High-pressure DTA Studies of the Phase Behaviors of 4-n-butyl-thiocyanobiphenyl (4TCB) and 4-n-pentyl-4'-n-phenyl-cyanocyclohexane (5HCP)

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DTA measurements of 4-n-butyl-thiocyanobiphenyl (4TCB) and p-cyano-p'-pentylphenyl-cyclohexane (5HCP) have been performed in the temperature range 220 K – 390 K and pressures up to 400 MPa. For 4TCB a transition from a crystalline to a liquid crystal phase (probably smectic E) could be detected at higher pressures > 90 MPa. The pressure dependence of the transition temperature has been established. At pressures lower than 88.7 MPa no transition of SmE into a crystal or into a glass has been found. For 5HCP only the melting curve was observed, in contrast to 5PCH, which displays a liquid crystalline nematic phase.

Key words: DTA; High Pressures; Phase Transitions; Liquid Crystals.

1. Introduction

The polymorphism of liquid crystalline (LC) materials can be studied using differential scanning calorimetry (DSC), differential thermal analysis (DTA), polarizing microscopy and dielectric relaxation spectroscopy [1–3]. It was found that many liquid crystals exhibit pressure-induced disordered phases [2, 3]. For 4-n-butylthiocyanobiphenyl (4TCB) the DSC and polarizing microscopy studies at normal pressure did not show any crystallization. Preliminary DSC measurements performed on heating allow to detect a very small anomaly at 218 K (the shape of which pointing rather to a glass transition than to crystallization) and then a much higher peak at 356 K [4]. The polarizing microscopy observations performed on cooling show at about 356 K the appearance of a texture typical for smectic E [5] which did not vanish down to liquid nitrogen temperatures. It was the aim of the pressure measurements (i) to find the conditions appropriate for the crystallization process and (ii) to clarify the evidence for a glass transformation. In turn, for p-cyano-p'-pentylphenyl-cyclohexane (5HCP) no LC-phase has been observed at normal pressure [6]. Therefore it should be checked, whether high-pressure DTA studies reveal new phase transitions.

2. Experimental

The molecular structures of 4TCB and 5HCP are presented in Figure 1. The 4TCB sample of 97% chemical purity was synthesized in the Military Technical University (Warsaw, Poland) by Dąbrowski. 5HCP was provided by Prof. de Jeu (Amsterdam, The Netherlands). The high-pressure DTA studies have been carried out with the help of computer-assisted equipments described in [7]. The measurements were performed in the temperature range from 220 K to 390 K on heating the sample at several pressures up to 400 MPa. To cover the whole pressure range two apparatus were used. In order to grow a crystal the sample was annealed during about 24 hours at several temperatures and pressures.

3. Results and Discussion

3.1 Butyl-thiocyanobiphenyl (4TCB)

In DTA measurements of 4TCB performed on heating at several pressures up to 110 MPa the anomaly con-
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The transition temperature of the smectic E - isotropic transition was observed. It was found that the transition temperatures increase linearly with pressure. In order to grow the crystalline phase from the smectic E phase with the help of a higher pressure the sample was annealed for 24 hours at 233 K and 215 MPa. Then, on slow heating the sample, a second small anomaly was detected in the DTA curve at 335.3 K. Later the same feature was found for several pressures up to 400 MPa at higher transition temperatures. The anomaly was identified as being connected with a second transition from crystal into smectic E phase, as the values of the transition temperatures were much lower than those expected for the SmE - isotropic transformation. The next goal was to observe a DTA curve that reveals both anomalies at the same pressure. It was expected to be observed at lower temperatures; for higher pressures the clearing temperature is beyond 390 K, which is the limit of the available temperature range. Thus, the pressure was reduced slowly, and at 88.7 MPa the anomaly connected with Cr - SmE was observed at 306.5 K. Then the temperature was increased slowly, and at 385.2 K the second anomaly connected with the transition from SmE - isotropic was found at somewhat higher pressure, i.e. at 99.2 MPa. Figure 2 presents the DTA curve with these two anomalies. It was found that further reduction of the pressure does not result in detection of the Cr - SmE transition, even after 24 hours of annealing. For pressures lower than 88.7 MPa the sample is still in the smectic E phase and may after supercooling transform into a glassy state as in polarizing microscopy observations at normal pressure. There a lowering of the temperature leads to a darkening of some parts of the microscopic image of the sample and to the appearance of fractures which disappear on heating [1, 4].

The phase behaviour under pressure is presented in Figure 3. The pressure dependence of the transition temperatures $T(p)$ for the two phase transitions is well described by the following polynomials:

$$S_{mE} - I: \quad T(p)/K = 355.3 + 0.322 (p/MPa) - 2.0 \times 10^{-2} (p/MPa)^2,$$

$$Cr - S_{mE}: \quad T(p)/K = 285.2 + 0.238 (p/MPa) - 0.46 \times 10^{-4} (p/MPa)^2.$$

The details of pressure and temperature conditions during annealing the sample are presented by squares and circles (explaining the starting conditions), and arrows showing the direction of changes. The dashed part of the lower line $T(p)$ exhibits the range of pressure where the sample exists in the smectic phase only. One can expect that below that $T(p)$ the smectic phase can be supercooled yielding a glass. There are two points marked by asterisks which show the transition temperatures (356 K and 218 K) observed in DSC at atmospheric pressure. The point with higher $T$, corresponding to SmE - isotropic transition, coincides well with the result from the pressure studies. The point with small $T$ lies definitely below the temperature which is extrapolated from the high pressure data. It seems that it corresponds rather to the temperature of transformation between the SmE phase and a glass G. DSC studies at atmospheric pressure with a scanning rate of 10 K/min detect the transition as a very small anomaly on cooling at 215 K and at heating at 218 K. Detailed description of the SmE - G transformation requires further studies. Although many different thermal treatments have been employed, it was not pos-
Table 1. Thermodynamic properties of 4TCB.

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<tbody>
<tr>
<td>SmE – Isotropic</td>
<td>355.3</td>
<td>12.09</td>
<td>34.0</td>
<td>10.96</td>
<td>0.332</td>
</tr>
<tr>
<td>Cr – SmE</td>
<td>285.2</td>
<td>3.8</td>
<td>13.4</td>
<td>3.2</td>
<td>0.238</td>
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In Table 1 the thermodynamic data for 4TCB estimated for phase transitions at atmospheric pressure.

The volume changes ΔV for SmE–I were estimated using the Clausius-Clapeyron equation. The transition enthalpy ΔH = 3.8 kJ/mol for the Cr–SmE transition (not observed at atmospheric pressure) was estimated from the ratio of the transition enthalpies at 88.7 MPa, i.e. 1 : 3.2, assuming that it is independent of the pressure. The same procedure was used for the calculation of the entropy and volume changes.

4TCB displays no nematic phase. Thus, it seems clear that the melting is connected with much smaller changes on the molecular level of the sample than the transition at the clearing point, in accordance with the ratio of the enthalpy changes. In the so-called low-temperature smectic E phase the 3-d positional order of the centers of gravity of 4TCB molecules as well as the long range orientational order of long molecular axes does not differ much from the case of the true crystal. During melting the molecules gain only a freedom of π-rotation and thus the ability of the ±direction of the long axes, while at the clearing point both the 3-d positional and orientational order is lost. The small ΔH, ΔS, and ΔV values at melting and the large ΔH, ΔS, and ΔV values at the clearing point reflect the relation between the magnitudes of those changes. Contrary to that for liquid crystalline materials possessing the nematic phase, the enthalpy changes are much larger for the solid – nematic transition than for the nematic – isotropic transition. For example for 5CB [3, 9] ΔH(Cr–N) = 13.4 kJ/mol and ΔH(N–I) = 0.33 kJ/mol. It seems worth to note that the sum of the transition enthalpies from the solid to the isotropic phase is nearly the same in both 4TCB and 5CB. For 6CHBT, a bit longer molecule [3] with the same CNS group as 4TCB (but with the hexane ring instead of benzene ring), the respective values are different, but the tendency observed is the same as for 5CB, i.e. ΔH = 26.8 kJ/mol at melting is much larger than ΔH = 1.6 kJ/mol at the clearing point. The much longer 6TPEB molecule [2] with CNS group reveals the most pronounced thermal effect at the solid – smectic B transition (ΔH = 21.3 kJ/mol). It is much larger than the effect at the smectic B – nematic transition (ΔH = 5.4 kJ/mol) and at the clearing point (ΔH = 2.95 kJ/mol). The mutual ratios of volume changes accompanying those transitions are similar to the ratios of the respective enthalpy changes. For 4TCB the pressure influence on the transition temperatures is more pronounced at the clearing point (ΔT/Δp = 0.33 K/MPa) than at melting (ΔT/Δp = 0.24 K/MPa). For liquid crystals with a nematic phase that tendency is the same, i.e. at the clearing point ΔT/Δp = 0.4 K/MPa is larger than at melting ΔT/Δp = 0.3 K/MPa [2, 3]. The values ΔT/Δp observed for liquid crystals at melting seems not to differ much from those observed for some plastic crystals [3, 7, 8].

3.2 Cyano-pentylphenyl-cyclohexane (5HCP)

In Fig. 4 we present the transition points, which have been observed under pressure. Their extrapolation to atmospheric pressure gives the melting temperature found previously. No other phase transition has been detected. The absence of a liquid crystalline phase even under high pressure seems to be an interesting experimental fact. Compounds with similar shape and length of molecules like 5CB with two phenyl rings, 5CCH with two cyclohexyl rings [10, 11] and 5PCH, where in comparison with 5HCP only the positions of phenyl and cyclohexyl rings are interchanged, all exhibit liquid crystalline phases [12]. There is a wealth of experimental data concerning the relationship between the mesomorphism and chemical constitution of rod-like molecules [13]. Unfortunately there is still lack of detailed theoretical predictions explaining the observed polymorphism by means of the molecular structure [14, 15]. Ordering of molecules leading
to an anisotropic phase is determined by many factors like sterical factor, anisotropy of electron polarization of molecules, dispersion forces between molecules and electron conjugation in molecular units. These factors are not the same for 5HCP and 5PCH.

4. Final Remarks

For 4TCB no transition of the smectic E to glass was found in the DTA studies. This can be caused by the fact that the DTA signal due to glass transition is generally very small [16]. But more important is that increasing the pressure applied to the sample during the annealing procedure favours the conditions for growth of crystalline nuclei into the crystal phase. Increase of pressure has a similar result as decrease of temperature. Application of pressure accelerates the kinetics for crystallization, lowering the annealing time. It can be observed that the higher the pressure the larger the melting and clearing temperatures as well as the temperature ranges of existence of crystalline and smectic phases. This agrees with the conclusions of experiments performed for other liquid crystalline materials [12].

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