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Room Temperature Two Component Nematic Mixtures of Thiobenzoates*

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Results of the polymorphism investigation of three nematic liquid crystalline mixtures made of four compounds belonging to the thioester homologous series: 4-n-pentylphenyl-4′-n-alkoxythiobenzoate (in short nOS5, where n=4,5,6,7 stands for the number of carbon atoms in the alkoxy chain) are presented. Three out of them 4OS5, 5OS5 and 6OS5 possesses only enantiotropic nematic phases whereas 7OS5 possess a monotropic smectic C phase. The principal component of the mixtures was 4OS5 and the following mixtures: 4OS5/5OS5, 4OS5/6OS5 and 4OS5/7OS5 were prepared. The transition temperatures of all compounds and the binary mixtures were determined by means of DSC calorimetry and polarizing microscopy methods. For all concentrations linear dependence of T_{cl} was observed. The widest temperature range of the nematic phase (from –6°C to 86°C) was obtained for the 4OS5/7OS5 system. For this system a tricritical point at cooling the mixture containing 63% of 7OS5 was obtained. For all examined mixtures the eutectic point is observed on heating.

Keywords: liquid crystals, room temperature nematic mixtures, thioesters homologous series, eutectic point

1. INTRODUCTION

Polymorphism investigations of bi- and multicomponent liquid crystalline systems at room temperatures are important from the point of view of practical applications in display technology [1]. Special attention is paid to extend temperature range of a mesophase considerably below room temperatures and to the

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induction of the smectic phases. Some systems exhibit slight deviations from linearity and some of them do not show additive behaviour [2].

Earlier investigations of the mesomorphic properties of the alkylalkoxy-thiobenzoates homologous series (nOS5) showed considerable differences in their phase situation and in dependencies on lengths of the terminal alkyl chain (see [3] and references therein). Also too essential changes surrender physical properties in the nOS5 series, in these dielectric properties. [4]. The crystal structures of 4,4′-disubstituted phenylthiobenzoates have recently been studied. X-ray diffraction analysis of crystal structure for 5OS5 [5], 4OS5 [13] and 6OS5 [6] showed that 4OS5 and 5OS5 crystallize in a monoclinic lattice (space group $P2_1/c$), and 6OS5 – in the orthorhombic lattice (space group Pbca). The results obtained from crystallographic investigations of 4OS5, 5OS5 and 6OS5 show that benzene rings lie in two different planes making an angle of 60°. The bond lengths and angles in the molecular body are nearing and both the terminal chains have the trans conformation. The principle differences exist in the molecular packing along favoured axis and arrangement of molecules in relation to oneself in layers.

Up to now only one binary mixture of thiobenzoates, namely 7OS5/8OS5 [7] has been thoroughly studied. One should point out that thioesters appear to be interesting components of the multicomponent liquid crystal mixtures as far as temperature range of the nematic phase and variety of phases are concerned. These substances exhibit low melting points and their clearing points are well below 100°C. For this reason systematic investigations of the binary thioester mixtures from the nOS5 series are interesting.

2. EXPERIMENTAL

The substances used for the binary mixtures (nOS5, n=4,5,6,7) have the following chemical formula:

$$H_{2n+1}C_nO\text{-}C_6H_4\text{-}COS\text{-}C_6H_4\text{-}C_5H_{11}$$

Four compounds with different alkoxy chains (n=4,5,6,7) were taken into account. They were synthesised in the Institute of Chemistry of University of Podlasie in Siedlce. The thioester contain two terminal groups: pentyl ($-C_5H_{11}$) and alkoxy ($-OC_nH_{2n+1}$), connected to the benzene rings. Two groups in this molecule are polar: -COS- and $-OC_nH_{2n+1}$ and they determine the dielectric properties and relaxation [8].

The transition temperatures of all the compounds and their binary mixtures were determined by means of a polarization microscope made by VEB Analitik (Dresden) with a LINKAM programmable heating stage THMSE 600.

DSC mesurements were performed in the Institute of Physics of the Jagiellonian University in Kraków using differrential scanning calorimeter (Pyris 1 DSC) with low temperature set-up CRYOFIL. The mass of samples was between 5 and 10 mg. The heating and cooling rates were +/-5 K/min, respectively.

3. RESULTS AND DISCUSSION

The basic substance in the binary mixtures of thiobenzoates examined was 4OS5, which possesses only enatiotropic nematic phase (Table I). The phase situation of 4OS5 is shown Figure 1. In particular mixtures as a second component were one of the substances: 5OS5, 6OS5 and 7OS5. These three substances also possess the enantiotropic nematic phase, and 7OS5 possesses additionally a monotropic smectic C phase [9] (Table I).

TABLE I Transition temperatures of nOS5 (°C)

nOS5	*Cr*	S_C	*N*	*I*
40S5	–	–	65.3	91.6
50S5	–	–	63.1	79.4
60S5	–	–	59.9	85.9
70S5	(22.1)	(36.9)	54.6	80.9

The phase diagrams received during heating and cooling for these of mixtures are presented in Figures 2, 3 and 6, respectively. For practical reasons the following abbreviated symbols of mixtures: 4/5 for 4OS5/6OS5, 4/6 for 4OS5/6OS5 and 4/7 for 4OS5/7OS5 are used below in the text. In addition, a number, e.g. 4/6 – 30 denoting wt% content of the second component, will follow each symbol. The phase diagrams of the mixtures studied do not take into account occurrence of polymorphism of the solid phases.

The 4OS5/5OS5 (4/5) mixture

The 4/5 mixture shows undisturbed miscibility in the nematic phase in the whole range of concentrations. As is seen the clearing temperature changes with concentration linearly (see Figs. 2, 3 and 6). The symbols in round brackets refer to the phase transitions occurring during cooling and this remark refers to all three phase diagrams.

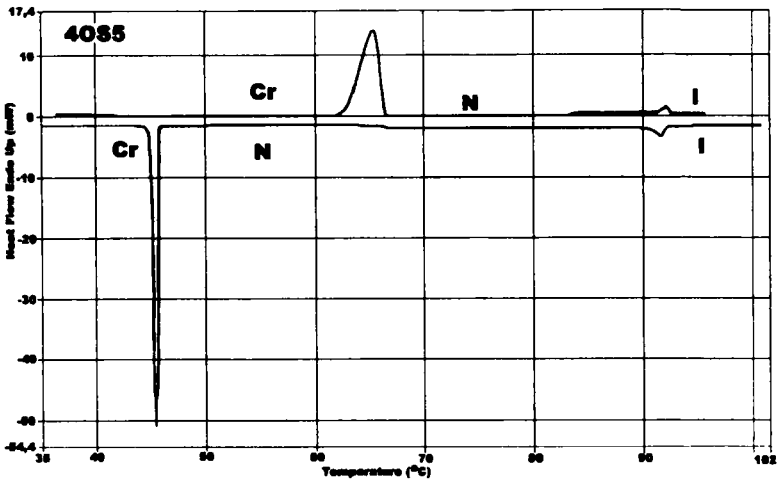

FIGURE 1 DSC curves for 4OS5 for heating (upper curve) and cooling (lower curve) of the sample

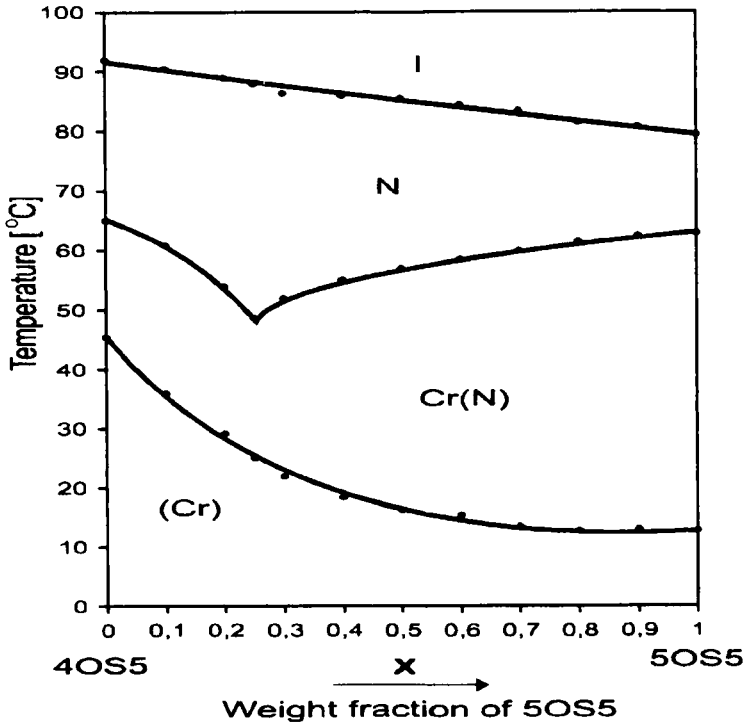

FIGURE 2 Phase diagram for the 4OS5/5OS5 mixture

As one can notice upon heating each mixture shows a minimum on the Cr-N transition line. It is a clear evidence of the eutectic point that for the 4/5 mixture shows up at 25% concentration of 5OS5 (0.24 mole fraction of 5OS5, Table II). For this point the greatest temperature range (ca. 37 °C) of the nematic phase is observed. The Temperature range of the nematic phase for the 4/5 –25 mixture is by ca. 7 °C and 18°C greater than for pure 4OS5 and 5OS5, respectively. In the whole range of concentration there is a narrow range of coexistence of nematic and crystalline phases. It varies from 0.5 to 1.5 °C (Table II). For these mixtures a solid polymorphism in the range 3–20 wt % of 5OS5 is observed. During cooling these mixtures a distinct supercooling of the nematic phase takes place leading to a pronounced extension of the nematic temperature range.

TABLE II Transition temperatures for the 4OS5/5OS5 mixture

Weight fraction	*Mole fraction*	*Cr - N*	*N - I*	*N - Cr*
4OS5	0	65.3	91.6	45.4
0.10	0.10	60.8	90.5	36.0
0.20	0.19	54.1	89.1	29.2
0.25	0.24	48.7	88.2	25.1
0.30	0.29	52.2	86.4	22.0
0.40	0.39	55.1	86.1	18.4
0.50	0.49	57.0	85.5	16.2
0.60	0.59	58.5	84.6	15.3
0.70	0.69	60.1	83.7	13.5
0.80	0.79	61.5	81.6	12.8
0.90	0.90	62.6	80.8	13.0
5OS5	1	63.1	79.4	12.8

The 4OS5/6OS5 (4/6) mixture

Figure 3 shows the phase diagram for the 4/6 mixture obtained during heating and cooling. As is known both components possess only nematic phase. The N-I phase transition temperature shows almost a straight-line character in the whole range of concentrations. During heating the temperature range of the nematic phase of mixtures reduced, attaining a maximum at the eutectic point for the equilibrium composition of mixture (Figure 3). At this point the range of nematic phase is ca. 59 deg. On cooling of the mixtures the temperature range of the nematic phase considerably increases in comparison to the nematic range of pure components on heating. In the case of the 4/6–65 mixture the nematic phase exists in the range of ca 86 deg (from 87,2 °C to 1.4°C, see Figure 3)

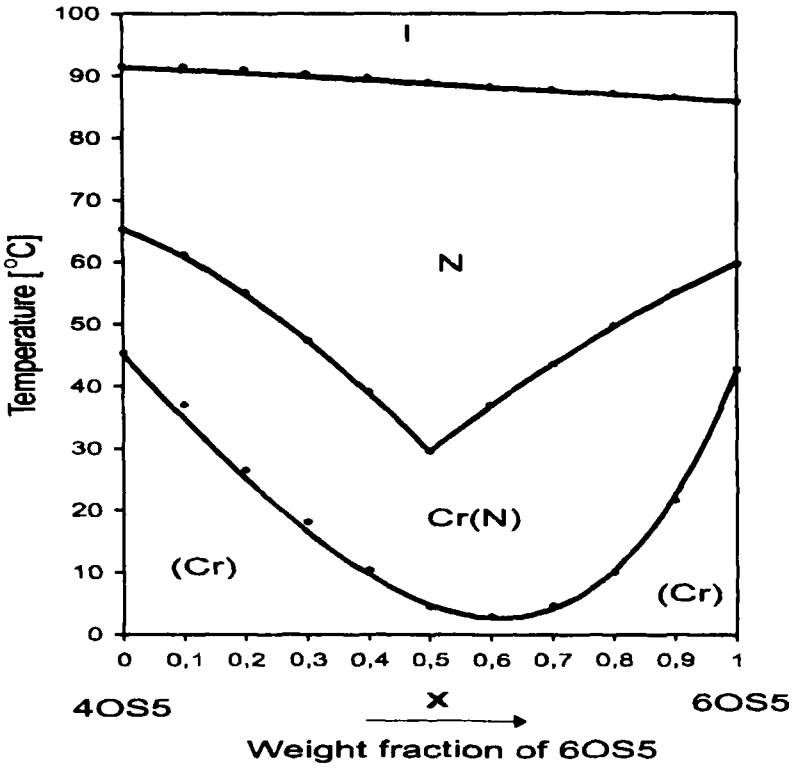

FIGURE 3 Phase diagram for the 4OS5/6OS5 mixture

On heating of the 4/6 mixture in the range of concentration from 10 to 40 wt% and between 60 and 75 wt% of 6OS5 a solid polymorphism exists which is visible both during observations under the polarizing microscope and DSC measurements. Independently from the composition of the mixture the CrII-CrI phase transition takes place at the same temperature equal 40°C. On cooling the 4/6 mixture to temperature -20°C the polymorphism of the crystalline phase is not observed.

Exemplary DSC thermograms obtained for two 4/6 mixtures are presented in Figures 4 and 5. On heating of the 4/6–30 mixture the phase transitions: CrII-CrI, CrI-N and N-I show up at 40.0°C, 45.6°C and 87.2°C, respectively, whereas on cooling the transitions: I-N (at 86.4 °C) and N-CrII (at 4.7°C) have been recorded. In this case a considerable supercooling of the nematic phase takes place. On cooling of the 4/6–30 sample down to room temperatures there was no crystallization process observed.

TABLE III Transition temperatures for the 4OS5/6OS5 mixture

nOS5	*Cr*	S_C	*N*	*I*
4OS5	0	65.3	91.6	45.4
0.10	0.09	61.2	91.5	37.1
0.20	0.19	55.1	91.0	26.5
0.30	0.28	47.5	90.4	18.2
0.40	0.38	39.1	89.7	10.4
0.50	0.48	29.6	89.1	4.5
0.60	0.58	37.0	88.3	3.0
0.70	0.68	43.5	87.8	4.6
0.80	0.79	49.7	87.2	10.1
0.90	0.89	55.0	86.5	21.6
6OS5	1	59.9	85.9	42.8

Figure 5 presents the DSC curves obtained in the present work for the 4/6–70 mixture on heating and cooling. In this case there are two crystalline phases CrI and CrII. The temperature range of the CrI phase is 6.1 deg. After cooling of the sample to room temperature and again heating the range of the phase CrI increased to 14.5 deg.

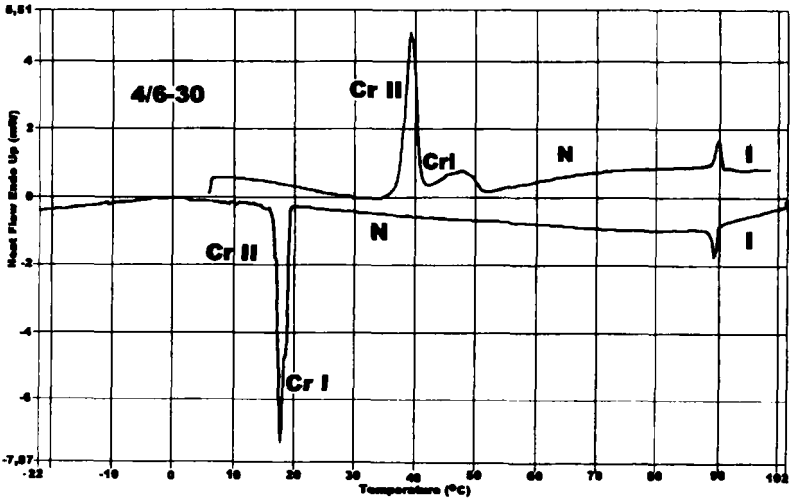

FIGURE 4 DSC results for the 4/6–30 mixture (see Table III)

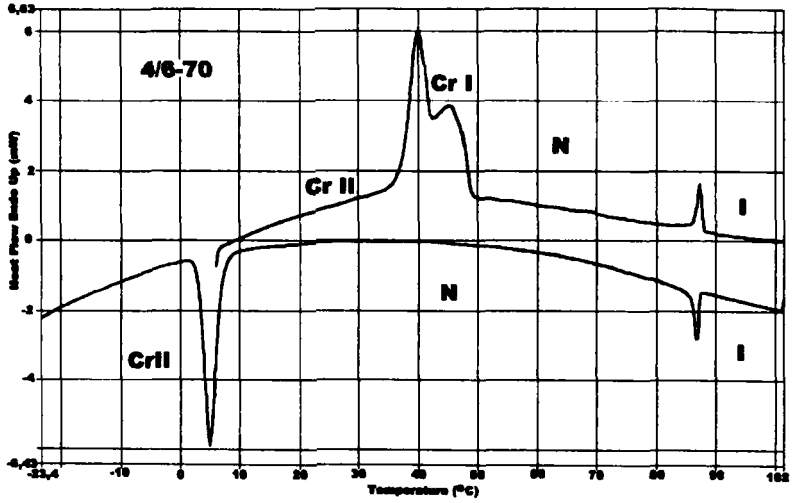

FIGURE 5 DSC results for the 4/6–70 mixture (see Table III)

The 4OS5/7OS5 (4/7) mixture

Two previous binary mixtures 4/5 and 4/6 their composed are of nematic substances. In the case of the 4/7 mixture one of the components, ie. 7OS5 possesses also a monotropic smectic C phase (Table IV). As seen in Fig. 6 the clearing point for the 4/7 mixture – similarly as for previous two mixtures – change with concentration in a linear way. The eutectic point occurs for equilibrium composition (50% 4OS5 and 50% 7OS5, 0.47 mole fraction of 7OS5) during heating. Temperature range of the nematic phase is the greatest for this composition and equal to 50 deg (Figure 6).

In the range of concentration from 10 to 40-wt% and between 60 and 80-wt% the 4/7 mixture exhibits a solid polymorphism (see Figure 7 and 8). As it has been shown there is a considerably greater extension of the nematic phase range on cooling of the 4/7 mixtures (Figure 6). The greatest range of the nematic phase (up to 90 deg, from 86°C to –6 °C) is observed for the 4/7 mixture in the concentration region from 40 to 60 wt% of 7OS5. For the 4/7–63 mixture (0.62 mole fraction of 7OS5) a tricritical point occurs connected with coexistence of three phases: N, SmC and Cr (Figure 6). It is also seen that the range of the smectic C phases widens with increasing concentration of 7OS5 in 4/7 and doesn't go beyond 15 deg.

TABLE IV Transition temperatures for the 4OS5/7OS5 mixture

weight fraction	*mole fraction*	*Cr – N*	*N – I*	*N-Cr (N-S_C)*	*S_C – Cr*
4OS5	0	65.3	91.6	45.4	–
0.10	0,08	61.5	91.0	36.5	–
0.20	0,18	56.1	89.7	25.6	–
0.30	0,28	50.2	88.6	13.2	–
0.40	0,37	44.0	87.4	–0.5	–
0.50	0,47	35.5	86.0	–6.0	–
0.60	0,57	37.8	85.1	–3.1	–
0.63	0,62	41.1	83.8	(-0.9)	–0.9
0.70	0,68	44.3	83.9	(9.6)	0.1
0.80	0,78	48.0	82.5	(19.2)	4.2
0.90	0,89	51.5	81.4	(28.3)	11.0
7OS5	1	54.6	80.9	(36.9)	22.1

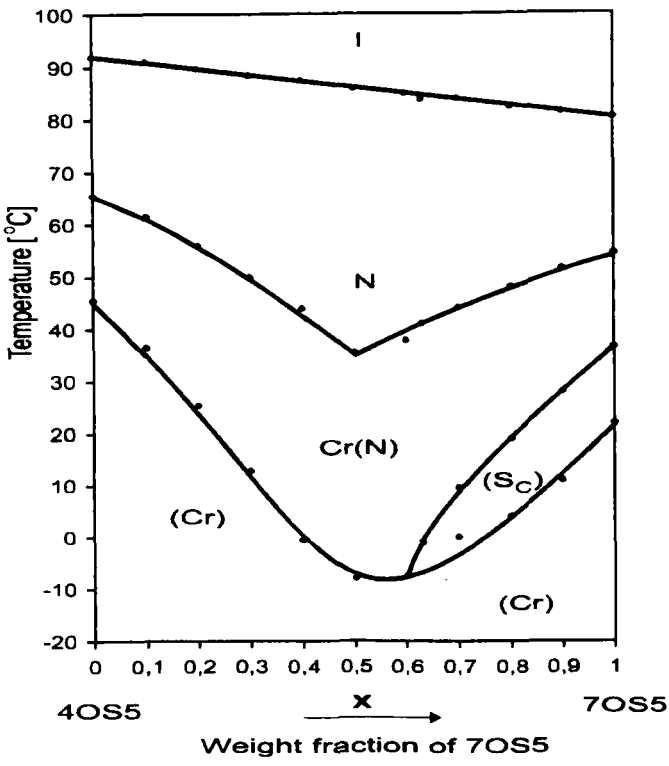

FIGURE 6 The phase diagram for the 4OS5/7OS5 mixture

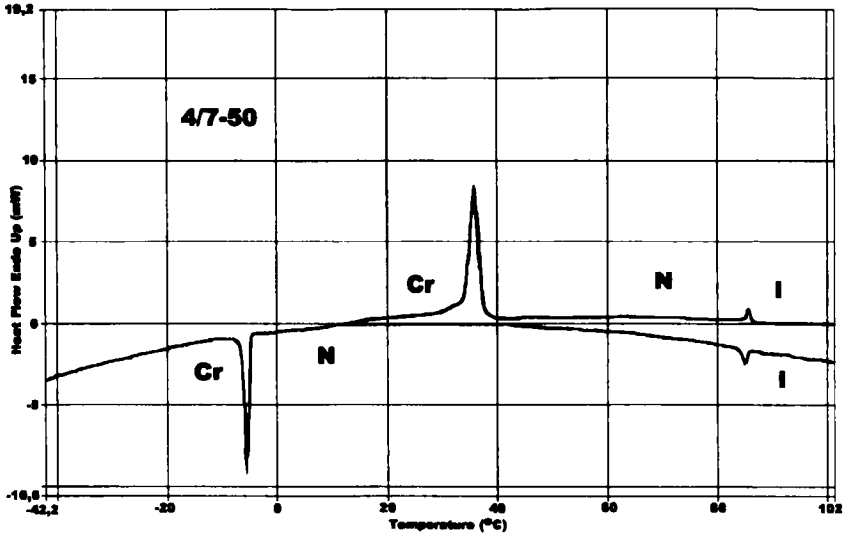

FIGURE 7 DSC curves for 4/7–50 mixture for heating (upper curve) and cooling (lower curve) of the sample

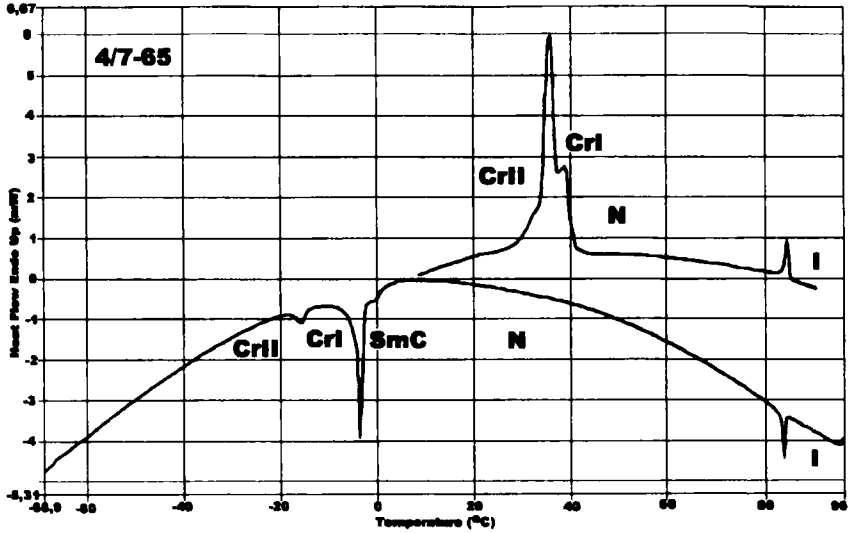

FIGURE 8 DSC curves for 4/7–65 mixture for heating (upper curve) and cooling (lower curve) of the sample

The eutectic composition of binary mixtures of 4/5, 4/6 and 4/7

From the theory of ideal solutions the following equations can be derived for calculating the solid phase – mesophase equilibrium curves:

$$\ln \frac{x_i^{\alpha}}{x_i^{\beta}} = -\frac{\Delta H_i}{R}\left(\frac{1}{T} - \frac{1}{T_i}\right) \tag{1}$$

where: $x_i^{\alpha}, x_i^{\beta}$ are the mole fractions of compounds "1" or "2" in the phases α and β, respectively; ΔH_i is the enthalpy of the phase transition of the pure components "1" or "2", T_i is the temperature of the phase transition of the pure components.

Equation (1) is called CSL equation, from the first letters of the surnames Le Chatelier, Schröder and van Laar. This equation was used by many authors for calculating equilibrium curves of mixtures composed of liquid crystal compounds [see e.g. 10–12]. If the compounds are completely mutually soluble in the nematic phase and in the solid phase they are insoluble, equation (1) assume the form:

$$T = \frac{\Delta H_{i(Cr-N)}}{\frac{\Delta H_{i(Cr-N)}}{T_{i(Cr-N)}} - R \ln x_{i(N)}} \tag{2}$$

where: $\Delta H_{i(Cr\text{-}N)}$ is the enthalpy of the solid-nematic phase transition of the pure components "1" or "2", $T_{i(Cr\text{-}N)}$ is the temperature of the solid-nematic phase transition of the pure liquid crystals "1" or "2", $x_{i(N)}$ is the mole fraction of liquid crystalline compounds "1" or "2" in nematic phase.

The melting points and enthalpy changes of the pure components are given in Table V. The data from Table V were used for calculating the theoretical solid-mesophase equilibrium curves Demus method using equation (2) [10]. In Fig. 9 and 10 eutectic points of binary mixtures of 4/5, 4/6 and 4/7 are shown. The experimental curves (solid lines, Figure 9) are compared with the theoretical ones (dashed lines, Figure 10). All the investigated systems yield simple eutectics. Position of the experimental eutectic point and theoretical one for 4/5 shows distinct difference (experimental: $T^{ex}_{E(4/5)} = 48.7°C$, $x^{ex}_{E(4/5)} = 0.24$ and theoretical: $T^{th}_{E(4/5)} = 42°C$, $x^{th}_{E(4/5)} = 0.47$) and for binary mixtures 4/6 and 4/7 similar values (experimental: $T^{ex}_{E(4/6)} = 29.6°C$, $x^{ex}_{E(4/6)} = 0.48$ and theoretical: $T^{th}_{E(4/6)} = 36°C$, $x^{th}_{E(4/6)} = 0.54$; experimental: $T^{ex}_{E(4/7)} = 35.5°C$, $x^{ex}_{E(4/7)} = 0.47$ and theoretical: $T^{th}_{E(4/7)} = 36°C$, $x^{th}_{E(4/7)} = 0.54$). These confrontation show that experimental eutectic point and theoretical one shift right with lengthen out of molecule which is a second component of the binary mixtures of thiobenzoates (the length of 5OS5 = 25,22 Å [5], 6OS5 = 26,25 Å [6] and 7OS5 = 27,31 Å [13]).

TABLE V Temperatures and enthalpies of the Cr-N phase transition for the nOS5

nOS5	$\Delta H_{i(Cr\text{-}N)}$ *[kcal/mol]*	$T_{i(Cr\text{-}N)}$ *[K]*
4OS5	5.70	338.5
5OS5	7.46	336.3
6OS5	5.37	333.1
7OS5	6.66	327.8

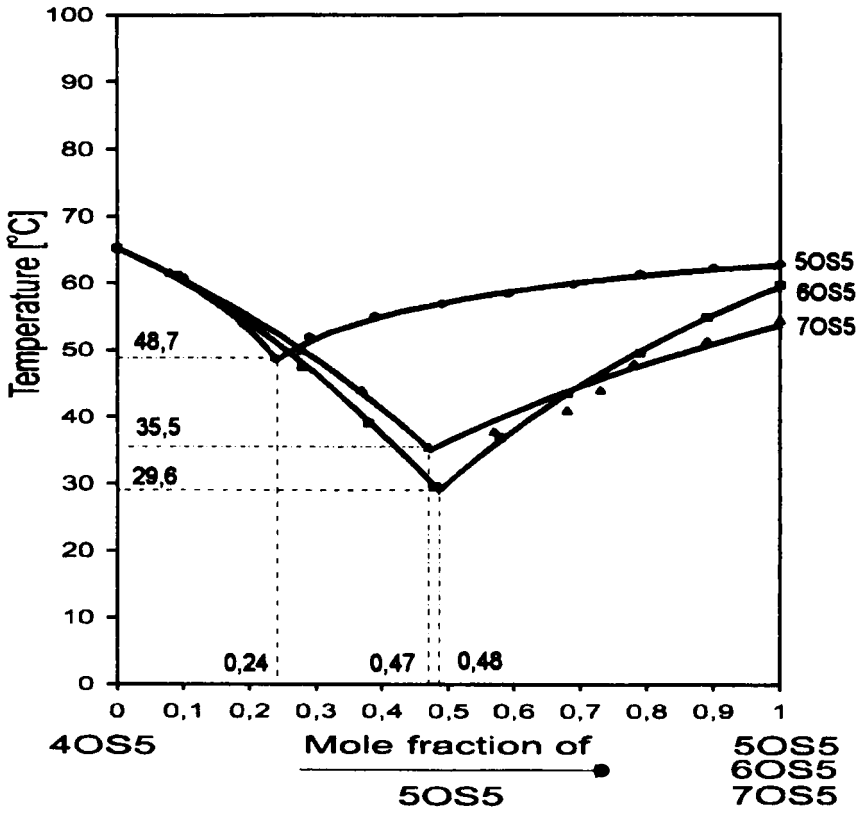

FIGURE 9 Experimental solidus curves for 4/5, 4/6 and 4/7 mixtures

The solidus curves for 4/6 and 4/7 mixtures given in Figure 9 are in good agreements with those calculated (Figure 10) from equation (2) for the branch corresponding to the melting of 6OS5 and 7OS5. The situation of experimental eutectic point for the last two mixtures takes place for the same weight fraction

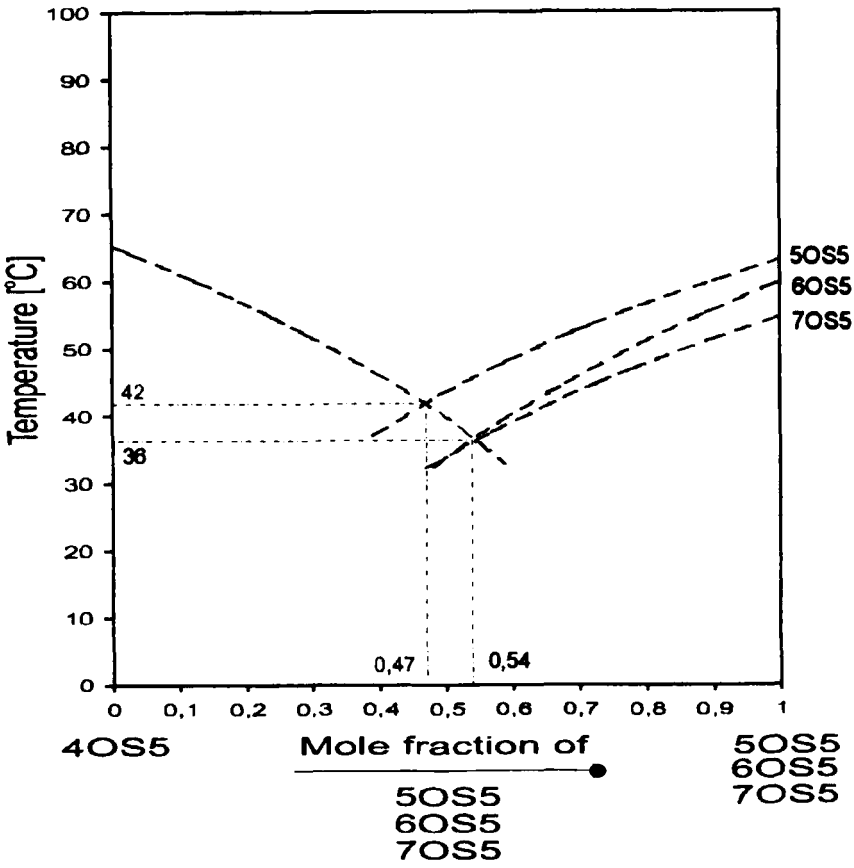

FIGURE 10 Theoretical solidus curves for 4/5, 4/6 and 4/7 mixtures

equal 0.5 (0.48 mole fraction for 6OS5 and 0.47 for 7OS5). From the calculated eutectic points for 4/6 and 4/7 mixtures appears that these points occur in the same place but for a little higher values of mole fraction equal 0.54 (for 6OS5 and 7OS5).

Different behaviour of mixture 4/5 in comparison with mixtures 4/6 and 4/7 can be probably explained by resemblances and differences of molecular structures between pure components of binary mixtures. 4OS5 [13] and 5OS5 [5] crystallizes in the monoclinic system, space group $P2_1/c$, with cell constants c equal molecular length of the 4OS5 and the 5OS5.6OS5 [6] and 7OS5 [13] crystallizes in the orthorhombic system, space group Pbca, with cell constants c equal about two molecular lengths. It leads to conclusion that mixtures composed of

compounds with similar molecular structure can have different position of eutectic point than mixtures composed of compounds with other molecular structures and cell constants.

Verification of this argument will be possible after comparison properties of next binary mixture of thiobenzoates and their molecular structures.

4. SUMMARY

All binary mixtures (4/5, 4/6 and 4/7) investigated show undisturbed miscibility in the nematic phase in the whole range of concentration. By mixing two nematic substances in the case of the 4/5 and 4/6 mixtures one did not observe induction of new liquid crystalline phases. The N-I phase transition temperature shows almost straight-line dependence on concentration for all of mixtures studied. By mixing two nematics a considerable extension of the nematic phase temperature range (up to 50 deg) in relation to pure mixture components. This range is even over 90 deg (from 86°C to –6°C) for the 4/7–50 mixture. For all examined mixtures the eutectic point is observed on heating. The tricritical point (N, SmC and Cr) was observed for the 4/7–63 mixture on cooling.

We confirmed possibility of delimitation of eutectic points basing on CSL equation in the binary mixtures of thiobenzoates.

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