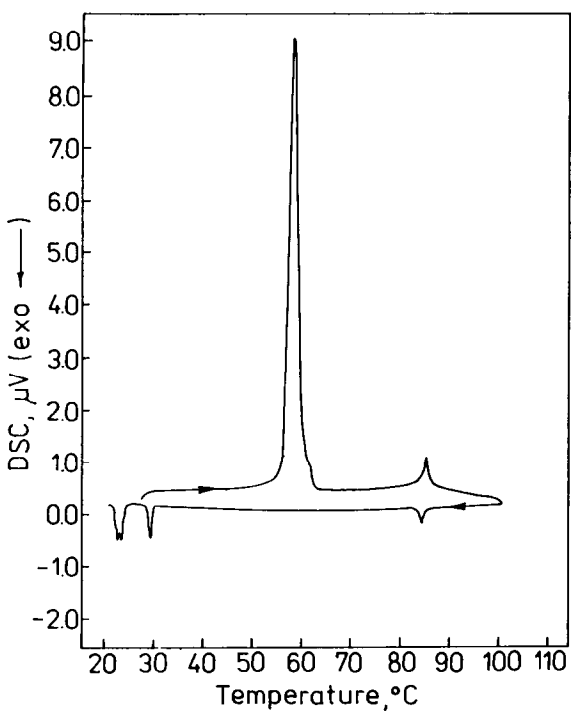


Fig. 1. DSC curve for $\overline{8}$S5 for heating (upper curve) and cooling (lower curve) of the sample.

Figs. 10–3 present the DSC curves obtained in the present work for $\overline{8}$, $\overline{9}$ and $\overline{10}$S5 respectively on heating and cooling of the samples. The photographs of the textures at various temperatures for $\overline{10}$S5 are shown in Figs. 4 and 5. The thermal parameters of the transitions detected are in good agreement with the literature data. As expected [1,2], in most DSC curves SmC–SmA transitions did not show strong enough anomalies to be detectable. Of special interest is the DSC curve obtained on cooling the samples. For $\overline{10}$S5 at 30°C, a distinct anomaly is observed (see Fig. 3), which has not been reported previously. Also, in our microscopic measurements there is a change in texture at that temperature (see Fig. 5(b) and (c)). So between 39 and 30°C, a new low-temperature monotropic phase is observed for this compound. The same situation takes place for $\overline{9}$S5 (Fig. 2). Apart from the phases known earlier, i.e. SmA, SmC and SmJ, there is a new phase on cooling of the sample between 35 and 30°C. It is interesting to note that for $\overline{8}$S5, the lowest temperature anomaly is split (see Fig. 1). This might suggest that the new phase is a highly ordered smectic phase which becomes wider for higher homologues, as it is known that longer chains favour the formation of smectic phases

However, on the basis of the present measurements alone, it is not possible to decide whether the new phase belongs to the class of crystal smectics or if it is a solid crystalline

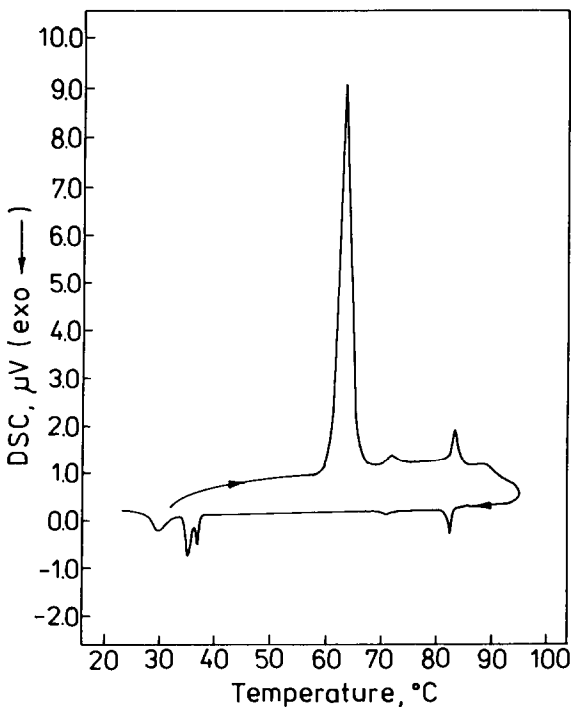


Fig. 2. DSC curve for $\overline{9}$S5 for heating (upper curve) and cooling (lower curve) of the sample.

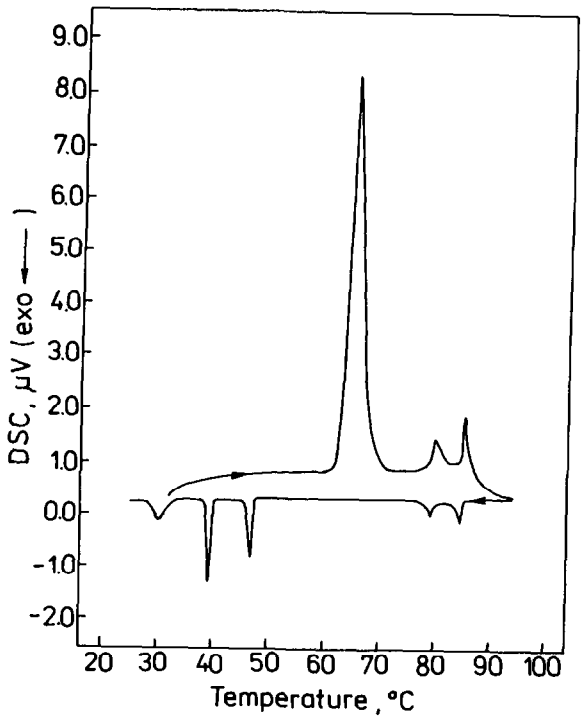


Fig. 3. DSC curve for $\overline{10}$S5 for heating (upper curve) and cooling (lower curve) of the sample.

Fig. 4. Textures of $\overline{10}$S5: (a) in the nematic phase, (b) in the smectic A phase at 61 °C, (c) in the smectic C phase at 52 °C.

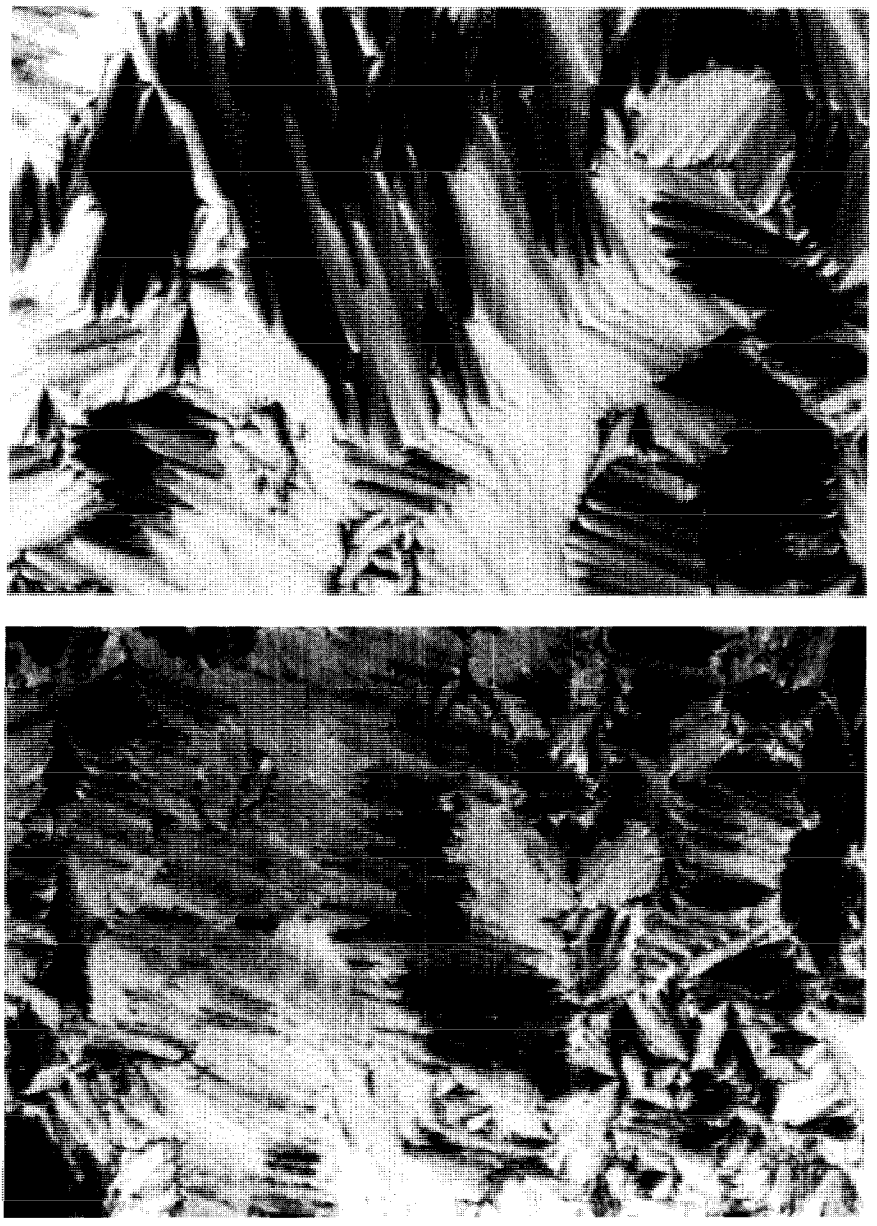


Fig. 4. *(Continued)*

state. To decide whether it is a highly ordered smectic with higher degree of order than smectic J or a modification of a crystalline state, additional studies should be performed. X-ray data would be of great value here. Also, it would be interesting to perform dielectric measurements at lower temperatures. The molecules of the $\bar{n}$S5

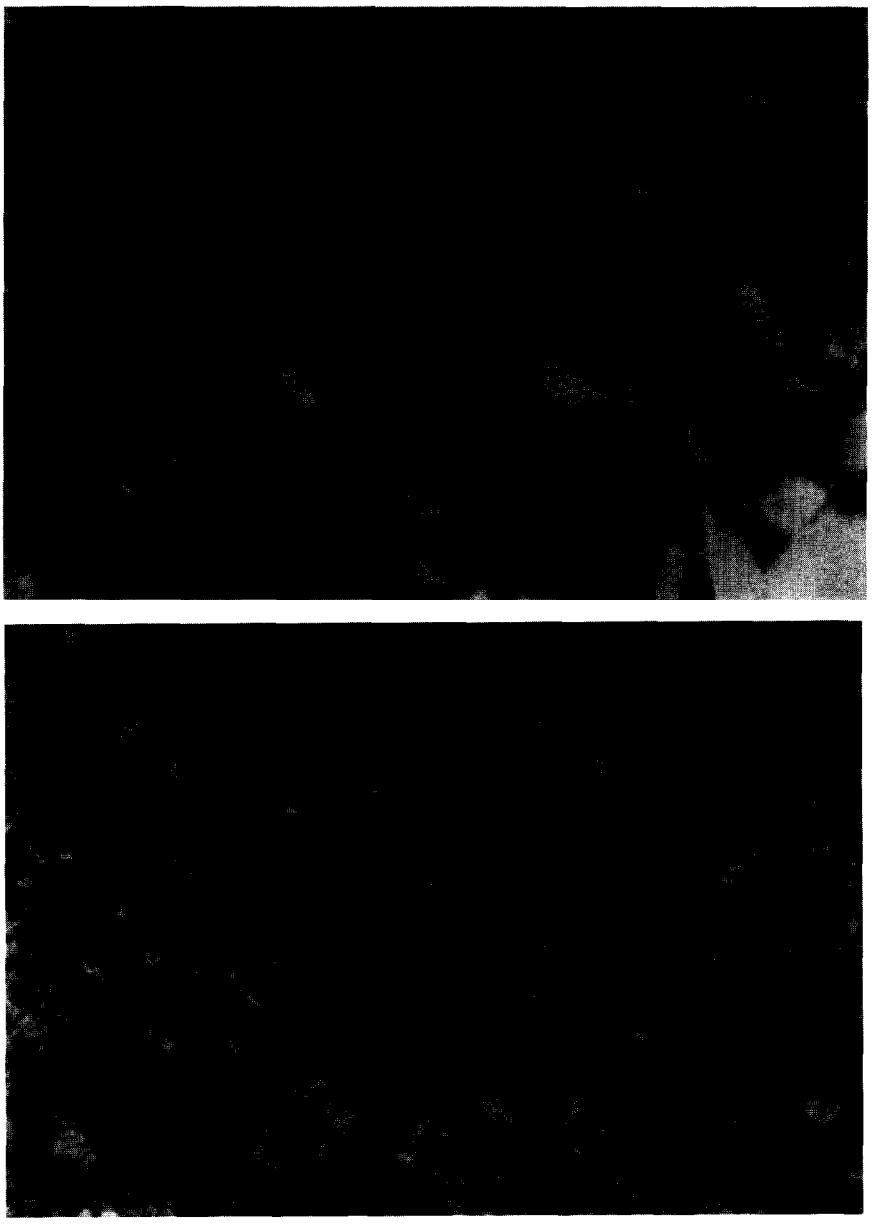


Fig. 5. Textures of $\overline{10}S5$: (a) in the smectic J phase at 41 °C, (b) in the C_x phase at 36 °C, (c) in the crystal phase at 31 °C, (d) in the crystal phase at 21 °C.

series possess a permanent dipole moment. Various phases of thiol esters have been extensively studied by dielectric methods [3, 6, 7] but mainly at higher temperatures. It has been shown that both principal molecular motions exist in the nematic, liquid-like SmA and SmC phases and also in the highly ordered SmJ phase. The detailed dielectric

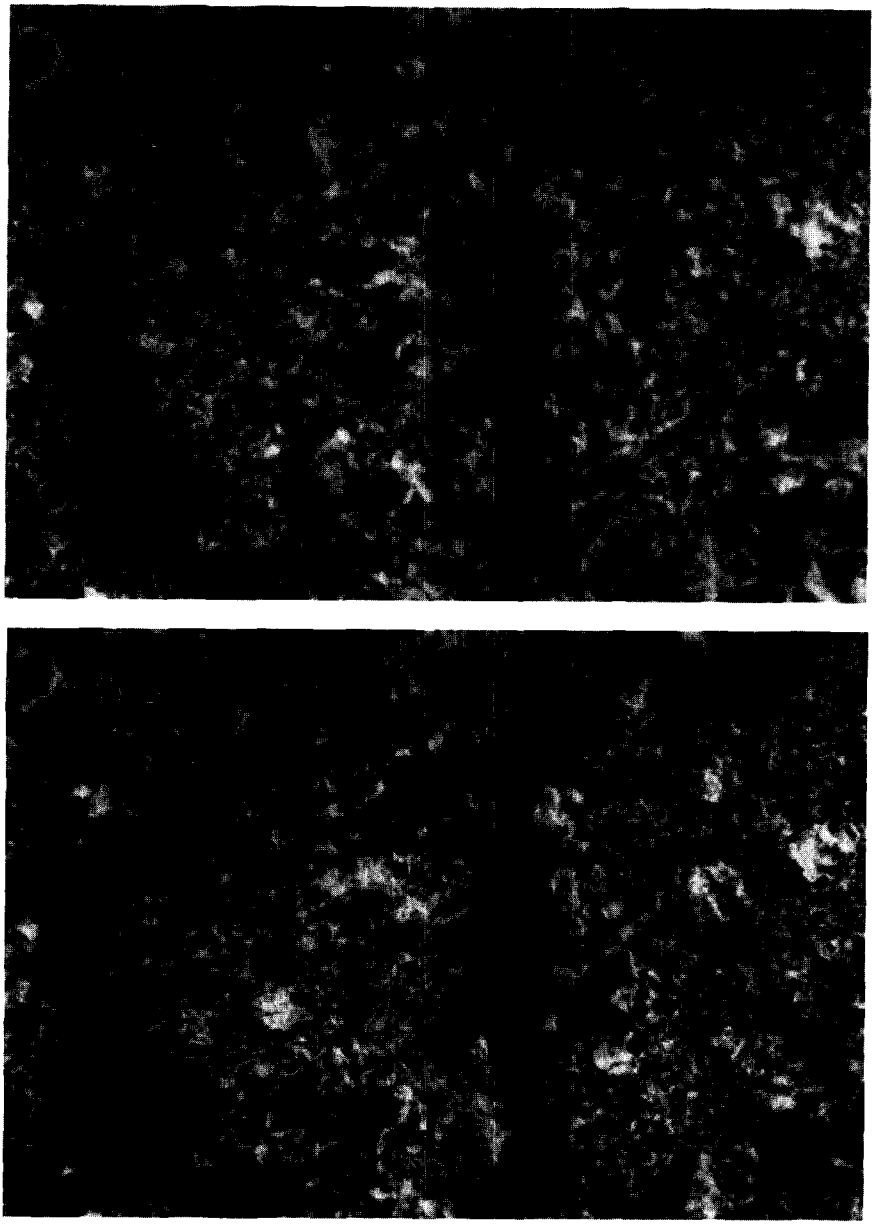


Fig. 5. *(Continued)*

measurements for $\bar{9}$S5 and $\overline{10}$S5 below 40°C could give information concerning whether there is any molecular reorientation in the new phase, thus indicating whether this phase belongs to the class of crystal smectics.

4. Conclusions

DSC and microscopic measurements were performed for three members of the thioester homologous series. In addition to the phases known previously, the present measurements revealed the existence of a new highly ordered phase in 9S5 and 10S5.

Further studies, in particular dielectric relaxation and X-ray (or neutron) diffraction, are needed to explain the nature of this phase.

Acknowledgement

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