

Rate Effects in the Measurement of Polymer Transitions by Differential Scanning Calorimetry

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Synopsis

Depending on heating rate, differences as large as 15°C in polymer transition temperatures may be observed in DCS measurements. A heat transfer analysis of the method shows that this rate dependence is a result of a lag in the heat path to the test sample and lag in heat transfer within the sample. Experiments confirmed the analysis. Methods for obtaining the correct values of transition temperatures are given.

INTRODUCTION

Differential scanning calorimetry (DSC) has become a widely used method for measuring phase transitions in polymers. Essentially, the method consists of measuring the rate of the electrical energy input to a sample chamber and sample needed to keep the heating rate of some area of the sample chamber constant. Note that the sample temperature is not directly measured. Because of the small sample size used (~10 mg) and the small size of the chamber, it has been tacitly assumed¹ that the sample temperature is uniform and equal to that of the chamber. Thus, the effect of heating rate on measured transitions is usually considered negligible.

Recently, Karasz, Bair, and O'Reilly² measured the T_g of PPO polymer using both an adiabatic calorimeter and a DSC. Employing heating rates of 2.4×10^3 °K/hr and 5 °K/hr, respectively, they found a value of T_g 18° higher by DSC than that from the calorimeter. Such a large discrepancy cannot be explained as an increase of T_g because of overshoot in free volume.³ We have observed similar discrepancies.

It is our contention that the observed discrepancies are a result of a heat transfer lag in attaining equilibrium conditions when the test sample undergoes a phase transition. We shall show that there is a significant dependence of the indicated value of a phase transition on the heating rate and that this dependence is a result of a lag in the heat path to the sample and lag in heat transfer within the sample.

THEORETICAL

Figure 1a shows a typical arrangement for the DSC. For analysis, the arrangement in 1a can be approximated by that in Figure 1b. In 1b, the sample holder and sample are taken as infinite slabs, and the free surface of the sample holder has a monitored heat input such that its surface is heated at a fixed rate. The simplest case is shown in Figure 1c where one surface of the sample slab is heated at a constant rate, the other surface being insulated so that the temperature gradient is zero at this surface. The situation of the sample undergoing a step change in specific heat or thermal diffusivity at some temperature will be analyzed. It has been shown⁴ that such an analysis is relevant to a polymer undergoing a glassy transition (C_p is sigmoidal at T_g) and also to melting phenomena. The analysis follows:

Let the sample surface be heated at some fixed rate, β . Assume a material of thermal diffusivity, k_1 , is heated at a rate β up to $t = \lambda$, where λ is large enough so that thermal equilibrium has been established. Heating of the k_1 material is then abruptly stopped; its surface at $x = l$ is held at $\theta = \beta\lambda$, and it is insulated at $x = 0$ (Case A). At this time, the material of diffusivity, k_2 , begins heating at the rate β (Case B). The sum of the temperatures of the k_1 and k_2 materials for $t \geq \lambda$ is now the temperature of the actual sample. Note that there is some approximation in assuming that the diffusivity of the whole sample changes at $t = \lambda$. This, of course, is not really so since there is a temperature gradient in the sample.

Carslaw and Jaeger⁵ give a solution for the slab, $-l \leq x \leq l$, with boundary conditions: $\theta = \beta t$; $x = \pm l$, and initial conditions: $\theta(x) = 0$; $t = 0$:

$$\theta_B = \beta(t - \lambda) + \frac{\beta(x^2 - l^2)}{2k_2} + \frac{16\beta l^2}{k_2\pi^3} \sum_{i=0}^{\infty} \frac{(-1)^i}{(2i+1)^3} \\ \times \left[\exp\left(-k_2(2i+1)^2\pi^2(t-\lambda)/4l^2\right) \cos \frac{(2i+1)\pi x}{2l} \right]; t \geq \lambda \quad (1)$$

which is also the solution for case B:

$$0 \leq x \leq l; \left. \frac{\partial \theta}{\partial x} \right|_{x=0} = 0$$

$$\theta = \beta t \text{ at } x = l$$

Case B also gives the initial conditions for case A:

$$\theta = \frac{\beta(x^2 - l^2)}{2k_1}$$

The boundary conditions are:

$$\theta = \beta\lambda; x = l$$

$$\frac{\partial\theta}{\partial x} = 0; x = 0$$

Using the methods of Carslaw and Jaeger, the following solution is obtained:

$$\theta_A = -\sum_{i=0}^{\infty} \frac{(-1)^i 16\beta l^2}{(2i+1)^3 \pi^3 k_1} \times \exp\left[-\frac{k_1(2i+1)^2 \pi^2 (t-\lambda)}{4l^2}\right] \cos \frac{(2i+1)\pi x}{2l} \quad (2)$$

The solution for the temperature in the sample after a step change in diffusivity at $t = \lambda$ is then (ignoring terms $i > 0$ and taking λ as zero)

$$\theta \doteq -\frac{16\beta l^2}{k_1 \pi^3} \exp(-k_1 \pi^2 t / 4l^2) \cos \frac{\pi x}{2l} + \beta t + \frac{\beta(x^2 - l^2)}{2k_2} + \frac{16\beta l^2}{k_2 \pi^3} \exp(-k_2 \pi^2 t / 4l^2) \cos \frac{\pi x}{2l} \quad (3)$$

Now the rate of heat input, $\partial H / \partial t$, is the measured quantity. Now $k = K / \rho C_p$

where:

K = thermal conductivity

ρ = density

C_p = specific heat

and K and ρ are taken as constant. Then from (3)

$$\frac{\partial H}{\partial t} = -K \frac{\partial^2 \theta}{\partial t \partial x} \Bigg|_{x=l} = \frac{2K\beta}{l} [\exp(-k_1 \pi^2 t / 4l^2) - \exp(-k_2 \pi^2 t / 4l^2)] \quad (4)$$

Equation 4 shows that the heat input changes, when C_p goes thru a step change, and takes time to reach a new equilibrium value. The shape of the $\partial H / \partial t$ vs. t curve is sigmoidal and has an inflection point, t_i^c at

$$t_i^c = \frac{4l^2}{(k_1 - k_2)\pi^2} \log_e \frac{k_1}{k_2} \doteq \frac{4l^2}{k_2 \pi^2}; \text{ for } k_1 \sim k_2 \quad (5)$$

and in terms of a temperature error,

$$\Delta\theta^c \doteq \frac{4\beta l^2}{k_2 \pi^2} \quad (6)$$

Equation (6) allows estimating the error from the geometry and thermal properties of the sample.

As to the situation illustrated in Figure 1, an estimate of the error involved because of the path through the sample chamber can be made as follows. Assume the sample has only a small effect on the temperature

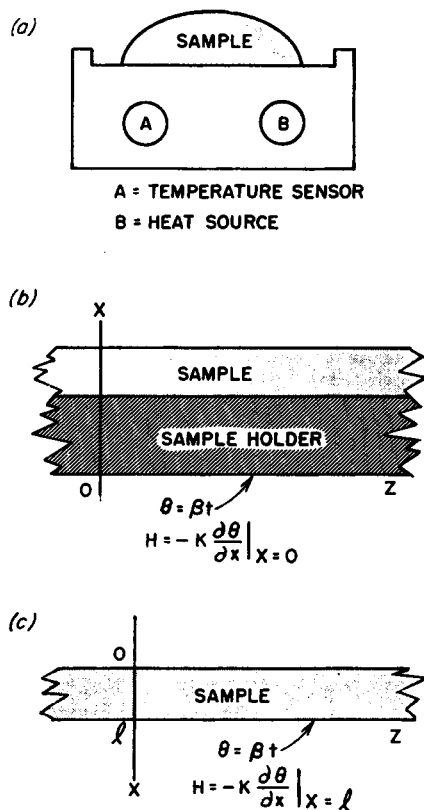


Fig. 1. (a) Typical arrangement for differential scanning calorimetry; (b) simplified model; sample and sample holder paths considered; (c) only sample paths considered.

profile in the sample chamber. Then from eq. (1), the sample-sample chamber surface lags the heated surface by a temperature:

$$\frac{\beta l_{sc}^2}{2k_{sc}}$$

where sc indicates sample chamber.

Accordingly, the estimate of error is from 6 and 7:

$$\Delta\theta \sim \beta \left[\frac{l_{sc}^2}{2k_{sc}} + \frac{4l_s^2}{\pi^2 k_s} \right] \quad (8)$$

where S refers to sample.

The first term in the bracket is a machine parameter and is best evaluated experimentally. The second term will depend on the sample. An estimate of its magnitude can be gotten by assuming typical values for polymer samples, e.g., $k = 0.001$, and $l = 0.1$ cm (for a 10 mg powder sample). For these values, t_i^e is about 4 sec. Thus, an error of the order of 4°C or more should be seen at a scanning rate of $60^\circ\text{C}/\text{min}$ for such a sample.

EXPERIMENTAL

All experiments reported here were made on the Perkin-Elmer Model 1 B. The machine temperature calibration setting was adjusted to some arbitrary value. Figure 2 shows uncorrected maximum rate of melting point ($T_{m\dot{m}i}$) data on a 0.040 mg sample of indium. We note a reasonably linear relationship between $T_{m\dot{m}i}$ and β . For such a small sample of a high diffusivity material the sample effect (eq. (6)) should be negligible. Figure 3 shows data on Indium for samples of different weight; only a small effect

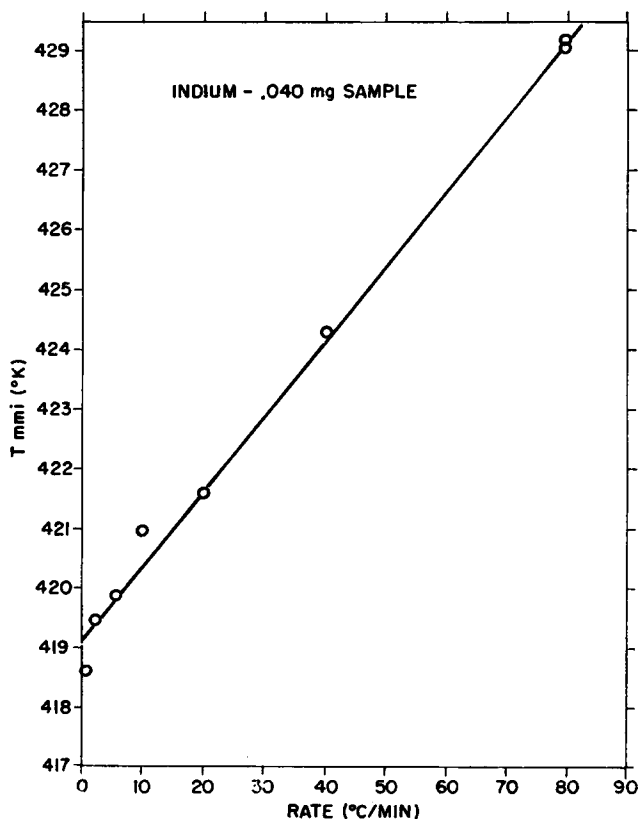


Fig. 2. Indicated temperature of maximum rate of melting ($T_{m\dot{m}i}$) vs. heating rate for indium.

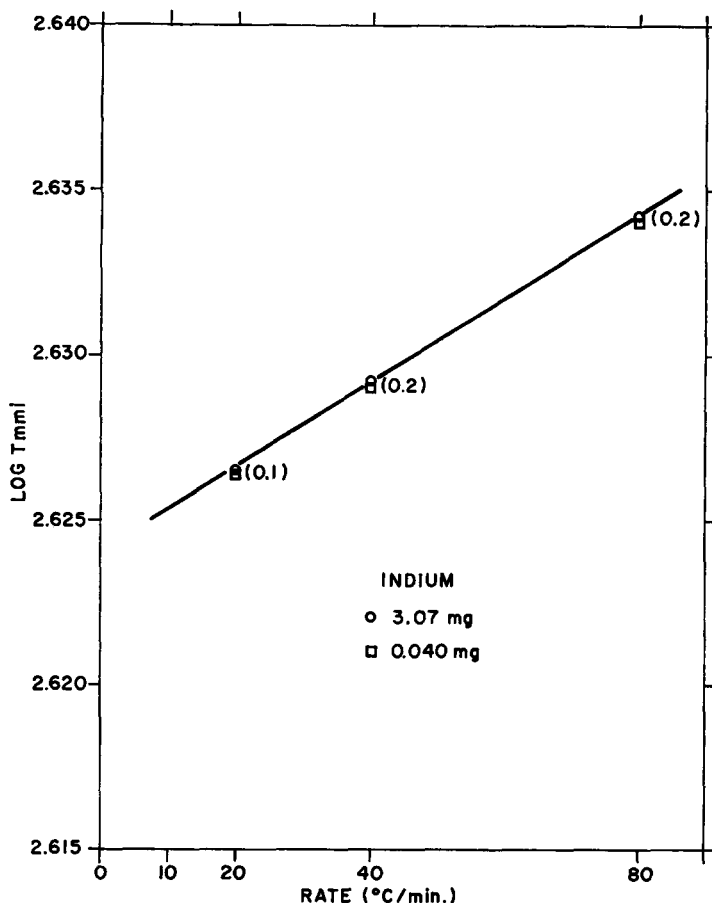


Fig. 3. Logarithmic plot of T_{mmi} vs. heating rate for indium samples of differing weights.

of sample size is seen. Thus, the rather large dependence of T_{mmi} on β is, for this sample, the machine path error. Although the linear line is a reasonable fit, a plot of $\log T_{mmi}$ vs. β is somewhat better at the very low heating rates. Considering the assumptions, and as has been shown from DTA measurements of T_g and T_m on polymers⁴ that a $\log T$ vs. β plot is more appropriate; the log plot shall be used from here on.

Figure 4 shows T_g data on a monodisperse high molecular weight polystyrene ($M_w = 500,000$) for different sample sizes. The method of reading T_g is to take the midpoint (or inflection point) of the T_g sigmoid transition. This method is more consistent with other means for measuring T_g since this point corresponds to the break in the enthalpy-temperature (or volume temperature) curve. The toe of the sigmoid which is often taken as T_g is really the onset of T_g . At $80^\circ\text{C}/\text{min}$ the 10 mg sample has $T_{g,i}$ about 2.2° higher than the 2 mg sample. This is about the magnitude to be expected from eq. 6.

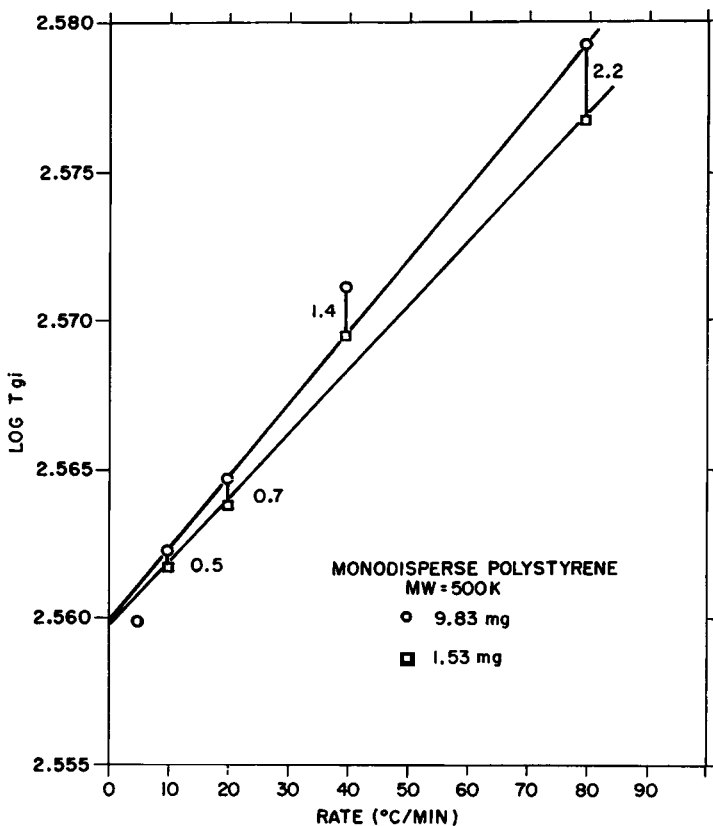


Fig. 4. Indicated glass transition temperature (T_{gi}) vs. heating rate for polystyrene samples of differing weights.

Figure 5 shows melting point data on naphthalene and *p*-nitrotoluene. Note that the slopes are nearly equal and quite close to that for indium. The T_{mm} values for naphthalene and *p*-nitrotoluene can be used as measures of the combined machine and sample errors at the two fixed points corresponding to the respective T_{mm} 's. By interpolation, the polystyrene T_{gi} data are corrected for both rate and average temperature calibration settings. The resulting line for polystyrene is shown in Figure 5b. The slope of this corrected line is now very close to that expected from the effects of the heating rate on free volume.³ Thus, a decade change in heating rate produces a change in T_g of about 3°C, for nominal heating rates.

CONCLUSIONS

We have shown that there is a dependence of the indicated value of a transition such as a T_g or T_m on the rate of heating employed in a DSC measurement. This dependence on heating rate can result in a large error depending on how the machine has been calibrated. Further, this

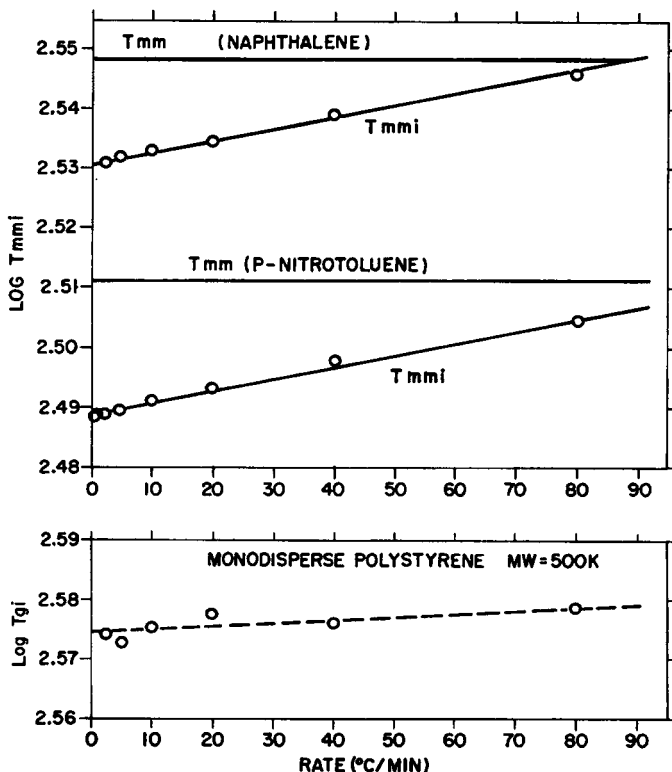


Fig. 5. T_{mni} for naphthalene and *p*-nitrotoluene and also T_{gi} for polystyrene, the latter corrected for heating rate error.

error or rate dependence is a result of: (a) a time lag in the sample, (b) a time lag in the heat path thru the sample, and for T_g 's, (c) the free volume effects.

The manner of correction is the choice of the experimenter. He can calibrate the machine at some specific heating rate, then obtain a T_m - β curve (for, say Indium) and use this to correct his data when other heating rates are employed. However, for precise comparison of data, particularly T_g , we feel the machine should be calibrated at a very low β ($\beta \sim 0$) and that zero heating rate extrapolations should be then made to obtain the correct T_g , since the extrapolation essentially eliminates all effects, including that from free volume.

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Received November 22, 1968