

PHASE TRANSITIONS OF ODD *n*-ALKANES OF HIGH PURITY — PRESSURE DEPENDENCE OF THE
TRANSITION TEMPERATURES DETERMINED BY HIGH PRESSURE DTA

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ABSTRACT

Polymorphic transitions of *n*-pentacosane, *n*-heptacosane and *n*-tritriacontane were examined under high pressure up to 500 MPa by high pressure DTA. The samples used were very pure and showed at atmospheric pressure solid-solid transitions, whose number depends on the carbon number in a molecule, beside the rotator transition. Their phase diagrams are presented. As well as the rotator phase, the other high temperature phases showed the upper pressure limit for their existing regions.

INTRODUCTION

Solid-solid transition of *n*-alkanes has been discussed, from an early stage of its studies, in correlation to molecular motion of the chain molecule in a crystalline lattice. In this case, the transition was a change of a stable phase at room temperature to a phase called the rotator phase. Recent studies, however, elucidated the complex polymorphic phase behavior of *n*-alkanes, especially the odd ones. Strobl and co-workers (ref. 1) reported that for *n*-tritriacontane (abbreviated by C₃₃) a stable orthorhombic phase A passes through phase B and C to the rotator phase D. Packing modes of the chain molecule for these phases were also determined. We studied the polymorphic transitions of some *n*-alkanes from C₃₂ to C₆₉ (ref. 2). All the *n*-alkanes examined showed the phase C below the rotator or melting transition irrespective of the parity of the carbon number. The phase C for higher homologues complicated oblique structures. Solution-crystallized samples of C₃₇ and C₄₅ have four modifications, as does C₃₃. On the other hand, Snyder and co-workers (ref. 3) found that C₂₅, C₂₇ and C₂₉ show another transition at lower temperatures. This transition is very weak and seems to have been missed before. It is necessary to get more precise information on these polymorphic transitions in many aspects. An important point in doing this work is to use the purest samples free from homologues. Otherwise the transitions become obscure. This report concerns one of our experiments on the phase behavior of pure C₂₃ to C₃₅.

The work on phase diagrams of *n*-alkanes has shown the existence of the triple point of the rotator phase / the stable phase / liquid (ref. 4-8). There has been

no report on the phase diagram of these weak solid-solid transitions. While the rotator transition leads to a large change in lateral packing of the chains, the high temperature phases of B and C maintain the same subcell structure as the orthorhombic phase has. We want to find out how these structural features, which accompanied in the transitions, affect the phase diagrams. We anticipate this will throw some light on understanding the intrinsic nature of *n*-alkane crystals.

In general, thermal analysis is a useful means to study subtle transitions. Here, we will describe a high pressure DTA to be used in this study. It enabled us to detect the weak transitions even under high pressures.

EXPERIMENTAL

Samples

Both *n*-pentacontane (C_{25}) and *n*-heptacontane (C_{27}) were synthesized, respectively, from *n*-tridecanoic acid and *n*-tetradecanoic acid through ketene dimer. A detailed description will be given elsewhere. The samples were finally purified by a preparative GPC [column: HF2003 2 x 20 mm ϕ x 500 mm (Showa Denko)]. By using GC [column: silicone OV-17 (Shimazu)] their purities were determined as above 99.9 %. The sample used of *n*-tritriacontane (C_{33}) was the same described in ref. 2. Its GC purity was over 99.9 %.

Apparatus

A DTA assembly was installed in a cylindrical pressure vessel, whose inner diameter was 25 mm. Sensors were supported on a top plug and a heater on a bottom plug (see Fig. 1-a and -b). The heater consisted of a Ni-bobbin (1) fitted with a pyrophyllite sleeve (2), on which a heater wire was wound noninductively.

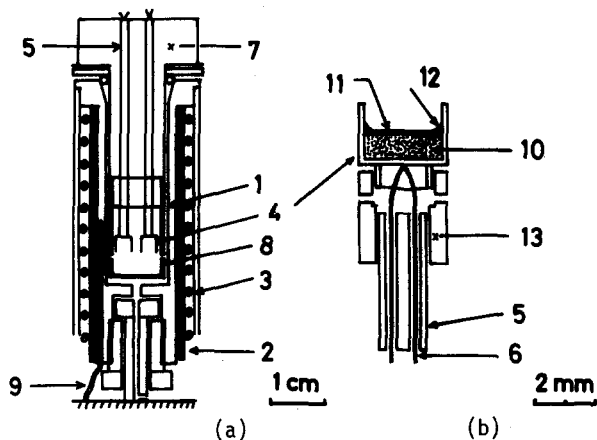


Fig. 1. Drawings of (a) DTA assembly and (b) details of the sensor (see Text)

The wire was coated with Sauereisen No. 8 cement. A sheathed thermocouple for temperature control (9) was placed in a groove of the bobbin. A sample container was a cup (4) made of platinum-rhodium alloy, whose size was 2.6 mm in diameter and 2 mm in depth. Alumel-Chromel thermocouple (6) was soldered on the bottom of the cup. It was supported on a ceramic tube (5). A Cu-made enclosure (8) was placed around the sensors in order to reduce thermal noise by convection. The tube was fixed by a holder (7) made of Macor glass. Detailed construction of the sensor is shown in Fig. 1-b. A sample (10) was placed in the cup and covered with a lead lid (0.15 mm thick) (11). The sample was sealed completely from a pressure transmitting liquid by using epoxy resin (12). Hydrostatic pressure in the liquid was anticipated to completely transmit to the sample. This type of sensor follows the design of high pressure quantitative DTA (ref. 9) and, in addition, has good durability.

The high pressure DTA system is schematically illustrated in Fig. 2. Hydrostatic pressure in dimethylsilicone oil (10 cS) generated by a pump was fed to the DTA vessel through a container for a manganin gauge. This DTA system with the inside heater resulted in a large change in pressure during DTA runs due to its relatively large dead volume in the vessel. A pressurestat was installed. Its principle is based on thermal pressure effect of the liquid. Another pressure vessel was connected, in which a heater similar to that used for the DTA was set. Deviation from an equilibrium of the manganin bridge was compensated by controlling the heater current. Overheating of the pressurestat heater arising from a sudden leakage in pressure was protected. The vessel was cooled to obtain a satisfactory cooling rate. Variation in pressure on present work was within 0.1 MPa. The DTA vessel had a cooling jacket and was held at a low temperature by a bath cooler (Neslab). Rigaku's PTC-10 and DTA-6 were used as

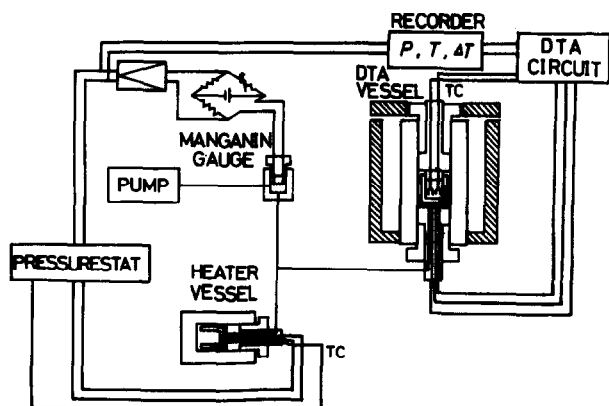


Fig. 2. Schematic diagram of high pressure DTA system (see Text).

an electrical system for DTA measurements. The calibration of the thermocouple was performed using the melting point of Ga (302.8 K at 10.0 MPa), In (430.3 K at 10.0 MPa), and Sn (505.3 K at 10.0 MPa). The sample temperature recorded on a chart was read with ± 0.1 K. The manganin gauge was calibrated against the fixed point, 756.9 MPa at 273.2 K.

RESULTS AND DISCUSSION

Odd *n*-alkanes ranging from C_{25} to C_{33} were verified to show the δ transition reported in ref. 3. Holding the notation for the phases proposed in ref. 1, the phase just above the δ transition is called phase A'. The heat of the transition is very small (an order of 0.5 KJ/mol). Its powder X-ray diagram did not show any distinct structural change from the phase A. Table 1 lists the transition temperatures of C_{25} , C_{27} and C_{33} , determined at atmospheric pressure by DSC (5 K/min). For the determination of the A \rightarrow A' transition a large sample size of 4 mg was needed. Others were determined on 1 mg sample. All the samples were crystallized from the melted liquid at a cooling rate of 0.625 K/min. Although ref. 3 and 10 reported that C_{25} has the phase B just below the rotator transition, the phase disappeared as the sample purity increased. We missed the A \rightarrow A' transition of C_{33} in the previous work (ref. 2).

Bulk crystallization of the chain molecule probably resulted in crystal imperfection when structural change in the obliquity occurred during cooling. It is desirable to use thick solution-crystallized crystals. At atmospheric pressure single crystals of C_{33} gave sharper transition peaks than bulk crystals did. But, the peak positions were almost identical. Fig. 3-a shows a comparison of DTA curves at 10 MPa for C_{33} samples different in crystallization condition: 1) cooled at a rate of 2 K/min at the pressure and 2) crystallized from dilute solution at atmospheric pressure. The latter shows broad peaks. Pressurization seems to have introduced some kind of defect in the crystals. To discern the A \rightarrow A' transition the measurements were done on large size sample. At this low pressure C_{33} has five modifications as at atmospheric pressure. Other transition temperatures were determined on sample of small size. In Fig.

TABLE 1

Solid-solid transition temperatures for *n*-alkanes at atmospheric pressure

<i>n</i> -Alkanes	Transition temperature ^a /K			
C_{25}	313.5/A \rightarrow A'			320.1/A' \rightarrow D
C_{27}	316.1/A \rightarrow A'	323.2/A' \rightarrow B		325.6/B \rightarrow D
C_{33}	320.7/A \rightarrow A'	330.3/A' \rightarrow B	339.3/B \rightarrow C	341.4/C \rightarrow D

^aLetters denote the phases. see Text.

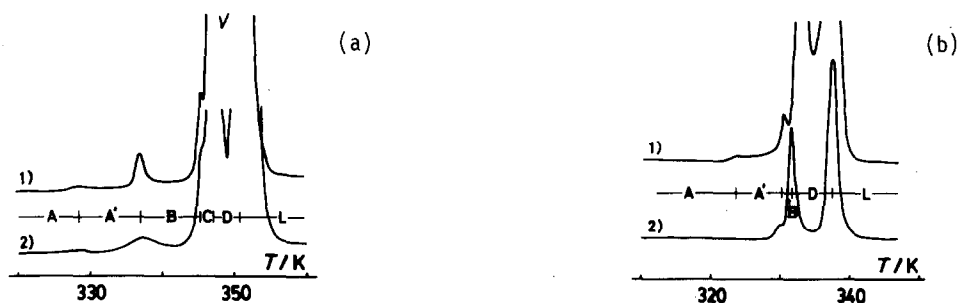


Fig. 3. Comparison of high pressure DTA curves. (a) crystallization conditions for C_{33} (see Text) and (b) sample size for C_{27} , 1) 4 mg and 2) 1 mg.

3-b, the effect of sample size on the DTA curve is seen. Fig. 4 shows some DTA curves of C_{33} for different pressures. Only the low temperature side of the curve is drawn to indicate clearly the $A \rightarrow A'$ and the $A' \rightarrow B$ transition peaks. The steep rise is due to the rotator transition. Even at 150 MPa the $A \rightarrow A'$ peak can be detected. The gradual rise near the rotator transition may be ascribed to a temperature gradient in the sample cell.

Phase diagrams are shown in Fig. 5. They are complicated, but the existing regions of the phase A' , B and C, as well as the rotator phase, are limited. Initial values of the pressure coefficient of the transition temperature, $(dT/dP)_0$ are listed in Table 2. The $A \rightarrow A'$ transition gives the highest value of $(dT/dP)_0$ and the melting of the lowest. The table suggests a correlation between the initial slope, that is, the ratio of the volume change of transition to the entropy change and the changes in packing modes of the chain molecule. A more detailed discussion has been left for a future study.

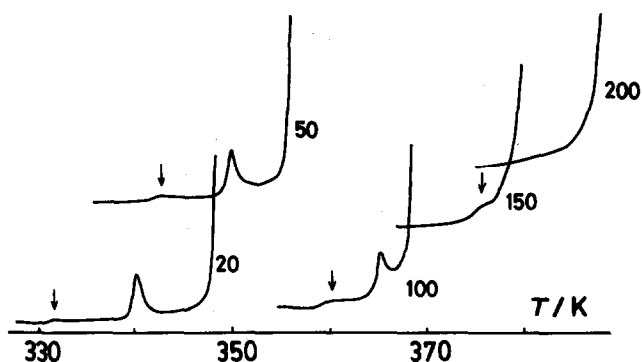


Fig. 4. DTA curves for C_{33} at different pressures, with attention to the $A \rightarrow A'$ (by an arrow) and $A' \rightarrow B$ transitions. Numerals are pressure in MPa.

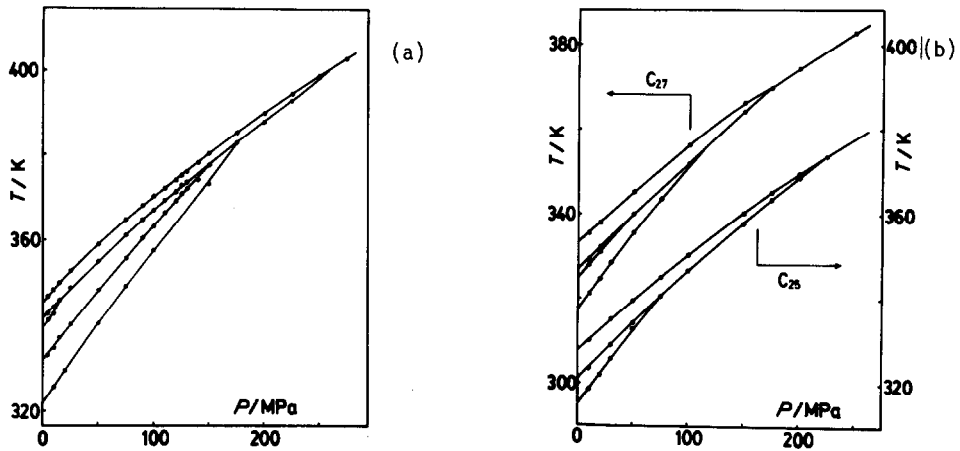


Fig. 5. Phase diagrams of *n*-alkanes. (a) C_{33} and (b) C_{27} and C_{25}

TABLE 2

Initial slope of the transition temperatures against pressure

<i>n</i> -Alkanes	$(dT/dP)_0 / K/100 \text{ MPa}$				
C_{25}	36.4/A → A'			28.5/A' → D	22.6/melting
C_{27}	39.0/A → A'	(33) ^a /A' → B		(27) ^a /B → D	22.2/melting
C_{33}	38.8/A → A'	34.1/A' → B	(30) ^a /B → C	(28) ^a /C → D	26.4/melting

^aNumerals in the parenthesis were estimated from two experimental points.

The triple point of liquid/D/A is 225 for C_{25} , 175 for C_{27} and 245 MPa for C_{33} , respectively. These values are nearly the same as those reported by Würflinger and Schneider (ref. 6). There, however, is no distinct correlation between the triple point and the chain length.

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