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Effect of Sample Weight on Micro DSC Measurements of Heptacosane

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Micro DSC measurement of solution-crystallized heptacosane was confirmed to be reliable down to a sample weight of 0.01 mg order. However, a close contact between the sample of such a slight amount and the sample pan resulted in a decrease in the transition enthalpy. This effect was interpreted from an entropic standpoint.

In recent years there has been an increased interest in the growth mechanism and aggregative states of vacuum-deposited chain molecules. DSC measurements could be utilized as one of characterizing methods. When deposited on metal foil, the sample can be punched out with the substrate and used as a DSC specimen. Amount of deposited samples usually ranged up to 0.15 mg/cm^2. The sample weight of the DSC was of the order of 0.01 mg/punch. Because heat-flux type DSC instruments which are currently available have a good sensitivity even at a low scanning rate, they may be applied to the thermal characterization of the deposited samples. Since the sample weight mentioned above is extremely small, it is desirable to examine the effect of the sample weight on the DSC. This paper concerns on the micro DSC of pure heptacosane (abbreviated as C27) crystallized from dilute solution as a preliminary study for the deposited sample. It was noticed that a kind of surface effect could not be ignored in the measurements when the sample weight was decreased and the sample was in close contact with the sample container.

The C27 sample used was synthesized through ketene dimerization reaction from tetradecanoic acid chloride. Tetradecanoic acid free from homologues was obtained by using a preparative liquid chromatography. Details of the purification and synthesis were described in a previous paper.1) The purity of the C27 sample was 99.98% by a capillary gas chromatography (Shimadzu GC-14A with a column of CBP1-M25-025, eluted at 260 °C). The sample was crystallized by slow cooling to 2 °C from a 1% hexane solution and filtered off at the temperature.

A Rigaku DSC 8240 was used. Temperature calibration was performed with the melting point of In and the equilibrium melting point of C27, which we determined as 332.0 K.1) Transition heat was calibrated by using In and Ga. A scan rate of 0.5 K/min was used as a standard one. Signals obtained were treated by a personal computer.

Recent studies on phase transitions of pure odd *n*-alkanes revealed that they showed several solid-solid transitions, on which the type of subcell structure did not change, below their hexagonal or melting transitions.2-5) C27 transforms from the orthorhombic phase (abbreviated as A) through a monoclinic modification of the space group Aa (abbr. B) to the hexagonal phase (abbr. H), and then melts. With an assumption that experimental base line may be expressed as a quadratic curve over the whole, it was determined by a least squares method from the data points over about 307-314 and 334-339 K, and used for the curve drawing and the calculation of transition heat. The DSC curves in Fig. 1 show three transitions described above. The enthalpy changes for the A→B, B→H, and melting transition were 2.9, 28.8, and 65.8 kJ/mol, those were determined on the sample of 1.30 mg. From an enlarged drawing of the DSC curve, a very small peak could be discerned at 316.9 K, whose area corresponded to 0.2 kJ/mol. Although this transition seems to be first-ordered, it is disregarded in this work because of its subtleness.

Figure 1 clearly shows that even if the DSC sample weight is decreased to one hundredth of a usual weight of mg order, the smallest peak can be discerned despite of relatively large S/N ratio. Temperature read off from an intersection point on the melting peak front was identical irrespective of the sample weight. This temperature was calibrated to the equilibrium melting point of 332.0 K. The A→B and B→H transition temperatures were also independent of the sample weight, and 324.4 and 326.5 K, respectively. Small peaked shoulder below the B→H peak of the curve a and b in Fig. 1 may result from that the solution-crystallized *n*-alkanes are generally less stable than bulk-crystallized ones.

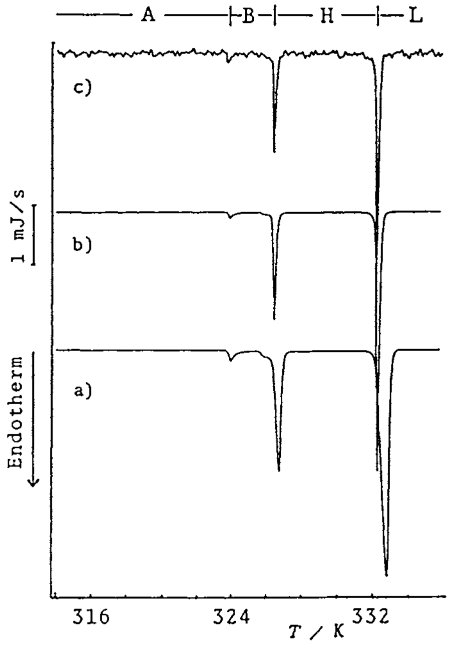

Fig. 1. DSC heating curves of C27. Heating rate: 0.5 K/min. Sample weight in mg and magnification: a) 1.30, x1 b) 0.13,x5 c) 0.013,x50; On the upper the phase notations are given.

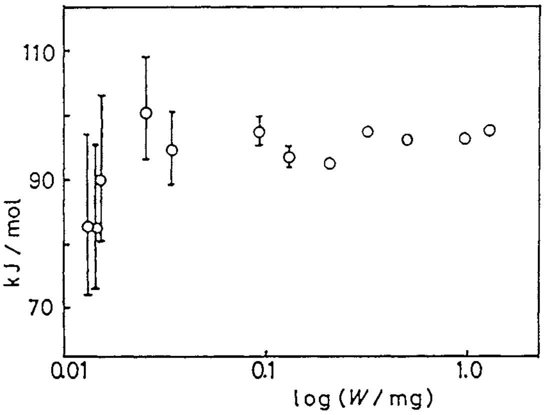

Fig. 2. Total transition enthalpy of C27 *vs.* logarithm of the sample weight. On error bar, see text.

In Fig. 2 the sum of the transition enthalpies is plotted against logarithm of the sample weight. Error bars on the data points represent uncertainty calculated from probable error in weighing. A micro balance (Metler M5SA) was used, whose accuracy was of the order of ± 2 μg. It may be said that the total transition enthalpy can be determined irrespective of the sample weight, although the error becomes very large on the sample of 0.01 mg order.

While the definite values on the transition temperatures and enthalpy were obtained from the usual DSC procedure on the micro samples, the second and third run of the C27 sample of 0.013 mg gave peculiar DSC curves, as shown in Fig. 3 a and b. These runs were done on the sample that was slowly cooled (about 3 K/min) in the DSC furnace after the heating scan. The B→H and melting peaks become broad and doubled. The A→B peak can not be discerned. For the 2nd run of the 0.13 mg sample (curve c) the A→B transition temperature becomes higher by 0.6 K than that of the 1st run and the peaked shoulder below the B→H peak disappears. These features agree with those observed on the bulk-crystallized sample.[1)]

In Fig. 4 the ratio of the total transition enthalpy of the 2nd to that of the 1st run is plotted as a function of the sample weight. That the ratio decreases steeply below 0.1 mg suggests the existence of a kind of surface effect. The ratio of the 3rd run to the 1st becomes lower than that for the 2nd. Error bars were calculated with an uncertainty of ± 0.2 mJ in the peak area determination. GC examination on the sample after the multiple run did not show any indication of thermal degradation.

It can be presumed that the surface effect correlates to a close contact of the sample with the surface of the aluminium sample pan. The situation is demonstrated in SEM photographs of Fig. 5. The photo a shows two pieces of solution-crystallized C27 (about 0.015 mg) placed on a sample pan. Thermal history similar to the DSC 1st scan was given to them (the photo b). After the heating up to a temperature about 15 K higher than the melting point, a part of the specimens transforms to thin layer, as shown as the dark part in the photo. The observation under a high magnification showed that the thin layer was composed of lamellar texture. When the sample was enclosed by crimping a pan with a cover, it transformed more effectively to such thin layer. The layer being in a close contact with the metal surface may lead to the anomalous thermal behavior.

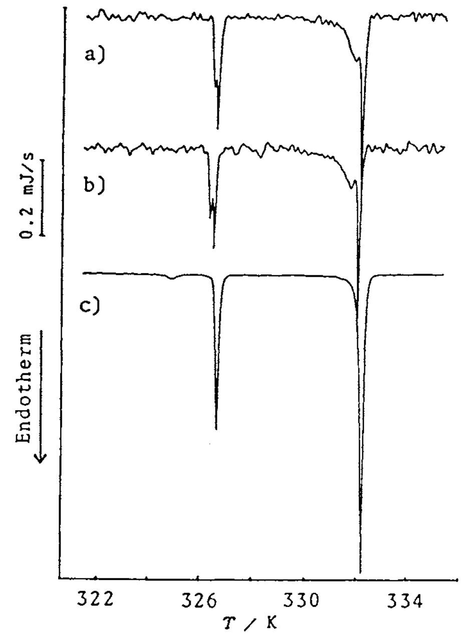

Fig. 3. DSC heating curves of C27. a) 2nd and b) 3rd run of the 0.013 mg sample; c) 2nd run of the 0.13 mg sample.

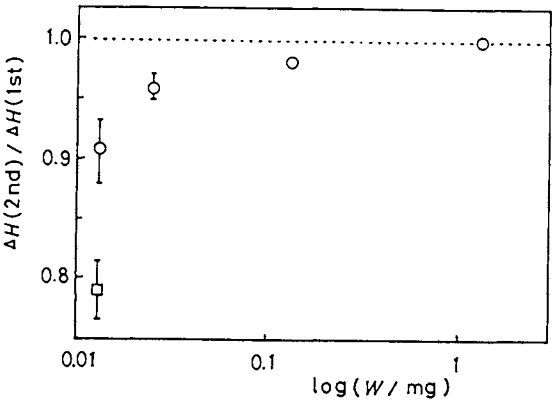

Fig. 4. Ratio of total transition enthalpy for the 2nd ( ) and 3rd run ( ) to that for the 1st run as a function of the sample weight.

Shibasaki already reported a kind of surface effect on DSC sample pan on micro DSC on the melting of stearic acid.[6)] With decreasing in the sample weight, the melting point decreased while the melting enthalpy increased. That was ascribed to a strong interaction between the carboxylic group and the aluminium surface.

In the present case of the non-polar *n*-alkane, the anomaly was observed only when the sample of 0.01 mg order was in the close contact with the metal surface. In this connection, it may be desirable to reexamine Shibasaki's data from the viewpoint of the degree of contact of the sample with DSC pan and of an accuracy of the sample weighing. We assume that on the 1st run there is no surface effect. The SEM observation confirmed that C27 molecules in the thin layer crystallized with vertical orientation of their axes to the metal surface. There does not seem to be a strong interaction between the methyl end group and the metal surface. It is, however, possible that a kind of ordered state in the liquid forms near the surface. Christenson et al. reported from measurements of solvation forces between mica surfaces in liquid *n*-alkanes that the chain molecules had some tendency towards a parallel orientation near the surface.[7] If this tendency is generally valid irrespective of kinds of the surface, C27 molecules in the liquid thin layer are to some extent oriented by the surface of the DSC pan. It may result in a small decrease in entropy in the liquid. For the quantitative estimation of this effect it is necessary to know the entropy of the ordered liquid and the ratio of the surface to volume of the sample in the DSC pan. If we assume that the transition entropy of the ordered liquid layer of 5 nm thickness is negligible, rough estimation that the thin layer thickness of the 0.013 mg sample ranges from 100 to 400 nm may give a decrease in the transition enthalpy of 3 to 10 per cent. These values seem to be somewhat low to explain the observed decrease of the enthalpy. Another factor for it may be a lowering of the crystallinity, which is suggested from the disappearance of the A→B transition peak described previously. The lowering may arise from crystalline defects introduced near the surface. Moreover, the double peaks on the curves a and b in Fig. 3 are not essential to the present argument. Often we observed only broadening of the peaks.

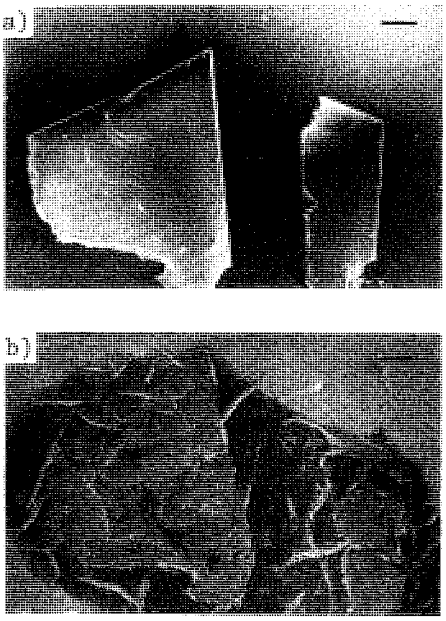

Fig. 5. SEM photographs of C27 on DSC pan. a) before and b) after thermal history similar to DSC scan. Bar equals 0.1 mm.

The present result suggests that on the thermal characterization of vacuum-deposited samples it must be paid attention to close contact between the sample and the substrate even if the sample is non-polar such as *n*-alkanes.

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