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The Effect of the Particle Size on the Anomalous Peaks observed with the DSC Measurements on Henpentacontane and Dopentacontane

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DSC curves for henpentacontane and dopentacontane, when crystallized from the melt, showed anomalous sharp endothermic peaks on the region of the high-temperature phases. Grounding the samples made the peaks disappear. The appearance of the peak may be ascribed to the kinetic factors, not to the first order phase transition.

One of the thermal characteristics of the higher *n*-alkanes is the polymorphic transition, on which the subcell remains unchanged in the orthorhombic form.[1,2] The crystal structures of *n*-alkanes, stable at room temperature, are orthorhombic for the odd-numbered ones and monoclinic for the even-numbered ones.[3] These stable forms could be obtained from dilute solutions of good solvents, whereas it seemed that the number of the carbon atoms in a molecule for even-numbered *n*-alkanes to crystallize in the monoclinic form was limited to approximately 66.[4] Despite of this structural difference at room temperature, the crystals of the even and the odd *n*-alkanes transform to high-temperature modifications.[2] Their structural feature is that the end methyl plane inclines to the chain axes. Recently, we are working on an X-ray determination for the high-temperature structures for henpentacontane and dopentacontane, abbreviated as C51 and C52, respectively. The numeral indicates the number of carbon atoms. When crystals were grown from a dilute propanol solution at a high temperature, single crystals were obtained and their structures could be determined at room temperature. Preliminary results indicated that the frozen-in structures for C51 and C52 belonged to monoclinic crystal but the space group differed.[5] We have to pay much attention to the freezing-in phenomena on the crystallization.

This paper is concerned with the effect of the crystallization modes, namely, solution- and melt-crystallization on DSC curves. DSC measurements were performed with a Rigaku DSC 8240B-TAS100 system. Standard operational conditions for the DSC measurement were: sample weight of about 1.00 mg and a heating rate of 0.5 K/min. C51 and C52 were synthesized and their purities, determined with capillary gas chromatography, were 99.4% for C51 and 99.8% for C52, respectively.[5]

DSC curves of the solution-crystallized samples of C51 and C52 show small solid-solid transition peaks before the melting, as drawn in Figs. 1 and 2, respectively. In order to clearly show the small peaks, the curves with a high magnification of about 25 times for the ordinate scale is also drawn. Two small peaks for C51 may be ascribed to the transition of the orthorhombic (abbr. as A phase) to Aa (B) to A2 monoclinic crystal (c), based on the structures determined for tritriacontane.[1] C52 transforms from the room-temperature monoclinic (M) to the high-temperature one (C'). The symbols given at the top of the figures indicate the phases.

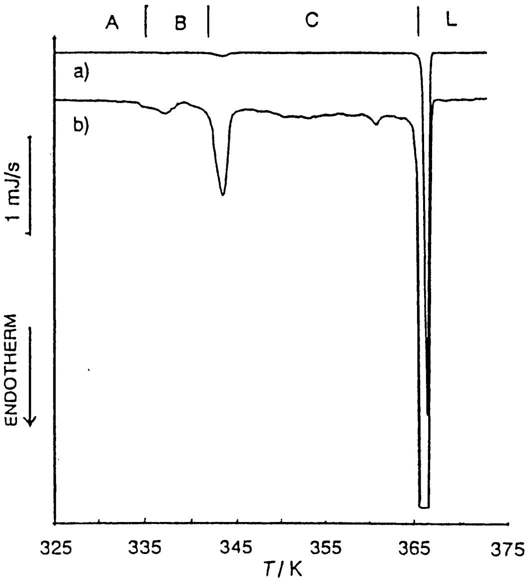

Fig. 1. DSC curves of C51 sample crystallized from heptane solution. Sample weight 1.00 mg and heating rate of 30 K/h. b) With a magnification of 25 times.

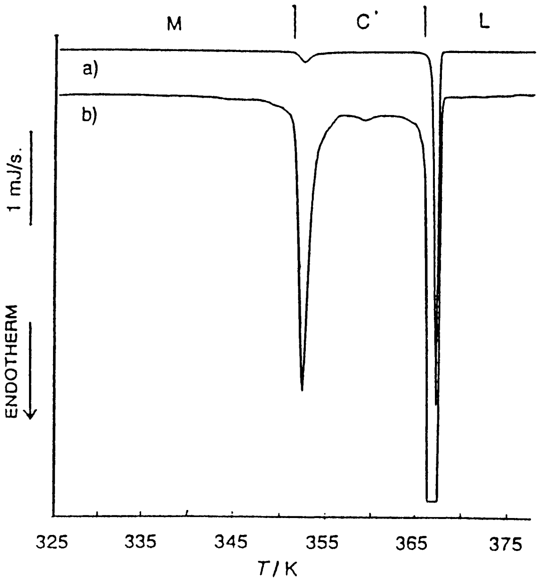

Fig. 2. DSC curves of C52 sample crystallized from octane solution. Measuring conditions are same as in Fig. 1. b) Magnification of 25 x.

On the other hand, C51 samples crystallized in bulk at a cooling rate of 1 K/h did not give the solid-solid transition peaks. The DSC curves in Fig. 3 have the same magnification as in Fig. 1. The disappearance of the transition peaks can be interpreted as the result that the C phase structure was frozen during the cooling of the melt-crystallization. An oblique structure was also confirmed by the change in X-ray long spacing. The gradual increase of the base line is also observed over the temperature region corresponding to the C phase, as it is seen on the solution-crystallized sample. The cause for this thermal feature for the C phase is still unknown. The presence of longitudinal disorders in the C phase for C33 was already suggested.[6]

If the conformational disorders in the C or C' phases need a very long time to attain an equilibrium state, it seems difficult to define these states unequivocally in a usual experimental time scale.

A very small peak, observed at about 360 K for the solution-crystallized C51, becomes very sharp for the bulk-crystallized sample. Its sharpness seems to be too large for the peaks of the first-order phase transition. We have to search another mechanism to give such a peak. There was a report that α form of sulphathiazol crystal showed many spike-like peaks on a DSC curve with a slow heating rate. Grounding the sample resulted in the disappearance of the spike-like peaks.[7)] This was ascribed to be the relaxation of strained states related to the polymorphic transition.

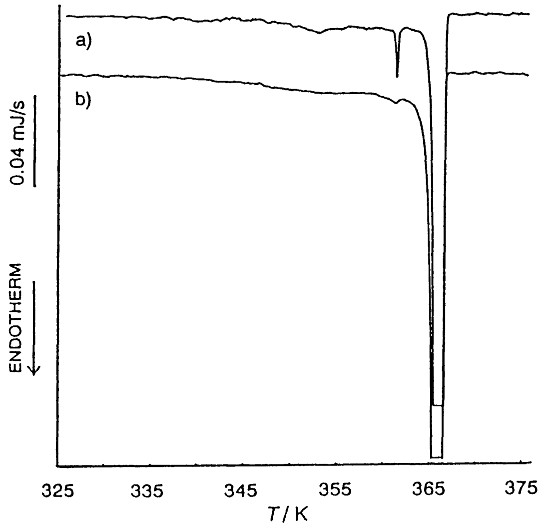

Fig. 3. DSC curves of C51 sample crystallized in bulk at a rate of 1 K/h. Measuring conditions are same as in Fig. 1. Magnification 25 x. a) Unpulverized and b) Pulverized samples.

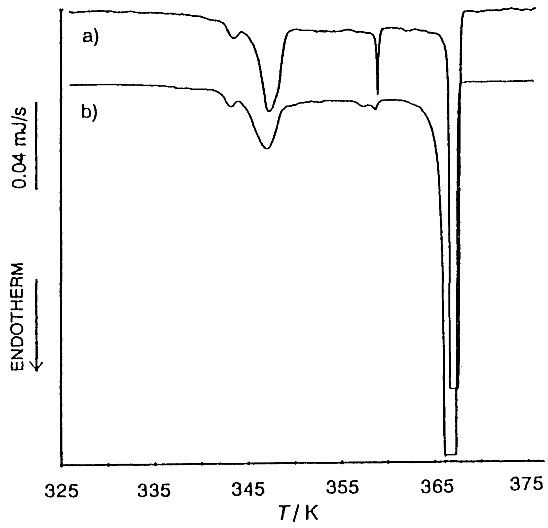

Fig. 4. DSC curves of C52 sample crystallized in bulk at a rate of 1 K/h. Measuring conditions are same as in Fig. 1. Magnification 25 x. a) Unpulverized and b) Pulverized samples.

For the present case a similar phenomenon may occur. The SEM observation revealed that when the solution-grown samples were annealed at the C phase region the original flat crystallites changed to a ridged structure whose surface was inclined, corresponding to the oblique structure.[5)] The solid-solid transition may proceed by the mechanism of nucleation and growth in the solid state. The top or the bottom of the ridged structure may act as a nucleus. As previously stated, the long chain compounds may need a very long time to transform to new states in the solid state. Therefore, the superheated or the strained state remained in crystals during the heating process of DSC measurements. These states abruptly relaxed at some temperatures and the sharp peak might appear. When the grounded sample is used, the size of the domain to cooperatively transform may become small and the probability of the appearance of the anomalous peak may be reduced.

The DSC curve of a grounded bulk-crystallized sample of C51 is compared in Fig. 3. The sample was pulverized in liquid nitrogen in a mortar with a pestle to an average size of about 0.1 mm in diameter. After dried in a vacuum, the measurement was done. As was expected, the sharp peak became very small. It can be interpreted as an artifact. That the pulverization did not affect the thermodynamic state of the crystals was confirmed by the comparison of the heat of the M to C' phase transition with that of melting for C52 crystals grown from solution. The ratio were 0.119 for the original crystal and 0.115 for the grounded, respectively.

A similar effect of the grounding was also observed for C52 crystals. The DSC curves for the original and pulverized samples of the bulk-crystallized C52 are given in Fig. 4; in which the solid-solid transition peak does not disappear, but the peak area decreases and its location moves to a lower temperature compared with the solution-crystallized sample. The transformation in the C52 crystals may proceed with a more complicated mechanism than in C51, because the direction of the monoclinic axis rotates by 90°.5) This may result in such complicated peaks. For the ground sample, the sharp peak at about 359 K becomes very small. We conclude that these anomalous sharp peaks observed on bulk-crystallized C51 and C52 samples need not to be taken into consideration as phase transition. At last, we would like to point out that the appearance of the anomalous peak is restricted to the crystals of a suitable chain length.

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References

1) W.Piesczek, G.R.Strobl, and K.Malzahn, *Acta Crystallogr. Sect. B,*, 30, 1278(1978).
2) K.Takamizawa, Y.Ogawa, and T.Oyama, *Polym. J.*, 14, 441(1982).
3) M.G.Broadhurst, *J. Res. Natl. Bur. Std.*, 66A, 241(1962).
4) K.Takamizawa, T.Nagano, S.Saita, and Y.Urabe, unpublished work.
5) K.Takamizawa, Y.Urabe, J.Fujimoto, H.Ogata, and Y.Ogawa, unpublished work.
6) B.Ewen, G.R.Strobl, and D.Richter, *J. Chem. Soc., Faraday Discuss.*, 69, 19(1980).
7) H.Nakamzchi, The 13th Couse for Thermal Analysis, held by the Society of Calorimetry and Thermal Analysis, Japan, Osaka, May 1986, p.18.

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