Differential Thermal Analysis under High Pressure on 6-TPEB

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The high pressure phase behaviour of a new liquid crystal, belonging to the series 1-[4-*n*-alkyl-biphenyl]-2-[4-isothio-cyanato-phenyl]ethane (*n*TPEB), $n=6$, has been studied with differential thermal analysis. The pressure dependence of the phase transitions has been determined up to 300 MPa. No pressure-induced or pressure-limited phases are observed in this pressure range, the phase behaviour, however, depends on the thermal treatment. Enthalpy and volume changes accompanying the phase transitions have been calculated using the Clausius-Clapeyron equation.

1. Introduction

Many homologous series of liquid crystals were studied in order to check the influence of different molecular cores on the thermodynamic and dielectric properties [1, 2]. Recently, dielectric relaxation studies were performed on some representatives ($n=7, 8, 9$) of 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 [3, 4]. For $n \geq 4$, the following sequence of phases is observed: crystal – smectic B (SmB) – nematic – isotropic. In this paper we investigate the polymorphism of 6-TPEB, using differential thermal analysis (DTA).

2. Experimental

6-TPEB was synthesized and purified in the Institute of Chemistry, Military Academy of Technology (Warsaw, Poland). The phase behaviour of the liquid crystal was studied in the temperature range 290 to 450 K and up to pressures of 300 MPa. The measurements were carried out with a computer-assisted high-pressure DTA apparatus [5, 6]. For each run, 40–50 mg of the samples were filled in lead cells, which were then closed, in order to avoid any contact of the pressure-transmitting gases (Ar, He) with the substance. The transition temperatures were usually obtained in heating runs at a rate of 2 K/min. Details of the DTA apparatus and the experimental technique are described in [6]. The enthalpy changes at atmospheric pressure have been determined in Warsaw with a Setaram calorimeter DSC 92 and in Bochum with a DSC 7 (Perkin Elmer) [7].

3. Results

Figure 1 displays the heating and cooling runs at atmospheric pressure, obtained with the DSC92 calorimeter. A considerable supercooling is observed for the freezing of smectic B; the splitting of the DSC peak indicates the formation of a metastable phase. A similar splitting is observed in DTA heating runs recorded at atmospheric pressure, see Figure 2. When the sample is cooled to the crystal phase and immediately reheated, the transition crystal → Smectic B is observed at 329 K (Figure 2a). However, annealing in the crystal phase shifts the transition temperature to 333.5 K (Figure 2b, c). Obviously, a metastable phase (denoted as solid I′) is formed on cooling that slowly converts to the thermodynamically stable phase solid I during the thermal treatment. Other phase transitions are not affected by the annealing procedure: smectic B (372.6 K) → nematic (403.8 K) → isotropic.

The annealing time can be reduced by the application of pressure. The phase diagram of 6-TPEB is given in Figure 3. At higher pressures, the lower transition did not completely vanish, even after annealing for 50 hours. An additional peak is observed (see Fig. 4) that probably is also connected with a metastable phase transition, because its peak area decreased with increasing annealing time. The transitions from metastable phases are presented as dashed lines. The pressure dependence of the phase transitions has been

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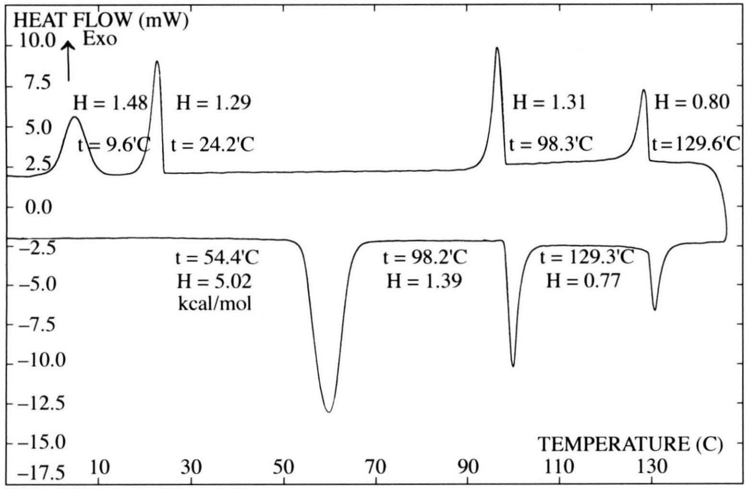

Fig. 1. Heating and cooling runs at atmospheric pressure obtained with the DSC92 calorimeter.

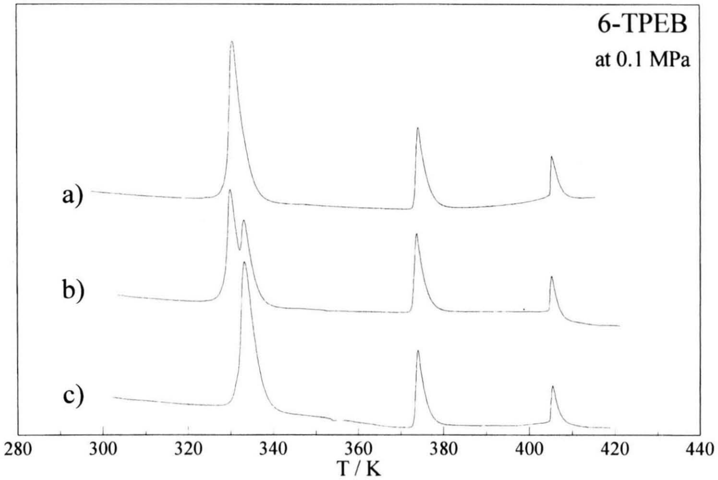

Fig. 2. DTA traces of 6-TPEB at atmospheric pressure, a) without thermal treatment, b) after annealing of 3 hours, c) after annealing of 50 hours.

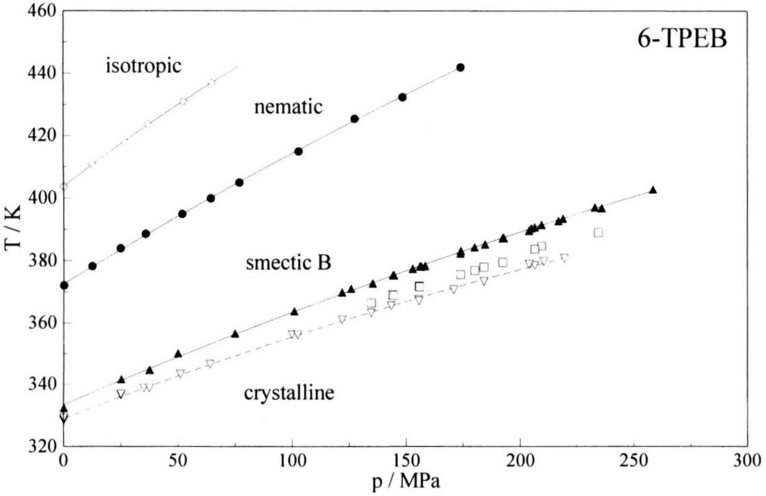

Fig. 3. Phase diagram of 6-TPEB, metastable phase transitions are presented as dashed lines.

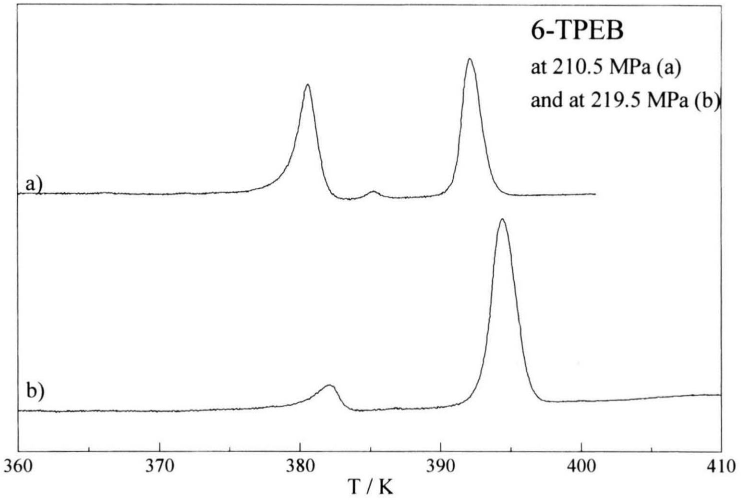

Fig. 4. DTA traces of 6-TPEB at elevated pressures, a) 210.5 MPa, without thermal treatment, b) 219.5 MPa, after annealing of 72 hours.

Table 1. Pressure dependence of the phase transition temperatures of 6-TPEB.

solid I′ → smectic B	$T/\mathrm{K} = 329.1 + 0.286\ (p/\mathrm{MPa}) - 2.28 \cdot 10^{-4}\ (p/\mathrm{MPa})^2$
solid I → smectic B	$T/\mathrm{K} = 333.5 + 0.319\ (p/\mathrm{MPa}) - 2.05 \cdot 10^{-4}\ (p/\mathrm{MPa})^2$
smectic B → nematic	$T/\mathrm{K} = 372.6 + 0.442\ (p/\mathrm{MPa}) - 2.55 \cdot 10^{-4}\ (p/\mathrm{MPa})^2$
nematic → isotropic	$T/\mathrm{K} = 403.8 + 0.557\ (p/\mathrm{MPa}) - 7.00 \cdot 10^{-4}\ (p/\mathrm{MPa})^2$

Table 2. Thermodynamic properties of 6-TPEB at normal pressure.

Transition	T/K	$(\mathrm{d}T/\mathrm{d}p)/$ $\mathrm{K\ MPa^{-1}}$	$\Delta H/\mathrm{kJ\ mol^{-1}}$	$\Delta V/\mathrm{cm^3\ mol^{-1}}$
solid I → smectic B	334.0	0.319	21.3 (21)*	20.3 (20.1)
smectic B → nematic	372.0	0.442	5.4 (5.8)	6.4 (6.9)
nematic → isotropic	403.5	0.557	2.95 (3.2)	4.1 (4.4)

* Values in brackets are obtained with the DSC92 calorimeter with somewhat different transition temperatures, see Figure 1.

smoothed by polynomials, the parameters of which are given in Table 1. Enthalpy changes were 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.

In conclusion, we note that the phase behaviour of 6-TPEB corresponds to the findings of related liquid crystals, namely 1) an increase of the nematic and smectic phase regions with increasing pressure [1, 2], 2) the observation of metastable phases [8].

Acknowledgements

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