Vol. **122** (2012) *ACTA PHYSICA POLONICA A* No. 2

Proc. VII National Conference of Neutron Scattering and Complementary Methods, Chlewiska, Poland, June 12–16, 2011

Equimolecular Mixture of Calamitic and Bent-Core Thiobenzoates

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This article reports on the new results on phase transitions, mesomorphic and electro-optical properties of new equimolecular mixture of calamitic and bent-core thiobenzoates. Two following liquid crystals were the components of the binary mixture: (S)-(+)-4-(1-methylheptyloxy)biphenyl 4′-octylthiobenzoate (MHOBS8) having rode-like, calamitic-chiral molecules possessing among others ferroelectric smectic C (SmC*) and bis [4-(4′-octylphenyl-thiocarbonyl)phenyl] isophtalates from a homologous series of banana-shaped thioesters, referred to as IFOS8, where $n = 8$ denoted the number of carbon atoms in terminal alkyl chains in both mesogens, synthesized by us. The IFOS8 compound has two enantiotropic phases: $B2$ with antiferroelectric order and $B6$. The mesomorphic properties were investigated by means of three complementary methods: differential scanning calorimetry, polarized light optical microscopy, and transmitted light intensity. Electro-optical measurements were also carried out.

PACS: 61.30.–v, 64.70.M–, 78.15.+e

1. Introduction

The binary and multicomponent mixtures are the subject of intensive research due to their potential application in e.g. liquid crystal displays. The E7 mixture is an example of such liquid crystalline commercial mixture [1]. Equally important are also electro-optical applications of liquid crystal mixtures [2]. Recently, the researchers have been vividly interested in mixtures characterized by ferroelectric properties (e.g. [3, 4]), and especially in the mixtures of bent-core and calamitic liquid crystals, in which an equimolecular binary mixture are the important object of the investigations (e.g. [5-8]).

The subject of this publication is an equimolecular binary mixture composed of a ferroelectric calamitic chiral liquid crystal and an achiral banana-shaped mesogen from thiobenzoesan homologous series. The chemical structures of both components, MHOBS8 (calamitic liquid crystal) and IFOS8 (bent-core liquid crystal), are presented in Fig. 1.

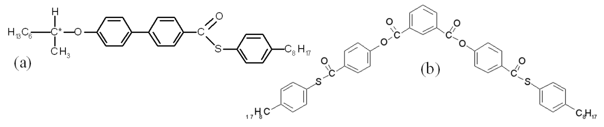

Fig. 1. Chemical structures of the components of the equimolecular mixture: MHOBS8 (a) and IFOS8 (b).

Besides the high-ordering phases SmI* and SmG* as well as chiral nematic N*, MHOBS8 possesses the enantiotropic ferroelectric SmC* phase [9] in the considerably wide temperature range (103 °C–79 °C, Table). IFOS8 possesses the enantiotropic antiferroelectric $B2$ and $B6$ phases [10]. The temperature range of phases is as follows: $B2$ 195 °C–174 °C and $B6$ 174 °C–160 °C, during cooling (Table). An interesting problem was to study the changes occurring in the phase situation and mesomorphic properties of an equimolecular mixture of calamitic and banana-shaped molecules.

2. Experiment

DSC measurements were performed by 822^e Mettler Toledo equipment. The temperature, enthalpies and entropies were determined (the values of parameters obtained during cooling in Table were shown, because of the larger temperature ranges of phases occurrence in cooling). The sample was placed in aluminum crucible of 40 μl capacity. TLI measurements were performed using a home-made setup [11]. The temperature was controlled with a Linkam controller (Linkam hot stage THMSE 600). The texture observation (POM) were performed using polarizing microscope Nikon, Model Eclipse E200 (a magnification of about 1×180). For the measurement of electro-optical reorientation (EO) of the sample, a reversal current method was employed using triangular voltage driving pulses (generated by the HP 33120A pulse generator) [12]. POM, TLI and EO measurements were conducted on planar aligned samples, using the ITO HG AWAT electro-optic cell of 7.8 μm thickness. In order to ensure a comparison of results between DSC, TLI, POM,

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and EO methods all the measurements were carried out with the rate of 2 °C min^{-1}. Thus the phase transition temperatures obtained agreed among the methods of detection within the accuracy of 0.1–0.3 degree. The measuring error value of enthalpy and entropy was *ca.* 5%.

3. Results and discussion

Figure 2 shows the phase situation of the equimolecular mixture of MHOBS8/IFOS8 (EM) in the comparison of calamitic liquid crystals. As one can see, the phase sequences of EM and MHOBS8 are identical, even the temperature range of particular phase are different.

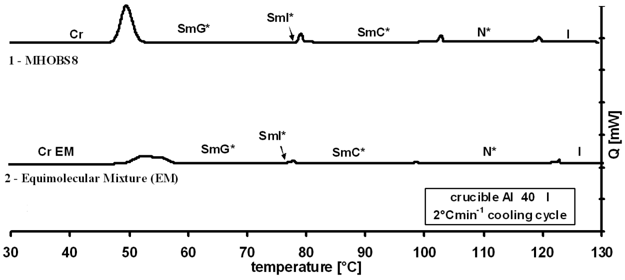

Fig. 2. DSC curves obtained during cooling (−2 °C min^{-1}) for (S)-MHOBS8 (1) and EM (2).

Further analysis of temperature ranges of the phases in the EM mixture suggests that the equimolecular system leads to the disappearance of the antiferroelectric $B2$ and $B6$ phases present in an achiral bent-core liquid crystal IFOS8. The destabilization of the phases coming from the banana-shaped liquid crystal occurs in the temperature range between the isotropic phase and the crystal phase. The results obtained by the DSC method have been confirmed by the TLI studies which well identify the phase transitions. The SmC*–SmI* phase transition in MHOBS8 and binary mixture can be well observed using the DSC method and has been confirmed unequivocally with the TLI method (Fig. 3). The enthalpy value in the EM mixture of the SmI*–SmG* transition is very low (see Table). This transition is observable only at a considerable magnification of the SmI*–SmG* transition interval, but is well observed on the TLI diagram (Fig. 3). The textures of the equimolecular mixture under study were presented in Fig. 3. Similar textures were observed in the SmG* and N* phases in other chiral thioesters from the MHOBSn homologous series [13].

The total temperature range of phases occurring in the EM mixture is somewhat smaller than in MHOBS8. The range of the N* phase in the EM mixture is larger than in MHOBS8, with a smaller range of the ferroelectric SmC* phase originating from a rod-like MHOBS8. The enthalpy values of all transition phases in the EM mixture are lower in comparison with MHOBS8 (Table). A similar dependence can be observed when comparing the changes in the entropy values of transition phases between the MHOBS8/IFOS8 mixture and MHOBS8. Optical transmittance vs. electric field (±1.5 V/μm) was measured for MHOBS8 and for EM put in 7.8 μm HG cells at 10 Hz of the applied triangular-wave electric field. The representative results obtained during cooling of the equimolecular mixture of MHOBS8/IFOS8 in the same temperature in the ferroelectric SmC* phase are presented in Fig. 4.

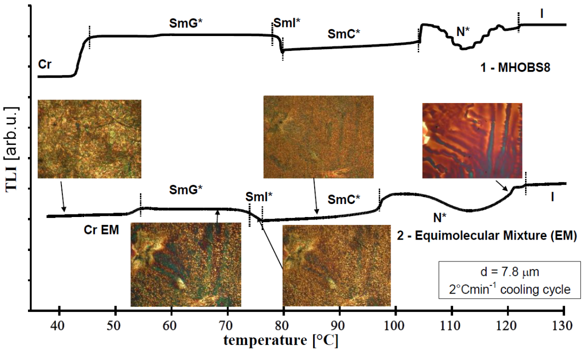

Fig. 3. TLI curves obtained during cooling (−2 °C min^{-1}) for MHOBS8 (1) and EM (2) and textures of the N* (120.0 °C), SmC* (85.5 °C), SmI* (75.0 °C), SmG* (67.8 °C) and Cr (41.2 °C) phases observed during cooling.

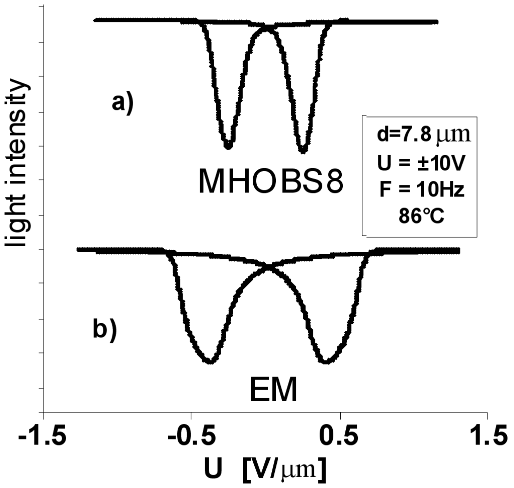

Fig. 4. Transmitted light curves obtained during cooling in the SmC* phase (86.0 °C) vs. applied triangular wave for MHOBS8 (a) and EM mixture (b). Electric field of frequency 10 Hz and amplitude ±10 V/7.8 μm has been applied.

At a frequency of 10 Hz the W-shaped switching for MHOBS8 was observed. A slight modulation of the hysteresis loop was noticeable in the whole range of the SmC* phase for the equimolecular mixture EM. Similar changes were observed in SmC* for other compounds [14, 15].

TABLE

Phase transition temperatures, enthalpy and entropy changes for MHOBS8, IFOS8 and EM.

Substances	Cooling					
	DSC		TLI	ΔH	ΔS	Type of phase transition
	T_P [°C]	T_0 [°C]	[°C]	[J/g]	[kJ/(g K)]	
MHOBS8	119.6	120.0	118.4	2.30	5.85	I–N*
	103.0	103.4	103.1	2.32	6.16	N*–SmC*
	79.3	79.8	76.0	4.01	11.36	SmC*–SmI*
	75.0	76.0	73.0	0.81	2.30	SmI*–SmG*
	49.9	51.6	48.0	46.3	144.08	SmG*–Cr
IFOS8	194.7	195.5	200.8	15.72	33.55	I–*B*6
	173.8	174.3	176.8	1.31	2.93	*B*6–*B*2
	158.2	162.2	162.0	45.47	104.48	*B*2–Cr1
equimolecular mixtures	122.8	123.0	122.6	0.91	2.28	I–N*
	98.7	99.2	95.8	0.72	1.93	N*–SmC*
	–	–	77.0	–	–	SmC*–SmI*
	77.8	78.5	75.3	0.22	0.63	SmI*–SmG*
	52.5	57.6	53.7	2.21	6.68	SmG*–Cr

4. Conclusions

The equimolecular participation of the calamitic chiral liquid crystal MHOBS8 and of achiral bent-core mesogen IFO8 destabilizes the antiferroelectric *B*2 and the *B*6 phases in the achiral bent-core mesogen. Such behaviour is unexpected in relation to the properties of other mixtures of a bent-core and a calamitic liquid crystal [5]. The effect observed comes most probably from significant differences between the chemical structure of the achiral banana-shaped molecule and of the chiral calamitic liquid crystals.

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