

## DSC studies on the phase transition of micro-weight polyethylene \*

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### Abstract

In order to establish an experimental method for micro-weight analysis of polymers, polyethylene (PE) was analysed in a weight range from 0.5 to 100  $\mu\text{g}$  using heat-compensation and heat-flux differential scanning calorimeters. Two types of PE crystal, extended chain and folded chain, were prepared. Purified hexacosane was used as a reference material. The temperatures of melting and crystallization were constant, regardless of the sample weight in the above weight range. It is possible to estimate the enthalpy of melting  $\Delta H_m$  when the sample weight was about 5  $\mu\text{g}$  or greater for PE samples and about 0.5  $\mu\text{g}$  or greater for hexacosane. The  $\Delta H_m$  of extended chain crystals of PE maintained a constant value whereas the  $\Delta H_m$  values of folded chain crystals of PE and hexacosane started to decrease at around 10  $\mu\text{g}$ . The results suggest that the enthalpy deficiency at the surface of each crystalline sequences varies when the sample weight decreases in the order of micrograms. This effect cannot be ignored when the sample contains a large amount of defects.

### INTRODUCTION

Recently, particular attention has been paid to the functional properties of micro-fine powders and ultra-thin films derived from polymers. In order to investigate the thermal properties of ultra-small samples, it is important to develop techniques for measuring micro-weight samples. Shibazaki [1] reported that the melting enthalpy of stearic acid was twice the normal enthalpy value when the weight of the sample was less than 10  $\mu\text{g}$ . The author attributes this increase to the chemical interaction between the carboxylic group and the oxidized aluminium surface of the DSC sample

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vessel. Takamizawa and Urabe [2] reported the transition enthalpy of pure heptacosane, indicating that the melting enthalpy decreased when the sample weight was less than 10  $\mu\text{g}$ . This decrease in the enthalpy of melting was attributed to the entropic change in the sample which was affected by contact with the aluminium surface of the sample vessel. The above conflicting results indicate that the surface of the sample vessel markedly affects the phase transition behaviour of micro-weight samples.

The above results are concerned with the problem that the thermal properties of polymers are affected by the surface of the polymers when the weight of the sample is within 10  $\mu\text{g}$ . It is important to study the effect of sample surface on the thermal behaviour of polymers and, at the same time, it is necessary to establish an experimental method for micro-weight analyses in the field of polymer application. Polymeric samples are inhomogeneous, even if the sample for thermal analysis is obtained from the same sample piece. This micro-scale inhomogeneous structure may be attributed to the thermal conditions prevailing during polymer processing. The evaluation of micro-weight polymeric material is necessary in order to obtain the correct information and for the precise application of the thermal data in polymer processing.

In this study, polyethylene in the weight range from 2 to 100  $\mu\text{g}$  was investigated using differential scanning calorimetry.

## EXPERIMENTAL

### *Sample*

High density polyethylene (PE, Sholex) was fractionated using a column method [3]. The molecular weight ( $M_w$ ) was  $1.3 \times 10^4$  and the molecular weight distribution ( $M_w/M_n$ ) was 5.0. The sample was pressurized at 500 MPa at 235°C. After crystallization for 20 h, the sample was cooled to 20°C and depressurized. The sample preparation was as previously reported [3].

*n*-Hexacosane (Wako Chemical Co.) was recrystallized four times from ethanol solution. The purity calculated from the melting peak was 99.4% [4].

### *Measurements*

Perkin-Elmer DSC-II and Seiko SSC 5000 thermal analysers were used to measure the temperature and enthalpy of melting; the former analyser is the heat-compensation-type DSC and the latter is the heat-flux-type DSC (quantitative DTA). The melting and crystallization enthalpy were determined using indium as a reference material. The sample weight ranged from 0.5 to 100  $\mu\text{g}$ . The samples were weighed using a Sartorius micro-bal-

ance at 22°C and 45% relative humidity. The balance was calibrated before measurement by the ordinal calibration method. The accuracy of the balance was  $\pm 0.2 \mu\text{g}$ . Measurements were carried out at the heating rate of  $10 \text{ K min}^{-1}$  in  $\text{N}_2$  gas. An open aluminium sample vessel was used. Each sample was heated to a temperature 30 K higher than the melting peak and cooled to 50 K lower than the crystallization temperature. The procedure followed was as reported previously [5,6].

A Hitachi scanning electron microscope (S-500A) and a Leitz polarizing light microscope (Othoplan Pol) were used for the morphological observation.

## RESULTS AND DISCUSSION

When polyethylene is crystallized under high pressure, extended chain crystals (ECC) are obtained [7]. The crystal size of the ECC is in the range 1–500  $\mu\text{m}$  depending on the crystallization conditions and the molecular weight of the sample [7]. It is also known that the melting temperature of ECC is around 10 K higher than that of the folded-chain-type crystals (FCC) [8,9]. When ECC was distorted during the sampling process, the DSC melting peak changed from a smooth melting peak to a peak with a subpeak on the low temperature side of the main peak. Thus it is obvious when the original crystal structure has been maintained during the sampling process.

Figure 1 shows representative DSC heating curves (the first run) of crystallized PE with various sample weights, measured by heat-compensation DSC. The peak observed at 410 K is attributed to the melting of ECC. Although DSC curves of samples less than 4.7  $\mu\text{g}$  in weight are not shown in

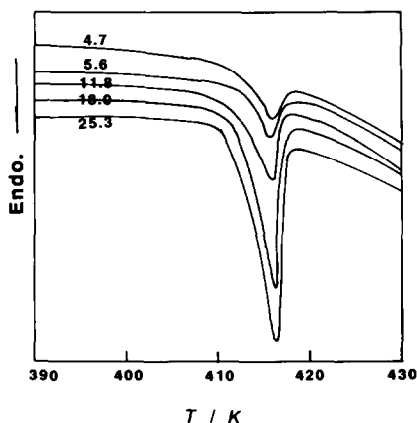


Fig. 1. DSC melting curves of extended chain polyethylene. Numerals in the figure show the sample weight in micrograms.

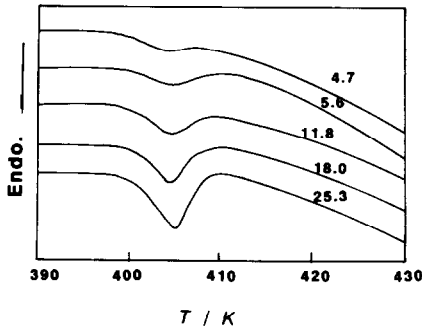


Fig. 2. DSC melting curves of folded chain polyethylene. Numerals in the figure show the sample weight in micrograms.

Fig. 1, the endothermic peak could be distinguished for the sample around 1  $\mu\text{g}$  in weight. After melting, the sample was cooled and an exothermic peak due to crystallization was observed at around 388 K.

The reheating curve of PE is shown in Fig. 2. The higher order structure of PE changed to FCC, because of the recrystallization during the cooling process. The melting peak was about 10 K lower than that of ECC as shown in Fig. 1.

Similar DSC heating curves were obtained using heat-flux DSC, although the signal-to-noise ratio was slightly higher than that obtained by heat-compensation DSC owing to the measuring conditions described above in the experimental section.

DSC heating curves of hexacosane in the weight range 0.5–100  $\mu\text{g}$  were also obtained. Both melting and a crystal-crystal transition could be observed, as shown in Fig. 3.

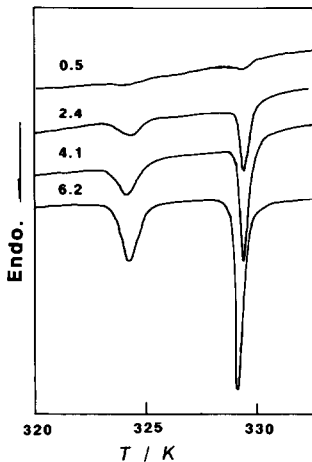


Fig. 3. DSC melting curves of hexacosane. Numerals in the figure show the sample weight in micrograms.

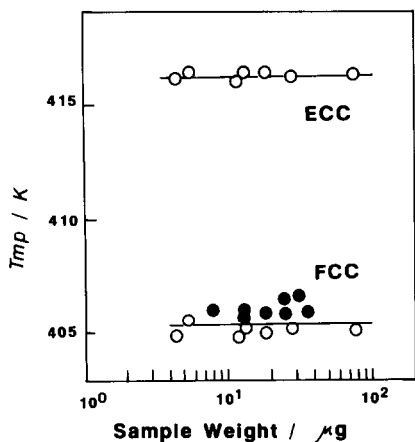


Fig. 4. Relationship between the melting temperature ( $T_{mp}$ ) and sample weight:  $\circ$ , heat-compensation DSC;  $\bullet$ , heat-flux DSC; ECC, extended chain crystal; FCC, folded chain crystal.

Figure 4 shows the melting peak temperature ( $T_{mp}$ ) of FCC and ECC PEs. The  $T_{mp}$  and the peak temperature of the crystal-crystal transition ( $T_t$ ) of hexacosane maintained constant values in the sample weight range 0.5–100  $\mu\text{g}$ , as shown in Fig. 5. In both PE and hexacosane, the  $T_{mp}$  and  $T_t$  showed constant values regardless of large weight variations. The temperature of crystallization also showed a constant value similar to  $T_{mp}$ .

Figure 6 shows the enthalpy of melting ( $\Delta H_m$ ) of ECC and FCC. The  $\Delta H_m$  value of ECC is around 260  $\text{J g}^{-1}$  over the whole range of sample weight. The  $\Delta H_m$  of FCC, however, varied as shown in Fig. 6, starting to decrease at around 10  $\mu\text{g}$ . The  $\Delta H_m$  value was 138  $\text{J g}^{-1}$  when measured by heat-compensation DSC with sample weights higher than 10  $\mu\text{g}$ ; the  $\Delta H_m$  value obtained by heat-flux DSC was slightly higher. The above difference is reasonable: a large variation in  $\Delta H_m$  data has been observed in the same PE sample [6].

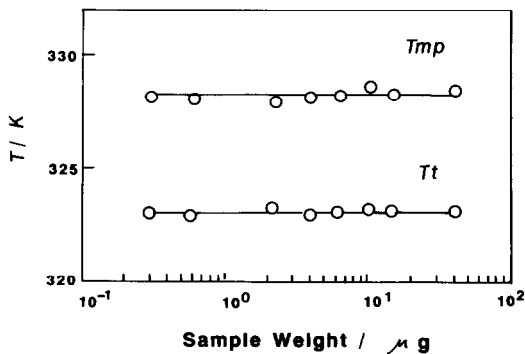


Fig. 5. Relationship between the melting temperature ( $T_{mp}$ ) and the temperature of the crystal-crystal transition ( $T_t$ ) of hexacosane and the sample weight.

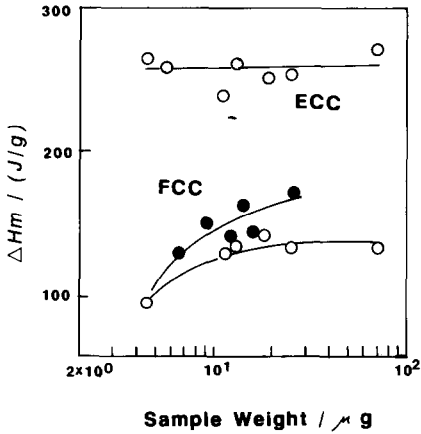


Fig. 6. Relationship between the melting enthalpy ( $\Delta H_m$ ) and sample weight of polyethylene:  $\circ$ , heat-compensation DSC;  $\bullet$ , heat-flux DSC; ECC, extended chain crystal; FCC, folded chain crystal.

Figure 7 shows the  $\Delta H_m$  and the transition enthalpy of the crystal-crystal transition of hexacosane as a function of sample weight. Both enthalpies decrease at around  $10 \mu\text{g}$ . The variation in  $\Delta H_m$  was almost identical to that obtained by Takamizawa and Urabe [2].

Manderkern et al. [10] defined the enthalpy ( $H$ ) of PE crystal prior to fusion as

$$[N_0 H = (N_0 - n\xi\rho)H_a + n\xi\rho(1 - \alpha)H_c + n\xi\rho H_d + 2n\rho\Delta H_e] \quad (1)$$

$$[(1 - \lambda) = (n\xi\rho)/N_0] \quad (2)$$

where  $N_0$  is the total number of units,  $n$  is the number of crystallites having uniform size which contain  $\rho$  crystalline sequences each of length  $\xi$ ,  $H_a$  is the enthalpy per unit of the non-crystalline units,  $H_c$  is the enthalpy per unit

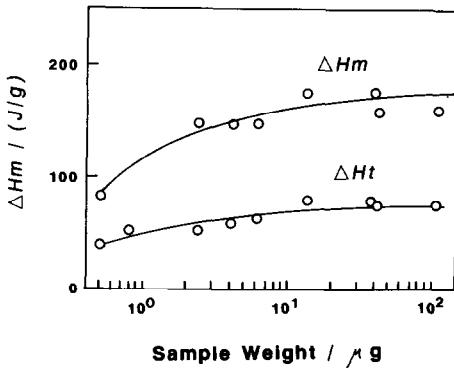


Fig. 7. Relationship between the melting enthalpy ( $\Delta H_m$ ) and the transition enthalpy of the crystal-crystal transition of hexacosane and the sample weight.

in the completely crystalline state,  $\alpha$  is the fraction of units per sequence within the interior of the crystals having defects,  $H_d$  is an excess enthalpy from the defects,  $H_e$  is the enthalpy deficiency per sequence at the terminus of each crystalline sequence and  $(1 - \lambda)$  is the degree of crystallinity.

$$[\Delta H_m = (1 - \lambda)[\Delta H_u - (2\Delta H_e/\xi) + \alpha\Delta H_d]] \quad (3)$$

where  $\Delta H_m$  is the measured enthalpy of fusion per repeating unit,  $\Delta H_u$  is the enthalpy of fusion for a completely crystalline polymer, and  $\Delta H_d = H_c - H_d$ .

In the case of ECC, we may ignore possible contributions from the interfacial region or defects within the interior of the crystal; then

$$[(1 - \lambda) = \Delta H_m/\Delta H_u] \quad (4)$$

The crystallinity  $(1 - \lambda)$  of the ECC sample used in this experiment was about 91%. The reported enthalpy value of 100% crystalline PE ( $\Delta H_u$ ) was  $286 \text{ J g}^{-1}$  [11].

In contrast, the  $\Delta H_m$  of FCC was almost half that of ECC. Therefore, it is difficult to ignore the effects of both the interfacial region between the folded crystals and the defects within the interior of the crystals formed during the recrystallization on cooling. This suggests that the value of the second term in eqn. (3) must be taken into account. The results shown in Fig. 5 indicate that the  $(1 - \lambda)(2\Delta H_e/\xi)$  term also varied as a function of the sample weight of FCC-PE when the sample weight was about  $10 \mu\text{g}$  or less.

Takamizawa and Urabe [2] measured the  $\Delta H_m$  of pure heptacosane as a function of the sample weight. The  $\Delta H_m$  obtained from the second DSC run decreased when the sample weight was about  $20 \mu\text{g}$  or less. Scanning electron micrographs indicated that the sample came into contact with the aluminium surface of the sample vessel after melting. The  $\Delta H_m$  and SEM results suggest that the aluminium surface affected the crystallization and that defects were introduced near the surface.

In contrast with samples of low molecular weight, such as heptacosane, the viscosity of PE in the molten state is high. The PE samples were easily detached from the sample vessel after melting and recrystallization, even though the aluminium surface was not smooth. The change in the appearance of the sample while on the aluminium surface was not remarkable in the PE samples. SEM revealed the unevenness of the aluminium surface of the sample vessel and this cannot be ignored, considering the sample size. At the same time, the heat distribution of the DSC sample holder must be taken into account. When the sample size is less than  $1\text{--}2 \text{ mm}^2$ , the inhomogeneous structure of the heater is also thought to affect the thermal data of the sample; this might influence the signal-to-noise ratio in the curves obtained from both heat-flux and heat-compensation DSC.

The results shown in Figs. 6 and 7 indicate that the  $\Delta H_m$  values of both FCC-type PE and of hexacosane decrease when the sample weight is about 10  $\mu\text{g}$  or less even though the  $\Delta H_m$  value of ECC maintained a constant value. This suggests that various types of defects, such as chain ends, irregularly folded chains and interfacial regions between crystallites, affect the molecular mobility of the local order of the molecular chains and the subsequent melting. It is appropriate to consider that a large free surface area of the crystallites enhances the molecular motion of the above defects, even though the molecular motion of the crystallite is restricted by adjacent molecules in the solid state. The constant  $\Delta H_m$  value of ECC is reasonable, because these are fewer defects in ECC-PE than in FCC-PE.

The results of this study suggest that the  $(1 - \lambda)$  value decreases with decreasing sample weight. Therefore the enthalpy of melting of samples containing large amounts of defects decreases when the sample weight is about 10  $\mu\text{g}$  or less.

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