

Differential Thermal Analysis of Polymers. II. Melting

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The first paper¹ of this series dealt with the manner in which a glass transition is manifested in a differential temperature analysis (DTA) thermogram and with the method of arriving at the real value of the glass transition temperature. This paper shall concern itself with the analysis of the polymer melting process.

In the previous paper¹ of this series it was shown that the equilibrium differential temperature $\Delta\theta$ between the center and surface of a cylindrical sample, whose surface temperature is raised at a constant rate β , is:

$$\Delta\theta = \theta_{r=a} - \theta_{r=0} = \beta a^2/4k \quad (1)$$

where a is the radius of the sample and k is the thermal diffusivity.

$$k = K/\rho C_p$$

where K is the thermal conductivity, ρ is the density, and C_p is the specific heat. Further, it was shown that the response of the differential temperature to a step change in the thermal diffusivity (k goes from k_1 to k_2 at time $t = 0$) is

$$\Delta\theta \doteq \frac{a^2\beta}{4k_2} (1 - e^{-k_2\alpha_1^2 t}) + \frac{a^2\beta}{4k_1} e^{-k_1\alpha_1^2 t} \quad (2)$$

where α_1 is the first root of $J_0(\alpha a) = 0$.

Now consider the manner in which C_p changes when a crystalline polymer goes through its melting transition,² as shown in Figure 1.

The heat of fusion ΔH^* per gram of polymer would be

$$\Delta H^* = \int_{T_1}^{T_2} \delta C_p dT, \text{ cal. g.}^{-1} \quad (3)$$

where the integral represents the area above the dotted line. The heat of fusion ΔH per gram of the completely crystalline phase would be:

$$\Delta H = \Delta H^*/W_c \quad (4)$$

where W_c is the weight fraction crystallinity of the sample.

Now, if the $\Delta\theta$ thermogram of polymer melting is corrected for the time lag error¹ so as to be a direct measure of the instantaneous sample thermal diffusivity, that is

$$\Delta\theta_s = \beta a^2/4k$$

Then

$$C_p = 4K\Delta\theta_e/\rho\beta a^2 \quad (5)$$

and thus

$$\delta C_p = (4K/\rho\beta a^2) \delta(\Delta\theta)_e \quad (6)$$

Thus obtaining C_p from the thermogram will allow using the established techniques for calculating crystallinity from the C_p vs. T behavior.²

The heat of fusion ΔH is

$$\begin{aligned} \Delta H &= (1/Wc) \int_{\theta_1}^{\theta_2} (4K/\rho\beta a^2) \delta(\Delta\theta_e) d\theta_s \quad (7) \\ &\doteq (4K/Wc\rho\beta a^2) \int_{\theta_1}^{\theta_2} \delta(\Delta\theta_e) d\theta_s \end{aligned}$$

or, conversely

$$W_c \doteq (4K/\Delta H \rho\beta a^2) \int_{\theta_1}^{\theta_2} \delta(\Delta\theta_e) d\theta_s \quad (8)$$

It is thus seen that in order to calculate the crystallinity of a sample, K , ρ , and the $\delta(\Delta\theta_e) - \theta_s$ values must be known. For utmost rigor one should account for the fact that K , ρ , and C_p vary with both phase and temperature. The problem now is to obtain the $\Delta\theta_e - \theta_s$ curve from the DTA melting thermogram.

It was shown that an inherent error in $\Delta\theta$ is always experienced when the C_p of the sample changes because of the time lag of the machine response.¹ If the methods are employed then it is realized that:¹

(1) $\Delta\theta$ vs. θ_s should have the approximate shape of C_p vs. T for polymer melting.

(2) The magnitude of the $\Delta\theta$ change should be proportional to rate of heating.

(3) The maximum value of $\Delta\theta$, T_{mmt} (the indicated temperature of maximum melting rate) should rise in temperature with increasing rate of heating.

(4) Log T_{mmt} vs. heating rate should be linear, with the zero rate extrapolation being the correct T_{mm} .

(5) Contraction of the θ_s coordinate of the melting $\Delta\theta - \theta_s$ curve by the temperature error, $T_{mmt} - T_{mm}$, should give a reasonably accurate $\Delta\theta_e - \theta_s$ curve. Thus, using the previous equation for W_c (or knowing W_c) the W_c vs. T curve may be calculated.

The problem of the determination of the temperature at which melting is completed still remains. This problem may be solved by considering the following. For an infinitely sharp melting material, C_p changes from one value to another, with its value at the melting point being indeterminate; that is, the slope of C_p vs. T at the melting point is infinite. For a real polymer, however, the melting is diffuse, with C_p increasing to some maximum value and then dropping to some lower value as illustrated in Figure 1. If the slope of this drop in C_p is infinite then this point is the terminus of melting. However, if C_p does not decrease with an infinite slope, then the

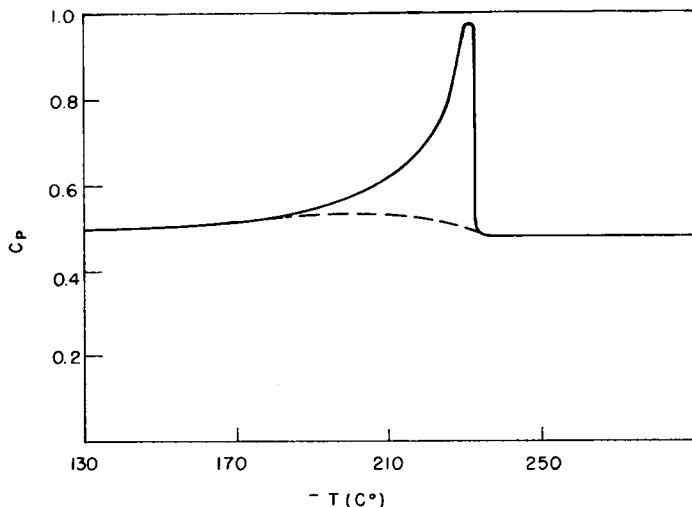


Fig. 1. Behavior of C_p at polymer melting.

point at which C_p reaches its final low value is the terminus of melting. (This is based on the present understanding of polymer melting behavior.)

Now, from eq. (2), it was seen that a step change in C_p or k will result in an approximately exponential dependence of $\Delta\theta$ on temperature. Therefore, the $\Delta\theta - \theta_s$ curve will show an exponential decay even though the polymer's C_p drops with an infinite slope to the final post melting value. The question remains to be answered as to whether the observed $\Delta\theta$ decay is caused by a step change in C_p or an actual toe in the polymer melting-temperature behavior. This may be resolved by calculating the system response for a step change in k of magnitude determined by $\Delta\theta_m$ and $\Delta\theta_b$ (Fig. 2). The exact procedure would be to calculate k_m and k_b from $\Delta\theta_m$ and $\Delta\theta_b$ using eq. (1) and then calculate the system response using eq. (2). If the slope of the system decay is 10 or more times greater than that of the observed $\Delta\theta$ decay then the $\Delta\theta$ decay is a reasonably correct measure of a toe in the melting curve. However, if the slope factor is less than 10 then the system response is an important part of the $\Delta\theta$ decay. Analytical techniques could then be used to calculate the actual drop in C_p but the value of such an effort is questionable.

Let us reconsider the problem of determining the weight fraction crystallinity at temperatures lower than melting. Recalling eq. (8), one sees that, beside knowing the $\Delta\theta_s - \theta_s$ curve one must also know the correct values of a number of parameters. This may be a formidable task. However, the more usual application is to assess the crystallinities of a number of different samples of a given system, e.g., polyethylene. The question thus is whether the instrument may be calibrated using a sample of known crystallinity and thereby compare other samples of the same system. Equation (8) indicates, that if the sample radius, heating rate, etc., were

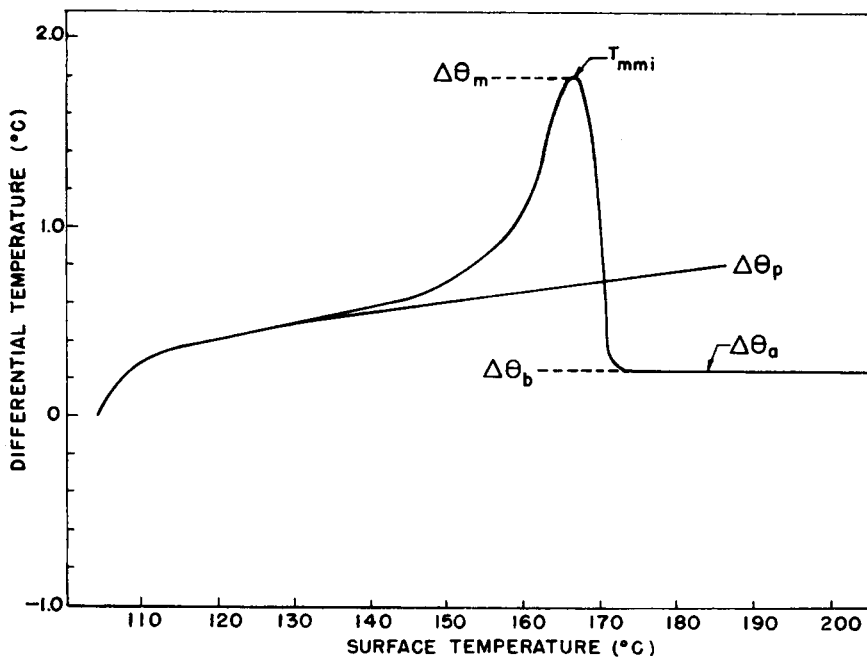


Fig. 2. Typical polymer melting thermograms.

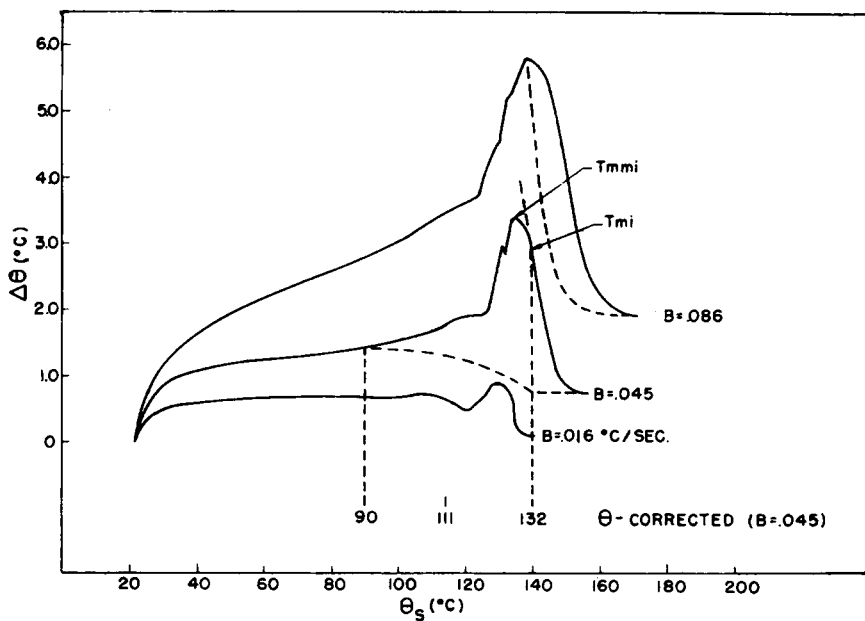


Fig. 3. Melt thermograms of linear polyethylene at several heating rates.

kept constant, then the area under the $\delta(\Delta\theta) - \theta_s$ curve would measure the crystallinities relative to the calibration sample. Even here, because of thermocouple placement, etc., there is room for error in measuring the $\Delta\theta$ values.

However, there is an alternative method of calibration. If the error in measuring $\Delta\theta$ is a constant factor (in a given run) and if one assumes the weight additivity of the C_p of crystalline and amorphous regions then the $\Delta\theta$ before melting, $\Delta\theta_p$, and the $\Delta\theta$ after melting, $\Delta\theta_a$ may also be used to calculate W_c . Since $\Delta\theta \propto C_p$ then

$$\Delta\theta_p = \Delta\theta_a(1 - W_c) + W_c\Delta\theta_c \quad (9)$$

where $\Delta\theta_c$ would be the value for the 100% crystalline material. A known W_c would then give the value of the ratio of $\Delta\theta_c$ to $\Delta\theta_a$, λ . Then, an unknown W_c , W'_c , could be calculated from

$$W'_c = \frac{1 - (\Delta\theta'_p/\Delta\theta'_a)}{1 - \lambda} \quad (10)$$

where the primes denote values from the new run.

Experimental

The DTA equipment used was that previously described. The samples were prepared by compressing the powders into a highly compacted $1/2$ in. diameter pellet. The samples were forced into the test well and then melted down. All differential temperatures were measured between the sample center and a point in the heating block adjacent to the sample.

Results

Experiments were performed to verify the prediction of the manner in which a DTA thermogram reflects polymer melting. $\Delta\theta$ vs. temperature for a crystalline polyethylene (PE) (Marlex 50) sample was measured at three different heating rates as shown in Figure 3. Prior to each run, the sample was annealed at 120°C. for four hours, and then slow cooled. One may readily observe (Fig. 3) that (a) the shape of the $\Delta\theta - \theta_s$ curves are similar to that observed for C_p vs. T ; (b) the magnitude of the $\Delta\theta$ change is proportional to the heating rate, and (c) the maximum value of $\Delta\theta$, $T_{m_{mt}}$, rises in temperature with increasing heating rate. Further, the log of $T_{m_{mt}}$ vs. heating rate gives a straight line as shown in Figure 4.

The system response time was calculated from $\Delta\theta_m$ and $\Delta\theta_b$ using eqs. (1) and (2); and is also shown in Figure 3 (transposed dotted line). As is seen, the calculated system decay is identical to the observed toe in the thermogram. Therefore, there is no toe in the melt behavior. Thus the terminus of melting, T_{m_t} , is as shown in Figure 3. Further the log of T_{m_t} versus β was also linear (Fig. 4) plot.

Contraction of the melt temperature range of the $\beta = 0.045^\circ\text{C./sec.}$ thermogram by $T_{m_t} - T_m$ ($\sim 7^\circ\text{C.}$) gave the $\Delta\theta_s$ vs. θ_s curve as shown in

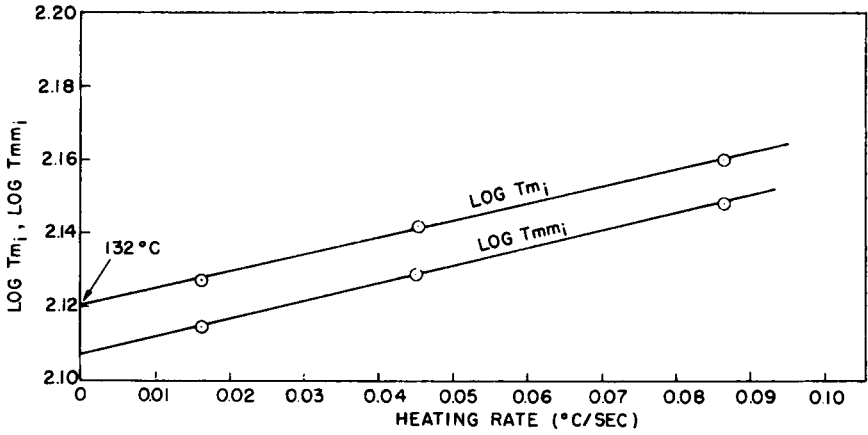


Fig. 4. Logarithm of the indicated temperature of maximum melting vs. heating rate.

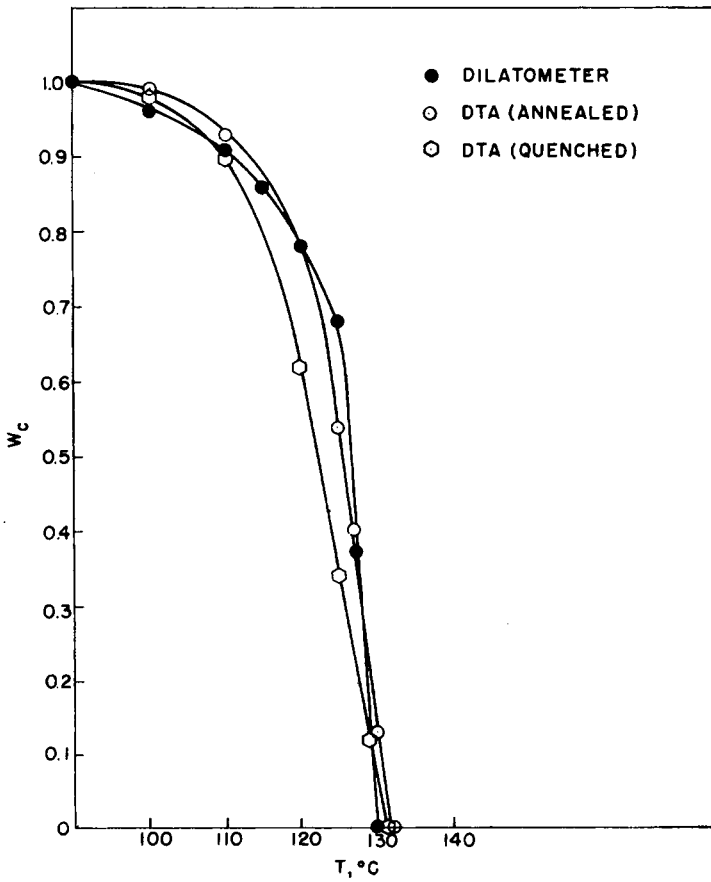


Fig. 5. Relative weight fraction crystallinity vs. temperature of linear polyethylene as determined by DTA and dilatometry.

Figure 3. This contraction was effected in the following manner. At about 90°C . the $\Delta\theta - \theta_s$ curve began to deviate from a steadily rising value. This point was taken as the onset of melting. Since an abrupt change in C_p immediately shows some change in $\Delta\theta$ this point is taken as correct (thermograms on ice show an abrupt change at exactly 0°C . though the maximum value of the $\Delta\theta$ change occurs at some higher temperature dependent on the heating rate). The indicated terminus of melting (139°C .)

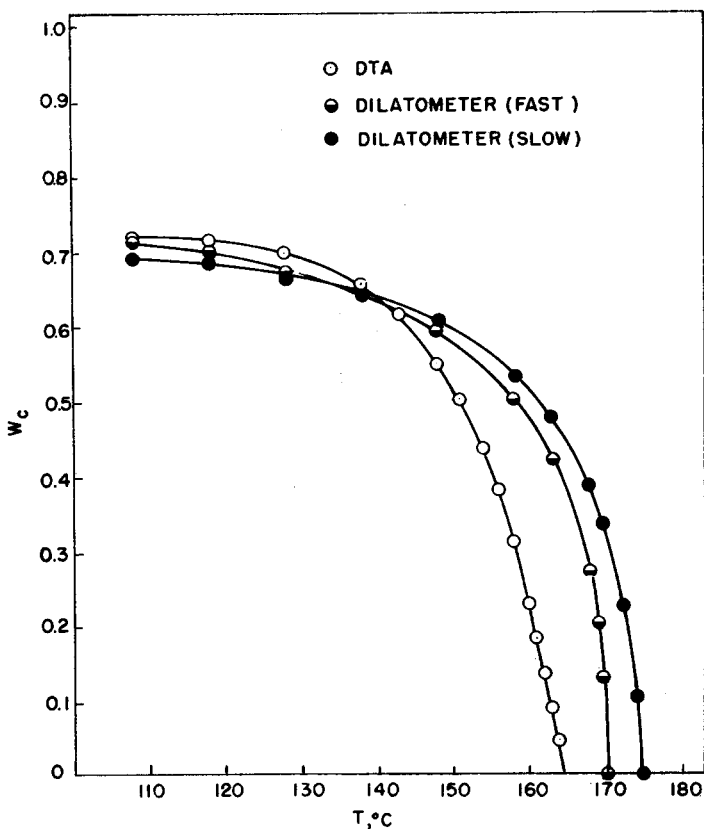


Fig. 6. Weight fraction crystallinity vs. temperature of crystalline polypropylene as determined by DTA and dilatometry.

was corrected by the error ($\sim 7^{\circ}\text{C}$.) to 132°C . and the scale between 90 and 132 was linearly divided. (This linear contraction is not quite correct since the contraction should be greater where more melting is occurring.)

Drawing in a base line (dotted line in Fig. 3)* by assuming that $K/\rho a^2$ changes most rapidly when $\Delta\theta_s$ is a maximum, and equating the area above

* This base line was manually drawn. Successive approximation techniques could have been used to obtain a more accurate base.

the base line to the known W_c permitted the calculation by numerical integration of crystallinity vs. temperature as shown in Figure 5.

Figure 5 also shows dilatometric data³ on the same polymer. Also shown is DTA data on a quenched sample (the sample well, containing the melted polymer was dropped in water). Quenching the sample had no effect on the total crystallinity (comparison of both the area under the thermograms, and the value of $\Delta\theta_p$ just prior to the start of melting and that of $\Delta\theta_a$, using eq. (10), gave negligible differences in total crystallinity).

Figure 3 shows evidence of recrystallization during the DTA runs with recrystallization being most apparent at the slowest heating rate. Considering that the dilatometer is a slow test compared to DTA, then the agreement between the DTA and dilatometry data is good.

Figure 6 shows both DTA and dilatometry melting data⁴ on a crystalline polypropylene (Profax polypropylene). The dilatometry data were obtained over two different time intervals (4 hr. and 8 days). The DTA thermograms showed no evidence of recrystallization. It should be pointed out that the dilatometric data showed that recrystallization becomes important above 140°C. This temperature corresponds to the point where the DTA and dilatometric data begin to diverge.

Thus, considering the phenomenon of recrystallization and the liberties taken in both the temperature scale contraction of the DTA melt thermogram and the drawing of the base line under the melt thermogram, then the results on both the polyethylene and polypropylene are in good agreement with the theory.

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References

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Synopsis

A theory is presented of the way in which the melting of a polymer is manifested in a differential temperature analysis thermogram. An analytical method based on this theory allows a precise determination of both the melting point and the crystalline weight fraction as a function of temperature. Experimental results for linear polyethylene and crystalline polypropylene confirm the theory.

Résumé

On présente une théorie de la façon par laquelle la fusion d'un polymère se manifeste dans un thermogramme d'analyse différentielle thermique. On décrit des méthodes analytiques basées sur cette théorie en vue d'obtenir le point de fusion précis. On décrit également le comportement de la fraction en poids de cristallinité en fonction de la température. Des résultats expérimentaux dans le cas du polyéthylène linéaire et du polypropylène cristallin confirment les divers aspects de la théorie.

Zusammenfassung

Eine Theorie dafür, wie sich das Schmelzen von Polymeren im Thermogramm einer Differentialthermoanalyse äussert, wird vorgelegt. Auf dieser Theorie beruhende analytische Methoden zur Ermittlung des korrekten Schmelzpunktes und der Temperaturunabhängigkeit des kristallinen Anteils werden beschrieben. Durch Versuchsergebnisse an linearem Polyäthylen und kristallinem Polypropylen werden die verschiedenen Aspekte der Theorie bestätigt.

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