

Some Problems encountered in DSC Measurements and Data Analysis

Shoji Ichihara, Tomohiko Takahama and Hideaki Nakagawa

(Received 20 July 1977)

Abstract

DSC has been widely used for thermal analysis of various materials. But the methods of measurements and the reliability of the obtained data have been discussed very little. So we tried to investigate these problems from the point of view of temperature distribution in the sample and thermal balance of the sample. It was proved that the temperature distribution in the sample must be taken into consideration, even if the quantity of the sample used is small. Read out temperature diverges from the true temperature linearly with scanning rate. It is necessary to obtain the corrected base line for the measurements of heat of fusion of the materials of large temperature range of melting.

1. INTRODUCTION

It has been said that reliability of the results by Differential Scanning Calorimetry (DSC) are extremely influenced by the measurement conditions and the methods for correcting the data¹⁾. But it has been little discussed how to think about these. Therefore, it seems likely to us that quantities measured by DSC have not been utilized fully, and that the reliability limit of the data becomes questionable and discussed with errors.

In this study, we tried to investigate these problems from the point of view of temperature distribution in the sample and thermal balance of the sample

2. THEORY

2.1 Temperature distribution in the sample

As a model of the sample for DSC, we assume a flat one of thickness l , and the x axis is taken along the thickness direction. It is supposed that the scanning rate S is constant on the point at $x=0$ and the heat is transferred to the environment proportionally to the temperature difference between the sample and the environment, whose temperatures are $T(l, t)$ and T_{en} respectively, where t is the time. Using k for thermal conduc-

tivity, α for thermal diffusivity and h for heat transfer coefficient between the sample and the environment, the temperature distribution in the sample can be obtained by solving an equation of heat conduction ($\partial T/\partial t = \alpha (\partial^2 T/\partial x^2)$) under the boundary conditions of eq. (1) and eq. (2)

$$\frac{\partial T}{\partial t} \Big|_{x=0} = S = \text{const.} \tag{1}$$

$$-k \frac{\partial T}{\partial x} \Big|_{x=l} = h \{ T(l, t) - T_{en} \} \tag{2}$$

The temperature distribution in the beginning of the measurement should be derived under the condition of eq. (2). However, it is difficult to solve the equation of heat conduction under the conditions of eq. (1) and eq. (2), so that the boundary conditions are approximated as follows:

$$\frac{\partial T(x, t)}{\partial t} = S = \text{const.} \quad -k \frac{\partial T}{\partial x} \Big|_{x=l} = \beta = \text{const.} \tag{3}$$

The conditions of eq. (3) may be applicable approximately to the stationary state of heating in small temperature range and small time interval. Therefore, solving the equation of heat conduction under the conditions of eq. (3), we obtain eq. (4).

$$T(x, t) = \frac{S}{2\alpha} x^2 - \left(\frac{S}{\alpha} l + \frac{\beta}{k} \right) x + T(0, 0) + S t \tag{4}$$

where $T(0, 0)$ is the hypothetical initial tempera-

Mitsubishi Petrochemical Co., Ltd.

Toho-cho, Yokkaichi-city, Mie, Japan

ture of the stationary state of heating on the point at $x=0$. Let Δt represent the interval between the time when the temperature at $x=0$ reaches to T_m and the time when $T(x, t)=T_m$. From eq. (4), we have

$$\Delta t = \left(\frac{\rho}{k}\right)x \frac{1}{S} + \frac{1}{\alpha} \left(lx - \frac{x^2}{2}\right) \quad (5)$$

2.2 Calibration of read out temperature and temperature distribution in sample holder

The temperature distribution exists in the sample holder, too, as mentioned in the section 2.1. Therefore, we must consider two terms for the calibration of the read out temperature of DSC. One is related to the fact that the read out temperature is approximated, because the temperature dependence of the output signal of the sensor is approximated in some manner. The other is related to the temperature difference between the sample base and the sensor, and it depends on the scanning rate.

In the case of Perkin-Elmer DSC-1 and DSC-1B, the temperature is measured by temperature dependence of electric resistance of platinum. The temperature dependence of the resistance is expressed by a quartic equation²⁾. But it can be approximated by a quadratic square equation, considering the temperature range of DSC measurement and the accuracy of temperature measurement. Therefore, the electric resistance, R is written as the following

$$R = A + BT + CT^2 \quad (6)$$

where T is the temperature, and A , B and C are all constants. The relation between the read out temperature θ_r of DSC-1 and DSC-1B and R is expressed by a simple equation

$$R = A' + B' \theta_r \quad (7)$$

where A' and B' are constants. Therefore, the relation between θ_r and T is

$$\theta_r = a + bT + cT^2 \quad (8)$$

where a , b and c are constants, too. Eq. (8) expresses the approximation of the read out temperature.

Next, we consider the temperature difference ΔT between a position of the sensor and the sample base. The temperature distribution exists

also within the sample holder, as mentioned in the section 2.1. Hereupon we consider it by using a simplified model in which the space between the temperature sensor and the sample base is composed of uniform material. Using this model, temperature difference between the sensor and the sample base is given by eq. (4), where the position of the sensor and the sample are respectively $x=0$ and $x=l$, and temperature of the sensor is $T(0, t)=T(0, 0)+St$. Thus, $T(0, t)-T(l, t)$ is described by a simple equation for the scanning rate S . If this term is added to eq. (8), we can obtain eq. (9)

$$\theta_r = a + bT + cT^2 + dS + e \quad (9)$$

where d and e are constants. In the case of the cooling measurement, S is negative. Assuming that if the temperature distribution in this case is reverse of that in the heating measurement, e becomes also minus, then the relation between θ_r , T and S is

$$\theta_r = a + bT + cT^2 + dS \pm e \quad (10)$$

where S and e are both plus in the case of heating, and S is minus in the case of cooling.

In the isothermal measurement, ΔT can be estimated by using $-k(\Delta T/\Delta x)=\rho$. Substituting $2 \times 10^{-2} \text{ J cm}^{-2} \text{ s}^{-1}$ for ρ as is seen in the later description and 0.05 cm for Δx , ΔT are $-2.4 \times 10^{-4} \text{ }^\circ\text{C}$ and $-0.24 \text{ }^\circ\text{C}$ when k are $1 \text{ J cm}^{-1} \text{ s}^{-1} \text{ }^\circ\text{C}^{-1}$, and $10^{-3} \text{ J cm}^{-1} \text{ s}^{-1} \text{ }^\circ\text{C}^{-1}$, respectively. From these facts, it seems to be quite reasonable that the temperature difference between the sensor and the sample base is small in the isothermal measurement ($S=0$).

2.3 Base line and measurement of specific heat capacity

In this section we will consider thermal balance, but neglect the temperature distribution mentioned in the sections 2.1 and 2.2. The symbols used are as follows; C_p the specific heat capacity of the sample, M_x the sample weight, W_s the weight of sample pan, C_{sp} the specific heat capacity of the material of the sample pan, H_s the effective heat capacity of the sample holder, q_s the heat transferred to the sample side, f_s the heat transferred per unit time to the exterior from the sample holder, W_r the weight of another sample pan put into the reference holder, H_r the effective heat capacity of

the reference holder, q_r the heat transferred to the reference holder, and f_r the heat transferred per unit time to the exterior from the reference holder. The thermal balance of the sample side is

$$(M_x C_p + W_s C_{sp} + H_s) \frac{dT}{dt} = \frac{dq_s}{dt} - f_s \quad (11)$$

and the thermal balance of the reference side is

$$(W_r C_{sp} + H_r) \frac{dT}{dt} = \frac{dq_r}{dt} - f_r \quad (12)$$

Subtracting eq. (12) from eq. (11), we obtain

$$\{M_x C_p + (W_s - W_r) C_{sp} + (H_s - H_r)\} \frac{dT}{dt} = \frac{dQ}{dt} - F \quad (13)$$

where $Q = q_s - q_r$ and $F = f_s - f_r$. The term dQ/dt is the vertical read out of DSC, but the zero point can not be shown generally. It may be impossible to satisfy the following condition with enough accuracy: $W_s = W_r$, $H_s = H_r$ and $F = \text{const}$.

Then, we consider the case of blank measurement as standard. In this case, only the sample pan, whose weight is W_{sb} , is put into the sample holder, and we obtain the next equation replacing Q and F with Q_b and F_b

$$\{(W_{sb} - W_r) C_{sp} + (H_s - H_r)\} \frac{dT}{dt} = \frac{dQ_b}{dt} - F_b \quad (14)$$

From eq. (13) and eq. (14)

$$\{M_x C_p + (W_s - W_{sb}) C_{sp}\} \frac{dT}{dt} = \left(\frac{dQ}{dt} - \frac{dQ_b}{dt} \right) - (F - F_b) \quad (15)$$

Next, we consider the condition under which F can be approximated to be F_b . If $F - F_b$ is zero at the start and end of specific heat capacity measurements when dT/dt is zero, we can also approximate $F - F_b$ to be zero even during heating. The method, by which $F - F_b$ can be eliminated when $dT/dt = 0$, is to move the DSC curve of the sample or the blank along the longitudinal axis, i.e., dQ/dt axis, and to superpose the isothermal traces of the blank at the start and the end of heating upon that of the sample. By this operation, eq. (15) becomes

$$\{M_x C_p + (W_s - W_{sb}) C_{sp}\} \frac{dT}{dt} = \left(\frac{dQ}{dt} - \frac{dQ_b}{dt} \right) = \rho l_x \quad (16)$$

where l_x is the length between these two curves thus superposed and ρ is sensitivity (for instance, the sensitivity expressed by $\text{mJ cm}^{-1} \text{s}^{-1}$). In the case that sapphire, as the standard sample of specific heat capacity is put into the sample pan in place of the sample, we obtain eq. (17)

$$\{M_s C_{ps} + (W_{ss} - W_{sb}) C_{sp}\} \frac{dT}{dt} = \left(\frac{dQ_s}{dt} - \frac{dQ_b}{dt} \right) = \rho l_s \quad (17)$$

where C_{ps} is the heat capacity of the sapphire, M_s is the weight of the sapphire, W_{ss} is the weight of the sample pan for the sapphire, and Q_s and l_s are used instead of Q and l_x in eq. (16), respectively. Dividing eq. (16) by eq. (17), and rearranging it,

$$C_p = \frac{l_x M_s}{l_s M_x} C_{ps} + \left\{ \frac{l_x}{l_s} \frac{W_{ss} - W_{sb}}{M_x} - \frac{W_s - W_{sb}}{M_x} \right\} C_{sp} \quad (18)$$

We usually don't use the condition that l_x/l_s becomes extreme large. Therefore, using the sample pans for which $M_x \gg W_{ss} - W_{sb}$ and $M_x \gg W_s - W_{sb}$, eq. (18) becomes eq. (19).

$$C_p = \frac{l_x}{l_s} \frac{M_s}{M_x} C_{ps} \quad (19)$$

Eq. (19) coincides with the equation derived by O'Neill³⁾.

If $H_s = H_r$ and $W_s = W_r$, eq. (13) becomes eq. (20)

$$M_x C_p \frac{dT}{dt} = \frac{dQ}{dt} - F \quad (20)$$

The sample holder is made in the way that $H_s \approx H_r$. Therefore, if we use sample pans of almost equal weight, eq. (20) is approximately applicable. This equation expresses that the apparent sensitivity increases when the heating rate increases, and that the linearity of base line is very affected by difference in heat transfer from the sample and reference holders to the exterior.

3. EXPERIMENTAL

3.1 Apparatus and samples

The apparatuses used were DSC-1 and DSC-1B manufactured by Perkin-Elmer Co. Ltd.

The standard samples used are shown in Table 1. Purities of gallium, indium, tin, bismuth and lead are more than 99.99%. Benzoic acid, hexachloro-

Table 1. Samples used for calibration.

Materials	Melting point $T_m/^\circ\text{C}$	Transition point $T_t/^\circ\text{C}$	Heat of fusion $\Delta H_f/\text{J g}^{-1}$	Note
Hg	-38.9			easily form alloy with aluminium
Ga	29.8		80.1	
Benzoic acid	122.3			
In	156.4		28.5	
Sn	231.9		59.6	
Bi	270.9		52.6	
Pb	327.3		23.0	
Hexachloro-ethane	187 (in sealed tube)	71.4*		easily sublimate
Hexamethyl-benzene	166	110.4**		

* monoclinic \rightarrow tetragonal
 ** rhombic \rightarrow hexagonal

ethane and hexamethylbenzene are special grades on the market. As polymer samples, we used low density polyethylene (LDPE), high density polyethylene (HDPE) and ethylene-vinylacetate copolymer (EVA) on the market. We did not characterize these polymers, because these characteristics do not affect the conclusions. We made the sample base as flat as possible and thermal contact of the sample pan with the sample holder good.

3.2 Measurement of temperature distribution in sample

We made samples of indium contained in LDPE by the following technique. At first, we made LDPE film of about 0.01cm thickness by press. Then, this film was superimposed to thickness of about 0.1cm. Thin layers of indium were inserted into a suitable position of these films, and were pressed again. These samples were put into the sample pans, and the onsets of melting were measured at various heating rates without cover on the pan (Fig. 1 (b)). After the measurements, the samples were taken out of the pans and the distances x from the base of LDPE to the base of indium were measured. We assumed that the difference of the onset of melting for $x=0$ from that for the distance x is the temperature difference between the points at $x=0$ and $x=x$.

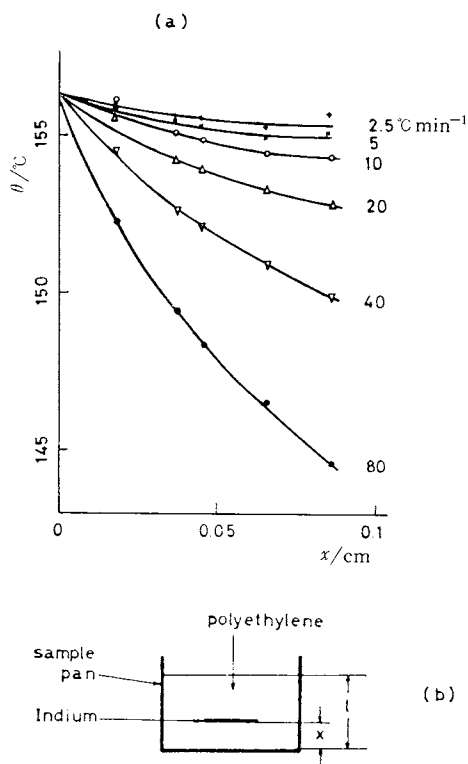


Fig. 1. (a) Temperature distribution in DSC sample (low density polyethylene) at various heating rates. +, 2.5 $^\circ\text{C}\cdot\text{min}^{-1}$; \times , 5; \circ , 10; Δ , 20; ∇ , 40; \bullet , 80. (b) Method to obtain temperature distribution.

3.3 Calibration for read out temperature

Calibration of the read out temperature for the heating measurement were done by the method described elsewhere³¹. For the cooling measurement we used the transition temperatures of hexachloroethane and hexamethylbenzene at 71.4°C and 110.4°C, respectively. For the isothermal measurement we used iron-constantane thermocouple of 0.1 mm diameter adhered on the sample pan with Arardite (the binding agents). For the case of heating and cooling, we obtained the relation of θ_r and the temperature indicated with the thermo-couple T , and determined the values of $S \rightarrow 0+$ and $S \rightarrow 0-$, i.e., the values extrapolated to $S=0$ from the heating and cooling direction, respectively. We observed change of the temperature with time after heating up at $S=40$ and $S=80^\circ\text{C min}^{-1}$ and then maintaining at $\theta_r = 200^\circ\text{C}$.

3.4 Other measurements

The measurement of heat capacity was done by the method which O'Neill described⁴⁾. In the measurements of melting and glass transition, care was taken of thermal contact between the sample pan and the sample holder.

4. RESULTS AND DISCUSSION

4.1 Temperature distribution in DSC sample

The observed data for the temperature distribution in LDPE, which was in molten state during the DSC measurement, were compared with eq. (4). These results are shown in Fig. 1 (a). This result indicates that the temperature distribution in the sample must not be ignored, even if the small sample was used.

If we assumed the specific heat capacity and the density of LDPE at 165°C is $2.65 \text{ J g}^{-1} \text{ K}^{-1}$ and 0.788 g cm^{-3} ,⁵⁾ respectively, we obtained the values of k and β from the plot of Δt versus $1/S$ and from eq. (5); k was $1.59 \times 10^{-3} \text{ J cm}^{-1} \text{ s}^{-1} \text{ K}^{-1}$ and β was $1.97 \times 10^{-2} \text{ J cm}^{-2} \text{ s}^{-1}$. As a reported value⁶⁾ of k is $2.43 \times 10^{-3} \text{ J cm}^{-1} \text{ s}^{-1} \text{ K}^{-1}$, it is in good agreement with the value estimated above, taking into account of the assumptions assumed to obtain eq. (5) and the structure of the practical sample holder.

4.2 Correction of read out temperature

For the examination of validity of eq. (10), we obtained the read out temperatures at onset of melting of Ge, In, Sn, Bi and Pb by changing the heating rate, and calculated (a+e), b, c and d, which are the coefficients of eq. (10), by the least squares method. Next, we calculate the read out temperature for the melting point of benzoic acid, $\theta_{r(\text{calc})}$, and compared this value with observed ones. The standard deviations, i.e., $\{(\theta_{r(\text{obs})} - \theta_{r(\text{calc})})^2(n-1)\}^{1/2}$, for the samples used in the calibration and benzoic acid, were all about 0.26°C. Therefore, eq. (10) seems to be an excellent equation for correction. In the case of cooling measurement, the values of a, b and c may be the same as the heating. Therefore, if we obtain the values of (a-e) and d, the read out temperature in the cooling measurement can be calibrated. In Fig. 2, the differences of the read out temperature, θ_r , of the onset of DSC transition curves from their transition temperatures, T_t are plotted against the scanning rate for hexamethyl-benzene at 110.4°C and that of hexachloroethane at 71.4°C. For slow cooling rate, small deviations from the straight lines are observed, but the value of d is considered to be nearly equal to that for heating. The value of e and a are obtained from the difference between the values of $S \rightarrow 0+$ and $S \rightarrow 0-$.

Fig. 3 shows the temperature change after heat-

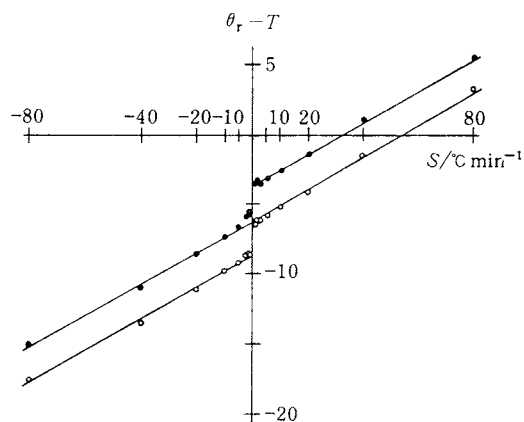


Fig. 2. Relations of deviations of read out temperatures, θ_r , of DSC transition onsets for hexamethylbenzene, at 110.4°C and for hexachloroethane at 71.4°C from their transition temperatures, T_t , vs. scanning rate. ●, hexamethyl-benzene; ○, hexachloroethane.

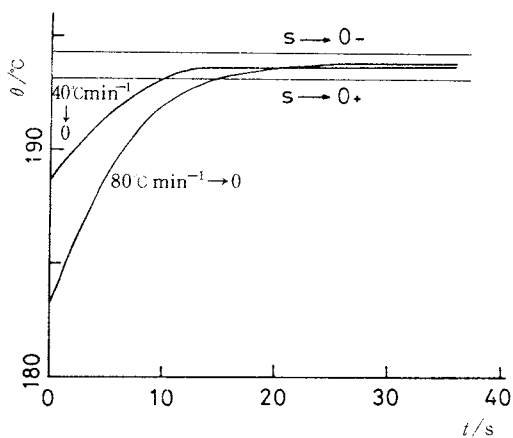


Fig. 3. Temperature change of sample pan after heating is stopped at $\theta_r=200^\circ\text{C}$. The values denoted with $S \rightarrow 0+$ and $S \rightarrow 0-$ are obtained by extrapolation of read out temperature at heating and cooling to zero scanning rate, respectively.

ing at the rate of 40 or $80^\circ\text{C min}^{-1}$ is stopped at some temperature and it is measured with the thermocouple. From this figure, it is apparent that about 30 s is necessary to heat up to a constant temperature and that the read out temperature at the zero heating rate is intermediate between the values extrapolated to the zero rate, namely e in eq. (10) becomes zero for the case that $S=0$.

4.3 Measurement of specific heat capacity and heat of fusion

Specific heat capacities, that are the average of ten measurements, for poly(α -methylstyrene) of different degrees of polymerization are shown in Fig. 4(a). The deviation of the measured value from the average and the standard deviation are shown in Fig. 4(b) for the sample, whose degree of polymerization is 1000. The standard deviation is lower than 1.5%.

DSC melting curves for HDPE were obtained under the conditions of sample weight of 6.78 mg, sensitivity range of 16 , heating rate of $10^\circ\text{C min}^{-1}$ (curve 2 in Fig. 7). The heat of fusion determined from the peak area obtained by drawing a straight base line is 218 J g^{-1} . This is the value estimated by neglecting non-linearity of the base line mentioned in the section 2.3. The heat of fusion was estimated by obtaining the base line by the same technique as in the measurement of the

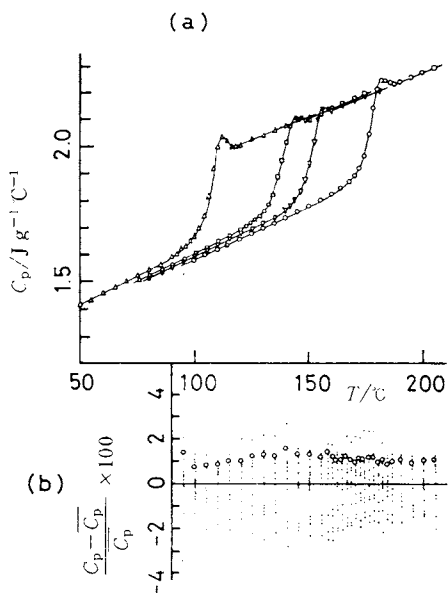


Fig. 4. (a) Specific heat capacities of poly(α -methylstyrene) obtained by DSC. Heating rate is $16^\circ\text{C.min}^{-1}$. Degrees of polymerization are: Δ , 15; \square , 20; ∇ , 30; \circ , 1000. Each points are mean value of 10 measurements.

(b) Deviations from mean values of specific heat capacity of poly(α -methylstyrene) of degree of polymerization of 1000. Temperature scale corresponds to Fig. 6 (a), and open circles in the figure are standard deviations.

specific heat capacity mentioned in the section 2.3, and it is 259 J g^{-1} . For the measurements of heat of fusion of materials with large melting temperature range, it is necessary to obtain the corrected base line.

4.4 DSC melting curves

Certainly, even if the corrected base line is obtained, the problem for obtaining the heat of transition is not resolved, when the specific heat capacity changes largely at the transition. For this reason, analysis which will be discussed in this section is necessary.

O'Neill discussed DSC curves of sharp first order transition, such as the melting of low molecular weight materials of high purity⁷⁾. The sample holder was represented as shown in Fig. 5 (a). But he calculated for a model simplified further as the followings. Namely, he neglected the heat capaci-

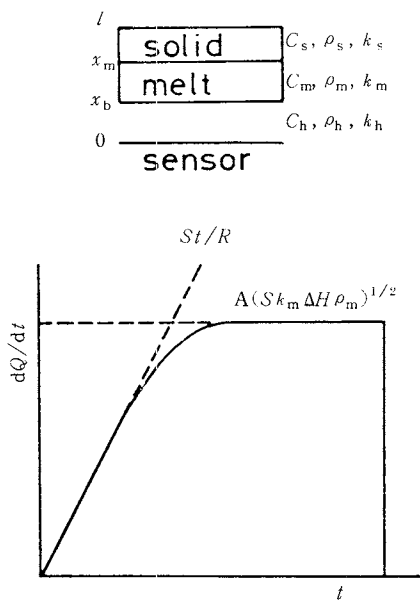


Fig. 5. (a) Schematic drawing of sample holder and sample in DSC apparatus. x_b is distance from temperature sensor to bottom of sample; x_m , to the plane where melting is just proceeding; l , to upper surface of sample. C , ρ and k are specific heat capacity, density and thermal conductivity, respectively. A is area of cross section. Suffices h, m and s indicate sample holder, molten phase and solid phase, respectively.
 (b) DSC curve of melting calculated by O'Neill. S , t , R and ΔH are heating rate, time, thermal resistance of sample holder and heat of fusion of sample per unit weight, respectively.

ties of the samples and the holder (it was a matter of course to neglect also the change of temperature distribution within the sample and the sample holder caused by absorbing the heat of melting). He assumed that total heat absorbed in the sample was used to move the melting plane and that the heat conduction between $0 \sim x_b$ and $x_b \sim x_m$ in the model in Fig. 5 (a) occurs on linear temperature gradient. The results of his derivation are shown in Fig. 5 (b). When small quantities of sample was used, the region where dQ/dt is constant does not appear, and the DSC curve is a regular triangle. Practical DSC curves are the shape as is shown in Fig. 6. The shape of the peak is

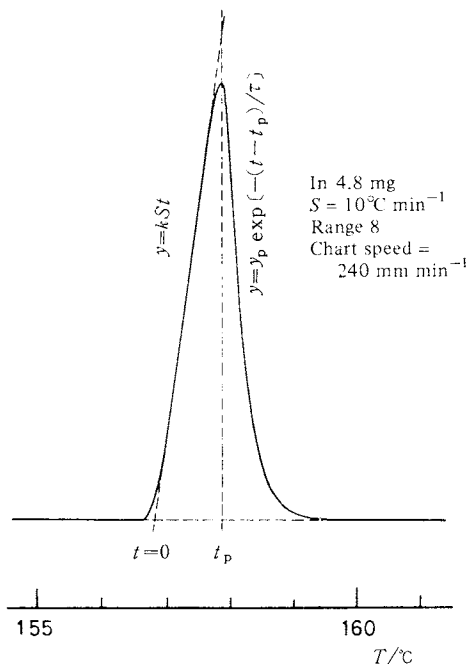


Fig. 6. DSC curve of melting of indium. Sample weight, 4.8mg; heating rate, $10^\circ\text{C} \cdot \text{min}^{-1}$.

expressed approximately with eq. (21).

$$y = kst \quad (0 < t < t_p)$$

$$y = y_p \exp\left\{-\frac{-(t-t_p)}{\tau}\right\} \quad (t_p < t) \quad (21)$$

where the height from the base line is y , the time at the starting point of the peak is zero, the time at the peak is t_p , the peak height is y_p , the heating rate is S and the time is t , and k and τ change a little with different material. For instance, k is 0.13 for In, 0.15 for Sn and 0.23 for Pb, respectively, and τ is 1.83 s for In, 1.92 s for Sn, 1.96 s for Pb and 2.08 s for HDPE, respectively (these are the values with Perkin-Elmer DSC-1B).

The term shown with exponential function may be considered to express the process that temperature distribution in the sample holder and the sample, which changes by absorbing the heat of melting, approaches to that of the stationary state after melting. Though the derived results by O'Neill does not contain this term, it is natural, considering his model of over-simplification. When we determine the heat of fusion from the peak area, the area of this part is also included, because this term originates in the change caused by the

absorption of the heat of melting.

For the cases that the peak deviates from the above-mentioned normal shape and/or that the specific heat capacity changes largely at the transition, method of drawing the baseline is necessary to be derived by taking into account of the theoretical considerations that have been done by Smyth⁸⁾. For instance, it is reasonable to consider that dQ/dt is regulated by the difference of temperature gradient at the point of $x=0$ between the sample and the reference, or by the heat for temperature increase of each side and movement of the melting plane. Further, we assumed the followings. In the model as shown in Fig. 5 (a), the equation of heat conduction holds in each section, such as $0 \sim x_b$, $x_b \sim x_m$ and $x_m \sim l$. The initial conditions is the same as in the section 2.1 and the boundary conditions are $(\partial T/\partial t) = \text{const} = S$ for $x=0$, $k_h(\partial T/\partial x)_{x_b^-} = k_m(\partial T/\partial x)_{x_b^+}$ for $x = x_b$, $-k_m(\partial T/\partial x)_{x_m^-} = -k_s(\partial T/\partial x)_{x_m^+} + \rho \Delta H (\partial x_m/\partial t)$ for $x = x_m$ and $-k_s(\partial T/\partial x) = \text{const} = -\beta$ for $x = l$.

For the response of DSC, Ozawa set forth detailed measurements and discussion⁹⁾. He confirmed that DSC curves can be superimposed on each other and DSC shows linear response when energy is evolved in the sample electrically or optically with infrared ray, but it shows nonlinear response for transitions and reactions.

4.5 Melting temperature for polymers

The melting temperature for polymers have been taken at the final point of S-shape volume change in the case of temperature-volume curves and at the end point of the peak in the case of heat capacity curves. These points correspond to the temperature at which the crystals of the highest melting point melt completely. For many DSC measurements, the peak temperature¹⁰⁾ or the end point of the peak¹¹⁾ are taken as the melting temperature. The peak temperature is close to the melting point determined with optical microscopy, and the end temperature is close to that determined with X-ray diffraction, but there are also suggestions that the melting temperature by DSC must be taken at the end point since the melting temperature by X-ray diffraction is reliable rather than that by optical microscopy¹¹⁾. But these points change with the sample weight, as shown in Fig. 7. Since it is not unreasonable that the melting

point of polymers changes with the measurement condition and the principle, it is necessary to discuss which points is reasonable to be taken considering the principle of DSC.

Geometrical relation between the sensor and the sample base is designed to be nearly constant in DSC. When the samples of little temperature range of melting, such as low molecular materials of high purity, start to melt from the side near the sensor, onset point of the peak is the melting point. The peak is corresponding to the read out temperature at which the upper side of sample melts completely. This temperature changes by sample weight and the state of the sample in the pan, since the geometrical relation of the upper side to the sensor is not constant. After the melting finishes, DSC curves descends exponentially to the base line. Considering the above facts, the maximum melting temperature of samples of some temperature range of melting must be obtained by extrapolating the

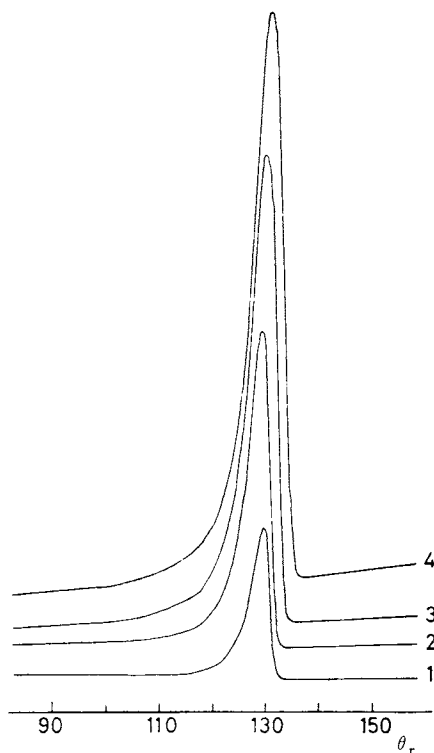


Fig. 7. DSC curves of melting of high density polyethylene of different sample weight. Heating rate, $10^{\circ}\text{C min}^{-1}$. Sample weights: curve 1, 1.98 mg; curve 2, 6.78 mg; curve 3, 11.44 mg; curve 4, 14.67 mg.

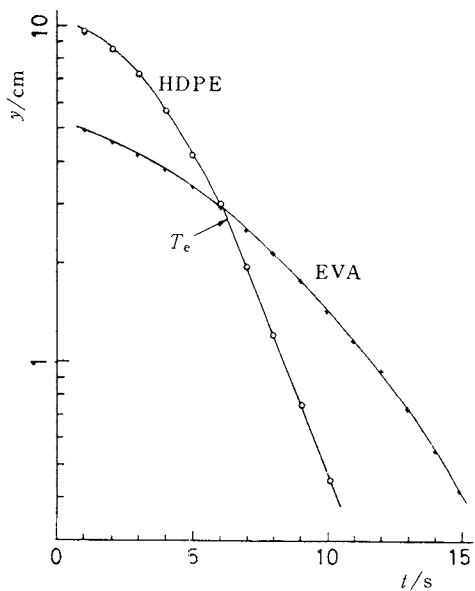


Fig. 8. Height of DSC melting curve from baseline in higher temperature portion. \circ , high density polyethylene; $+$, ethylene-vinyl acetate copolymer.

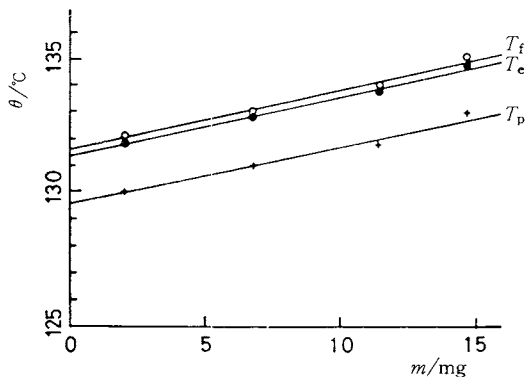


Fig. 9. Sample weight dependence of peak temperature, T_p , starting temperature of exponential DSC curve, T_e and end point of melting curve, T_f .

temperature, at which the DSC melting curve becomes exponential, to zero sample thickness. Fig. 8 shows the result that the logarithm of the height (y) from the baseline is plotted against the time for the higher temperature side of the peak of HDPE and EVA. The HDPE curve has a straight line part, but the EVA curve has not. Therefore, it may be plausible that the melting point is the extrapolated temperature of the following points to the zero sample thickness. For HDPE the point is that at which the relation between $\log y$ and the time begins to be on a straight line, and for EVA it is the end point of the peak. In Fig. 9, the peak temperature, the starting point of exponential DSC curve and the end point of the melting curve are plotted against the sample weight instead of sample thickness.

REFERENCES

- 1) H. Kanetsuna, "Calorimetry, Thermometry and Thermal Analysis", p.93, Kagaku Gijyutsu Sha, (1972)
- 2) K. Amaya, "Jikken Kagaku Koza", vol. 5, p.97, The Chemical Society of Japan. (1958)
- 3) S. Ichihara, *News Letter* (The Society for Calorimetry and Thermal Analysis, Japan), 2, 7 (1971)
- 4) M.J. O'Neill, *Anal. Chem.* 38, 1331 (1966)
- 5) K. H. Hellwege, W. Knappe and P. Lehmann, *Kolloid Z.* 183, 110 (1962)
- 6) J. von Hennig, W. Knappe and P. Lohe, *ibid.*, 189, 114 (1963)
- 7) M.J. O'Neill, *Anal. Chem.* 36, 1238 (1964)
- 8) H. T. Smyth, *J. Am. Ceram. Soc.* 34, 221 (1951)
- 9) T. Ozawa, 12th Japanese Calorimetry Conference, Nagoya (1976), and *Netsusokutei* 4, 45 (1977)
- 10) E. Hellmuth and B. Wunderlich, *J. Appl. Phys.* 36, 3039 (1965)
- 11) ISO interlaboratory study of melting point method for preparation of ISO recommendation, 1218 (1970)