

## The Determination of Glass Transition Temperatures by Differential Thermal Analysis

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### INTRODUCTION

Differential thermal analysis (DTA) had its beginnings in Le Chatelier's<sup>1</sup> early work with analytical procedures involving thermal transitions. Since this time DTA has been used extensively in the fields of ceramics and mineralogy for identification and analytical purposes. It is only recently, however, that the technique has been applied to the study of polymers. Most of these applications have been limited to the detection of first-order changes such as decomposition, isomerization, or melting.<sup>2-7</sup>

The particular interest of these laboratories has been the determination of glass transition temperatures by differential thermal analysis. Coste<sup>8</sup>

briefly mentions the possibility of such an application but gives no specific experimental results. Chackraburty<sup>9</sup> gives a DTA curve for polyvinyl acetate showing an inflection at 28°C., the reported value<sup>10</sup> for the glass temperature, but does not identify it as such. Other than this, no extensive use of thermal analysis in this area has been reported. It is interesting, however, to note that DTA has been used to detect Curie points in magnetic materials.<sup>11</sup> This application is analogous to the determination of glass temperatures by DTA. In both cases, the discontinuous changes in specific heat result in deflections in the differential temperature curves.

Because glass transitions involve no latent heats, the DTA curves do not show the peaks typical of first-order transitions. Instead, the change in specific heat occurring at the glass transition results only in a shift in the base line of the DTA curve. This effect is small, compared to that observed for transitions with latent heats, and high sensitivity and good base line stability are required. The apparatus described meets these requirements.

### EXPERIMENTAL

In order to obtain maximum stability, the holders for the sample and reference materials are an integral part of the DTA furnace block itself. This was accomplished by constructing the furnace from a solid metal cylinder cut approximately in half perpendicular to its axis. Both sections are externally wound with heater wire, and the sample and reference wells are drilled directly in the top face of the bottom block. Aluminum has proved to be a satisfactory material for the furnaces since it is rarely necessary to go above 300°C. Two furnaces of the general type shown in Figures 1 and 2 have been used for a wide variety of samples.

The wells for the sample and reference materials are cylindrically shaped,  $\frac{1}{2}$  in. deep and  $\frac{1}{2}$  in. in

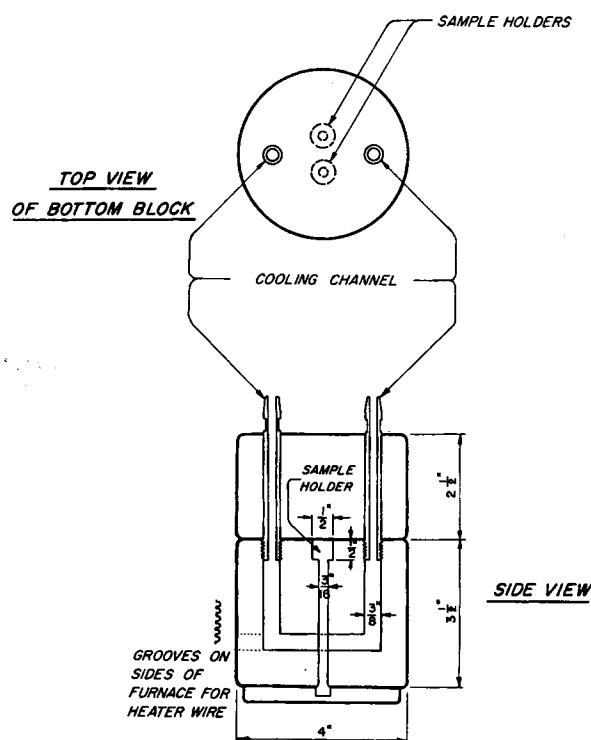


Fig. 1. Differential thermal analysis furnace.

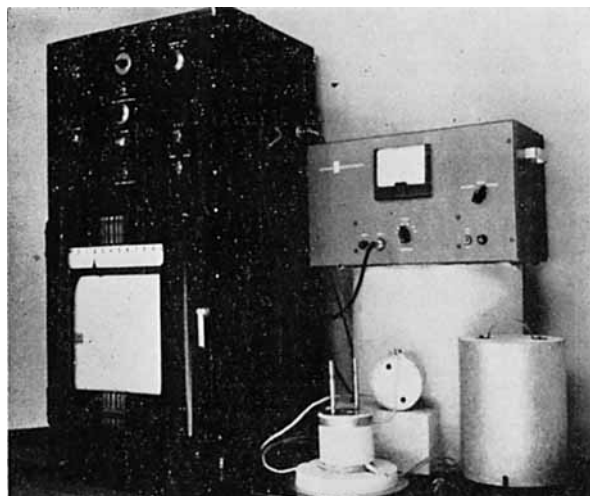


Fig. 2. Photograph of DTA apparatus showing recorder, amplifier, and furnace.

diameter. The thermocouples are inserted into the bottoms of the wells through  $\frac{3}{16}$  in.-diameter holes drilled through the lower block. Chromel and alumel wires (B and S No. 28) are used for both the absolute and differential thermocouples. As indicated in Figure 3, the two differential junctions are placed symmetrically in the reference and sample holders and project about  $\frac{1}{4}$  in. into the cells. The absolute couple is located immediately next to the differential one in the sample cell, and for symmetry, a dummy thermocouple is placed in the reference side. The portions of the thermocouple leads lying within the furnace block

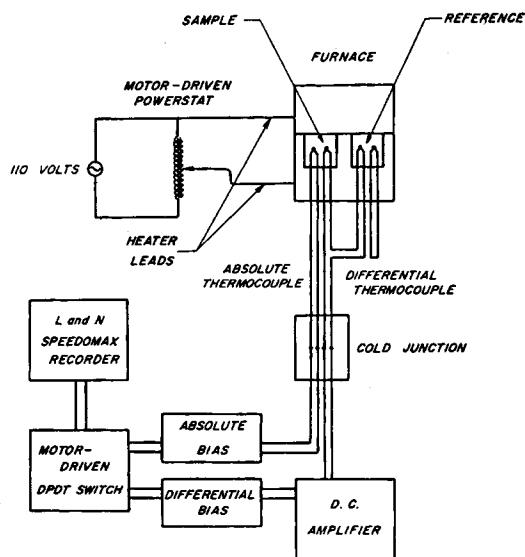


Fig. 3. Schematic diagram of DTA furnace and recording system.

are insulated with two-hole ceramic tubing. The thermocouple beads themselves are held in place and protected by a small amount of Alundum cement. The amount of cement used is kept to a minimum to avoid loss of sensitivity. A  $\frac{1}{2}$  in. thick transite disk containing a channel for the couple wires forms the base of the furnace. Nichrome heater wire (B and S No. 20, 0.635 ohm/ft.) covered with "fish spine" insulators is laid in a spiral groove machined in the sides of the two halves of the furnace. A coating of heat-resistant cement protects the heater element.

The furnace ordinarily used for studying transitions below room temperature contains a cooling channel through which cold acetone can be pumped. This was constructed by drilling  $\frac{3}{8}$ -in. holes in the bottom block as shown (Fig. 1). Two sections of steel pipe were screwed into the holes and extend through the upper block, which slides on and off over the pipes. A latch-type closure with a thumb screw is used to hold the two furnace halves firmly together. The rubber tubing of the cooling system is connected directly to the tapered ends of the steel pipes. A temperature of  $-60^{\circ}\text{C}$ . can be reached in ten to fifteen minutes by pumping acetone through a copper coil packed in Dry Ice and then through the DTA block. The second furnace differs from the first only in the elimination of the cooling channel and is suitable for samples having transitions above  $50^{\circ}\text{C}$ .

During operation the furnaces are electrically grounded and are covered with a cylindrical top of one inch thick insulation. The air gap between the furnace and the cover is about  $1\frac{3}{4}$  in. Without the electrical ground and the cover, the furnaces are not sufficiently stable for the detection of glass transitions.

Linear heating rates are obtained by using a motor driven Powerstat. The range of motor speeds available permits a rate of change of voltage from 0 to 1.4 v./min. A heating rate of  $2.5^{\circ}\text{C}/\text{min}$ . is used for most polymers.

A Leeds & Northrup Speedomax recorder with a range of 0–10 mv. is used to record both the differential and absolute temperatures. The differential signal is preamplified by a Leeds & Northrup 9835A stabilized d.-c. indicating amplifier (micro-volt type) having six ranges of amplification varying from 50 to 2000  $\mu\text{v}$ . full scale. A continuously variable bias of up to 10 mv. provides a means of zeroing the differential signal at any point on the recorder chart. The absolute temperature e.m.f. is recorded without preamplification. Full scale

is thus always 10 mv., but a zero bias varying in steps of 5 mv. permits measurements of e.m.f. from  $-5$  to  $+45$  mv.

The absolute and differential signals are fed to the two sides of a DPDT microswitch. The switch is activated by a cam driven by a synchronous motor operating in a five minute cycle (Cramer Controls Corp. Model 510A-1-5M). In normal operation, the differential signal is recorded for the majority of the cycle, and the absolute voltage, for a period of only 10 seconds. This latter interval, however, may be increased up to one-half the total time ( $2\frac{1}{2}$  minutes) of the full cycle. Controls are provided for switching to the absolute signal at any time during the differential period or for turning off the synchronous motor altogether. Thus it is possible to record only the absolute or only the differential signal.

Any material that does not itself undergo a transition, and whose thermal conductivity and heat capacity and rate of change of these quantities with temperature are comparable to those of the polymer sample, can be used as a reference. An organic material has generally been found to be more satisfactory than the commonly used alumina. Isophthalic acid is suitable for most runs of powdered polymers because of its high melting point ( $312-14^{\circ}\text{C}$ .). Samples of cut up polymer films are better matched against commercial polyethylene (satisfactory from about  $-60^{\circ}\text{C}$ . to its melting point, approximately  $100^{\circ}\text{C}$ .).

#### DISCUSSION

Typical DTA curves for glass transitions of polystyrene and polyvinyl chloride are shown in Figures 4 and 5, respectively. In each case, the curve *abcd* is the differential temperature  $\Delta T$ , whereas the vertical lines indicate the portions of the five-minute cycles during which the absolute temperature is measured. The point *a* is the zero point for the differential temperature curve; that is, the polymer sample and the reference material are at exactly the same temperature. Portions of the DTA curve below *a* indicate that the sample is at a lower temperature than the reference, whereas above, it is hotter. As heating is begun, small differences in heat capacity and thermal conductivity of the two substances as well as slight asymmetries in the thermocouple arrangement result in a temperature difference *a* to *b*. At *b* a steady state is reached and the differential temperature is essentially constant until the point

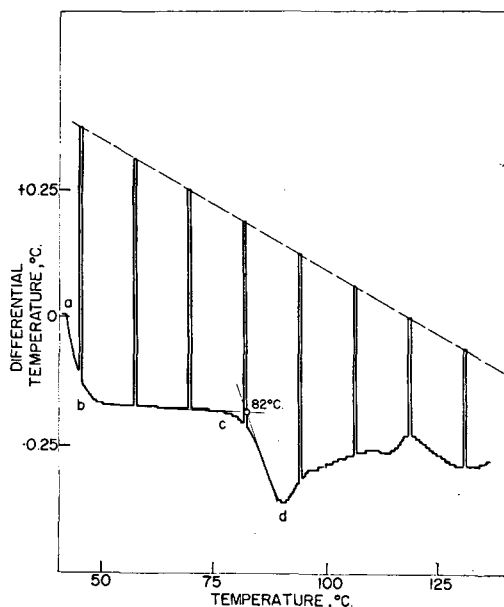


Fig. 4. Differential thermal analysis curve for glass transition in polystyrene.

*c*, corresponding to the beginning of the glass transition. Since an increase in heat capacity occurs at the transition, the temperature of the sample lags behind that of the reference and a definite "break" in the curve is observed. Extrapolation as indicated gives values of  $82$  and  $81^{\circ}\text{C}$ . for the glass transition temperatures of polystyrene and polyvinyl chloride, respectively, in excellent agreement with results obtained by other methods (Table I).

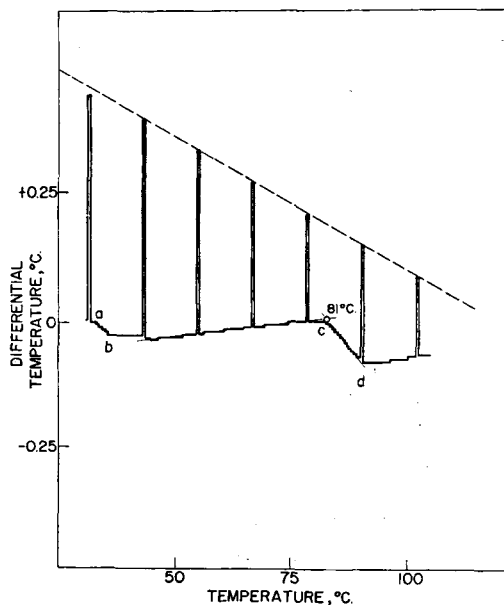


Fig. 5. Differential thermal analysis curve for glass transition in polyvinyl chloride.

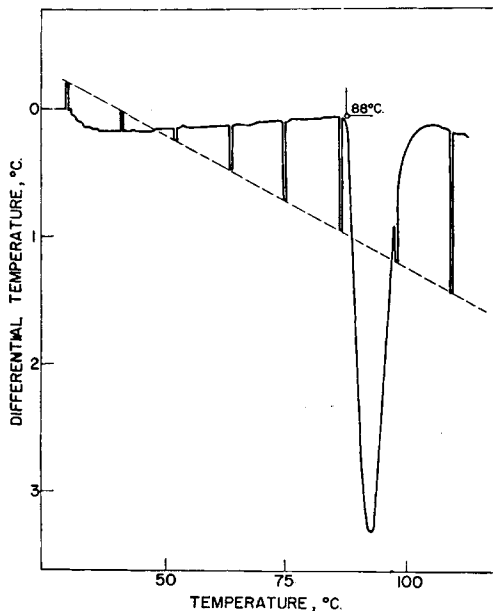


Fig. 6. Differential thermal analysis curve for first-order transition in ammonium thiocyanate.

Eventually a new equilibrium state is reached (point *d*), and the differential temperature again becomes more or less constant.

For comparison, Figure 6 shows a DTA curve for a first-order transition. At 87.7°C.,<sup>12</sup> ammonium thiocyanate undergoes a crystalline transition; the peak in the DTA curve in this instance is due to the latent heat of the transition. A comparison of Figures 4 and 5 with Figure 6 serves to indicate the high sensitivity necessary for the detection of glass transitions. The base line shifts caused by the transitions in polystyrene and polyvinyl chloride are of the order of only 0.1–0.2°C., whereas with ammonium thiocyanate  $\Delta T$  is close to 3.3°C. The  $\Delta T$  for transitions involving changes of state are generally even larger since in these cases latent heats are several times greater than that for the ammonium thiocyanate solid-solid transition (10.4 cal./g.<sup>12</sup>).

The heating rate used in differential thermal analysis can affect the measured glass transition temperature in one of two ways. It has been shown<sup>13</sup> that in general the DTA technique is time dependent. Because a rate of heating is involved, true equilibrium conditions do not exist during a measurement. Furthermore, the phenomenon of a glass transition itself has been reported<sup>14,15</sup> to be a time effect and not a thermodynamic singularity. For example, equilibrium temperature-volume curves for polystyrene show no transition between

20 and 140°C., whereas the same material has an apparent glass transition at 82°C. when the heating rates ordinarily used for thermal expansion work are employed.<sup>15</sup>

Apart from the theoretical aspects of glass transitions and thermal analysis, the practical problem with the present measurements was to determine to what extent the data varied within the range of heating rates generally employed and how well these data agreed with results obtained by other methods. The transition temperatures of polystyrene and polymethylmethacrylate were determined at a variety of heating rates between 1 and 6°/min. Plots of these values (Fig. 7) show that, within the precision of the method, the glass temperature is independent of heating rate in this

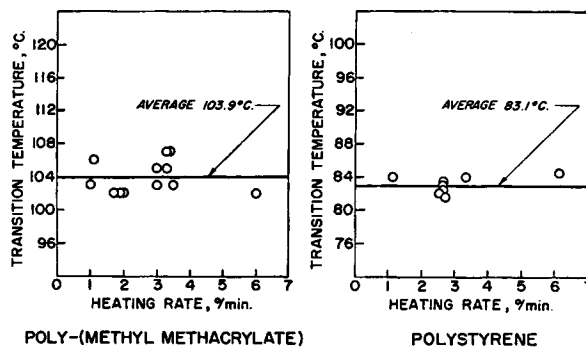


Fig. 7. Effect of heating rate on glass transition temperatures.

range. The shape of the DTA curve, however, is affected by the rate of heating, higher rates causing sharper breaks in the curves. More clear-cut results can be obtained for polymers showing only very gradual transitions at the customary heating rate of 2.5°/min. by increasing the rate to 5–6°/min.

Since differential thermal analysis depends upon heat conduction through the sample to the thermocouple imbedded within it, it is important to know what effect sample particle size and degree of packing have upon the measured transition temperature. The conclusions drawn from previous investigations<sup>13,16</sup> of these factors are not entirely consistent, but in general wide variations in either particle size or packing can be expected to influence the experimental results. In this apparatus, however, glass temperature measurements made on several polymers in different states of subdivision and degree of packing showed no more than the usual amount of variation. Thermal conductivity will, of course, determine the magnitude of the

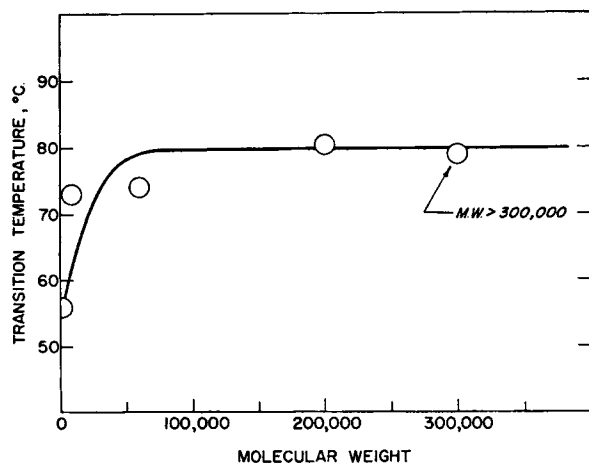


Fig. 8. Glass transition temperature vs. molecular weight for polyacrylonitrile.

initial temperature change  $a$  to  $b$  (Figs. 4 and 5). For this reason it is desirable to match the particle size and the packing of the sample and the reference as closely as possible. Powdered samples are generally analyzed as received, whereas fibers and films are cut into a size that can be conveniently put into the sample holder. The materials are packed as densely as possible since the magnitude of the temperature change  $b$  to  $c$  depends in part upon the weight of sample present.

Figure 7 shows that the precision of transition temperature data obtained by differential thermal analysis is good. In general, individual determinations agree within  $\pm 1.5^\circ\text{C}$ . The agreement between DTA transition temperatures and those obtained by other methods is also very good. Table I gives the average DTA transition temperature for several polymers of high molecular weight along with data reported in the literature. Since the transition temperature is dependent to a great extent upon the exact structure of a particular polymer and thus upon the way in which a polymerization is carried out, agreement within less than  $1\text{--}2^\circ\text{C}$ . is probably fortuitous.

#### GLASS TRANSITION OF POLYACRYLONITRILE

Because of the extensive commercial use of polyacrylonitrile (PAN), the glass temperature of this polymer has been of particular interest to these laboratories. Previously reported values differ considerably. Kolb and Izard<sup>23</sup> found the glass temperature of a sample of high molecular weight to be  $87^\circ\text{C}$ . by dilatometric methods, Roff<sup>17</sup> lists  $52^\circ\text{C}$ ., but Würstlin<sup>24</sup> was unable to detect a

TABLE I  
Comparison of Typical Transition Temperatures Determined by Differential Thermal Analysis with Reported Data

Polymer	Source	Transition temperature, $^\circ\text{C}$ .	
		DTA	Literature
Polyvinyl chloride	Marvinol VR-10 (Naugatuck Chemical Co.)	80.5	75-80 (ref. 17), 75 (ref. 18)
	Exptl. lab. sample	74	
Polymethyl methacrylate	Exptl. lab. sample	111	105 (refs. 19, 20)
Polystyrene	Dow 666K	83	82 (ref. 21), 82 <sup>a</sup> (ref. 17)
Vinylidene chloride-vinyl chloride copolymer	Saran wrap (Dow)	-5	-4 <sup>b</sup> (ref. 21)
Ammonium thiocyanate	Baker C.P.	88 <sup>c</sup>	87.7 (ref. 12)

<sup>a</sup> It has been reported<sup>22</sup> that when Dow polystyrene is precipitated from solution to remove all traces of solvent, the transition temperature increases from  $82^\circ\text{C}$ . to well over  $100^\circ\text{C}$ . A number of experimental polystyrene samples investigated by DTA showed transitions between  $82$  and  $100^\circ\text{C}$ ., depending upon the method of preparation. Since most authors report  $80\text{--}82^\circ\text{C}$ ., it is probable that their samples were comparable to Dow 666K.

<sup>b</sup> This value was obtained with unplasticized Saran B, a vinylidene chloride-vinyl chloride copolymer, 18.7% crystallized. Increases in crystallinity do not significantly affect the glass temperature for the unplasticized material.<sup>21</sup>

<sup>c</sup> First-order transition.

transition below  $100^\circ\text{C}$ . by dielectric measurements. It is conceivable that the discrepancy between the two values of  $52$  and  $87^\circ\text{C}$ . could be accounted for by large differences in molecular weight, since it is well known<sup>25</sup> that glass transition temperatures are dependent upon this variable in the low molecular weight range. It is difficult, however, to explain a value greater than  $100^\circ\text{C}$ . on this same basis. There is other evidence that the glass transition phenomenon in polyacrylonitrile is not as clear-cut as with most other polymers. Kolb and Izard<sup>23</sup> report that the material showing a transition at  $87^\circ\text{C}$ . became partially opaque when heated above  $130^\circ\text{C}$ . X-ray analysis showed no change in structure. Furthermore, whereas most polymers become noticeably soft at the glass temperature, this was not observed with PAN.

Differential thermal analysis has been used to study a number of polyacrylonitrile samples, rang-

ing in molecular weight from approximately 1500 to greater than 300,000. The polymers, their molecular weights, and the various methods of preparation employed are listed in Table II. The molecular weights were determined from intrinsic viscosity measurements according to a relationship established in these laboratories;<sup>26</sup> it is essentially identical to that of Cleland and Stockmayer.<sup>27</sup>

TABLE II  
Glass Transition Temperatures of Polyacrylonitrile Samples  
of Varying Molecular Weight

Sample and method of prepn.	Molecular wt.	Glass transition temp., °C.
(1) 42-83A (tributylphosphine-initiated at room temp.)	1500-2000	56 ± 1 Regular
(2) 68-1 (sodium ethoxide-initiated)	2600 ± 300	No detectable transition
(3) 48-34 (polymerized in isopropyl alcohol at 60°C. with (NH <sub>4</sub> ) <sub>2</sub> S <sub>2</sub> O <sub>8</sub> and Na <sub>2</sub> S <sub>2</sub> O <sub>5</sub> as catalysts)	8500 ± 15%	73 ± 2 Irregular
(4) 1-13 (emulsion-polymerized at room temp. with (NH <sub>4</sub> ) <sub>2</sub> S <sub>2</sub> O <sub>8</sub> and Na <sub>2</sub> S <sub>2</sub> O <sub>5</sub> as catalysts with butyl mercaptan)	60,000 ± 15%	74 ± 3 Irregular
(5) PAN 200,000 (chlorate-bisulfate redox-catalyzed)	200,000	80.5 ± 2 Very regular
(6) 1-10 (emulsion-polymerized at room temp. with (NH <sub>4</sub> ) <sub>2</sub> S <sub>2</sub> O <sub>8</sub> and Na <sub>2</sub> S <sub>2</sub> O <sub>5</sub> as catalysts)	>300,000	79 ± 1 Irregular

Several of the polymers gave anomalous DTA results comparable to those mentioned above. The transitions were almost always somewhat irregular and occurred over a wide temperature range. Successive runs on the same sample showed more than the usual amount of variation. Two of the polymers became soft and rubbery above their transition points. With the others, however, no such change was observed even where DTA showed a definite transition. In one instance, no transition could be detected in the differential curve up to 130°C.

Since the acrylonitrile polymers were prepared by several methods, it is not surprising that certain differences in their behavior upon heating were noted. Polyacrylonitrile has a moderate tendency

to branch and the extent of branching, of course, depends upon the method of polymerization. The amount of branching undoubtedly influences the glass temperature.

The PAN glass temperatures determined by thermal analysis are listed in Table II and plotted against molecular weight in Figure 8. The plot is of the same general shape as that established for polystyrene and polyisobutylene.<sup>28</sup> The temperature increases rapidly in the region of low molecular weights and levels off at molecular weights of approximately 75,000-100,000. The maximum glass temperature is 80°C. Although these results cannot be considered conclusive, nevertheless they are undoubtedly representative of a great many acrylonitrile polymers. Considerably more extensive investigation will be necessary to characterize completely the thermal behavior of PAN.

In general, the accuracy and reproducibility of glass transition temperatures determined by differential thermal analysis are at least comparable to those obtained by other methods. The great advantage of DTA lies in the rapidity with which measurements can be made. An accurate determination of the glass temperature of a typical polymer takes only one to three hours. (The attention of the operator is required during only a small portion of the overall time since an automatic recording system is used.) The method is non-destructive and no particular sample purification or preparation is necessary. Differential thermal analysis is not limited by sample opaqueness as is the refractive index method. Furthermore, if desired, melting and decomposition points may be determined subsequent to the glass transitions simply by continuing the run to higher temperatures.

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### Synopsis

Differential thermal analysis has been applied to the study of glass transitions in polymers; DTA can detect the discontinuous changes in specific heat which are associated with such transitions. The apparatus used must have considerably greater sensitivity than that required for measuring transitions involving latent heats. Amplification of the differential-thermocouple e.m.f. permits detection of temperature changes of 0.01°C. An aluminum block furnace having the high stability necessary for this amplification has been constructed. The DTA glass temperatures are comparable to those obtained by other methods, and the precision of the determinations is usually better than 1-2°C. This technique appears to be superior to others in convenience and speed. Wide variations in particle size and heating rate have no significant effect on the measured transition temperature. The glass temperature of poly-

acrylonitrile has been the subject of disagreement. Differential thermal analysis has shown that it rises from 56°C. for a sample of molecular weight 1500 to 80°C. for samples of molecular weight greater than 75,000.

### Résumé

L'analyse différentielle thermique (DTA) a été appliquée à l'étude des températures de transition vitreuse dans le cas de polymères. La méthode DTA peut détecter les changements discontinus dans la chaleur spécifique, qui sont associés à de telles transitions. L'appareil employé dans ce cas doit posséder une sensibilité considérablement plus grande que celle qui est requise pour mesurer des transitions dépendant des chaleurs latentes. L'amplification de la force électromotrice du thermocouple différentiel permet la détection de changements de température de 0, 01°C. On a construit un four en bloc d'aluminium ayant une grande stabilité, indispensable pour cette amplification. Les températures de transition vitreuse mesurées par la méthode DTA sont comparables à celles qui sont obtenues par d'autres méthodes et la précision des déterminations est d'ordinaire supérieure à 1-2°C. Cette technique apparaît être supérieure aux autres en commodité et vitesse. De grandes variations dans la grandeur de la particule et dans la vitesse d'échauffement n'ont pas d'effet significatif sur la température de transition vitreuse mesurée. La température de transition vitreuse du polyacrylonitrile manifeste un désaccord: la méthode DTA a montré qu'elle s'élève de 56°C, pour un échantillon de poids moléculaire 1500, jusqu'à 80°C, pour des échantillons de poids moléculaire supérieur à 75.000.

### Zusammenfassung

Die thermische Differentialanalyse (DTA) wurde zur Untersuchung der Glasumwandlung bei Polymeren herangezogen. Mittels der DTA kann man die diskontinuierlichen Änderungen der spezifischen Wärmen feststellen, die mit solchen Umwandlungen verknüpft sind. Das verwendete Instrument muss eine weitaus grössere Empfindlichkeit besitzen, als sie für die Messung von Umwandlungen mit latenten Wärmen erforderlich ist. Eine Verstärkung der EMK des Differentialthermoelements erlaubt die Feststellung einer Temperaturänderung von 0,01°C. Es wurde ein Aluminiumblockofen konstruiert, der eine genügend hohe Stabilität besitzt, um eine solche Verstärkung zu ermöglichen. Die DTA-Glasumwandlungstemperaturen sind den nach anderen Methoden erhaltenen durchaus vergleichbar und die Genauigkeit der Bestimmungen ist normalerweise besser als 1-2°C. Die angegebene Methode dürfte den gebräuchlichen an Bequemlichkeit und Schnelligkeit überlegen sein. Verhältnismässig grosse Änderungen der Partikelgrösse und der Erhitzungsgeschwindigkeit haben keinen wesentlichen Einfluss auf die gemessene Umwandlungstemperatur. Die in der Literatur vorhandenen Angaben über die Glasumwandlungstemperatur von Polyacrylnitril sind widerspruchsvoll. Die DTA zeigt, dass sie von 56°C für eine Probe vom Molekulargewicht 1500 auf 80°C für Proben mit einem Molekulargewicht höher als 75000 zunimmt.

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