Differential Thermal Analysis under Pressure on Cyanocyclohexane, 1,2,3,4-Tetrahydro-5,6-dimethyl-1,4-methanonaphthalene, and 2-Methyl-2-propanol

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Differential thermal analysis has been performed on cyanocyclohexane (CCH), 1,2,3,4-tetrahydro-5,6-dimethyl-1,4-methanonaphthalene (TDMN), and 2-methyl-2-propanol (t-butanol) up to 300 MPa. The latter compound was also investigated dielectrically. CCH displays an ODIC phase that transforms only reluctantly to the low-temperature stable phase II. Annealing under pressure can appreciably accelerate this transformation. For all three compounds the phase diagrams were established. For CCH and TDMN also the pressure dependence of the glass transition has been determined.

Key words: High pressure; DTA; Phase transitions; Glass transition; Dielectric constant.

1. Introduction

Globular molecules are well-known candidates for "plastic crystals" [1]. Due to the ease of rotational motions in the solid state they form orientationally disordered phases (ODIC). These crystals exhibit low values for the entropy of fusion, whereas large enthalpy and volume changes are observed at an order disorder transition. Cyanocyclohexane (CCH) is a typical representative that has attracted much attention in the past [2]. This compound can be readily undercooled to the glassy state, but it crystallizes to the low-temperature stable phase II only reluctantly. Also 2-methyl-2-propanol (t-butanol) is of approximately globular shape, and in fact it displays several solid state transitions [3]. However, its phase situation is not yet clear. 1,2,3,4-tetrahydro-5,6-dimethyl-1,4-methanonaphthalene (TDMN) is a new compound that was recently synthesized and characterized by ^{13}C-NMR [4, 5]. In order to get more insight in the phase behaviours of these three compounds we performed a detailed DTA study.

2. Experimental

For details of the high pressure equipment used for the DTA [6, 7] and the dielectric measurements [8, 9]

cf. the citations. CCH (97.0%) was obtained from Merck, Germany, and purified with preparative gas chromatography. Tertiary butanol was obtained from Aldrich, dried with molecular sieve and distilled under a high reflex ratio, after which the purity was 99.8%. TDMN was synthesized by Andreas Dölle [4] and analysed by gas chromatography.

3. Results

3.1. Cyanocyclohexane

The phase diagram is presented in the Fig. 1, showing also the pressure dependence of the glass transition (T_g). The DTA signal due to the glass transition was very small and therefore detectable only in a limited pressure range, just sufficient to determine the initial slope dT_g/dp. As mentioned in the Introduction, it is extremely difficult to crystallize CCH in the low-temperature phase II. In a previous DSC study the crystallization was not achieved at all [2]. Using adiabatic calorimetry the same group succeeded in getting the phase II after a tedious annealing procedure [10]. The formation of the phase II can be significantly accelerated by the application of pressure [11]. It is advantageous to employ the following procedure: first to pressurize at room temperature, then to cool down and anneal under pressure, to decompress and to heat up at ambient pressure. Such a "detour" reduces the annealing time to a few hours, as opposed to thermal treatment of several days in atmospheric pressure
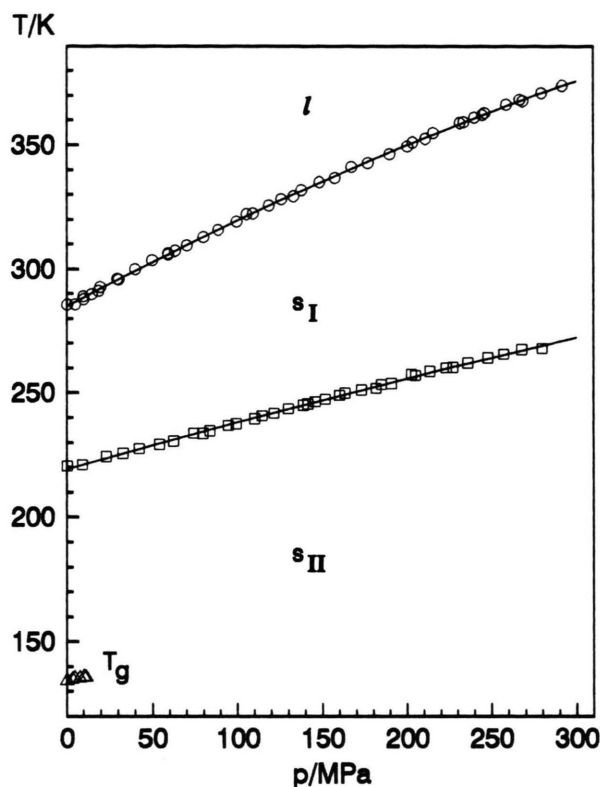
Fig. 1. Phase diagram for cyanocyclohexane. The glass transition (T_g) was only detectable in a limited pressure range.

Fig. 2. DTA traces for cyanocyclohexane, showing the solid II–I transition and melting at normal (a) and higher pressures (b).

Table 1. Thermodynamic properties connected with the phase transitions of cyanocyclohexane at 1 atm.

Transition	$\dfrac{T}{K}$	$\dfrac{\Delta H}{kJ\,mol^{-1}}$	$\dfrac{dT/dp}{K\,MPa^{-1}}$	$\dfrac{\Delta V}{cm^3\,mol^{-1}}$	Ref.
Solid I–	285.4		0.368	4.7	[7]
liquid	285.1	3.635			[10]
	281.9	3.88			[2]
Solid II–I	220.4		0.195	6.6	[7]
	215.0	7.425			[10]
Glass	134.0		0.14		[7]
transition	133.5				[10]
	134.7				[2]

studies. Even then, the solid II–I transition appears only sluggishly at atmospheric pressure. In Fig. 2 some DTA traces are presented, showing the transitions at ambient and elevated pressures. When the sample was cooled under pressure and reheated, an exothermic anomaly occurred due to the sol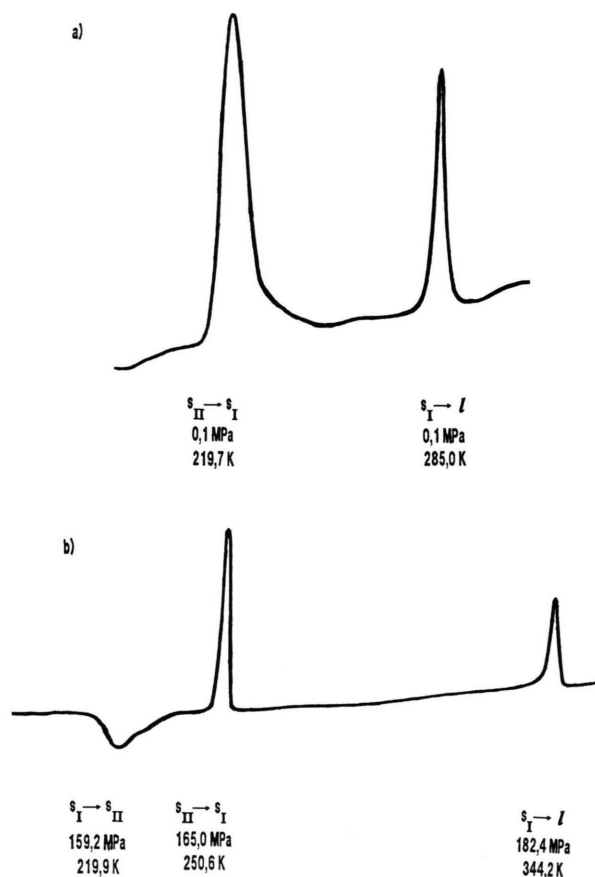id I–II conversion, immediately before the solid II–I transition takes place. At atmospheric pressure such an exothermic peak is not detectable because the solid I–II conversion needs much more time.

Some thermodynamic quantities are gathered in Table 1 and compared with literature data. The volume changes have been estimated with the aid of the Clausius-Clapeyron equation, using the enthalpies from Pinvidic [10]. A significant lower temperature was found for the solid II–I transition. This discrepancy is probably connected with the peculiar obstructions of the phase transition. There is good agreement for the melting and the glass transition temperatures.

The DTA transition temperatures have been smoothed by polynomials, yielding

melting:

$$T/K = 284.8 + 0.368\,(p/MPa) - 2.15 \cdot 10^{-4}\,(p/MPa)^2,$$

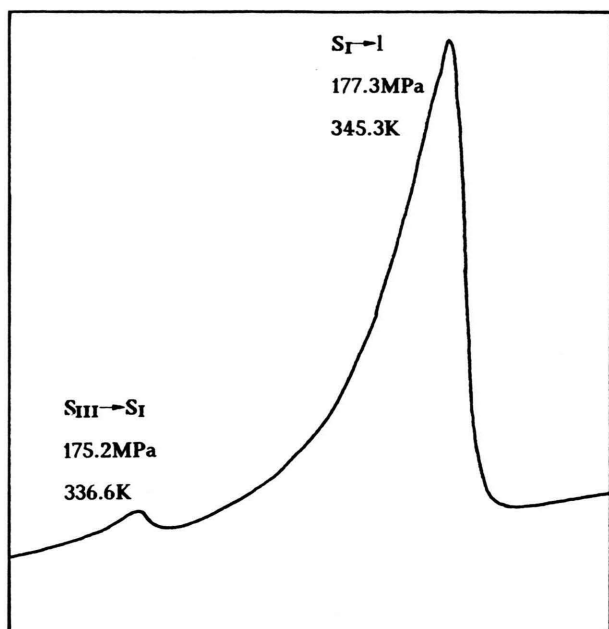Fig. 3. DTA traces for 2-methyl-2-propanol, showing the melting peak and the preceding solid III–I transition.

Fig. 4. Static permittivity of 2-methyl-2-2-propanol as a function of temperature at ambient pressure and 40 MPa.

Fig. 5. Phase diagram for 2-methyl-2-propanol. Solid line: melting (SI-l), dashed line: solid III–I transition.

solid II–I:

$$T/K = 219.2 + 0.195 \, (p/\text{MPa}) - 0.6 \cdot 10^{-4} \, (p/\text{MPa})^2,$$

3.2. 1,2,3,4-Tetrahydro-5,6-dimethyl-1,4-methanonaphthalene

The molecular structure of TDMN is rigid and asymmetric [4]. The shape deviates much from globularity, and therefore ODIC phases with low melting enthalpy are not expected. Surprisingly, only one transition, accompanied by a very small enthalpy change, has been found, although various thermal treatments have been employed. The shape of the DTA peak, however, looks rather like a glass transition. The pressure dependence of this transition is given by

$$T/K = 188.3 + 0.20 \, (p/\text{MPa}) - 6.6 \cdot 10^{-5} \, (p/\text{MPa})^2.$$

The slope dT/dp (0.20) is close to dT_g/dp for CCH (0.14), which in turn is significantly lower than the slope 0.37 for the melting curve of CCH. Similar results for the melting [12] and the glass transition [13] have been found for other plastic crystals. The unique DTA signal revealed in the measurements for TDMN is supposed to indicate the glass transition temperature.
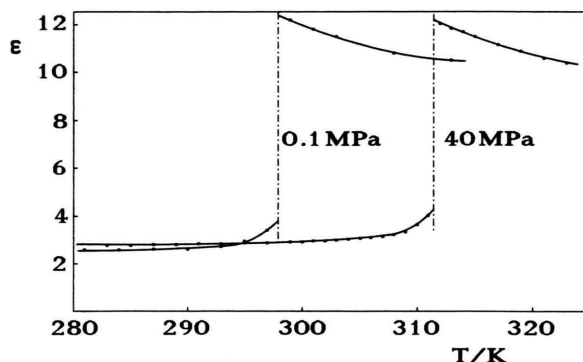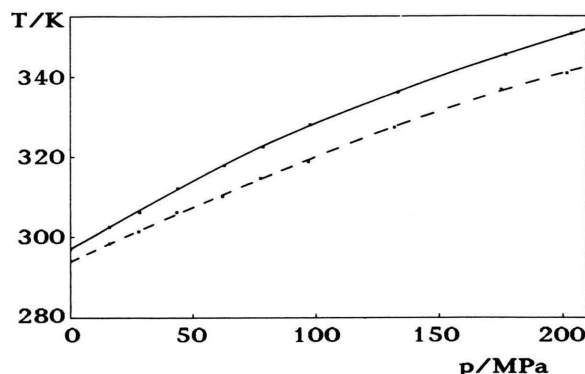
3.3. 2-Methyl-2-propanol

For this compound, two stable solid phases I and II and one metastable phase III are reported [3]. The solid I phase melts at 299 K with a low entropy of fusion and was therefore considered to be a rotator phase. All three phases could be identified by infrared spectroscopy, according to which phases I and III are disordered crystals built on chain polymers [14]. On the other hand, there is no evidence of a rotator phase due to a previous dielectric investigation [15].

In the present DTA study only one solid solid transition, preferably at higher pressures could be observed, appearing as a small peak immediately before the melting (see Figure 3). On cooling, however, the DTA traces sometimes revealed two transitions that are ascribed to the freezing to solid I and the solid I–II transition. The solid transition observed on heating is extrapolated to ambient pressure, yielding

294.3 K. This value is close to 294.5 K reported for the solid III – I transition, although there is not any indication of the solid II – III transition in the DTA traces. Therefore dielectric measurements were additionally performed in order to clarify the phase transitions.

Several runs have been carried out at ambient pressure in the freezing region. Low values of 2.5 are found for the permittivity in the solid state. Immediately below the melting temperature ε gradually increases, but there is no step indicating a solid phase transition (Figure 4). A similar behaviour was observed by Neu at atmospheric pressure [15]. Runs at higher pressures were hindered by pressure gradients in the brittle solid phase that limited the reproducibility of the measurements in the premelting region. Anyway, apart from

the melting no additional phase transitions could be detected. The phase diagram is shown in Figure 5.

From the static permittivity of liquid t-butanol we may derive the Kirkwood-g-factor [16]. At atmospheric pressure and room temperature $g \approx 2$, that is appreciably lower than g-factors for other alcohols [12, 17]. The smaller value for t-butanol is obviously caused by the steric hindrance of the tertiary butyl group [18].

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