Differential Scanning Calorimetry (DSC) under High Pressure on 10-TPEB

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The phase behaviour of a new liquid crystal, belonging to the series 1-[4-*n*-alkyl-biphenyl]-2-[4-isothio-cyanato-phenyl]ethane (*n*TPEB), $n = 10$, has been investigated with differential scanning calorimetry at ambient and high pressure. The phase behaviour depends on the thermal treatment. Phase transition temperatures have been determined as a function of pressure up to 300 MPa. No pressure-induced or pressure-limited phases are observed in this pressure range. Enthalpy- and volume-changes accompanying the phase transitions have been calculated using the Clausius-Clapeyron equation.

1. Introduction

Recently the phase behaviour of 6-TPEB (belonging to the series 1-[4-*n*-alkyl-biphenyl]-2-[4-isothio-cyanato-phenyl] ethane (*n*TPEB): C_nH_{2n+1}-ϕ-ϕ-CH_2CH_2-ϕ-NCS) was investigated, using high pressure differential thermal analysis (DTA) [1]. Some members of this homologous series have been studied dielectrically [2, 3] and by absorption of polarized light in studies of azo dye - mixtures [4]. In this paper we investigate the polymorphism of 10-TPEB using differential scanning calorimetry.

2. Experimental

10-TPEB was synthesized and purified (99.6%) at the Institute of Chemistry, Military Academy of Technology (Warsaw, Poland). The phase behaviour of 10-TPEB was studied at 250 to 450 K and up to 300 MPa. For the measurements a Setaram calorimeter DSC92 was employed at ambient pressure (in Warsaw) and a computer-assisted high-pressure DSC 7 (Perkin Elmer) apparatus [5, 6] (in Bochum). The transition temperatures as a function of pressure are usually obtained in heating runs at a rate of 2 K/min. For the experiments about 40 mg of the samples are filled in lead or indium cells. The closed cells transmit the pressure practically without hysteresis and prevent the pressure-transmitting gases (Ar, He) from being dissolved in the substance.

3. Results

Figure 1 displays heating and cooling runs at atmospheric pressure obtained with the DSC92 calorimeter. Starting from the solid phase (Cr_1 in the top of Fig. 1) the sample transforms to smectic B ($S_{B,cryst}$) at 316.4 K, then to the nematic phase (N) at 377.2 K, and finally to the isotropic phase (I) at 397.3 K. The smectic B_{cryst} phase, termed also as the smectic L phase ($S_{B,cryst} = S_L$) has been confirmed by X-ray diffraction. The charateristic 6 spots lying symmetrically inside the diffraction ring have been observed. The smectic B_{cryst} layer was slowly expanding with temperature from $d = 3.184$ nm at 350 K to $d = 3.203$ nm at 370 K. When the melt is slowly cooled and annealed for some hours after freezing, reheating yields additional peaks in the solid state, possibly indicating transitions between three different crystal phases (bottom of Fig. 1): $Cr_3 \rightarrow 302.6\text{ K} \rightarrow Cr_2 \rightarrow 311.9\text{ K} \rightarrow Cr_1 \rightarrow 316.5\text{ K} \rightarrow S_{B,cryst}$. The cooling runs exhibit only the transitions $I \rightarrow N \rightarrow S_{B,cryst}$.

The sample crystallizes only reluctantly, and therefore quick cooling may yield a glassy state resulting in an exothermic peak after reheating. Such a behaviour was observed several times in the high pressure DSC apparatus, see Figure 2. It is necessary to freeze the sample very slowly and to anneal after crystallization. At this point the formation of Cr_1-phase is favoured, as revealed by the large peak due to the transition $Cr_1 \rightarrow S_{B,cryst}$, which means that Cr_2 and Cr_3 are metastable

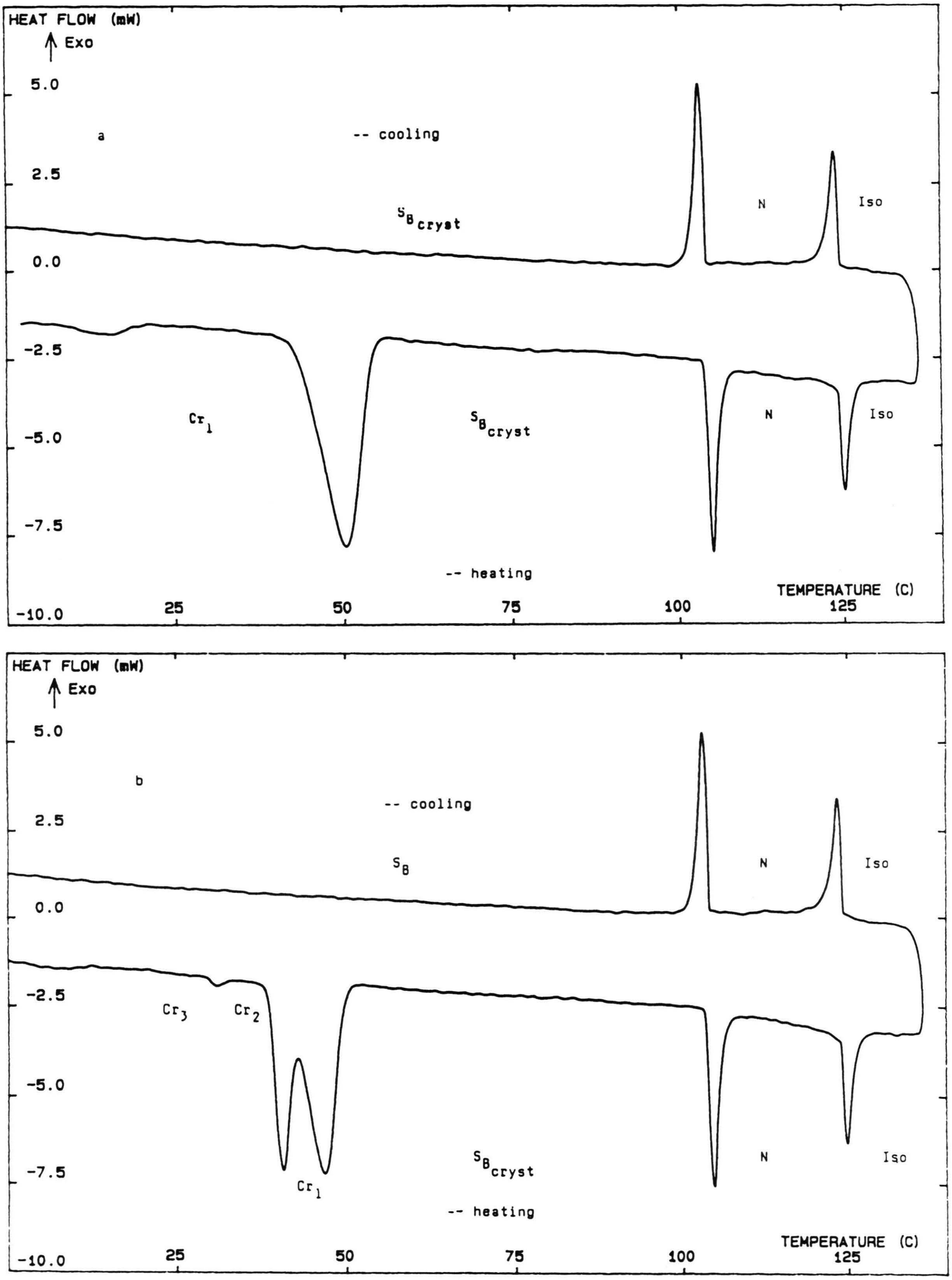

Fig. 1. Heating and cooling runs at amospheric pressure obtained with the DSC92 calorimeter, top: first heating and cooling, bottom: repeated after 24 hours.

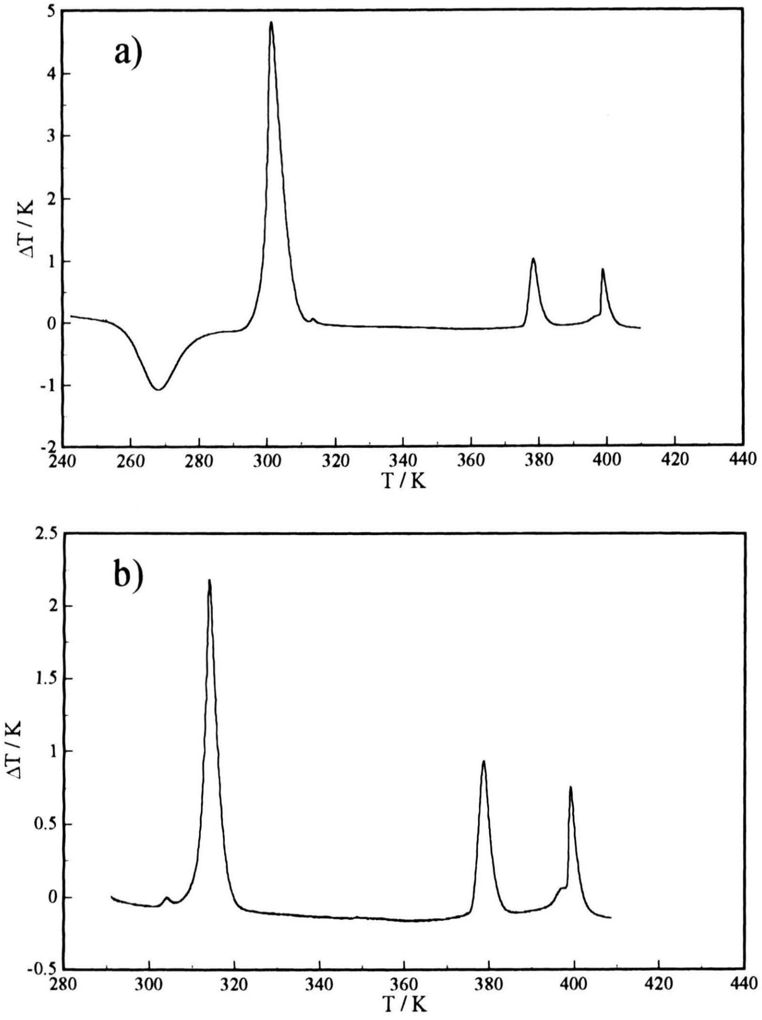

Fig. 2. DSC traces of 10-TPEB at atmospheric pressure obtained with the DSC 7 calorimeter, a) showing the exothermic peak, b) after annealing.

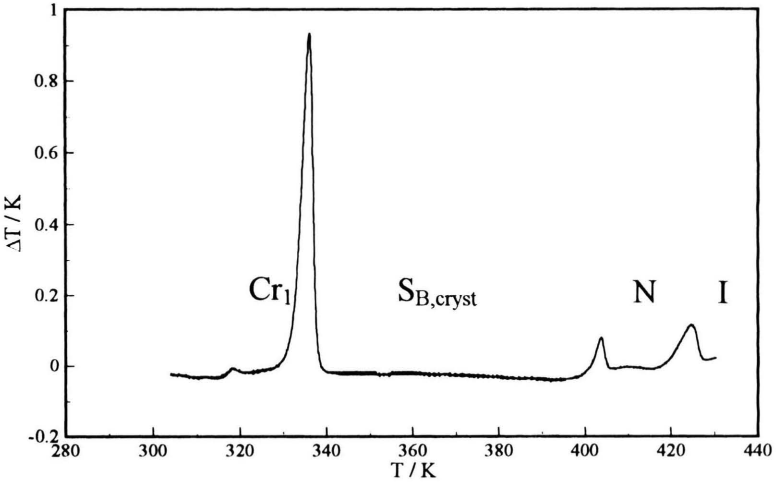

Fig. 3. DSC trace of 10-TPEB at pressures of (about 55 MPa).

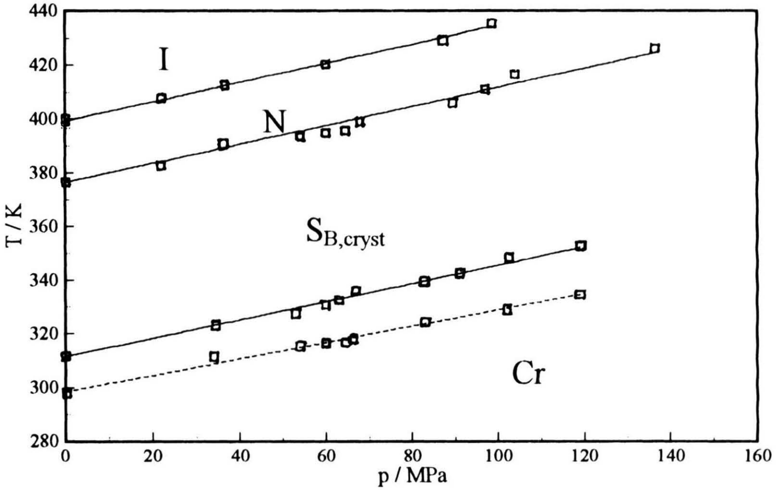

Fig. 4. Phase diagram of 10-TPEB.

Table 1. Pressure dependence of the phase transition temperatures of 10-TPEB.

$Cr_2 \rightarrow Cr_1$	T/K = 298.5 + 0.304 (p/MPa)
$Cr_1 \rightarrow$ smectic B	T/K = 311.5 + 0.340 (p/MPa)
smectic B → nematic	T/K = 376.5 + 0.352 (p/MPa)
nematic → isotropic	T/K = 399.4 + 0.355 (p/MPa)

phases. The sum of the transition enthalpies $Cr_3 \rightarrow Cr_2 \rightarrow Cr_1 \rightarrow S_{B,cryst}$, (0.35 + 10.80 + 16.20 = 27.3 kJ mol^{-1}) was the same as the enthalpy of the direct transition $Cr_1 \rightarrow S_{B,cryst}$ (27.3 kJ mol^{-1}). This conclusion is also confirmed by a previous high pressure DTA study [7], where the two low-temperature peaks disappeared after annealing at 280 K in favour to the transition at about 313 K. Figure 3 presents a DSC run at elevated pressures after appropriate annealing. The peak ratios show that the low-temperature transition practically disappeared.

The phase diagram of 10-TPEB is presented in Figure 4. Polynomials have been fitted to the pressure dependence of the phase transitions, the parameters of which are given in Table 1. Within the limits of experimental errors the phase boundaries can be presented by straight lines. The transition temperatures determined with DSC92 at atmospheric pressure are somewhat higher than those measured with the high-pressure DSC7 apparatus. Enthalpy changes have been calculated from the peak areas after calibration against substances of known transition enthalpies. The volume changes can be calculated from these data using the Clausius-Clapeyron equation. Some results of the thermodynamic calculations are collected in Table 2.

Table 2. Thermodynamic properties of 10-TPEB at normal pressure.

Transition	T/K (DSC92)	ΔH/kJ mol^{-1} (DSC92)	(DSC7)	(dT/dp) K MPa^{-1}	ΔV cm^{3}mol^{-1}
$Cr_3 \rightarrow Cr_2$	302.6	0.335			
$Cr_2 \rightarrow Cr_1$	311.9	10.80		0.304	0.010
$Cr_1 \rightarrow$ smectic B	316.4	16.20			
$Cr_1 \rightarrow$ smectic B	316.4	27.32	25.43	0.340	0.029
smectic B → nematic	377.2	5.92	9.54	0.352	0.005
nematic → isotropic	397.3	3.76	5.02	0.355	0.003

In conclusion, the phase behaviour of 10-TPEB is similar to that of 6-TPEB [1] in that both liquid crystals reveal metastable solid phases and stable smectic B_{cryst}, nematic, and isotropic phases. However, the coexistence range of the smectic and nematic phases show a significant chain length dependence [4]. For both n-TPEBs we find an increase of the nematic and smectic phase regions with increasing pressure as observed for many other liquid crystals [8].

Acknowledgements

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