Differential Thermal Analysis of Polymers.
I. The Glass Transition

STEPHEN STRELLA, *Monsanto Chemical Company, Research Department, Plastics Division, Springfield, Massachusetts*

I. INTRODUCTION

A number of articles[1-3] have recently appeared on the application of the technique of differential thermal analysis (DTA) to the determination of the temperatures at which phase or chemical changes occur in polymers. However, for most of the polymers that were studied, these temperatures such as the glass transition, T_g, and the melting point, T_m, were well known. The question thus arose as to whether a DTA thermogram could be correctly interpreted if one had no prior knowledge of a material's thermal behavior. This is of particular importance if the technique is to be utilized for the determination of the properties of new polymers.

This paper will be concerned with the manner in which the glass transition is manifested in a DTA thermogram and the method of evaluating correctly this transition from the DTA thermogram.

II. THEORY

A. Basic Principle

The basic principle involved in DTA is that a temperature gradient will exist within a sample if the sample surface is heated in some manner with time.

This temperature gradient is dependent on both the heating rate and on the thermal diffusivity, k, of the sample. (k = ratio of thermal conductivity, K, to the product of the specific heat, C_p, and the density, ρ). This dependence on the thermal diffusivity arises because the thermal conductivity determines the rate at which heat is transferred to a differential mass within the sample, and the specific heat determines the temperature rise of this mass.

If the sample's thermal properties change abruptly at some temperature, then the temperature gradient will change accordingly. Since C_p and/or K will change when the sample undergoes a chemical or phase transition (e.g., C_p is known both to increase sharply at the glass transition of a polymer and to go through a maximum at the melting point of a polymer), then observation of the behavior of the temperature gradient will indicate the presence of such transitions.

In practice, one does not measure the actual temperature gradient in the sample but the temperature difference between the center of the test sample and of an inert reference material that is being heated under identical conditions. The reason for this is that the sample's thermal diffusivity changes smoothly with temperature and thus the temperature gradient also changes. If a high degree of sensitivity is used for recording the temperature gradient (this will be necessary for secondary phase changes), then an unreasonable slope of the temperature gradient–time curve will be observed with this slope possibly masking small transitions. However, if the reference material's thermal diffusivity changes similarly to that of the test sample, then an approximately constant differential temperature will result, thus readily permitting the observation of small abrupt changes in the sample's thermal properties.

B. Analysis of the Heat Transfer Problem

In order to analyze the manner in which a glass transition will be depicted on a DTA thermogram, consider the situation of an infinite cylinder of radius a, whose surface is heated at a constant rate, β, beginning at time $t = 0$. The equation for the temperature, θ, at a point r within the cylinder may be found to be[4]

$$\theta = \beta \left(t - \frac{a^2 - r^2}{4k} \right) + \frac{2\beta}{ak} \sum_{n=1}^{\infty} \frac{J_0(r\alpha_n)}{\alpha_n{}^3 J_1(a\alpha_n)} \exp\{-k\alpha_n{}^2 t\} \qquad (1)$$

where α_n = the nth root of the equation, $J_0(\alpha a) = 0$. For the sample radius discussed here ($a \doteq 0.5$ cm.), terms higher than α_1 may be neglected. Thus the temperature difference between the center and surface of the sample is:

$$\Delta\theta = \theta_{r=a} - \theta_{r=0} \doteq (a^2\beta/4k)(1 - \exp\{-k\alpha_1{}^2 t\}) \qquad (2)$$

and the steady state temperature distribution [t in eq. (1) is large] is:

$$\theta = \beta \left(t - \frac{a^2 - r^2}{4k} \right) \qquad (3a)$$

$$\Delta\theta = \beta a^2/4k \qquad (3b)$$

Now if one considers that, at some time $t = \lambda$, the thermal diffusivity of the material undergoes an abrupt change (this is not actually correct since the thermal diffusivity of a material changes at a given temperature, not at a given time), that is, at the glass transition point the thermal diffusivity abruptly changes from one value to another, i.e., k goes from k_1 to k_2 at time $t = \lambda$, then the problem may be analyzed in the following manner: At time $t = \lambda$ or at times less than λ, the steady state temperature distribution through the sample is given by eq. (3) where k is equal to k_1. Now at $t = \lambda$ the surface temperature may be kept constant for the k_1 material, thus letting the parabolic temperature distribution of the k_1 material reduce to 0. Further, at time $t = \lambda$ one may consider that the k_2 material has had

an initial zero temperature distribution and will now begin to develop a differential temperature according to eq. (1). The sum of these two effects will give the correct differential temperature at time t greater than λ (Boltzman's Superposition Principle). The expression for the decay of the parabolic temperature distribution (again neglecting higher order terms of α_n) is found to be:

$$\Delta\theta \doteq (\beta a^2/4k) \exp\{-k\alpha_1^2 t\} \qquad (4)$$

Thus the equation for $\Delta\theta$ when k undergoes a step change is (λ is considered zero):

$$\Delta\theta = (\beta a^2/4k_2)[1 - \exp\{-k_2\alpha_1^2 t\}] + (\beta a^2/4k_1) \exp\{-k_1\alpha_1^2 t\} \qquad (5)$$

Insertion of typical values into eq. (4) will prove instructive. Taking k as 1.1×10^{-3} and k_2 as 1.0×10^{-3} (these values are of the magnitude found in polymers), a as 0.5 cm., and β as 0.1°C./sec. results in values of the differential temperature vs. time as shown in Figure 1. From Figure 1 it is observed that it takes at least 200 sec. for the differential temperature to come to its new equilibrium value. Thus, the system takes a considerable time to respond to a step function change in the thermal diffusivity.

Consider now the effect of this time lag on the differential temperature vs. surface temperature behavior. For a 1°/sec. temperature rise, the surface will have risen 200° in temperature before the differential temperature has approached its equilibrium value. For a 0.1°/sec. temperature
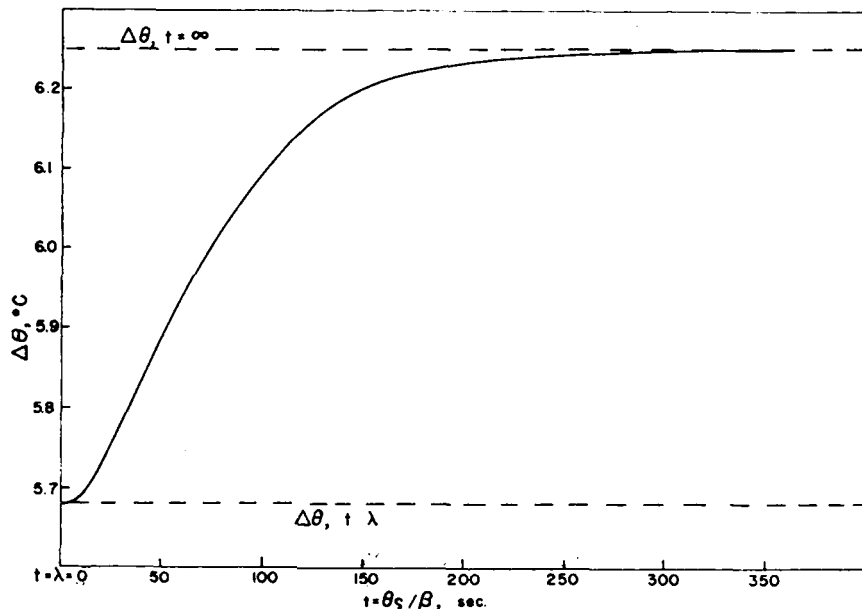

Fig. 1. Differential temperature vs. time or surface temperature for a step change in thermal diffusivity.

rise, the surface temperature will have gone 20° before reaching equilibrium and for a 0.01° rise the absolute temperature will have gone 2° before reaching equilibrium. Thus it is seen that on a $\Delta\theta$ vs. surface temperature basis, the change in $\Delta\theta$ is markedly dependent on rate. It is also observed from eq. (5) that the magnitude of the $\Delta\theta$ change is linearly dependent on β (the rate of temperature rise).

C. Analysis of the T_g Thermogram

Now consider the manner in which the thermal diffusivity actually changes at a glass transition for a real polymer. Figure 2 shows the manner in which C_p changes as a polymer goes through a glass transition.[5] If the assumed small change in thermal conductivity and minor change in
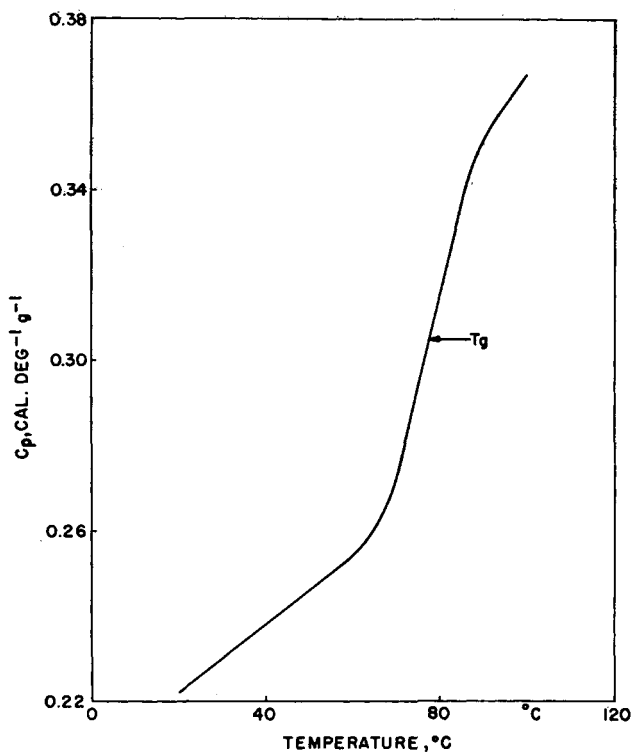

Fig. 2. Specific heat vs. temperature for a polymer about the glass transition.

density are neglected, then behavior of the diffusivity would be the reciprocal of that of the specific heat. The analysis shown previously might then be used to obtain the $\Delta\theta - \theta$ curve by dividing the diffusivity curve (reciprocal C_p curve) into small incremental step functions. However, this is actually not necessary. From the previous discussion of the response of the system on a surface temperature basis, it is seen that the

inflection point (the inflection point is taken as the indicated glass transition temperature, T_{gi}) of the thermal diffusivity curve for a true polymer would be displaced upwards in temperature as the temperature rate is increased. Therefore, the following deductions about the shape of the differential temperature curve as a real polymer goes through a glass transition can be made:

1. The shape of the $\Delta\theta$ vs. surface temperature curve should be of sigmoidal nature.

2. The maximum value of the $\Delta\theta$ change at the glass transition should be linearly dependent on the heating rate.

3. The inflection point T_{gi} should rise in temperature with the heating rate.

Further, considering the exponential nature of eq. (5), it is realized that a graph of log T_{gi} vs. rate should be linear and that on extrapolating this line to zero rate the effect of the lag in the system would be removed, the zero rate extrapolation being the correct glass transition temperature.

III. EXPERIMENTAL

A. Apparatus

The theoretical analysis indicated that three major requirements need be met for a DTA apparatus to be successful. The first of these is that the heating rate should be very uniform with time, preferably linear, since any erratic change in the heating rate will reflect itself if an erratic change of $\Delta\theta$, this change being possibly construed as some sort of transition. Second,
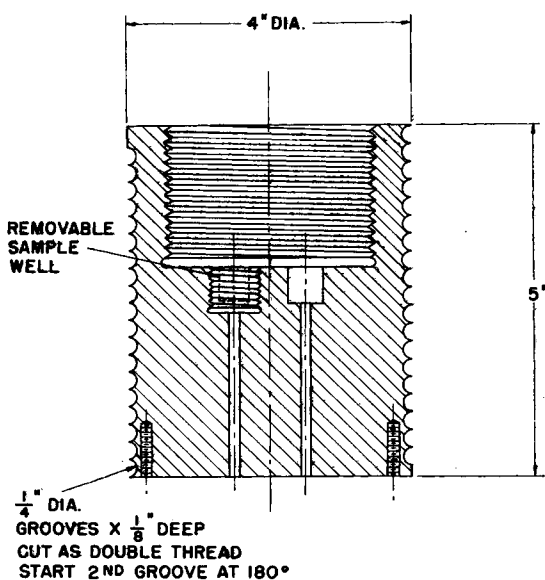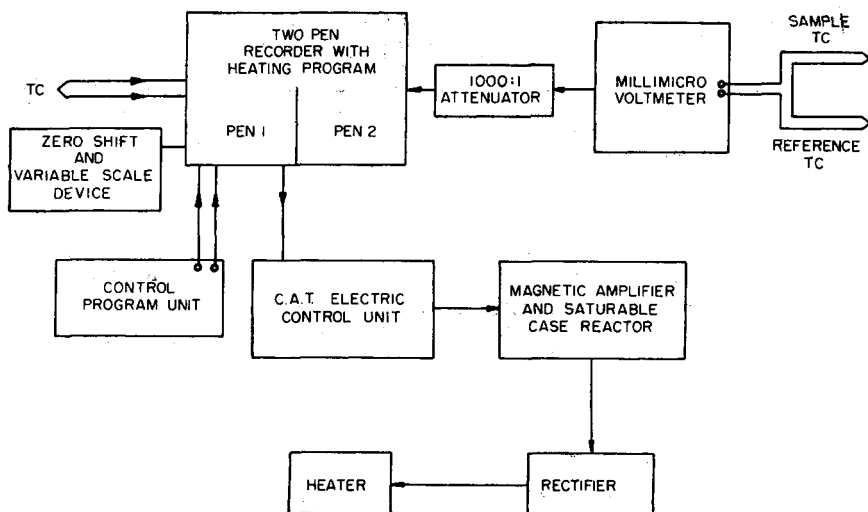

Fig. 3. DTA heating block.

Fig. 4. DTA heating and temperature indicating apparatus.

the sample geometry should not erratically change on heating since this also will manifest itself as a change in $\Delta\theta$. Third, because of the magnitude of the $\Delta\theta$ change in the glass transition, a great deal of sensitivity for measuring differential temperature is required. The following describes an apparatus which has suitably met the above requirements.

The equipment consists of a heating block and enclosure, a temperature controlling apparatus, and a temperature indicating apparatus, Figure 3. Pi wound Chromalux tubular elements are used for heating. This block is suitable for measurements up to a temperature of 650°C. It is cooled simply by surrounding it with crushed Dry Ice. The copper block can be housed in an evacuable chamber for atmospheric control. A block diagram of the heating and temperature indicating apparatus is shown in Figure 4. The block may be heated at linear rates of from 0 to 15°C./min. to about a maximum temperature of 650°C. The temperature controller may be used in two ways. One is to use a pre-cut cam to program the temperature rise of the sample. The second is to keep the energy input into the heater constant. The second method is preferable even though there is slight deviation from linearity when extremely high differential temperature sensitivities are being used, since any little erratic burr on the cam or any hunting of the cam program will reflect itself in an erratic differential temperature curve.

The recorder pre-amplifier used for amplifying the differential temperature has a maximum sensitivity of 0.1 μv. with an output of 10 v. with a noise level of about 2%. In practice though, because of source junction noise and other noise productive sources, this sensitivity is difficult to realize. However, it is relatively simple to obtain a sensitivity of 10 μv. of full scale and, with some caution, 1 μv. full scale. These two correspond

to 0.23° full scale of chart (10 in.) and 0.023° full scale of chart when using copper constantin thermocouples.   Fortunately 0.23° full scale of chart is more than sufficient (as will be seen later) for detecting the presence of glass transitions.

B. Sample Preparation Procedure

The sample preparation procedure used is first either to mole or compact the sample to a cylinder size of 0.375 in. diameter by 0.375 in. high (the well size is 0.5 in. diameter by 0.5 in. deep).   A small hole is then drilled halfway in from one face of this cylinder.   The sample cylinder is placed in the sample well (the thermocouple is already in place), and aluminum powder is carefully put around the sides of the sample.   Caution is exercised so as to not have aluminum powder form a conductive path between the top surface of the sample and the bottom part of the top copper plug.

600 mesh alundum powder, to which aluminum powder may be added to effect a good match, is packed in the reference well.

IV. RESULTS AND DISCUSSION

A. Verification of the Heat Transfer Analysis

In order to check the applicability of the preceding mathematics experimentally, an experimental determination of the thermal diffusivity of polymethyl methacrylate (PMMA) was made.   The method was to measure the equilibrium $\Delta\theta$ (Fig. 5) of the differential temperature and then to calculate the thermal diffusivity from eq. (3b), i.e.,
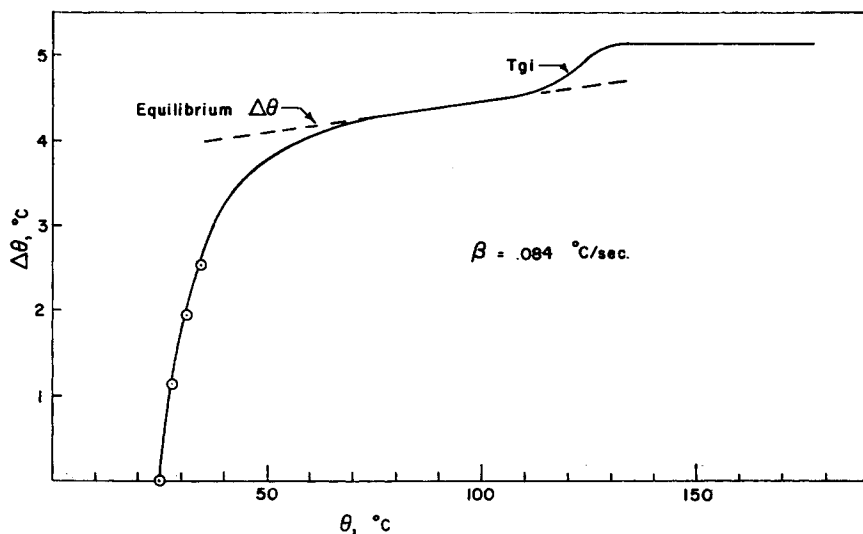
$$\Delta\theta = a^2\beta/4k$$

Fig. 5. Differential temperature vs. surface temperature for a PMMA sample.

The value determined for k was 1.26×10^{-3} cm.^{2} sec.$^{-1}$, in good agreement with the literature value[6] of 1.2×10^{-3} cm.^{2} sec.$^{-1}$. The mathematical analysis was thus considered applicable.
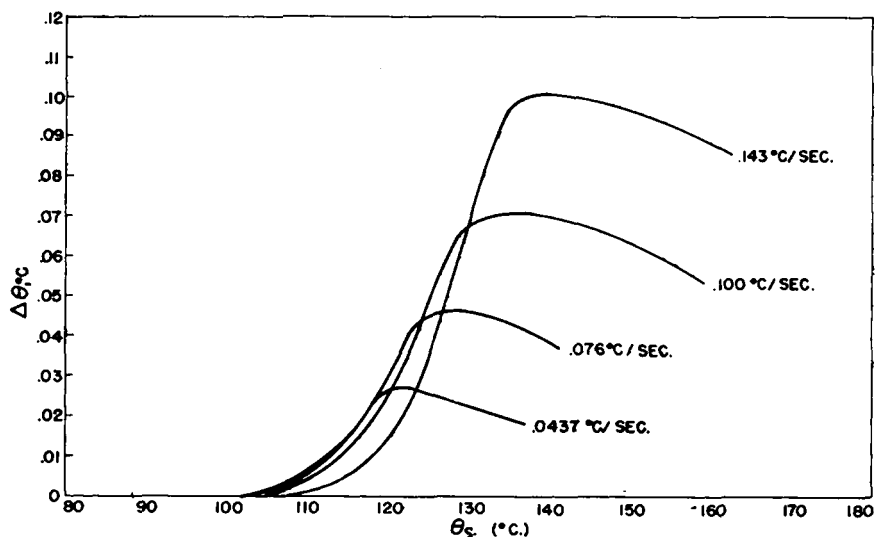

Fig. 6. Differential temperature vs. surface temperature for a PMMA sample heated at several rates.
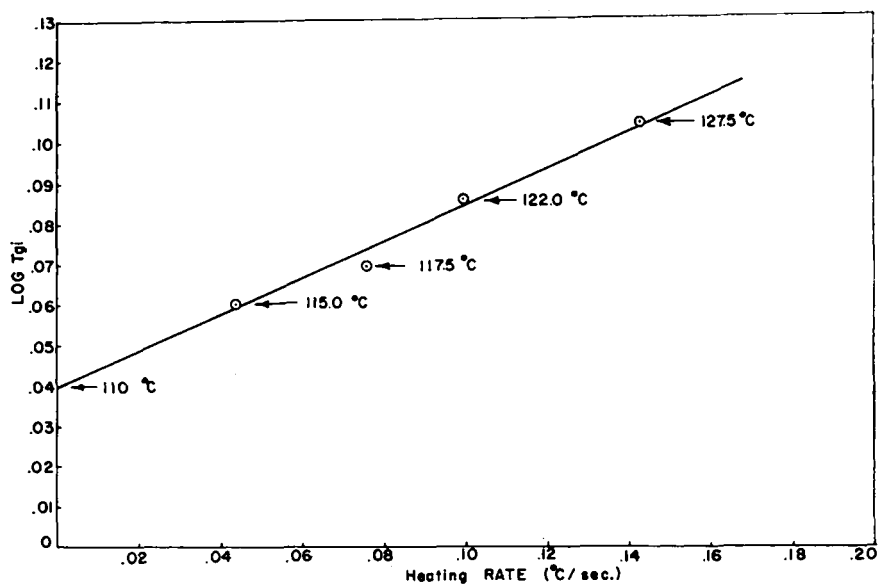

Fig. 7. Logarithm of the indicated glass transition temperature vs. heating rate, for PMMA.

B. Verification of the T_g Analysis

Experiments were performed to verify the prediction of the manner in which a DTA thermogram reflects a glass transition temperature. $\Delta\theta$ vs. temperature for a PMMA plus was measured at four different heating rates (as shown in Fig. 6). One may readily observe from Figure 6 that (a) the shape of the $\Delta\theta$ vs. surface temperature curve is approximately
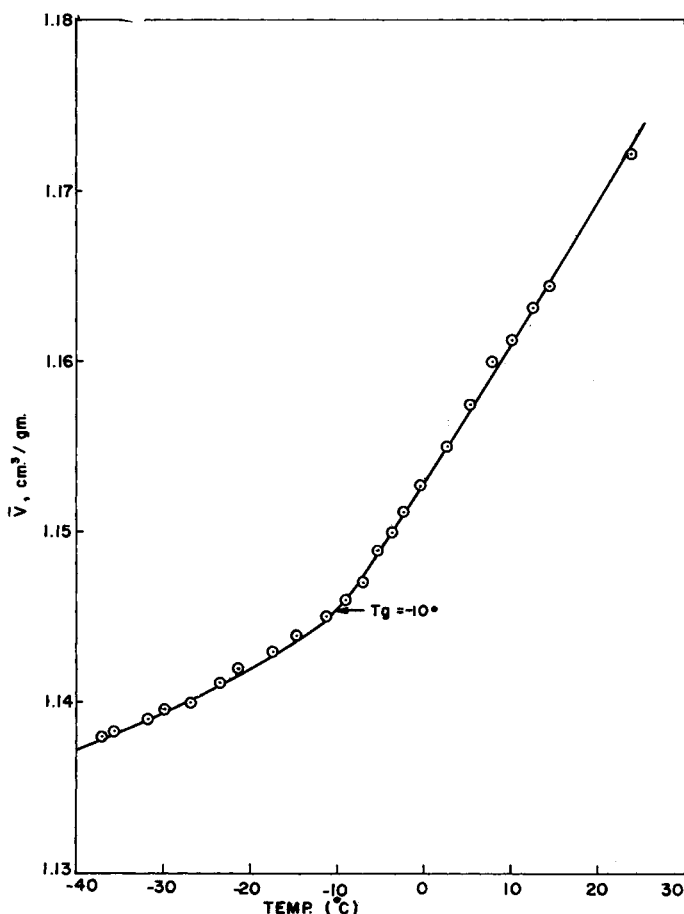

Fig. 8. Specific volume vs. temperature for atactic polypropylene.

sigmoidal, (b) the magnitude of the $\Delta\theta$ change at the glass transition is proportional to the heating rate, and (c) that the inflection point of the $\Delta\theta$ vs. surface temperature curve is displaced upwards in temperature as the heating rate is increased. Further, taking the inflection point as the indicated value of the glass transition temperature, T_{gi}, then a graph of the log of T_{gi} vs. the heating rate results in a straight line as shown in Figure 7.
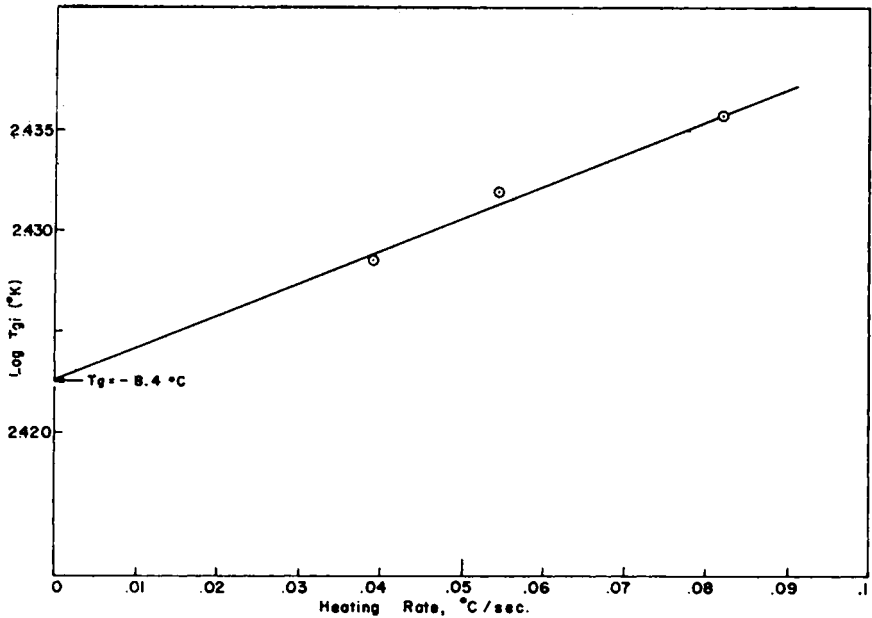
Fig. 9. Logarithm of the indicated glass transition temperature vs. heating rate for atactic polypropylene.

As is seen the zero rate extrapolation yields a glass transition temperature of 110°C. This value compares quite favorably with Mandelkern's value of 105°C.[7] Thus the prediction that the extrapolation of T_{gi} to zero rate would yield the value of the glass transition temperature is considered correct.

A more thorough check of this extrapolation procedure was made on an atactic polypropylene sample for which very accurate volume temperature data were available.[8] The volume temperature data (Fig. 8) gave a glass transition of −10°C. for this material. $\Delta\theta$ vs. absolute surface temperature for this material was measured at three different heating rates. The zero point extrapolation (Fig. 9) gave a value of −8°C. for the glass transition temperature. This value is in excellent agreement with the volume temperature data.

This writer would like to acknowledge the helpful discussions of Dr. S. Newman and Dr. F. D. Stockton. He would also like to thank Mr. A. A. Bibeau for his technical assistance.

References

1. Scott, N. D., *Polymer*, **1**, 114 (1960).
2. Schwenker, R. F., and L. R. Beck, *Textile Research J.*, **30**, 624 (1960).
3. Keavney, J. J., and E. C. Eberlin, *J. Appl. Polymer Sci.*, **3**, 47 (1960).
4. Carslaw, X. X., and X. X. Jaeger, *Conduction of Heat in Solids*, Oxford Univ. Press, 1959.
5. Dole, M., *Fortschritte Der Hochpolymerin.*, Forschung 2, Band 2 (1960).

6. *Technical Data on Plastics*, Manufacturing Chemists Association, Inc., 1952.
7. Rogers, S. S., and L. Mandelkern, *J. Phys. Chem.*, **61**, 985 (1957).
8. Unpublished data of S. Newman and A. A. Bibeau.

Synopsis

A differential thermal analysis device (DTA) for measuring the glass and other polymer transitions is described. A theory on the manner in which a glass transition is manifested in a DTA thermogram, and on the manner for obtaining the real value from the thermogram is presented. Experimental results on polymethyl methacrylate and atactic polypropylene verify the various predictions of the theory.

Résumé

On décrit un analyseur thermique différentiel (DTA) pour la mesure des transitions vitreuses et autres transitions de polymères. Une théorie sur la manière dont une transiton vitreuse est représentée dans un thermogramme DTA et sur la manière d'obtenir une valeur réelle à partir du thermogramme, est présentée. Des résultats expérimentaux sur le polyméthacrylate de méthyle et le polypropylène atactique vérifient les différentes prédictions de la théorie.

Zusammenfassung

Eine Vorrichtung zur Messung der Glasumwandlung und anderer Polymerumwandlungen durch Differentialthermoanalyse wird beschrieben. Theoretische Überlegungen über die Art des Auftretens einer Glasumwandlung in einem DTA-Thermogramm und über die Ermittlung des wahren Wertes aus dem Thermogramm werden mitgeteilt. Versuchsergebnisse an Polymethylmethacrylat und taktischem Polypropylen bestätigen die verschiedenen Aussagen der Theorie.