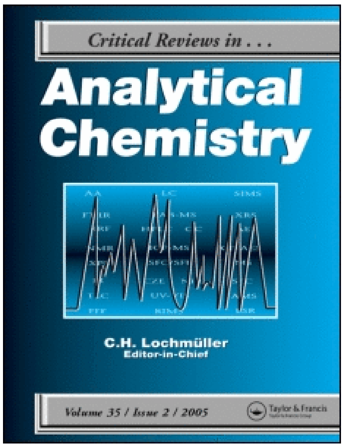

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RECENT DEVELOPMENTS IN THERMAL METHODS FOR THE CHARACTERIZATION OF POLYMERS

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I. INTRODUCTION

The growth of the general field of polymer analysis and characterization by thermal methods has been greater in the past 5 years than in the previous 50. This article attempts to report developments in the three areas which have grown the most rapidly: differential thermal analysis, differential scanning calorimetry, and thermomechanical analysis. Selected examples from the enormous recent literature are cited where applicable; however, this article does not intend to be a complete bibliography. For additional information on any particular topic, the reader is advised to consult the articles cited in the bibliography. A consideration of the fields of thermogravimetry, pyrolysis chromatography, hot stage microscopy, and the thermal aspects of light scattering from solids has been deferred to a later date. For general information and background on all thermal methods of polymer analysis the reader is referred to the series Techniques and Methods of Polymer Evaluation.[8, 73]

II. DIFFERENTIAL THERMAL ANALYSIS AND DIFFERENTIAL SCANNING CALORIMETRY

A. Introduction

The measurements of heat absorption, liberation, and content in polymeric systems have developed in the past decade into powerful techniques for polymer characterization. The application of classical thermodynamics to many problems in polymer analysis and physics was delayed somewhat until modern methods of differential thermal analysis and differential scanning calorimetry became available. The methods of equilibrium calorimetry, although of unsurpassed accuracy, are too tedious and time-consuming for general application to a large number of samples.

The thermodynamic properties of many narrow-molecular-weight or rare polymer systems were all but impossible to determine due to sample size requirements of older calorimetric techniques.

1. *Definition of Differential Thermal Analysis*

Differential thermal analysis (DTA) involves the measurement of the temperature difference between a sample and a reference material as the two are being heated or cooled at some known linear rate. Recommendations for nomenclature in thermal analysis are given in Appendix 2 of Volume 2 of *Thermal Analysis*, edited by R. F. Schwenker, Jr. and P. D. Garn, Academic Press, New York 1969. The temperature difference may also be measured as a function of time at a fixed temperature. No particular effort is made to keep the sample and reference temperatures balanced during a transition. Indeed, the sensitivity of the method is dependent on the degree of imbalance created during the period of transition.

2. *Definition of Differential Scanning Calorimetry*

Differential scanning calorimetry (DSC) requires the measurement of the power difference between sample and reference heaters as the sample and reference experience a linear temperature or time change. The method requires that sufficient power in the form of heater current be added to the sample or reference heater to keep the temperature difference between sample and reference substantially zero during both transition and heating. Any temperature difference which is not compensated will result in an error.

For no other reason than historical evolution the techniques of DTA will be considered prior to the techniques of DSC. As the two methods are for the most part measuring the same phenomena, DSC and DTA instrumentation can often be used interchangeably. Where specific advantages are obtained by one method over the other indication will be given in the text.

B. Differential Thermal Analysis

1. *Introduction*

The technique of differential thermal analysis, DTA, was introduced by LeChatelier in 1897. An interesting account of the development of this work has been given by Duval.[29] The field developed rapidly with most of the early work applied to the study of inorganic reactions and transitions. Two volumes report in detail on instrumentation and application to the mid 1950's.[56,74]

In polymer research the heat involved in transitions is relatively small compared to that in inorganic systems. Therefore, the instrumentation required for DTA is considerably more sophisticated. As there are now a considerable number of commercially available DTA instruments suitable for polymer analysis as well as specialized equipment described in the literature, an exhaustive review of equipment will not be included. Instead a comparison of the basic components with emphasis on recent developments will be given.

2. *Instrumentation*

The differential thermograph may be conveniently subdivided into a number of basic components. Figure 1 is a block diagram showing their relationship. The components are:

1. Temperature programmer and controller
2. Differential temperature measuring circuit
3. Absolute temperature measuring circuit
4. Sample container including heating/cooling system
5. Data recording device
6. Atmosphere control.

a. Temperature Programmer and Controller

In most polymer studies, differential thermal analysis is carried out at a steadily increasing or decreasing temperature although for certain cases isothermal operation is necessary. A number of theoretical analyses of the nature of the DTA curves are in agreement that the temperature increase or decrease must be linear.[15,49,70] The short-term fluctuations should be as small as possible. A number of controllers utilize a motor-driven voltage divider powered by a stable power supply to generate an increasing voltage which approximates a linear temperature increase for a specific thermocouple system. In order of increasing sophistication, desirability, and cost, the difference signal may be amplified and used to provide:

a. On-off control
b. Proportional control with fixed bandwidth
c. Proportional control with adjustable bandwidth and reset

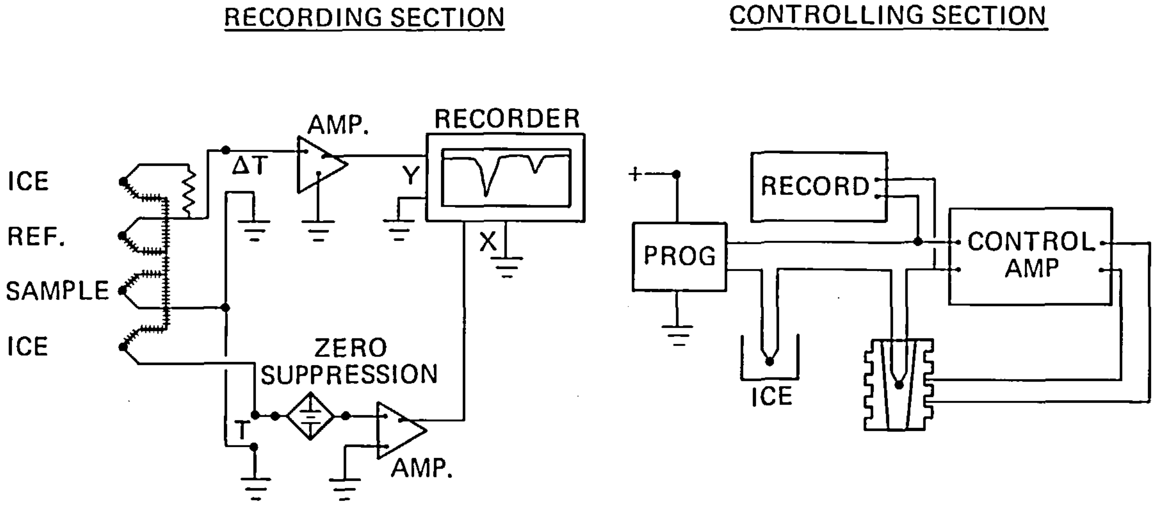


Figure 1. Block diagram of differential thermal analysis apparatus.[4]

d. Proportional control with adjustable bandwidth and reset and rate action.

Resistance temperature sensors can be used in place of thermocouples in systems operating on the same principle. Detailed descriptions are available in the literature.[72, 82, 88]

The temperature rates provided are usually in the range of 0.2 to 100°C per minute. The more commonly used ranges are probably 0.5 to 20°C/minute.

Recent developments in high-current semiconductors, silicon triodes and transference diodes, have resulted in the replacement in commercial instruments of the motor-driven rheostats, potentiometers, and relay galanometers common to most earlier instruments. Semiconducter controllers are available which are good proportional-band continuous programmers. These are smaller, more efficient, and, in most cases, less costly than mechanical methods. The heating modes provided are free of the temperature steps encountered with most relay galvanometric methods.

Figure 2 illustrates in an exaggerated fashion the effect of a temperature fluctuation in a temperature programmer. The shape of a peak that started at A, for example, would be badly distorted. Theall has described a simple test apparatus to be used in connection with the DTA to monitor the power input to the furnace.[81] A schematic diagram of this device is shown in Figure 3. A low wattage 120-volt bulb is connected in parallel with the heater. The bulb is mounted in a light-proof tube with a photovoltaic cell. The output of the cell is monitored by the DTA recording system to give a relative measure of power stability.

b. Differential Temperature Measuring Circuit

The temperature differential between the sample and reference is most frequently measured with thermocouples. Thermistors[44, 68] and resistance thermometers[64] have been used. Thermocouples combine sufficient sensitivity with a wide temperature range. While every standard thermocouple has probably been used, the ones most frequently employed are the higher output couples: copper-constantan, iron-constantan, and chromel-alumel. For high temperature or reactive systems platinum-platinum 10% rhodium may be required. Platine 2 is coming into common use.

In order to increase the sensitivity, multiple thermocouples in one sample have been used.[50] Another arrangement is to use several samples with a thermocouple in each. In effect, the signal is an average of several samples. This can remove any heating rate error, but it is important that there be no thermal gradient between the various sample holders or serious errors will result. Usually such arrangements are not necessary because present day amplifiers are sufficient to give almost any sensitivity desired.

c. Absolute Temperature Measuring Circuit

Thermocouples are usually employed to measure the absolute temperature of the sample or of the oven. It is important that either an ice junction

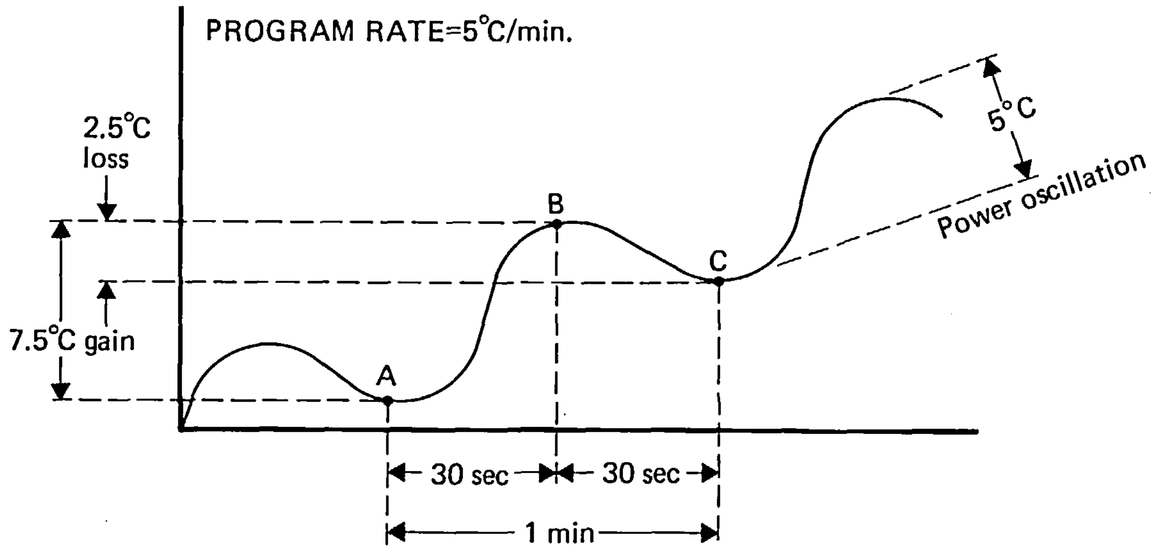


Figure 2. Effect of cyclic output power on the rate of temperature programming.[81]

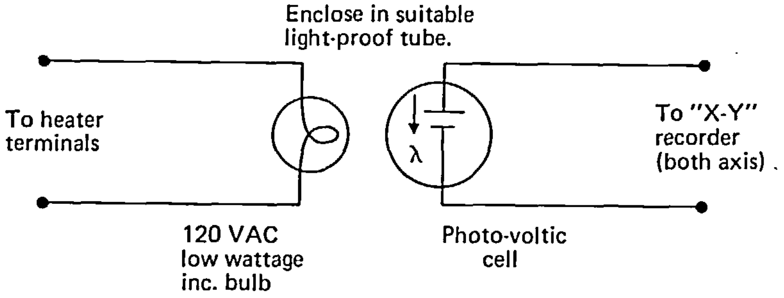


Figure 3. Apparatus for checking temperature programmer performance.[81]

or a careful compensation for changes in room temperature be provided. The location of the thermocouple measuring the temperature is of great importance. Figure 4 shows the marked differences observed with the thermocouple located at the center of the reference specimen, at the surface of the test specimen, or at the center of the test specimen. For convenience the symbol T_S is used to refer to measurements where the temperature of the sample is being measured and T_a where it is the temperature of the system, that is, of the furnace or of the heating block.

The determination of T_S, the temperature of the sample, is usually a more desirable parameter because it is least affected by differences in heating rate and is the parameter of most interest. Where heat uptake or liberation is the only important parameter, location of the temperature measuring thermocouple in the reference is more desirable.

Measurement of T_s poses the problem of putting two thermocouples in the center of the sample, one to measure ΔT and the other to measure T_S. Using one thermocouple eliminates the possibility of any temperature gradient between the two thermocouples. However, the large differences between ΔT and T_s may cause interaction. This is shown as an apparent drift in the ΔT abscissa.[4] It is possible to overcome this difficulty using the circuit shown in Figure 1. Here, a dummy thermocouple and resistor equal the resistance of the thermocouple and amplifier. In this way the back EMF's cancel, permitting measurement of T_s and ΔT. Very high impedance amplifiers should also be satisfactory in a limited temperature range

A very common arrangement to remove a portion of either the T or T_s signal and to expand the remainder on the recorder scale to any degree desired has been described by a number of

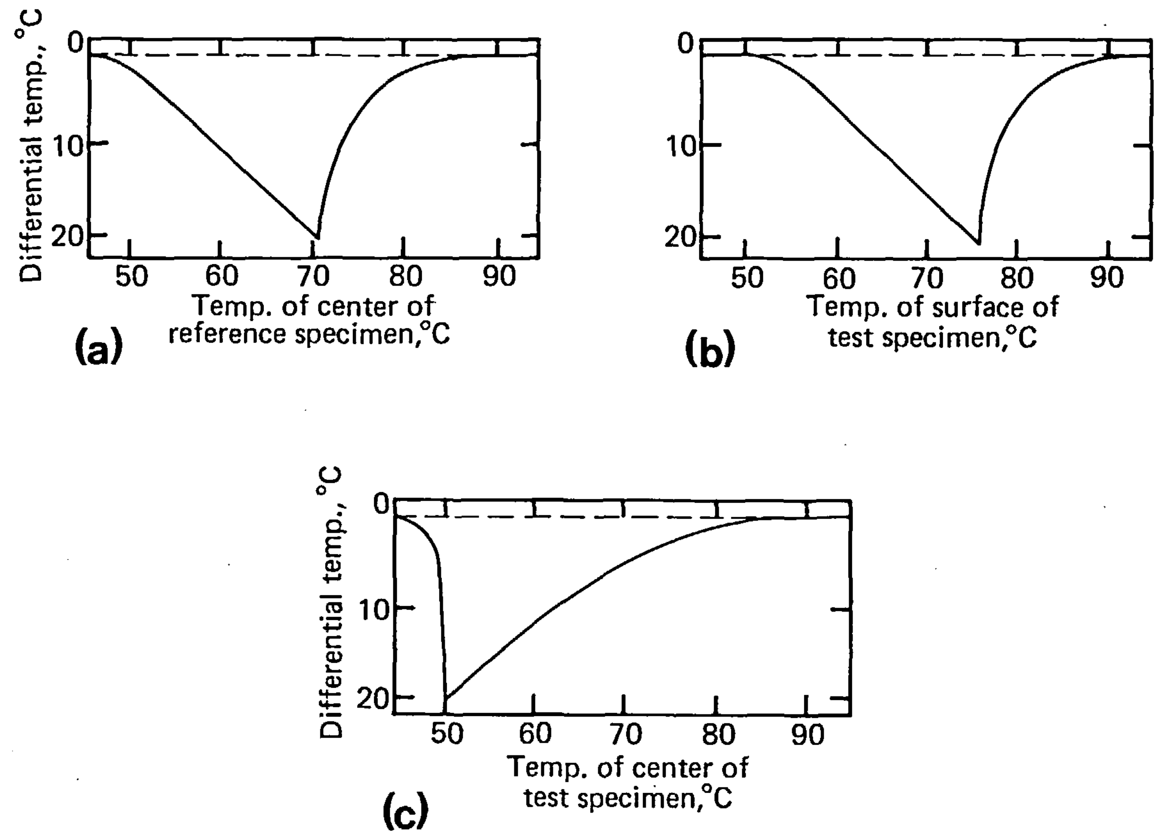


Figure 4. Effect of thermocouple location.[75]

authors.[4,30,82,88] These arrangements provide a reverse polarity EMF to remove most of the signal. Such arrangements are particularly useful when an XY recorder is being used. Actual potentiometric bucking is difficult, as the potentiometer must be thermostated to maintain high stability.[4]

A variety of DC amplifiers is available for amplifying either of the temperature signals. The amplifier must be linear within the range in which it is used. The effect of nonlinearity is shown in Figure 5. In Figure 5, amplifier A is functioning properly; that is, its response is linear throughout the range of use and passes through the origin. Amplifier B is offset from the origin, a zero effect that can be readily corrected. The nonlinearity in the point between the dotted lines, of course, will introduce a serious error into the signal recorded. While amplifier design is outside the scope of this article, it must be emphasized that recognizing performance that is not linear is necessary for the practicing thermal analyst. The simple circuit shown in Figure 6 can be used to check amplifier performance using a precision potentiometer. Another problem to be considered is that of amplifier response time. Frequently, an apparently obvious solution to problems of noise is to add a capacitative circuit that in effect decreases noise at the expense of increasing response time. If response time becomes too long, the erroneous result illustrated by the dotted lines in Figure 7 will be encountered.

d. Sample Container Including Heating and Cooling Systems

Design of the sample and reference holders and their geometry in relationship to the heating or cooling circuit is one of the more critical elements in constructing a DTA apparatus. The designs may perhaps be classified by the location of the thermocouple. As shown in Figure 8, the three principal types are (a) with the thermocouples located in the center of the sample and of the reference, (b) in a conductive wall outside the sample and reference, and (c) in the center and perimeter of the sample, i.e., without use of a reference. Cells have been constructed of glass, plastic, aluminum, ceramics, copper, nickel, platinum, etc. Most metals have the advantage of

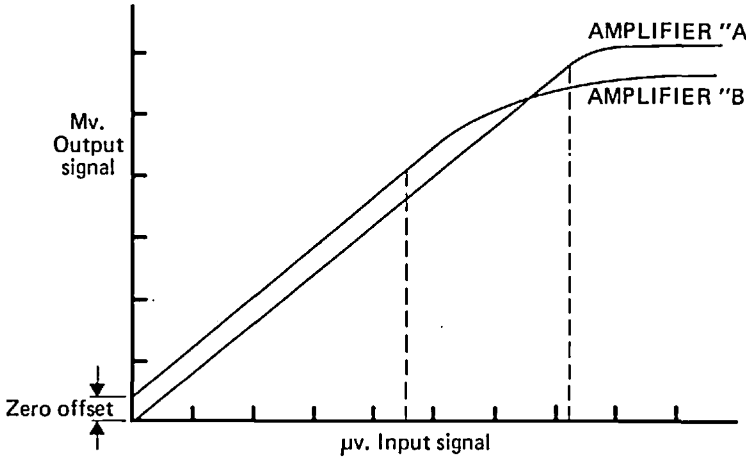


Figure 5. Amplifier response.[81]

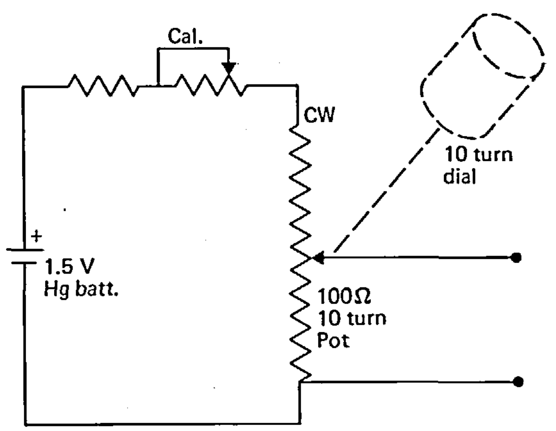


Figure 6. Apparatus for checking amplifier performance.[81]

being highly conductive, but reaction with the sample is always possible. Stainless steel has been generally found to be a poor material because of low thermal conductivity. Often some sort of a removable thin metal or glass cell is used to encapsulate the sample. Good thermal contact is important.

A considerable number of cell designs have been reported.[2, 14, 25, 28, 34, 41, 62, 77, 78, 82, 85, 86, 88] With the wide variety of commercial instruments now available the thermal analyst will need to produce a design of his own only for special purposes. An example of this is the microcell described by Yamamoto et al.[90,91] Cells specifically designed for calorimetry will be described in section 11.B.4.c and d.

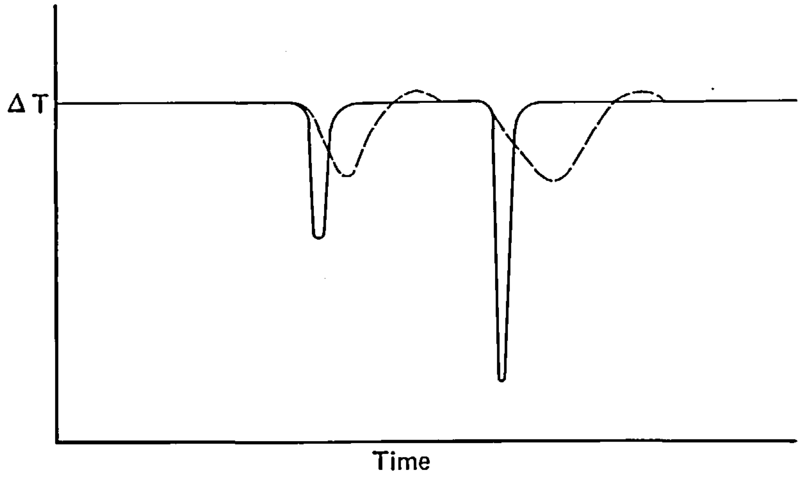


Figure 7. Effect of slow amplifier response.[11] Ordinate has no scale. Location of peak maximum only is significant.

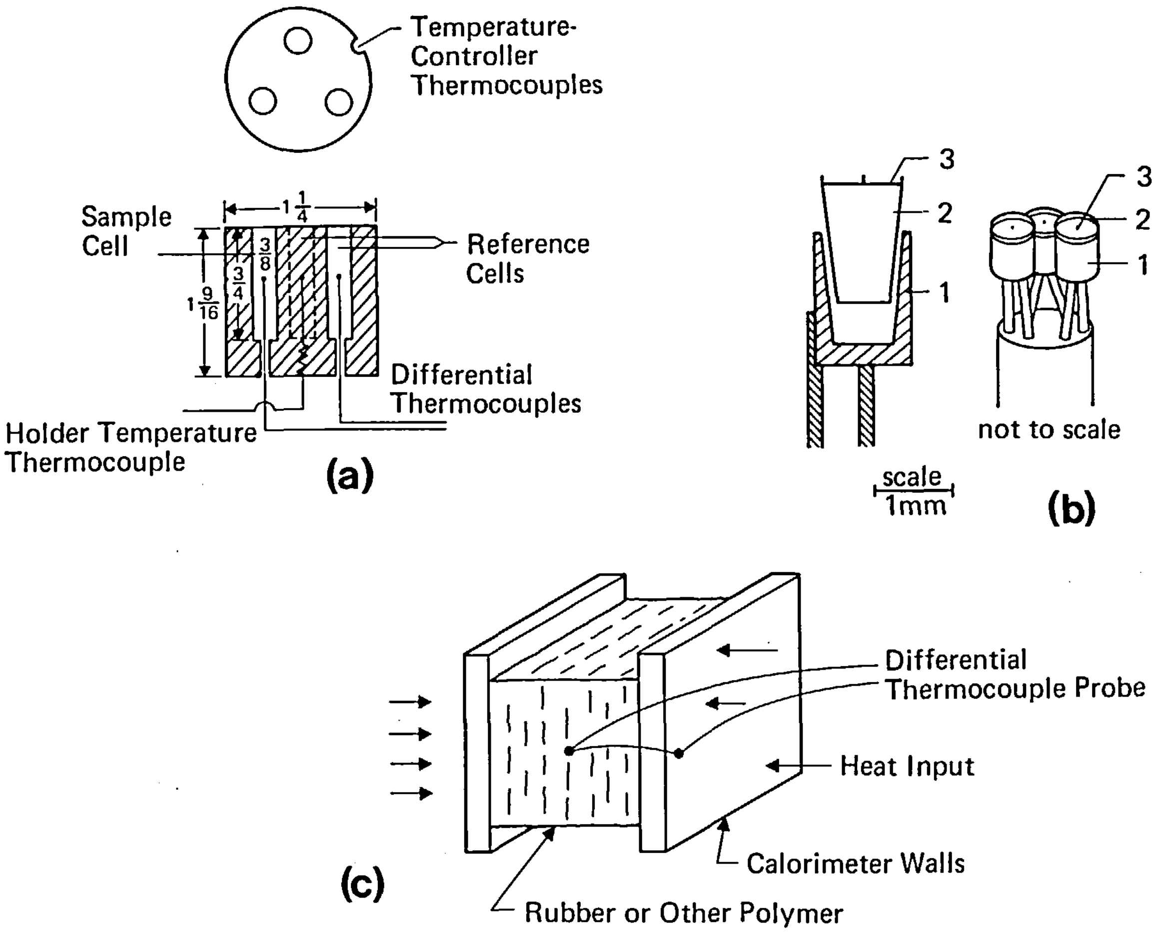


Figure 8. DTA cells. (a) Control thermocouples;[72] (b) external thermocouples, 1. thermocouple-cup, 2. sample encapsulation, 3. lid;[62] (c) wall reference cell.[22]

A variety of heating and cooling arrangements has been used. Usually heating is provided by resistance wire circuits or by enclosing the cell within a furnace. Liquid baths can provide very accurate control but are somewhat inconvenient to use and do not normally cover a wide temperature range. Design of cooling circuits is more difficult. Usually some form of refrigerant must be provided. Convenient methods are to precool a flowing gas or to inject small amounts of liquid nitrogen or liquid CO_2. To achieve control it is necessary to cool beyond the control point and provide the balance by using heat (see Figure 9). If the temperature differential between the cell and ambient is sufficient, control can be achieved without adding additional refrigerant.

e. Data Recording Device

The most common way of recording data in DTA is through the use of potentiometric recorders. Two main types are used: two unit or dual pen strip chart recorders where ΔT and T are plotted as a function of time, and x-y recorders where T is plotted on one axis and ΔT on the other. With a single strip chart recorder, the assumption is often made that if the temperature program is linear, one can substitute time instead of T by simply recording the initial temperature and heating rate. This incorporates any error encountered if the heating or cooling rate is not precisely linear. The advantage of this type recording is that the chart speed can be varied in order to present the peaks in a convenient fashion and the entire temperature range of the apparatus can be covered without interrupting the ΔT curve. Its disadvantage is that the data may appear in a rather extended chart. In addition a transform plot must be carried out if ΔT vs. time records are to be

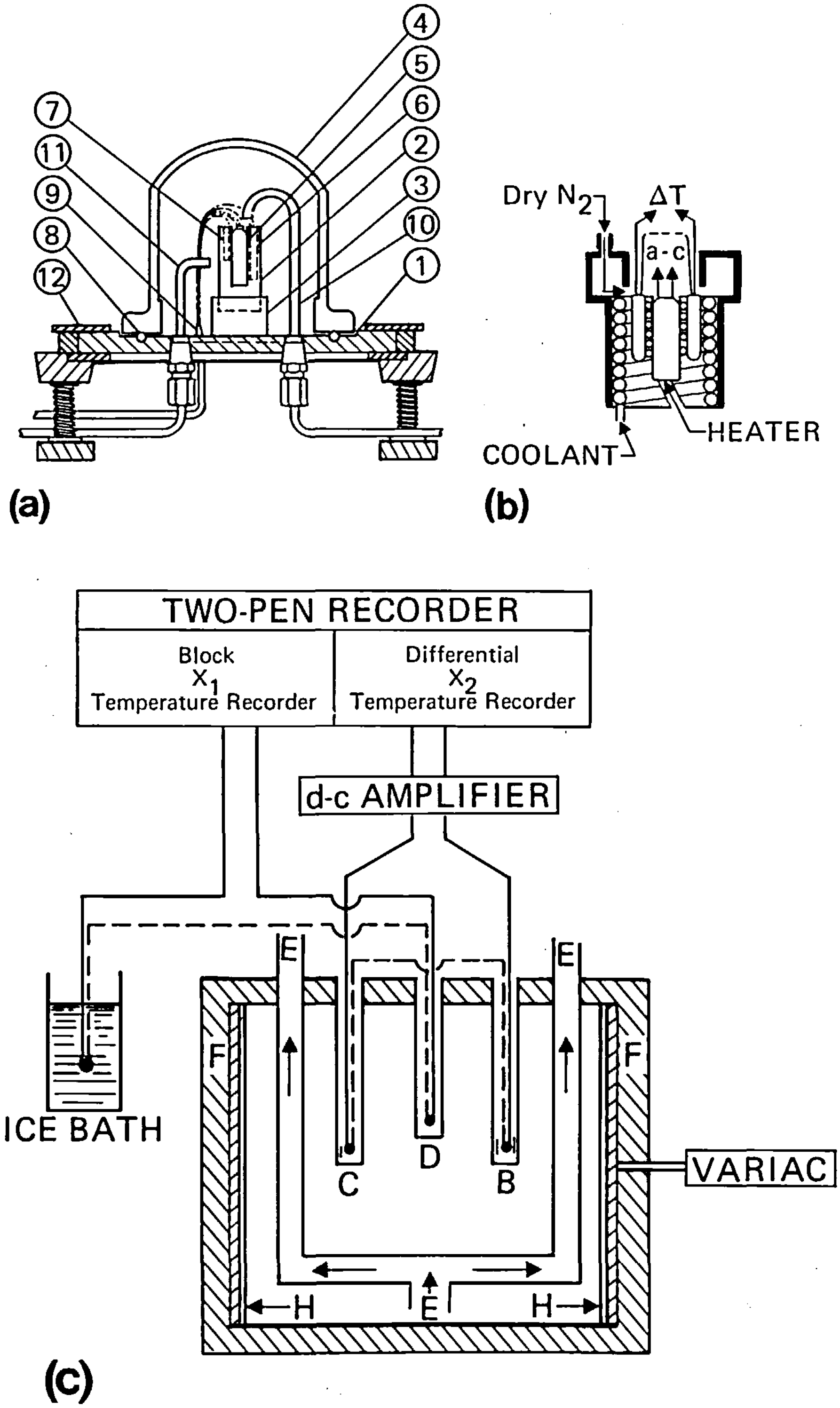


Figure 9. Cooling for DTA cells.[18,58,82]

used as valid ΔT vs. temperature curves. If a strip chart is used to record T_S vs. time, a smooth relationship between T_S and ΔT cannot be found directly from the chart because at T_S the process may be isothermal. However, if only calorimetric information is desired, stripcharts are not only satisfactory but also desirable. X-Y recording with the system temperatures measured in the sample is a convenient way for directly measuring ΔT at a given temperature. Also, x-y recording requires specialized potentiometric bucking if range expansion is desired. X-y recorders are generally less satisfactory for calorimetry as the ΔT vs. T function is less directly related to calories per unit time/than ΔT vs. time. Indeed, it is necessary to obtain a calorimetric constant for each heating rate if ΔT vs. T is measured.

More sophisticated data recording systems have been described. Usually these employ a high precision digital voltameter. The data can be presented either as a printed tape or on punched cards suitable to go directly to a computer or with the addition of an analog-to-digital converter they can be fed directly into a computer. These systems inherently take advantage of all the precision available in thermal analysis because the entire dynamic range of the amplifier may be used without incorporating attenuator circuits that are necessary if one is using a potentiometer recorder with its finite span. The difference in the degree of accuracy obtained, of course, is also a function of cost. The more sophisticated equipment is also considerably more costly. Without a doubt, future development and use of DTA will rely on direct digitization of the signal and subsequent computer processing of the data.

f. Atmosphere Control

The usefulness of being able to control the atmosphere in polymer analysis has been demonstrated by Ke.[46] This may consist of enclosing the sample in a static atmosphere which is established at the beginning of the run or using a flowing gas control to replace the atmosphere during the run.

Calibrations of the apparatus, if a controlled atmosphere or a flowing gas controlled atmosphere is used, should be carried out under the same conditions for highest precision.

3. Sample and Instrument Variables and Their Effects

a. Sample Thermal Conductivity

A number of sample variables affect the size, shape, and location of the resulting peak from DTA. These have been treated by a variety of theories. Only the most major and general qualitative effects will be considered here. If the thermocouples measuring the ΔT are located within the sample and reference, then the temperature at the junction is a function of heat flow from the sample walls through the sample to the thermocouple. Similarly, the reference temperature is also a function of the thermal conductivity of the reference. In practice it is not feasible to exactly match the thermal conductivities of the sample and reference.

A dilution technique has been widely used to reduce effects due to differences in thermal conductivity.[56, 74] The finely divided sample is mixed with an inert material. This minimizes differences in thermal properties at the expense of reducing the thermal effects.

b. Heat Capacity

During or slightly before a phase transformation the sample heat capacity changes.[55] This can cause errors in calorimetric measurements. Because the ΔT signal is simply that of the difference in temperature of the sample from that of a linearly heated reference, it is related to the heat absorbed or released acting on a fixed mass of material with a given heat capacity. If the heat capacity changes, the temperature difference will change. Again, the effect can be minimized by using highly dilute samples.

Berg and Egunov[12] in considering the mathematical problems of quantitative thermal analysis emphasize that at the start of the transition two phases exist. Also, there is no definite answer in the literature as to whether it is the thermophysical characteristics of the starting or final phase or both which determine the shape and parameters of the thermal curve. For example, on ammonium chloride the peak area of the cooling curve exceeds that of the heating curve by about 36% (see Figure 10). While the transition temperature may vary slightly with the direction of measurement it cannot account for this large difference. Further, the ratio of the peaks changes if an inert diluent is added. For example, Figure 11 for a 1:1 weight ratio of ammonium chloride

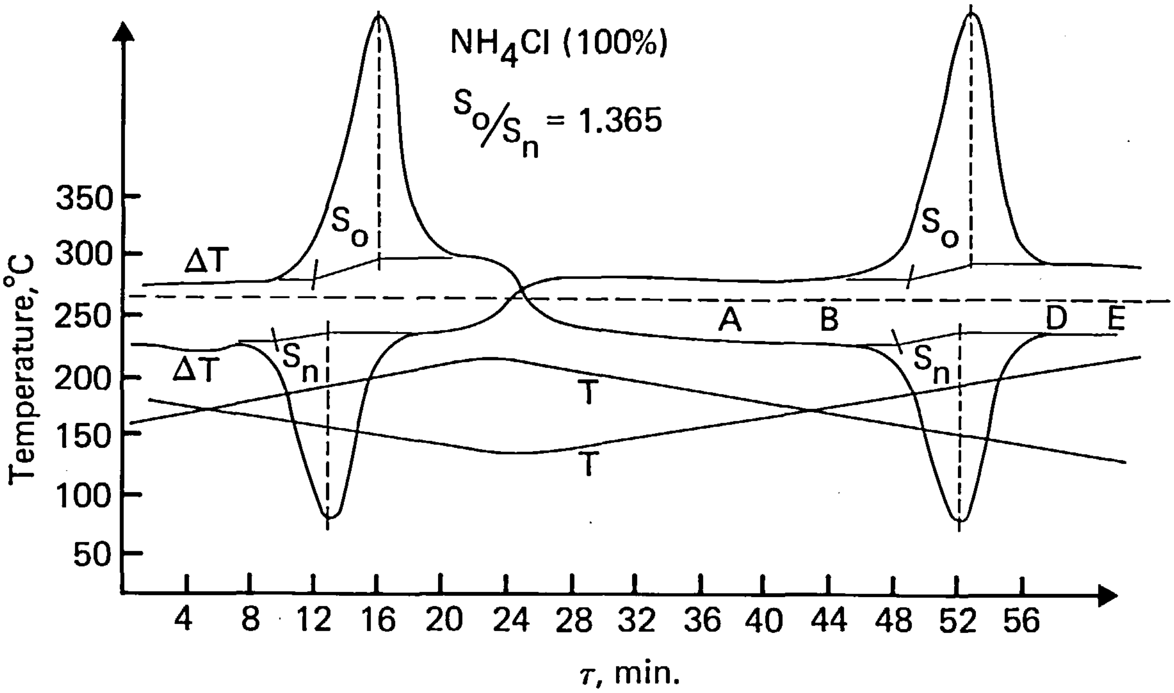


Figure 10. Heating and cooling curves of pure ammonium chloride.[12]

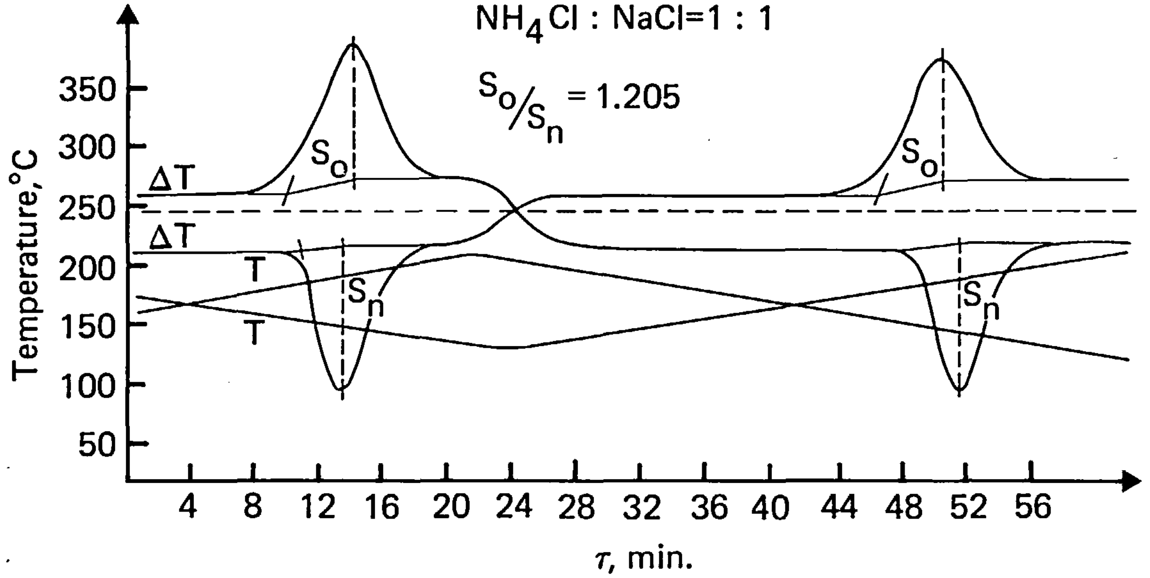


Figure 11. Heating and cooling curves of a mixture of ammonium chloride and sodium chloride (1:by weight).[12]

and sodium chloride shows a cooling to heating peak ratio of 1:2. Berg and Egunov[12] derive a simplified method of calculating the thermal effect and specific heat by (a) running with no sample or reference, (b) running a conventional thermogram on the pure material, and (c) running a thermogram on the material with a known amount of inert diluent. Although ingenious, this method appears to have no advantages over the use of special cells designed specifically for calorimetry, which are described in a later section.

4. *Techniques*

a. General Sample Preparation

Current practice is usually to place the sample and calibration standards in some type of disposable container that can be conveniently placed in the cell. By not having the sample in contact with the cell wall decomposition is minimized. Glass melting point capillaries and aluminum foil planchettes have been used.[5, 7, 76] Whatever the material, the container must be of sufficiently low mass so that weighing errors are not introduced.

As cited previously, diluents are used frequently. Some of those employed are alumina, calcined kaolinite, diatomaceous earth, carborundum, and silica. It is standard practice to dry these materials before use. As these materials are absorbents, caution should be exercised because some organic materials are retained above their boiling points and may give spurious results. For example, Manley[59] in a recent study soaked three diluents in organic liquids, filtered the solids, and dried them in a vacuum oven for one hour. Measurements on a thermogravimetric balance programmed at 3°C per minute from ambient to 300°C showed significant weight loss in some cases as shown in Table 1.

One possible approach to removing the errors caused by differences in thermal conductivity, heat capacity, sample size and shape, etc. between the sample and reference would be to calculate what these effects are and correct for them. This obviously requires an adequate model. Recently, Melling, Wilburn, and McIntosh[63] have developed a mathematical model that differs considerably from those described earlier. The sample and reference are considered to be held within cylindrical cavities in a block with very high thermal conductivity. Then finite difference equations are developed. The additional assumptions made are (a) that perfect thermal contact exists between the holder and sample and reference materials, (b) no heat leakage exists between the sample and reference, and (c) that although the physical properties of the sample and reference may be different they do not change during the thermal event being measured. With these assumptions Melling et al. develop finite difference equations. Using realistic values for the physical properties they have computed the effect of various parameters. This approach to analysis of DTA results appears to be promising. However, it is by no means completed.

TABLE 1

Weight Loss on Heating to 300°C, Percent[59]

Solvent	Celite	Kaolin	Silica
n-Butanol	4	0.2	0
Xylene	3	0.2	0.2 (Above 260°C)

b. Calibration for Temperature Measurement

Although the DTA cell designs given above are relatively unsatisfactory for calorimetry, they are useful for temperature measurements. Since thermocouples are used, only a few points of calibration are required. These points must be obtained with the standard sample mounted exactly as the sample is mounted in the block. A number of standard materials have been suggested.[8] The low fusing metals are very good calibration standards because they are readily available in high purity. Provided they are sealed in evacuated containers they may be remelted a number of times without decomposition.

Although ammonium nitrate is often used as a standard, there are a number of precautions that should be noted. It has been shown that only the 122 and 168°C endotherms are reproducible; the other transitions are subject to variations in both temperature and heat of transition.[84] Some samples decompose violently a few degrees above the melting point. Another commonly used standard, benzoic acid, sublimes and should be used only if it is encapsulated under nitrogen pressures. Water is a convenient low temperature standard, but must be degassed carefully. In addition, small droplets of water can supercool very easily by more than 20°C. Thus, adequate measures must be taken to insure the presence of the solid phase.

c. Heats of Transition Measurement

The determination of transition heats by DTA

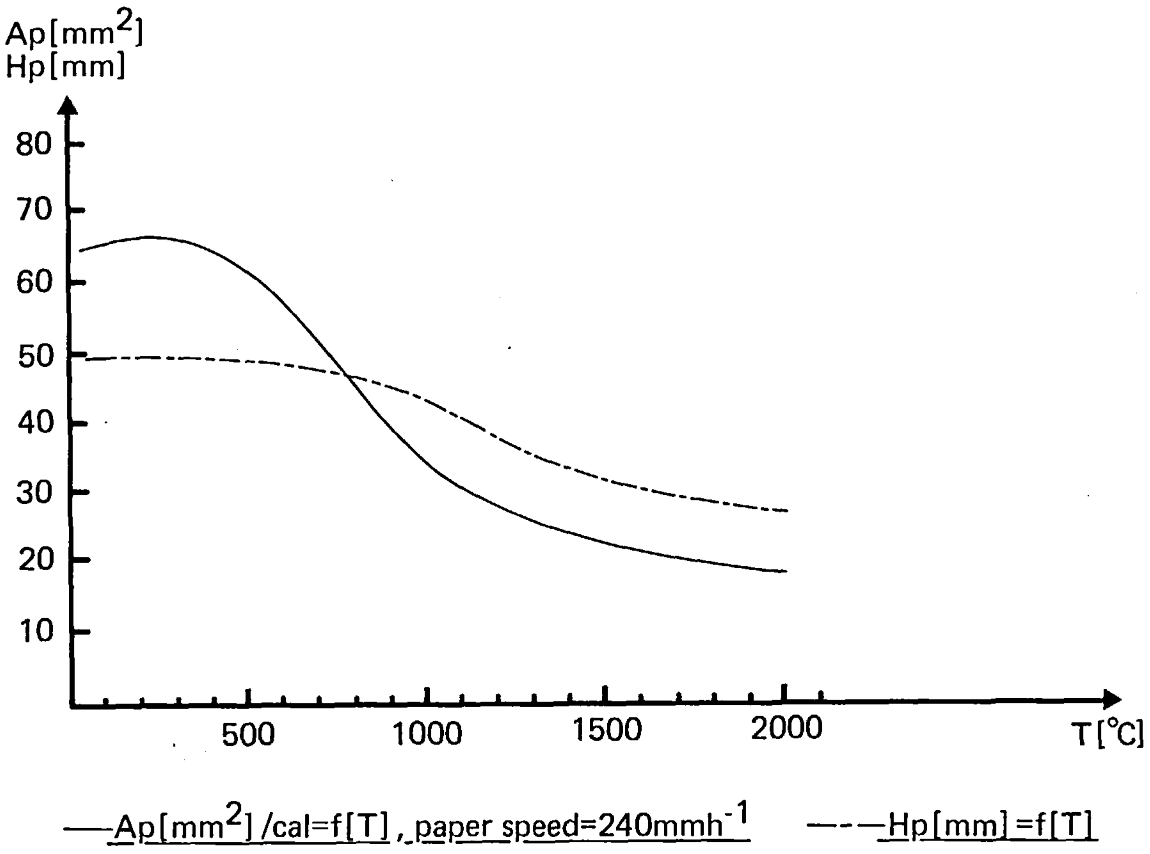


Figure 12. Sensitivity of DTA as a function of temperature.[52] Ap, peak area; Hep, peak height.

is more difficult than a simple transition temperature measurement. Certain fundamental requirements must be met by the DTA apparatus. Figures 12 and 13 emphasize the change in sensitivity in DTA as a function of temperature. In order to reduce as far as possible this variation, the design of the instrument should be such that variables which are not directly related to the heat absorbed or evolved by the sample during the transition are at a minimum. Among the variables that cause spurious effects are the heat capacity, thermal conductivity, heat loss due to vaporization, and heat loss due to thermal conductivity of the connecting wires. At this point it is helpful to consider briefly the current state of knowledge as far as the theory of measurement in differential thermal analysis.

Gray[35] has reported on a simple generalized theory for DTA measurements. Figure 14 shows the model for this analysis. Here T_s represents the temperature of the sample, C_s, the heat capacity, R, the thermal resistance, and T_p, the temperature of the heat reservoir which serves as the source of thermal energy. The rate of heat generation within the sample is dh/dt and dq/dt is the rate of heat transfer. Gray shows that it is possible to obtain an expression shown graphically in Figure 15 for the quantity Rdh/dt that is the sum of three terms. These terms are represented in Figure 15 by the lines I, II, III. It is apparent that the instrumental design should be such that the distance III is negligible compared to I and II. Similarly, since the recorded signal, $T_s - T_r$, is proportional to R, it is desirable to have a large R which in turn is incompatible with fast response. Thus, in most cases a compromise design must be selected. A number of cells designed for calorimetry have been reported (see previous section). A recent design by Baxter[9] will be discussed in detail. The cell is shown in Figure 16. A thermoelectric disc made of constantan serves as the major heat transfer path to the sample and is one half of the differential temperature thermocouple. The disc is attached to a silver surface that is temperature programmed

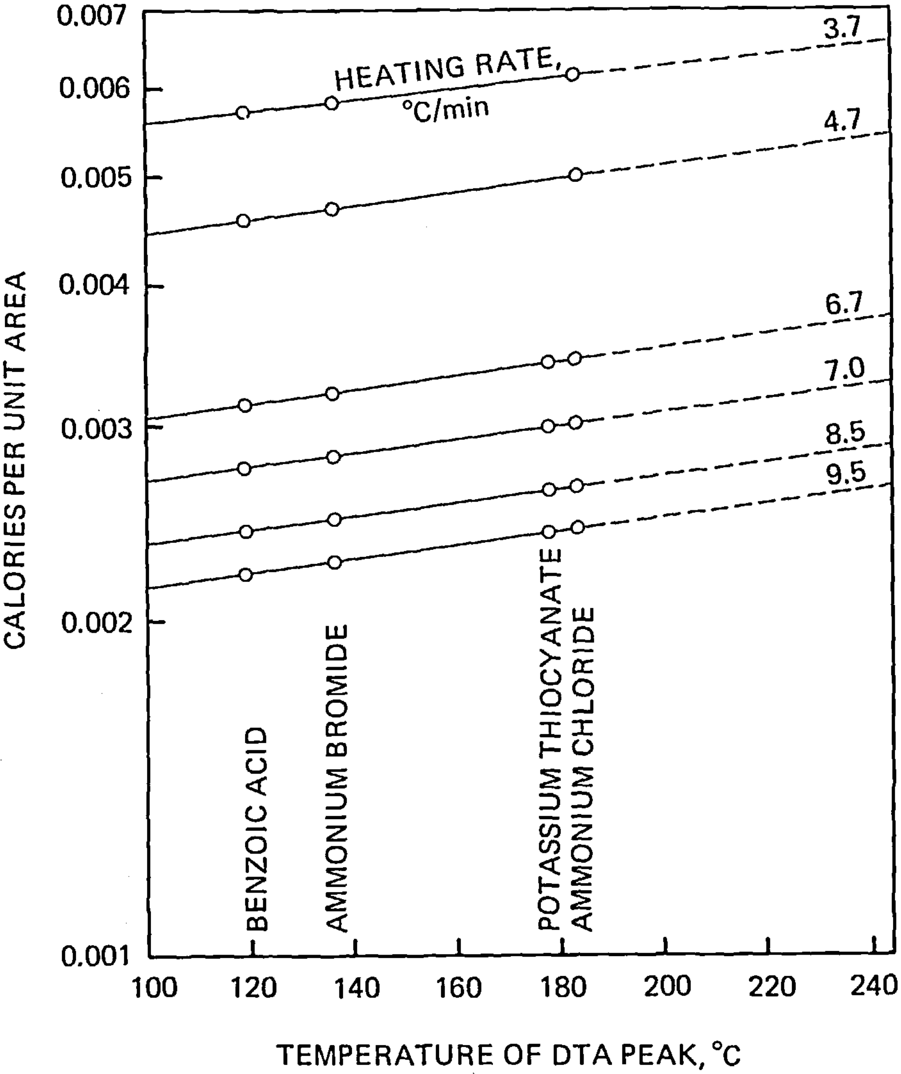


Figure 13. Variation of calories per unit area in DTA with temperature and heating rate.[5]

and has two raised platforms symmetrically positioned for the sample and reference. Each platform has a chromel wire attached to it to form a chromel constantan thermocouple. The calorimeter has a purge gas system. Working from a theory that is similar but not identical to that of Gray's, Baxter derives the equation for the idealized DTA curve shown in Figure 17 and the equivalent circuit for the cell shown in Figure 18. From this, he predicts that to increase the ordinate sensitivity it is necessary to make R_d large and R_o small. To increase resolution, R_D, C_{SH}, and C_s should all be small. A special base line circuit is used with the cell that gives a compensation independent of the temperature and heating range. Therefore, the total baseline deviation is less than 0.1 mcal/sec from ambient to 600°C as shown in Figure 19. The major improvement in cell performance can be shown by the plot of the sensitivity vs. temperature given in Figure 20. While the sensitivity is not constant, it is relatively constant as compared to those shown in Figures 12 and 13. Further evidence of the good performance of the design is given in Figure 21 where the calibration constant is shown as a function of sample size. In this case, the sample was indium varying from about 5 to 270 mg with less than a ±1% change in sensitivity. Similarly, the independence of the calibration constant with heating rate is shown in Figure 22. Major changes in heating

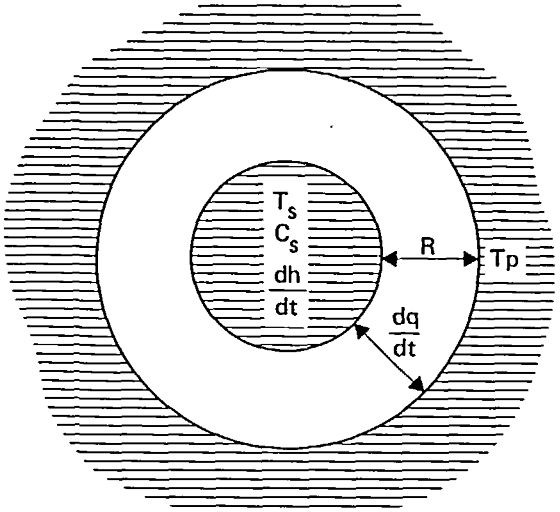


Figure 14. Model of a thermal analysis cell.[35]

rate produce less than a ± 1% change in the calibration constant. The operating characteristics of the cell are given in Table 2. With this design, calorimetric measurements can be conveniently made by DTA with high precision, ~ 1%, and good accuracy, of the order of ±5%.

d. Calibration for Transition Heat Measurement

Since the response of even well designed cells is not constant, calibration of the DTA instrument at several temperatures is desirable. Solid to liquid transitions are generally preferred. A convenient listing of standards has been given.[8] The amount of heat involved during the standard transition should be approximately equal to the heat of the materials under study. This insures that a variation due to sample thermal resistance and the thermal resistance between encapsulation and detector do not become important. The calibration of calories per area of chart should bracket the sample transition range. For most DTA cell designs (see previous exception) the calibration factor changes with heating rate may be quite large as shown in Figure 13.[5]

In addition to calibration with standards of known thermal properties special calibration holders containing a resistance wire to permit addition of known amounts of energy may be used.[52]

5. Specific Studies

a. General

Wendlandt[87] has reported on use of capillary tube sample holders for substances which react with the conventional aluminum sample cups in DTA and differential scanning calorimetry (DSC). These are melting point tubes 1.6 to 1.8 mm in diameter. The sample is placed in the tube, tamped gently into place, and the tube cut off to the length of 1.0 to 1.5 cm. The tube is then placed in the regular aluminum metal holder. This must increase the thermal resistance of the system.

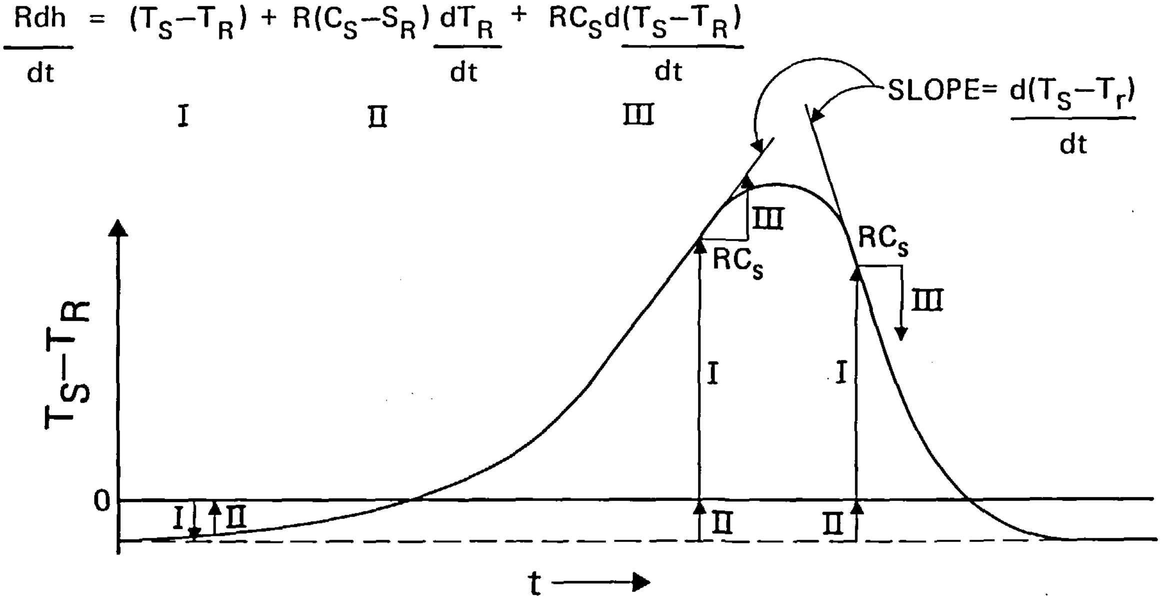


Figure 15. Graphical determination of Rdh/dt from a DTA curve.[35]

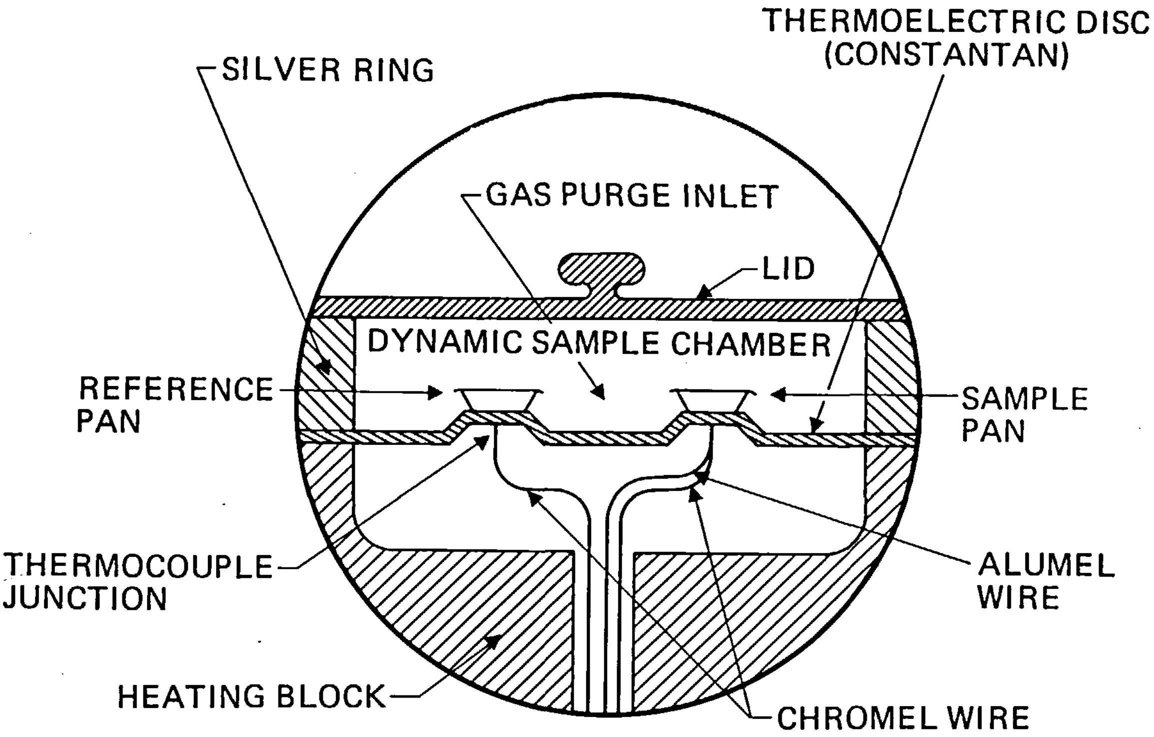


Figure 16. Calorimeter cell for DTA.[9]

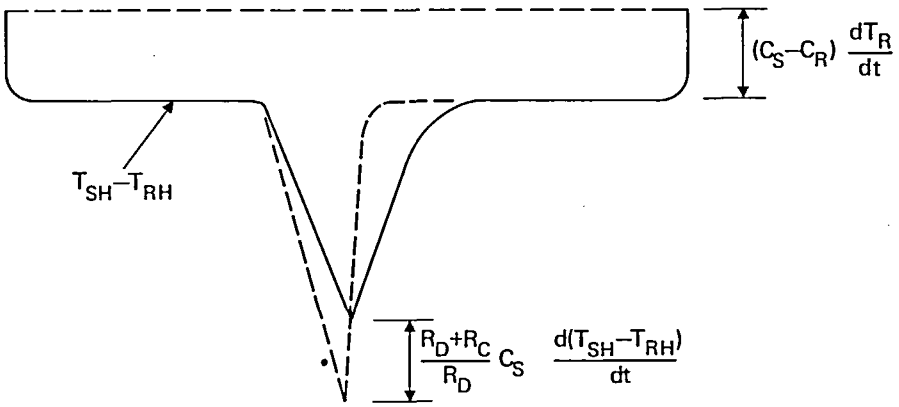


Figure 17. Idealized data for calorimeter DTA cell.[9]

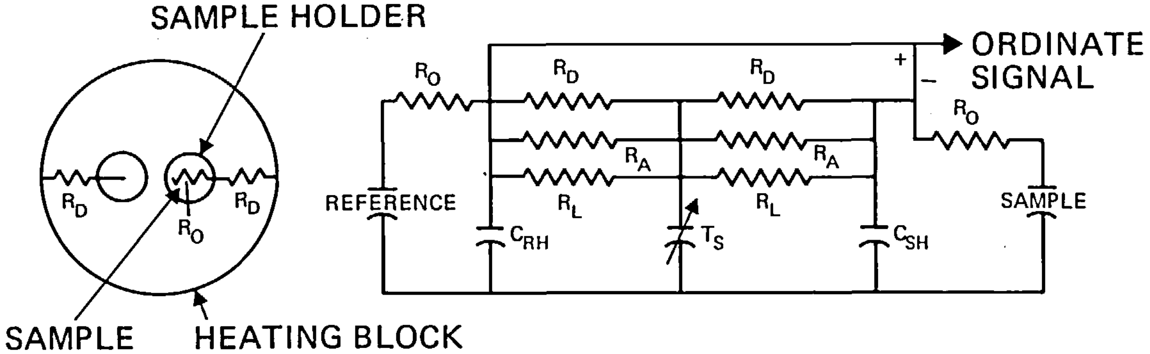


Figure 18. Equivalent circuit for DTA cell.[9]

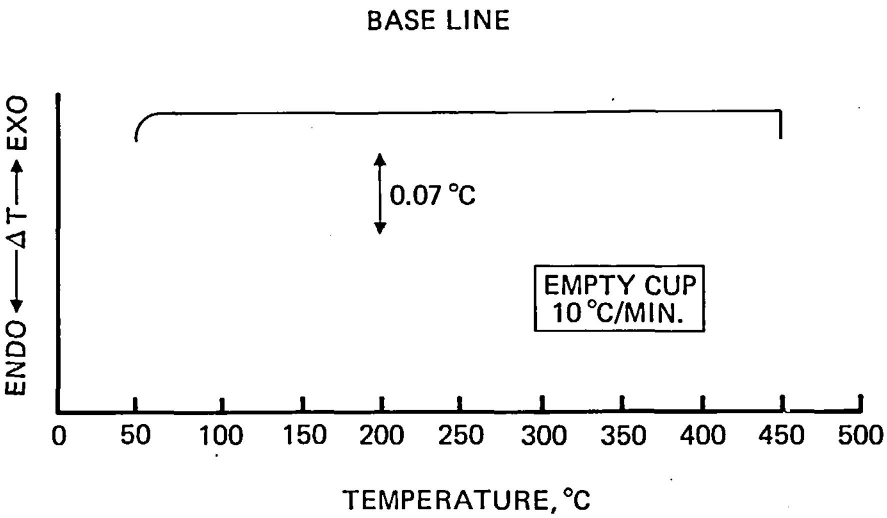


Figure 19. Test for base line stability.[9]

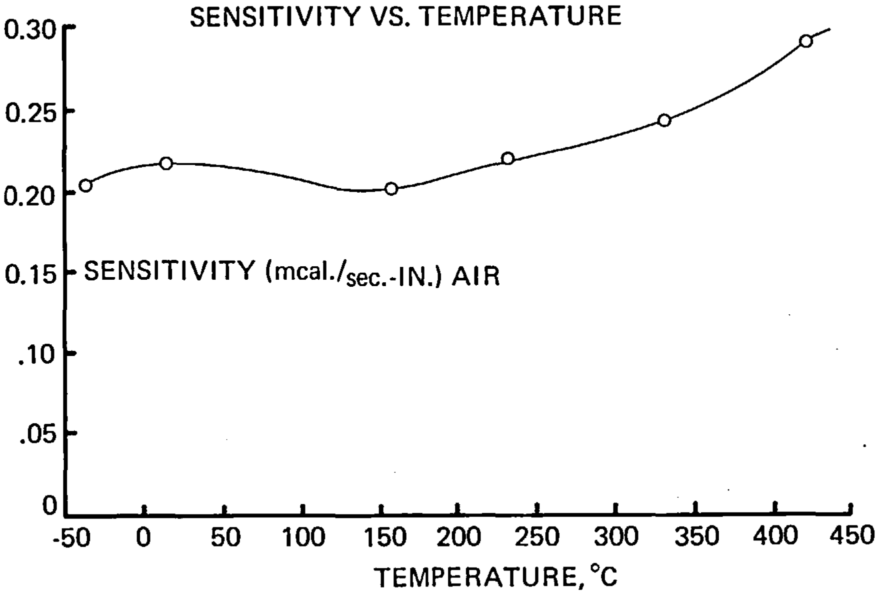


Figure 20. Sensitivity vs. temperature[9] for a conductive plate calorimeter cell.

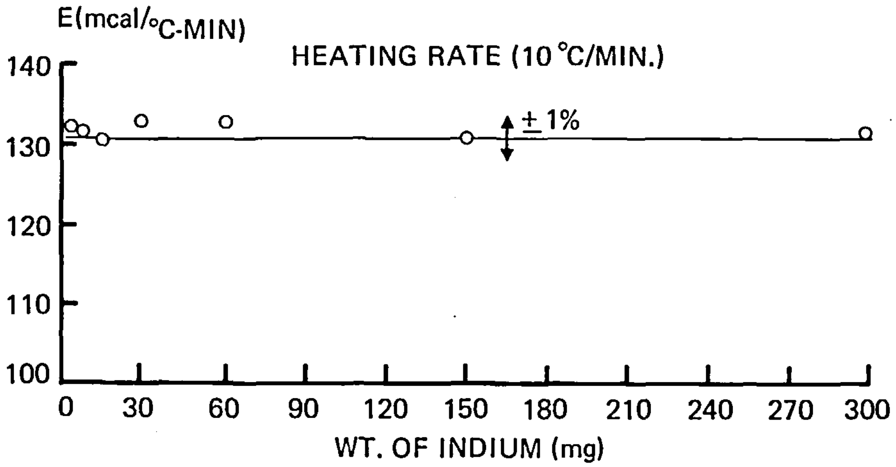


Figure 21. Effect of sample size on the calibration constant of a conductive plate calorimeter cell.[9]

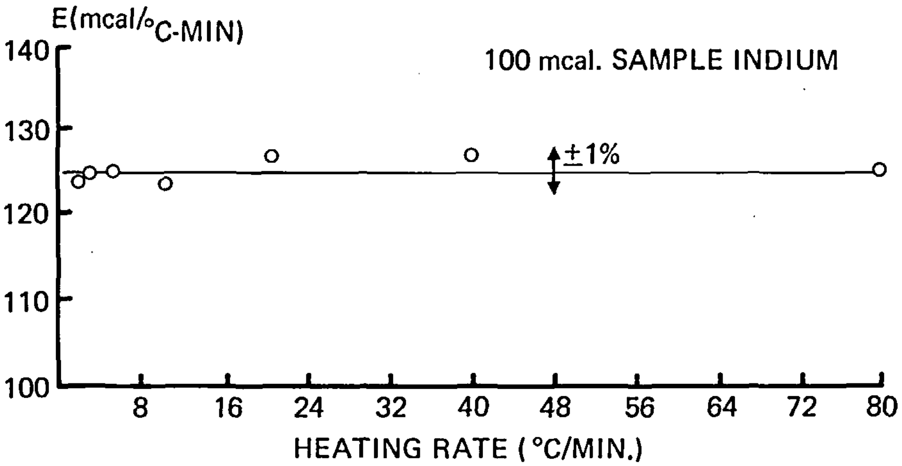


Figure 22. Dependence of thermogram area on heating rate.[9]

TABLE 2

Operating Characteristics of DTA Calorimeter Cell

Temperature Range:	-150°C to 600°C
Sample Volume	0.05 ml.
Sample Containers:	Aluminum (6.6 mm I.D.)
Atmosphere:	Atmospheric to 2 mm Hg - Purge to 100 ml/min.
Cell Volume:	2 ml.
Temperature Repeatability:	± 1° C
Calorimetric Sensitivity:	0.05 mcal/sec mv at ambient temperature
Heating Rates:	0.5 to 100 ° C/min.
Cooling Rates (Subambient):	0.5 to 10 ° C/min to -120° C
Baseline Performance:	<0.1 mcal/sec displacement to 600 ° C

However, in calorimetric measurements this is not as important as in temperature measurement.

Foltz and McKinney[32] utilize a quenched polymer sample as the reference material instead of the conventional inert reference or empty pan. Figure 23 shows a DSC curve with an inert reference material. The dashed line is the T_g curve for the amorphous polymer after heating at a temperature well above T_g and quenching. The solid line is for a specimen of the same polymer annealed during a long storage period. By contrast, Figure 24 shows the glass transition using a quenched polymer as a reference. This eliminates the base line shift associated with the change in specific heat. This technique is especially useful for determining small differences due to annealing.

Brennan et al.[16] have considered in detail methods of analyzing the data obtained by DTA calorimetry. In particular, they have developed methods of determining the true heat capacity base line for a system undergoing a thermal event. This is useful in determining heat capacity even though a thermal event is taking place. In particular, they analyze the curves associated with decomposition of polymethyl methacrylate and the pyrolysis of cotton.

b. Specific Heat Measurement

The calorimetric cells may be used with differential thermal analysis to measure specific heats. Figure 25 illustrates the principle of the method. The base line is established by measuring the base line with empty pans. A reference is then run, usually sapphire, to calculate a calibration constant. The sample is run and its deflection from the base line is compared with that of the reference of known weight and specific heat. The specific heat can then be calculated. This is discussed more fully in connection with differential scanning calorimetry.

c. Reaction Rate Studies

A number of studies have been made on polymerization reactions.[20, 37, 43, 66, 67] For example, the initiation temperature of the hard rubber reaction and approximate heat of reaction have been measured.[13]

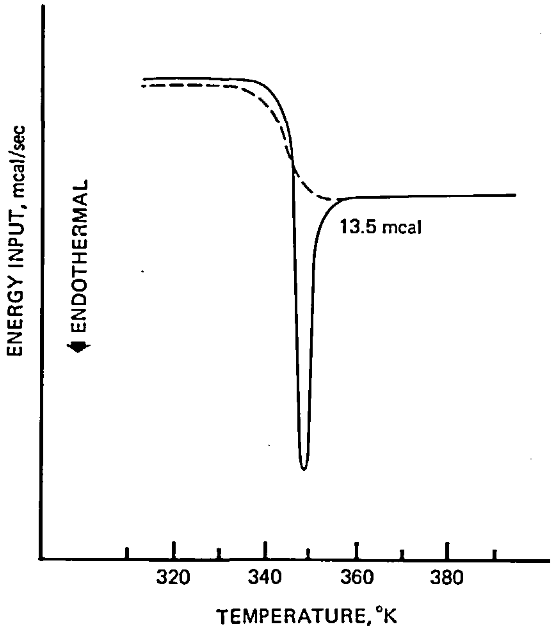


Figure 23. PVC copolymer. DSC curves for quenches - and annealed —.[32]

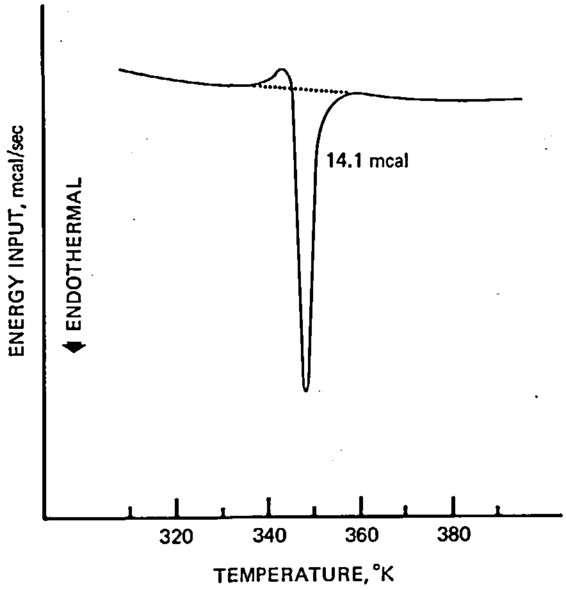


Figure 24. PVC copolymer. DSC curves for annealed vs. quenched polymer reference. Ruled line defines peak area.[32]

Figure 26 shows an example of the determination of kinetic data. Here, the deviation from the base line as modified by the time constant of the apparatus is proportional to the rate of a first-order reaction. The total area minus the area up to the temperature of the measurement is proportional to the fraction of samples remaining unreacted at that temperature.[9] This provides an easy method of calculating kinetic data. Morphological studies and polymer processing calculation

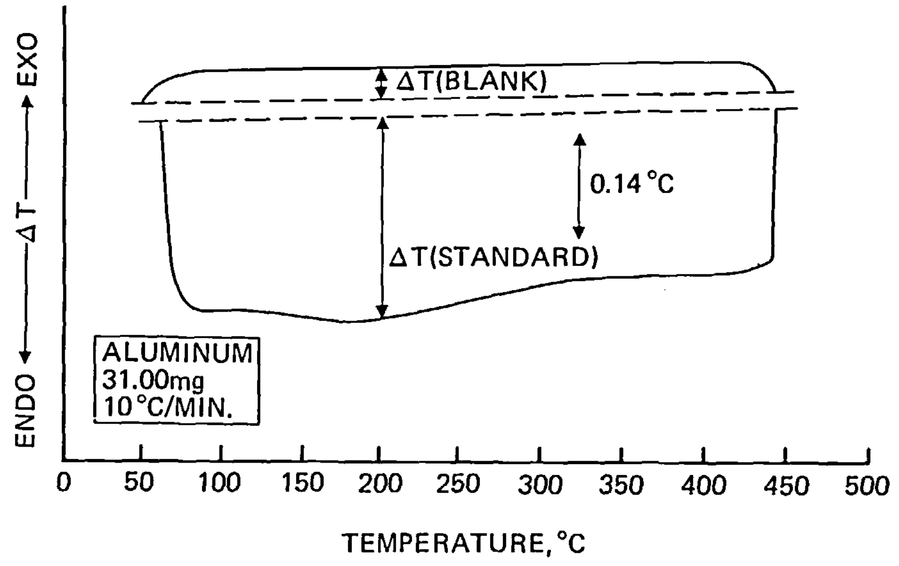
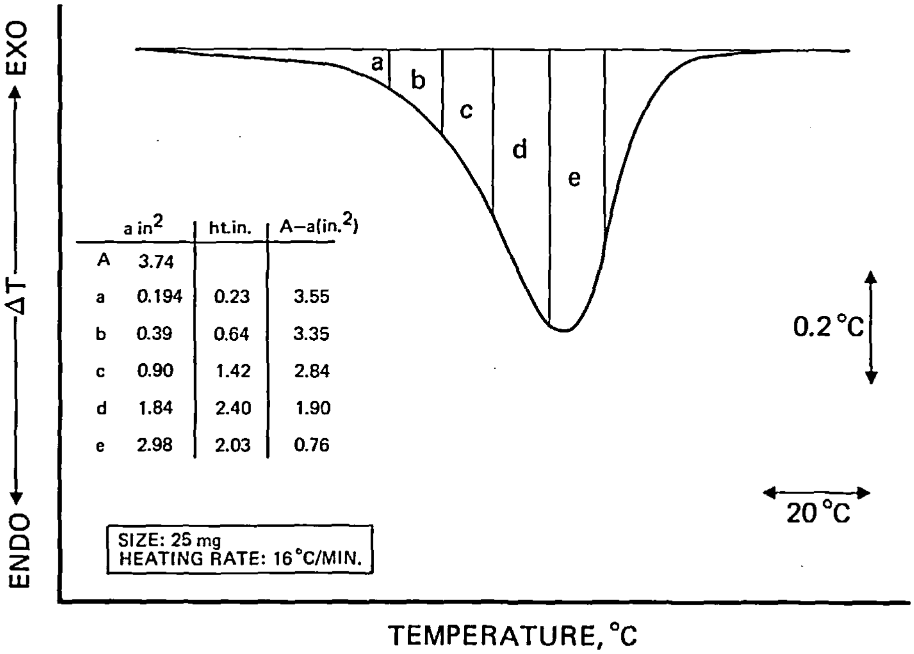


Figure 25. Determination of specific heat by differential calorimetry.[9]



	a in^2	ht.in.	A−a(in.^{2})
A	3.74		
a	0.194	0.23	3.55
b	0.39	0.64	3.35
c	0.90	1.42	2.84
d	1.84	2.40	1.90
e	2.98	2.03	0.76

Figure 26. Kinetic data on polymerization initiators by DTA.[9]

require a knowledge of isothermal crystallization rates. A convenient special cell for determining this is shown in Figure 27. The crystallization temperature is selected, usually somewhere near the freezing point, and this temperature is established by a temperature controller operating isothermally on the lower block. The upper block is set at a temperature that will destroy all crystal-

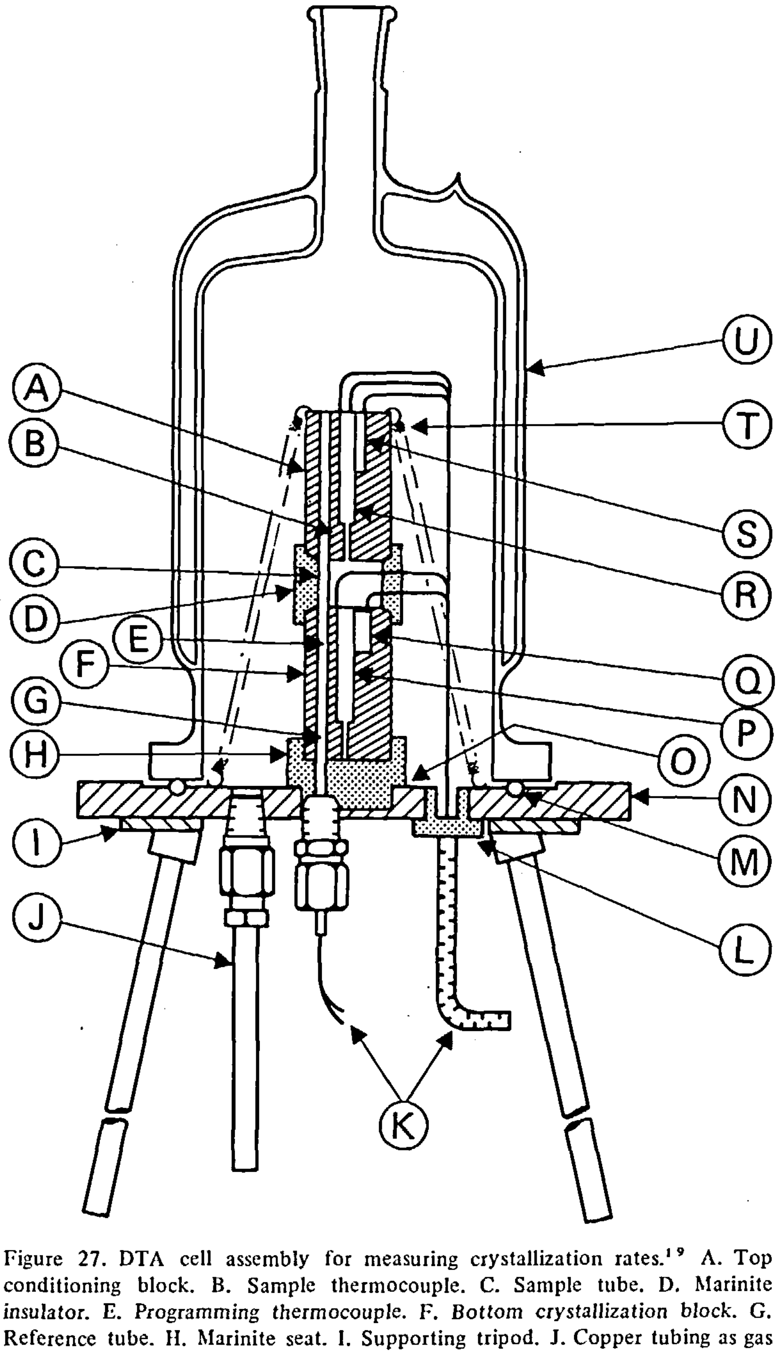


Figure 27. DTA cell assembly for measuring crystallization rates.[19] A. Top conditioning block. B. Sample thermocouple. C. Sample tube. D. Marinite insulator. E. Programming thermocouple. F. Bottom crystallization block. G. Reference tube. H. Marinite seat. I. Supporting tripod. J. Copper tubing as gas inlet. K. Electrical leads to recording system. L. Multiple-pin feedthrough connector or rubber stopper. M. Neoprene O-ring. N. Supporting aluminum plate. O. Reference thermocouple. P. and R. Cartridge heaters. Q. Platinum resistance thermometer. S. Temperature-controlling thermocouple. T. Tension springs. U. Vacuum-jacketed borosilicate glass bell jar.

linity and remove previous thermal history effects. When the sample is completely conditioned, the sample and reference are rapidly placed in the lower block. A conventional DTA is run with the exception that time is recorded rather than temperature. The fraction crystallized at any time, T, is proportional to the area of the curve at time, T, divided by the total area of the curve when crystallization is complete. Various conventional analyses of the data may be made.

d. Pressure Studies

A number of pressure DTA cells have been reported.[11, 26, 33, 53, 92] In general, these cells suffered from one or more of the following drawbacks: they were massive and therefore insensitive, their pressure range was very limited, or they were inconvenient to use. Currently there are a number of designs that oversome these defects. One of these is due to Levy and Miller.[51] This design is useful in a number of cases. First, they reduce vaporization or sublimation. This permits studies not attainable in cells at atmospheric pressure. For example, Hoyer et al.[40] used pressure DTA to determine activation energies for styrene polymerization. Figure 28 shows thermograms for: I. thermal polymerization of styrene. Such studies could not be carried out except with the aid of pressure DTA cells.

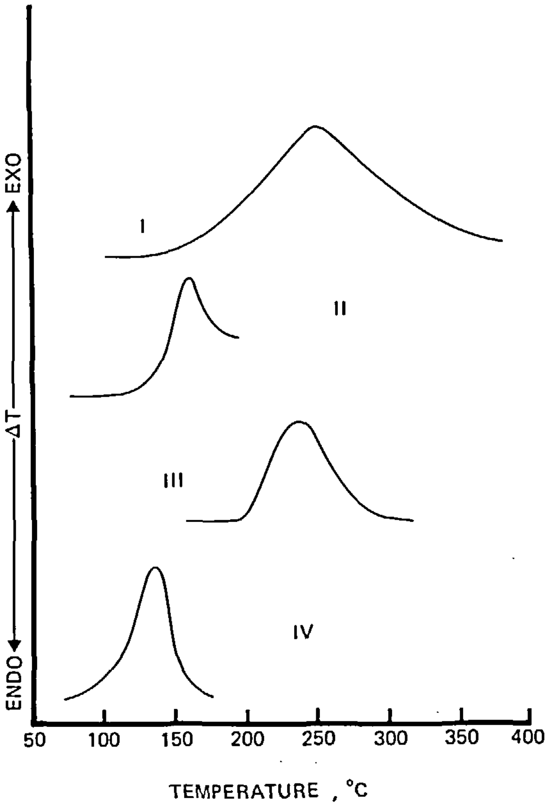


Figure 28. Thermograms for the measurement of activation energies.[40] I. Thermally polymerized styrene. II. Benzoyl peroxide polymerized styrene. III. Solution polymerized styrene. IV. Heterogeneous polymerized styrene.

Ezrin and Claver[31] have devised a DTA cell to contain the sample under pressure shown in Figure 29. An interesting application is illustrated in Figure 30. Here the curing behavior of thermosetting resins is studied. At atmospheric pressure a phenolic resin treated paper shows a broad endotherm peaking at 160°C and an exotherm at 270°C. No indication of an exotherm, i.e., curing, is observed below 200°C. Pressure DTA eliminates the endotherm because the volatile products are retained and an exotherm representing curing is observed.

For very high pressure DTA Davidson and Wunderlich[27] have used the cell design shown in Figure 31. This has been operated at pressures up to 3700 bars. Figure 32 gives an example of their work on the melting and crystallization of polyethylene under pressure.

C. Differential Scanning Calorimetry

1. Introduction

As stated previously, differential scanning calorimetry (DSC) operates on a principle fundamentally different from DTA. In many ways DSC approaches very closely classical calorimetry since the power difference between sample and reference is measured. The theory of DSC has been covered in detail by O'Neill.[65] A satisfactory apparatus was disclosed by Watson et al.[84] The routine technique and application of DSC has been given in detail elsewhere.[8]

2. Techniques

To obtain reasonably significant measurements it is essential that the following points be observed:

1. The sample and standards must be encapsulated in the same manner.
2. Every effort must be made to keep the thermal resistance of the system constant. As has been previously demonstrated serious errors in temperature measurement will occur if the thermal resistance is permitted to vary.[84]

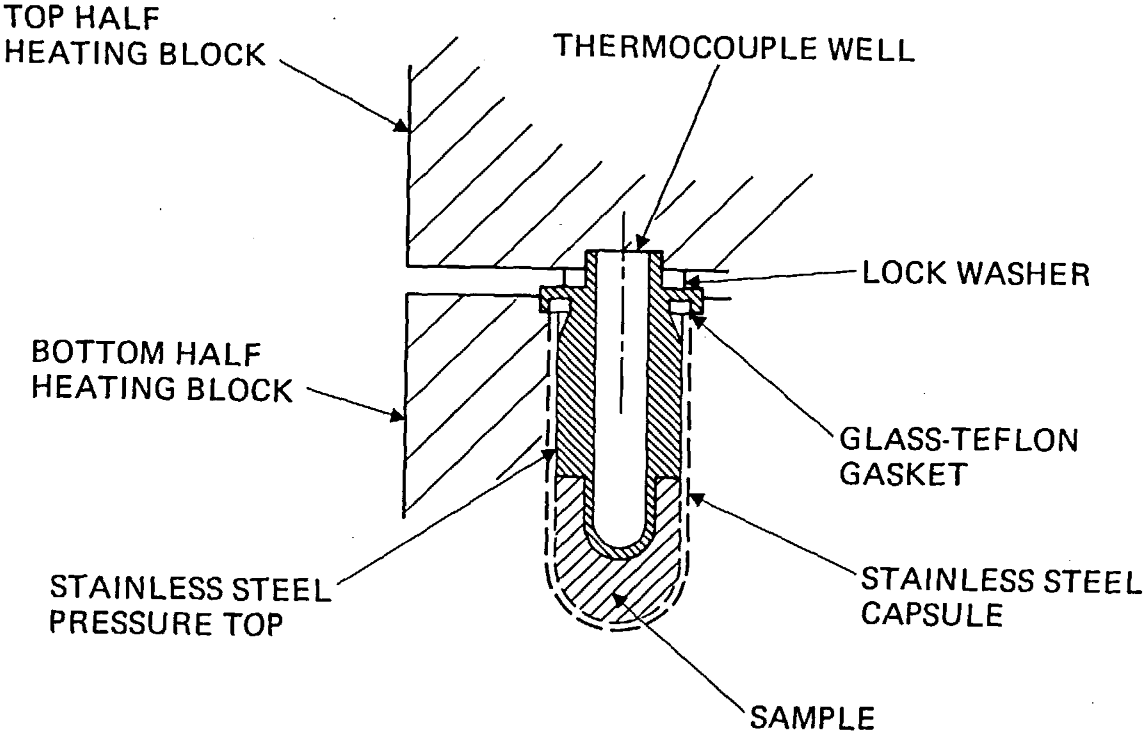


Figure 29. Pressure DTA cell.[31]

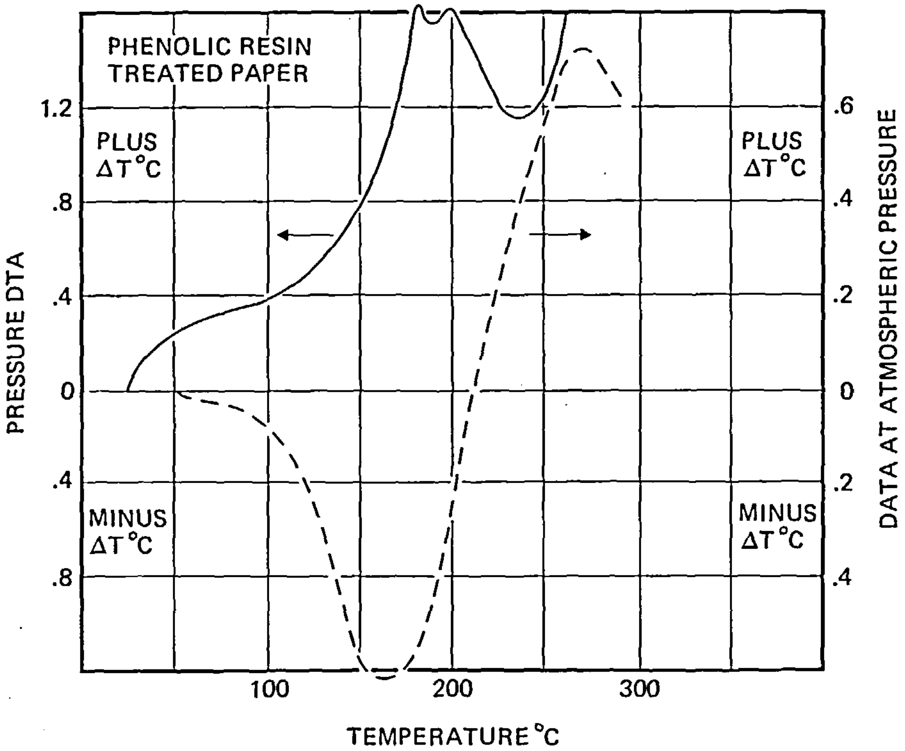


Figure 30. DTA curves of phenolic polymerization.[31] - - - Pressure Applied - - - Ambient Pressure

3. The temperature calibration must be carried out separately for each heating rate employed.[79,84]

4. The temperature calibration curve for presently available equipment is *hyperbolic*, not a simple curve function. Thus, a number of calibration points are required (see Figure 33).

5. The dependence of response on temperature is a linear function (see Figure 34). For precise calorimetry it is necessary to choose calibration standards throughout the temperature range studied.

6. Since most polymer samples are prone to oxidation, samples should be run in cold-welded sample holders sealed under nitrogen. Degassing of the sample for 30 to 60 minutes is desirable.

In general, measurements of heats of transition, second order processes, and heat capacity are slightly easier to carry out by DSC as opposed to DTA. Temperature measurements are more difficult by DSC due to item 4 above than by DTA. The ideal condition is to measure transition heat

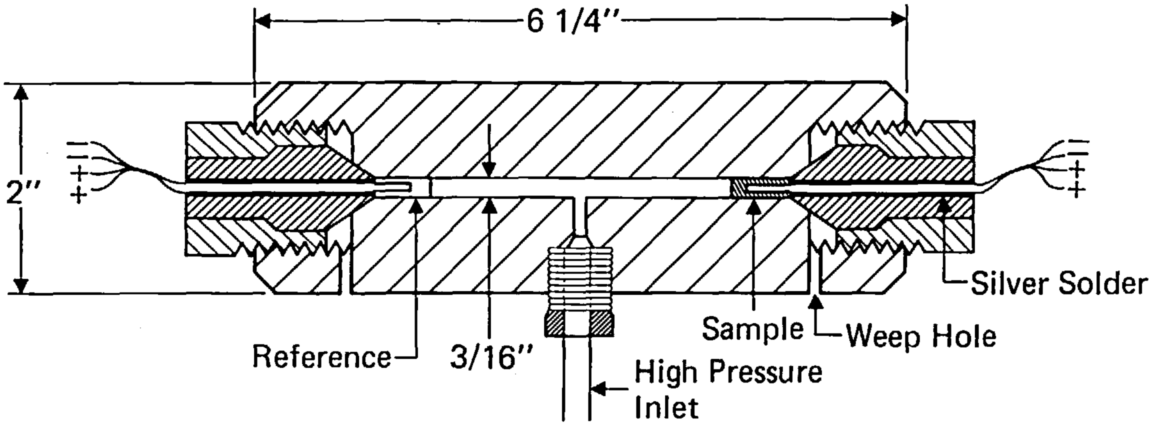


Figure 31. High pressure DTA apparatus.[27]

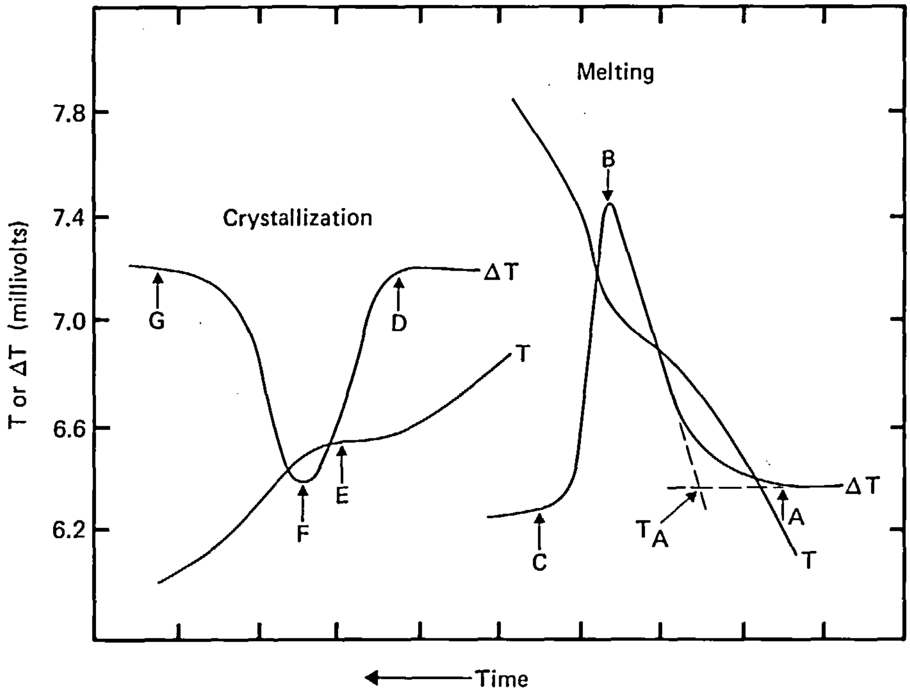


Figure 32. Melting and crystallization of polyethylene under pressure.[27]

and heat capacity by DSC and transition temperature by DTA.

D. Polymer Applications

1. Differential Thermal Analysis

a. First Order Transition Temperatures

The thermal energy of polymers released and adsorbed at freezing and melting temperatures is sufficiently large to make DTA determinations relatively simple.[17,23,24] The method of interpretation of the data has been the subject of a number of studies. Figure 35 shows the points that have been used as a measure of the transition temperature. Vassallo and Harden[82] studied the determination of a number of organic compounds. They concluded as have other investigators[4,80,83] that the point A, which is the intersection of the extrapolated straight line portion or an approximation to the straight line of the low temperature side of the peak with the base line, is the correct transition temperature when ΔT is plotted against either the furnace or block temperature and the surface temperature of the sample. Point C, which is the intersection of the two straight lines from the low and high temperature side, is the true transition temperature when ΔT is plotted in the center of the sample temperature. Apparently this holds true for both dilute and undiluted samples. The difference between point C and the temperature of the endothermal or exothermal minimum is frequently quite small and the latter is often reported as the transition temperature.

The observed transition temperature may be a function of heating rate. For polymers this is not an artifact but occurs because the sample, for example, may slowly melt and recrystallize in a form with a higher melting point. However, one should always be aware that such effects can occur. Figure 36 shows the temperature of the main melting peak when a linear polyethylene, M, of three fractions of this polyethylene, FR 1, FR 2, FR 3A, and, additionally, polyethylenes PM, III, and IV are cooled slowly. Note that there are significant changes in the transition temperature with change in heating rate.[36,69] Figure 37 shows the DTA curve of a mixture of low melting crystals and the initial melting of the high melting crystals, and D is the final melting of the high melting crystals. At high heating rates there is insufficient time for recrystallization, and the final endotherm disappears.

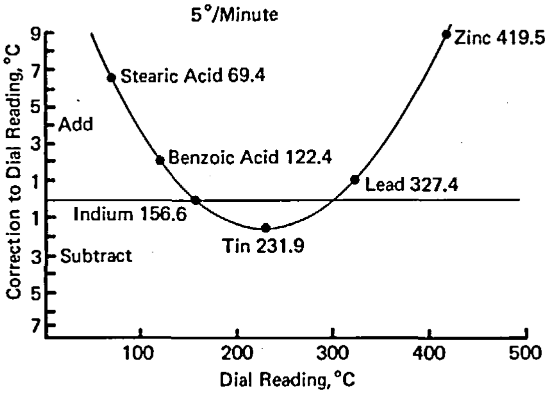


Figure 33. Typical temperature calibration correction curve.[72]

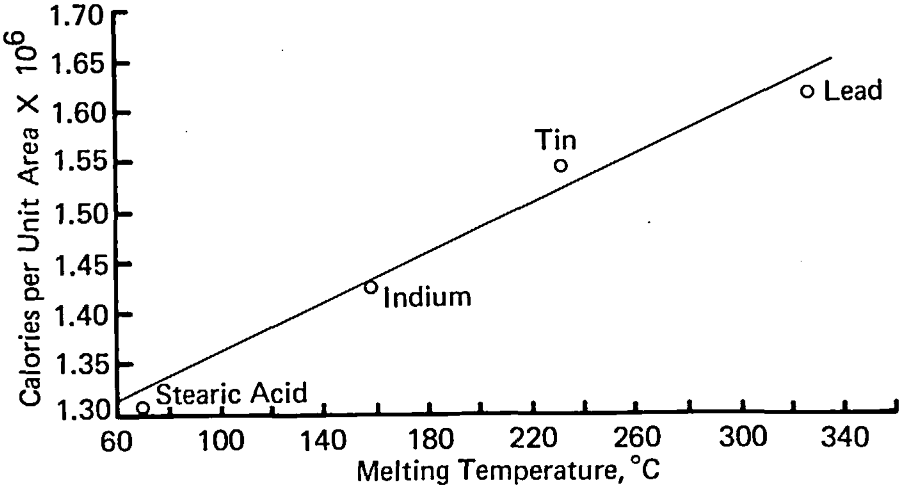


Figure 34. Variation in calibration factor, calories per unit area, with temperature.[72]

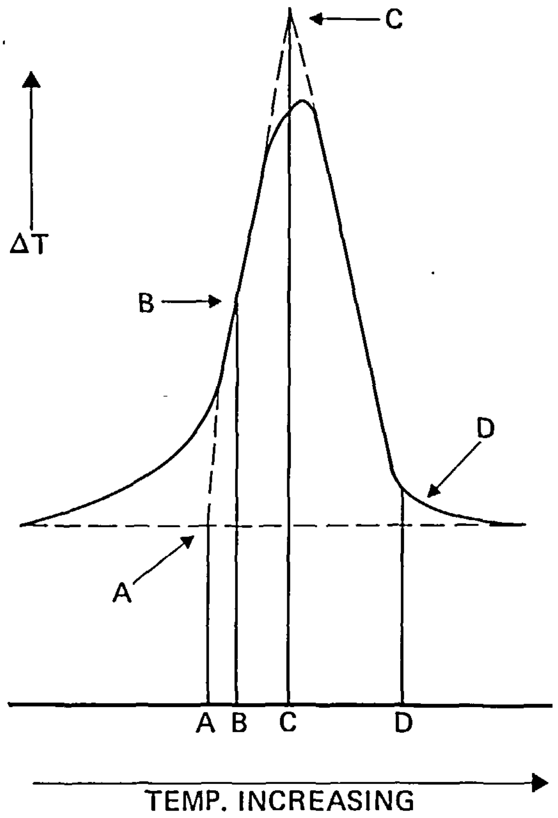


Figure 35. Methods of determining transition temperature.[82]

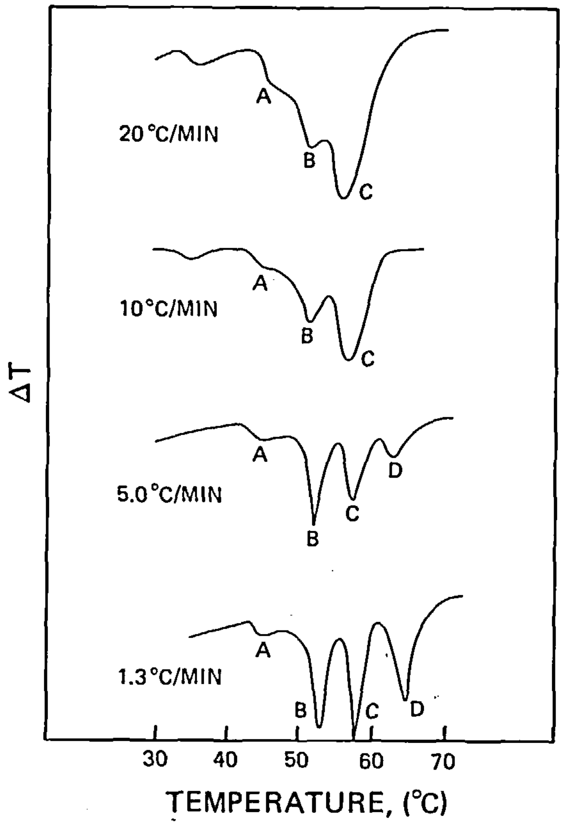


Figure 37. Melting temperatures as a function of heating rate for trans-1-4-polyisoprene.[54]

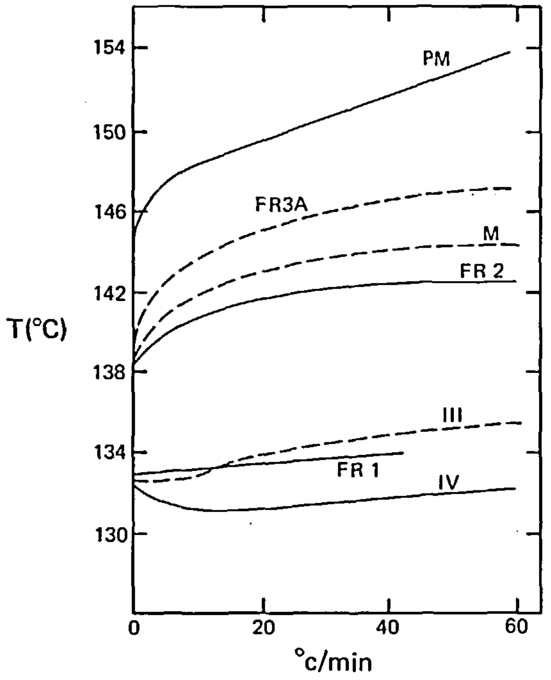


Figure 36. Melting temperatures as a function of heating rate.[36,69]

Thermal history can drastically affect the transition temperature observed. For example, Figure 38 shows the same mixture of low and high melting polyisoprenes crystallized at different temperatures. The high melting form predominates at crystallization temperatures of about 40° and above. At progressively lower temperatures, the low melting form begins to appear. Bell and co-workers have extensively studied the effect of crystallization temperature on Nylon 66 and on polyethylene terephthalate.[10] Figure 39 shows the DTA curve for Nylon 66 and illustrates the effect of slowly and rapidly cooling Nylon 66 from the melt. There are significant differences in the shape and position of the peak. When the same slowly and rapidly cooled samples have been annealed for 17 hours at 220° C, 2 forms were observed in one case, in only 1 form in another. The effect of annealing time on polyethylene terephthalate was studied. Figures 40 and 41 show the effect of annealing time on the peak area and peak temperature for the two forms of polyethylene terephthalate, respectively.

It is thus apparent that the thermal histories of

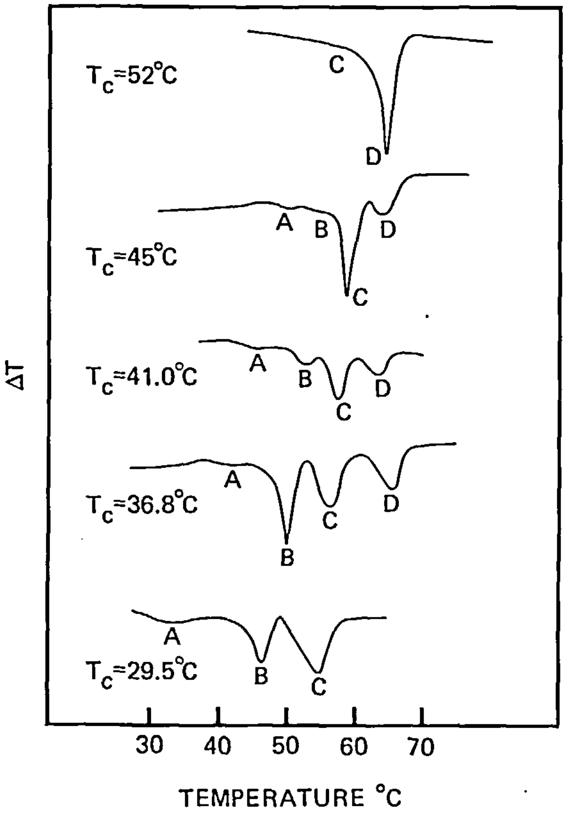


Figure 38. Effect of crystallization temperature on thermograms of low and high melting polyisoprene.[54]

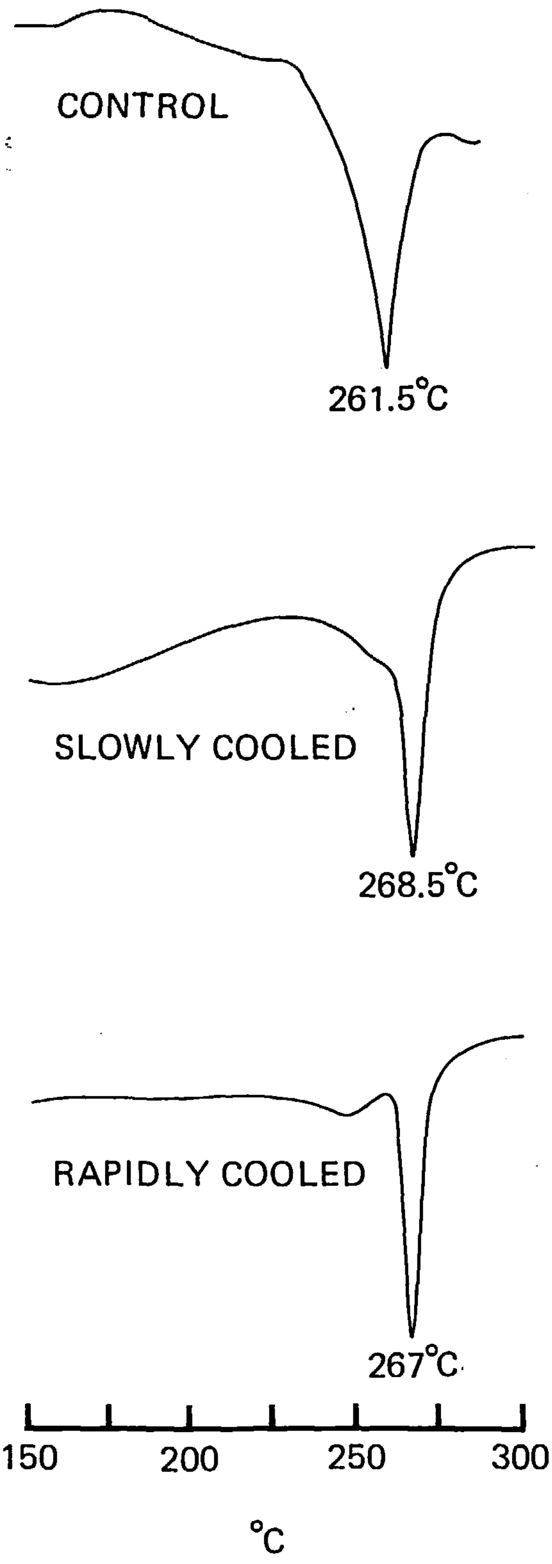


Figure 39. Effect of cooling procedure on Nylon66.[54]

the samples must be carefully controlled. Variations in the thermal treatment can be used to study the effect on various forms of the polymer and to produce different crystallite size distributions. An apparatus and cell both to produce conveniently and to record automatically a variety of thermal treatment have been described.[38,39]

b. Glass Transition Temperatures

Differential thermal analysis is among the several methods available for measuring glass transition temperatures. Since a polymer glass transition is associated not with an enthalpy change but with an increase in the rate of enthalpy gain with temperature, the DTA curves do not show peaks but simply a step change in T. This is usually observed as a shift in the baseline (see, for example, Figure 42a). The glass transition is a kinetic phenomenon and the observed transition occurs at temperatures at which the time scale of the experiment is of the same order as molecular relaxation time. Therefore, a number of various

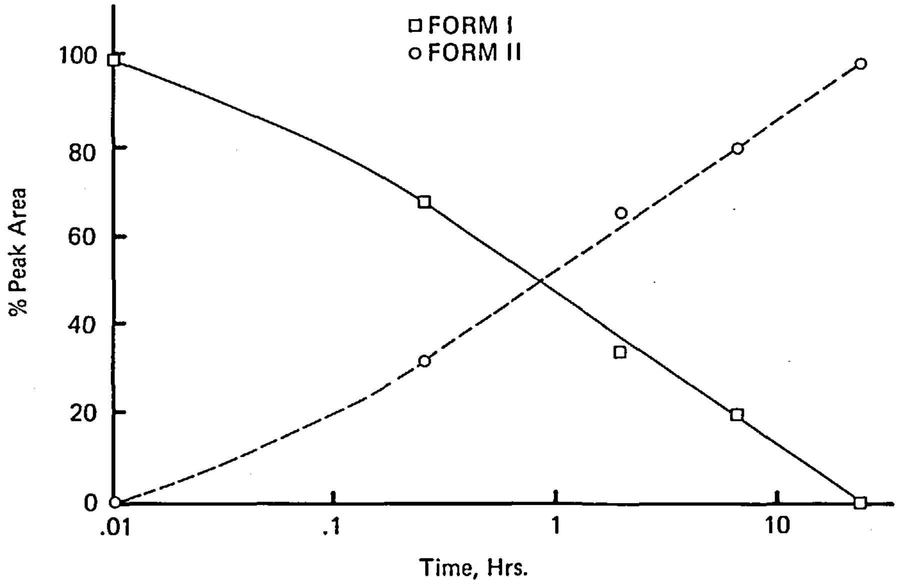


Figure 40. Effect of annealing time on peak area for polyethylene terephthalate.[10]

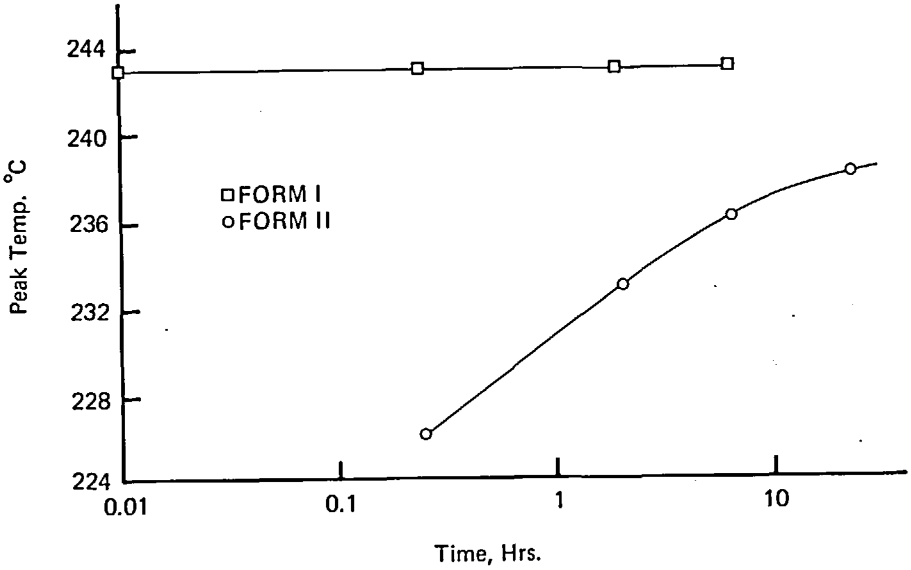


Figure 41. Effect of annealing time on peak temperature for polyethylene terephthalate.[10]

shapes for DTA curves have been reported. The more commonly encountered ones are shown in Figure 42b while those in 42c occur less frequently. Wunderlich, Bodily, and Kaplan[89] have given a detailed explanation of curves b and c. Briefly, when the heating rate through the transition region exceeds the rate at which the sample was cooled, curve b results. If the sample was rapidly cooled and then the DTA run at a slow heating rate, curves such as c will be observed. This comes about because on slow cooling, only a small fraction of the free column is frozen in at T_g. Roberts and Sherliker have reported an anomalous step in the DTA curve shown in Figure 42d.[71] In this case the change is in the direction of the exothermic sense. The polymer was a polyurethane. Curve d was obtained on cooling and then reheating. After further cooling and reheating the more normal phenomenon of 48a was observed. This behavior has been observed by them for a variety of polymers, polyesters, vinyl polymers, and polyamines. A possible explanation of this anomalous behavior is that it is due to the samples containing internal strains.

Figure 43 shows characteristic DTA curves for an ethylene-propylene copolymer and a butyl rubber.[61] There are three characteristic regions: region A, which is very nonreproducible and is generally thought to be due to heat capacity difference between the sample and the reference. In region B, T_g values may be calculated in two ways: the first is to use the "onset" temperature, that is, the temperature where the first departure from a base line is noted. This is sometimes difficult to estimate. Another way of calculating this is to use the extrapolated onset temperature. This is calculated by extrapolating the straight line portion of the curve above and below the break in the base line and using the intercept as T_{oo}. Region C, where changes are apparently taking place, is not completely understood. Several conflicting theories as to why this effect is noted have been advanced. Figure 44 shows the effect of the heating rate on the DTA traces. The upper curve is run at 5° per minute, the lower at 20°. There are changes in the curve although T_{oo} changes relatively little. However, the glass transition temperature as a kinetic phenomenon will definitely be influenced by the sample's thermal history and by the rate at which it is run. Table 3 shows results on a number of elastomers reported by Maurer.[61] The two reported values of T_g, calculated by the methods shown in Figure 43 and designated as T_o and T_{oo}, are given at two heating rates for replicate measurements and compared with values reported in the literature. It is apparent that T_{oo} is more reproducible and less affected by heating rate.

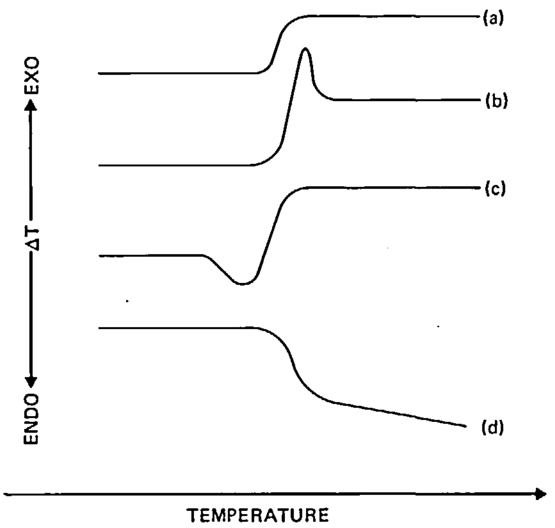


Figure 42. Examples of DTA curves in the glass transition region.[71]

Normally, no special instrumentation is used to measure glass transition temperatures by DTA. Dannis[22] modified the sample cup to take advantage of the fact that the glass transition is a function of the thermal diffusivity. He did not use a reference sample. The reference thermocouple was attached to the edge of the sample cup and the other thermocouple placed in the center of the sample. Thus, the shift in base line when T_g was reached was markedly increased.

Strella[78] has made a detailed study of interpretation of DTA curves in terms of T_g. Starting with the theoretical model, he concluded that measuring $\Delta\theta$, where $\Delta\theta$ is the difference in temperature between the center of the sample and the wall, and then extrapolating the log of the inflection point of the $\Delta\theta$ curve vs. the surface temperature curve an "indicated' glass transition temperature, T_{gi}, could be found. Values of T_{gi} were plotted against heating rate, and the T_g at zero heating rate agreed well with those measured by other methods. This is illustrated in Figure 45 where $\Delta\theta$ is plotted against the wall temperature and in Figure 46 where the extrapolation to zero heating rate is carried out. In most cases, the uncertainty in T_g due to thermal history is sufficiently large so that such an extrapolation to zero heating rate is probably not justified.

2. *Differential Scanning Calorimetry*

The application of DSC to polymer systems has been treated recently.[8] Strella and Erhardt[79] have studied the rate effects in the measurement of polymer transitions by differential scanning calorimetry. Figure 47 shows the change in the indicated maximum rate of melting, that is, the center of the melting peak, T_{mmi}, vs. Heating rate using indium as a standard. It is apparent that while quite high heating rates are involved there is an appreciable change in the measured melting point with heating rate. Juijn et al.[45] have made calorimetric studies of transitions in polyvinylchloride by DSC.

Jackson and Mandelkern[42] have studied the effect of various crystallization procedures by use of DSC fusion curves as shown in Figure 48. Similarly, Currie and Dole reported a number of measurements of specific heats of polymers.[21]

In a manner very analogous to DTA, DSC may be used to determine glass transition temperatures. Figure 49 shows glass transition temperatures for a narrow molecular weight distribution poly-

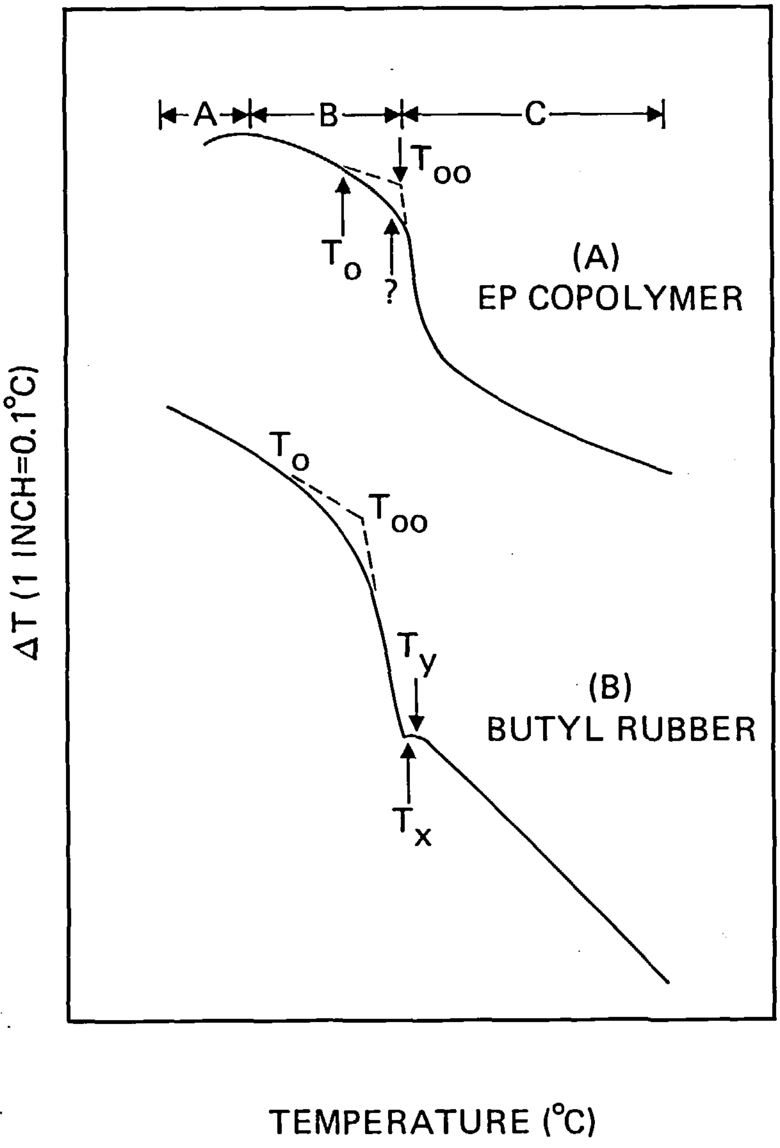


Figure 43. Characteristic DTA curves for elastomer glass transitions.[61]

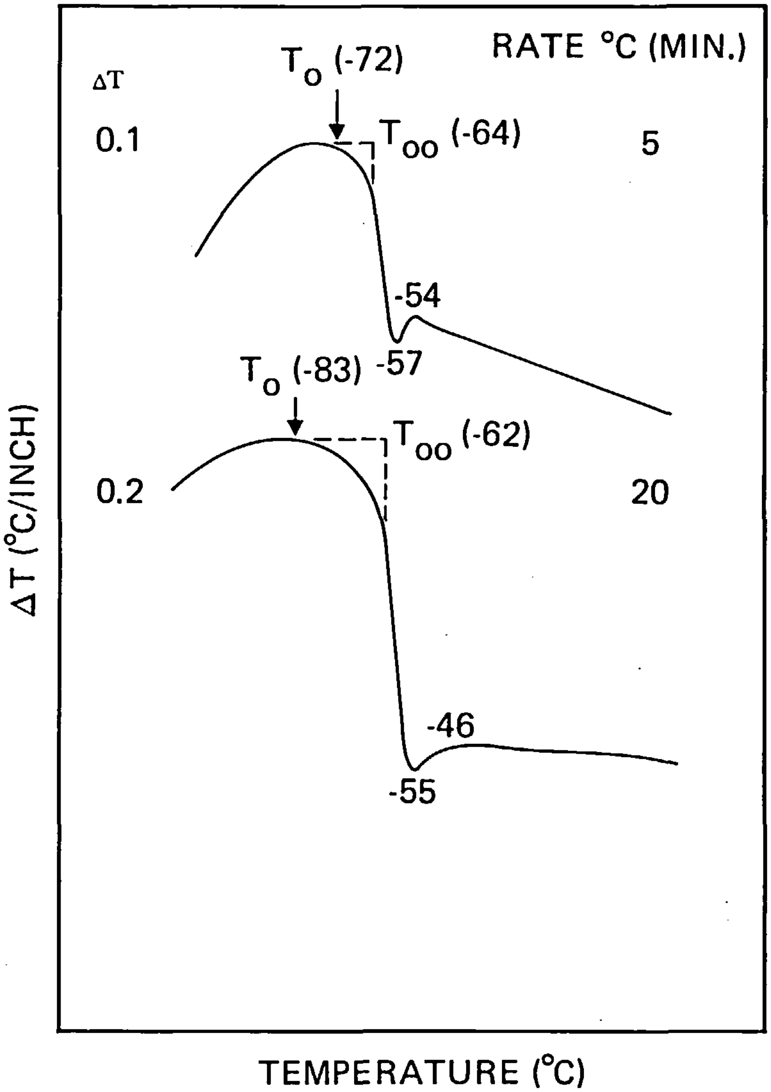


Figure 44. Effect of heating rate on glass transition of natural rubber.[61]

TABLE 3

T_g Values For Several Elastomers, °C[61]

Polymer	T_g Literature Values	Heating Rate °C/Min	T_0, Replicate Measurements			T_{00}, Replicate Measurements		
			1	2	3	1	2	3
Butyl rubber	−67 to −75	5	−73	−84	−78	−66	−66	−66
		20	−96	−83	−80	−65	−64	−64
Ethylene-propylene copolymer "A"	−55 to −60	5	−68	−73	−71	−59	−57	−56
		20	−88	−80	−98	−56	−56	−56
Neoprene W	−43 to −45	5	−47	−46	−45	−38	−38	−38
		20	−52	−52	−51	−38	−37	−37
Natural Rubber (smoked sheet)	−69 to −74	5	−69	−68	−72	−64	−64	−64
		20	−73	−83	−83	−61	−62	−64
S B R 1500	−59 to −64	5	−59	−56	−61	−52	−52	−54
		20	−62	−65	−81	−50	−50	−51

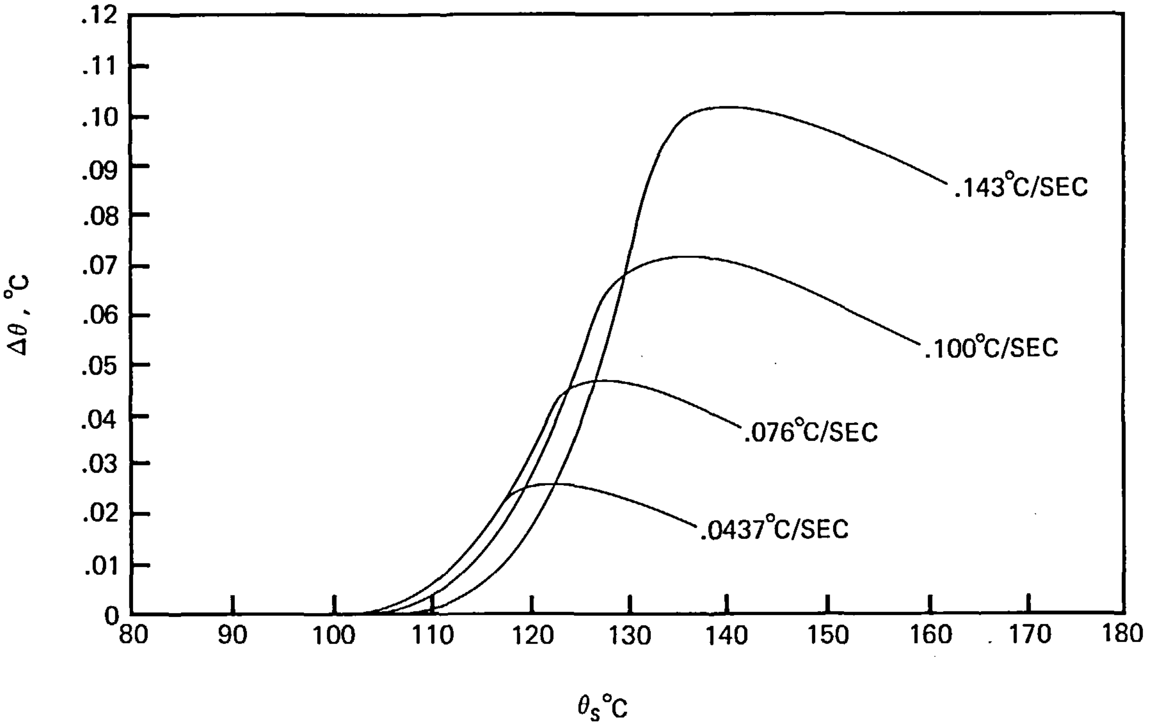


Figure 45. Differential temperature vs. surface temperature at various heating rates.[78]

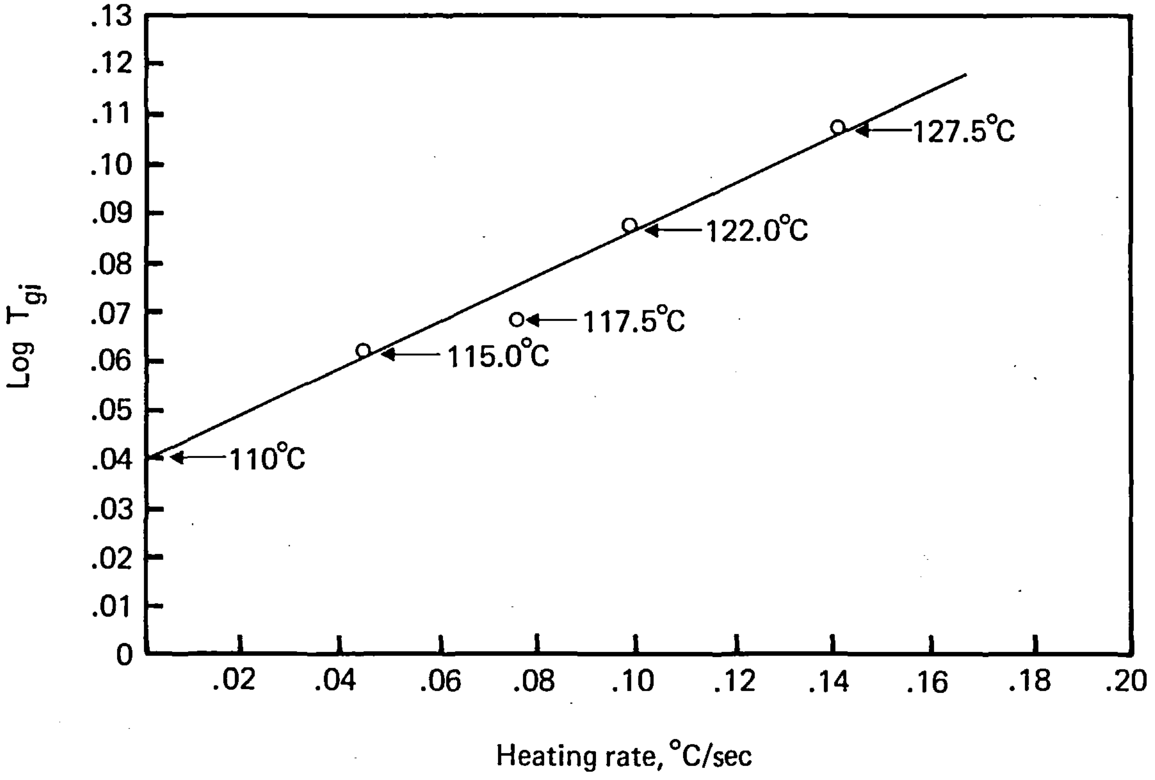


Figure 46. Log T_g vs. heating rate.[78]

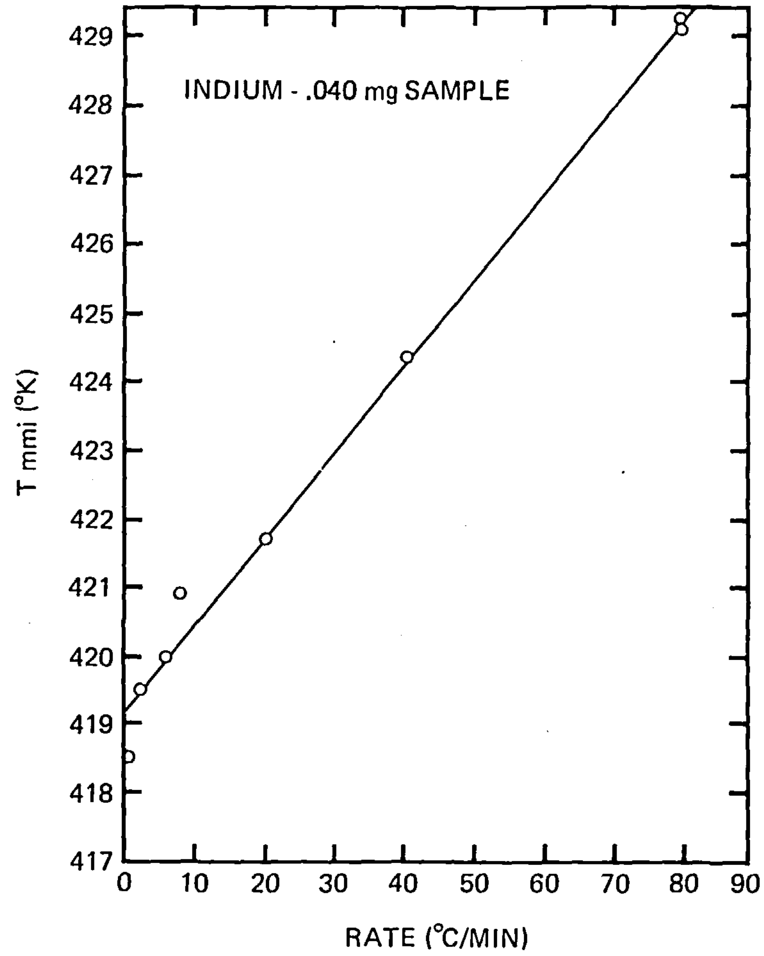


Figure 47. Indicated maximum melting temperature, T_{mmi} vs. heating rate for DSC.[79]

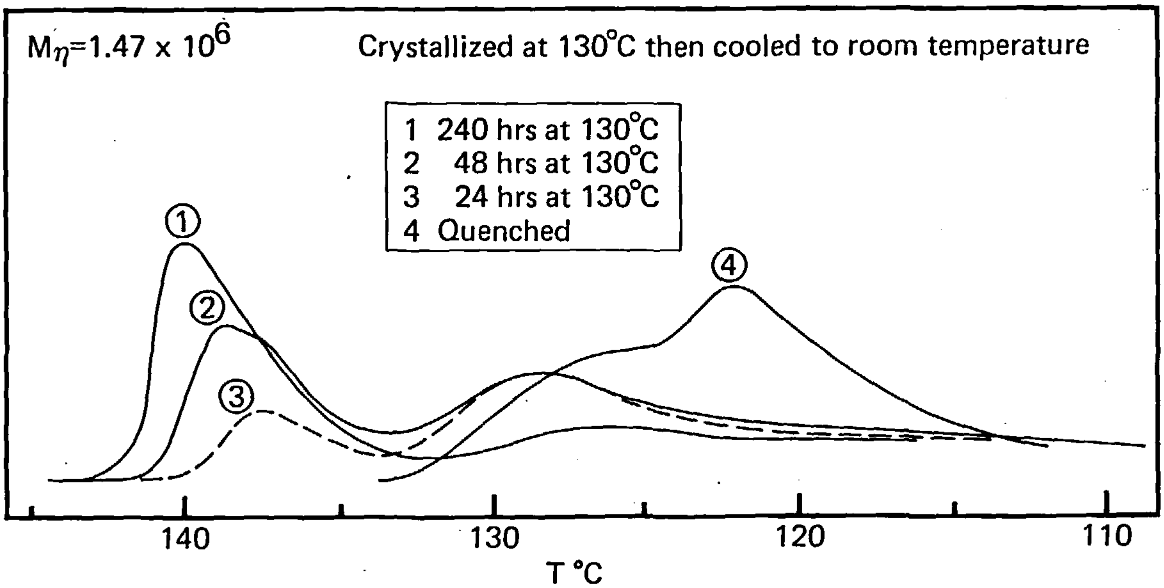


Figure 48. DSC fusion curves for polyethylene after various crystallization times.[42]

styrene.[79] Here again the results are a function of thermal history and of heating rate. Other typical studies include those of Arakawa[1] on Nylon 6.

Knox[47] has used DSC to determine the heat of fusion of crystalline polymers utilizing a melting point depression technique. Figure 50 shows the relationship of the reciprocal melting temperature to the volume fraction of solvent. This coupled with the Flory expression for the theory of melting point depression allows the calculation of the heat of fusion independently of the level of crystallization.

One of the problems of determining the equilibrium melting temperature is the fact that lamellar thickening of crystals occurs during temperature programming even for heating rates of the order of 100°C/minute. Bair et al.[3] have developed a technique to avoid this. They irradiated the crystals to produce a small amount of cross-linking, thus avoiding the lamellar thickening. Figure 51 shows DSC curves for irradiated and unirradiated polyethylene crystals. This would appear to be the most useful technique.

DSC may be used to study reaction rates in a manner analogous to that given previously for DTA. Thus, Knox[48] has studied the crystallization behavior of polypropylene using DSC as shown in Figure 52.

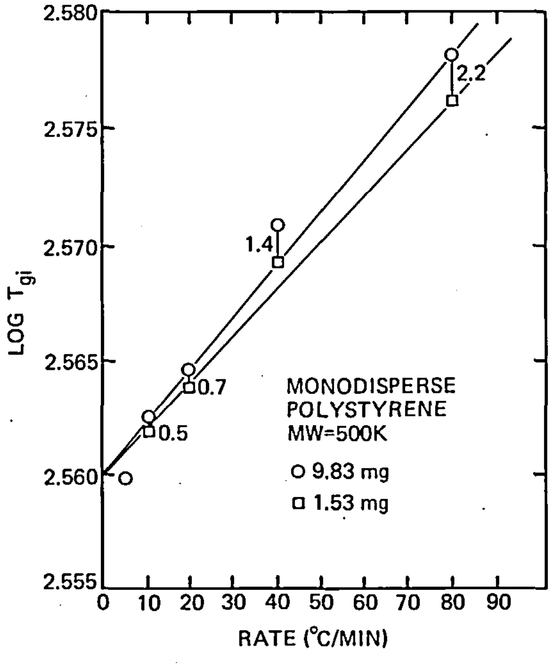


Figure 49. Indicated glass transition temperatures, T_{gi} vs. heating rate and sample size for polystyrene.[79]

III. THERMOMECHANICAL ANALYSIS

A. Introduction

In the past seven years the thermal expansion characteristics of polymeric materials have started to attract the attention of the theoretical as well as the applied polymer chemist. Prior to the introduction of modern instrumentation, classical dilatometry was second in tedium only to classical calorimetry. However, classical dilatometry furnished data of unsurpassed accuracy on samples ranging from liquids through crystalline solids. The present field of thermomechanical analysis (TMA) does not attempt to deal effectively with true liquids, but is restricted to dimensionally stable solids. Expansion is translated into a linear displacement of a transducer.

1. Instrumentation

There have been a number of instruments for TMA reported. Typical designs are given in references.[6,60]

In general, the equipment involves the use of a rod resting against the solid sample as shown in Figures 53 and 54. A movable core transformer or some other device is used to follow displacement of the rod. The temperature programmer and amplifier used in either the DTA or DSC apparatus may be utilized in conjunction with this simple auxiliary apparatus.

2. Applications

The thermal expansion curves, such as those shown in Figure 55 for polypropylene, change slope at the glass transition point, thus providing a convenient method for determining glass transitions. More complicated behavior is shown in Figure 56 for ethylene propylene copolymers with various thermal histories.

TMA may also be applied to anisotropic solids if crystal or stress directions are known. Recently developed equipment by DuPont Instrument Products division as well as by Perkin-Elmer Corp. permit the study of samples under tension in molded, film, and fiber forms. Little specific literature is currently available on this TMA application.

In addition to measurement of sample expansion, usually done using a simple flat foot resting on the sample, more complicated loading experiments can be carried out. Penetration studies normally done manually are readily automated by

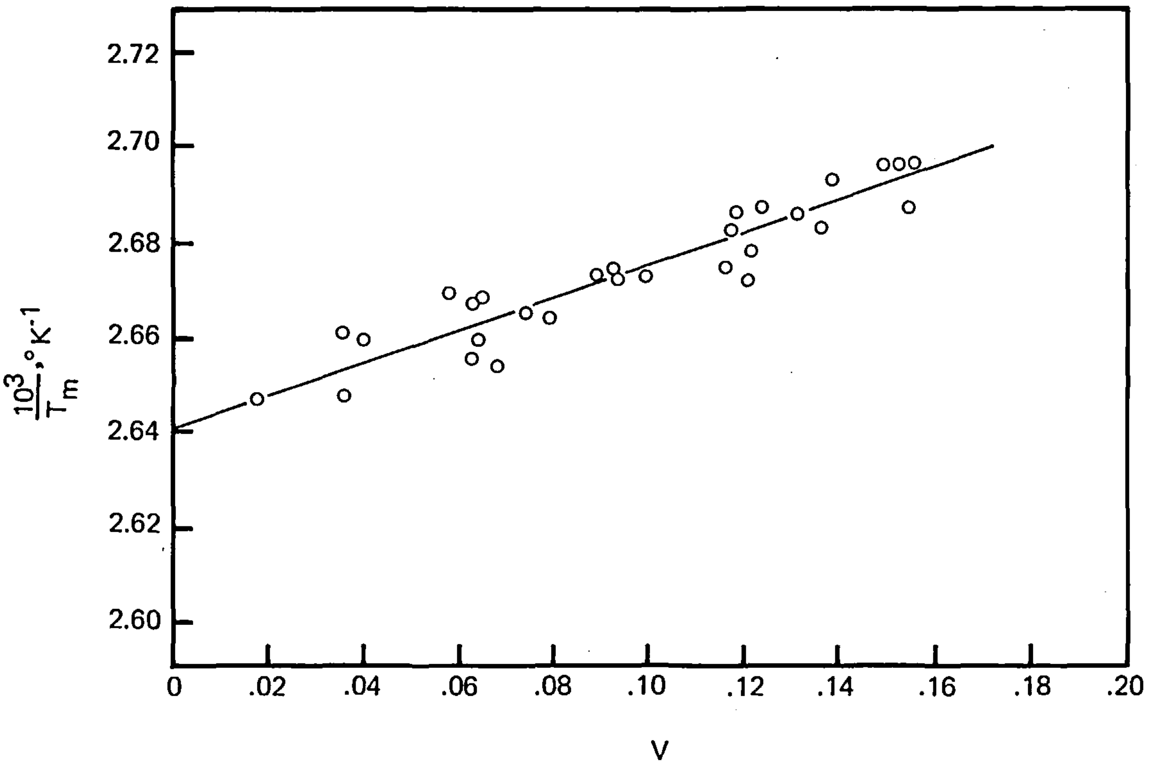


Figure 50. DSC determination of heat of fusion. Relationship of reciprocal melting temperature, T_0, to volume function of solvent.[47]

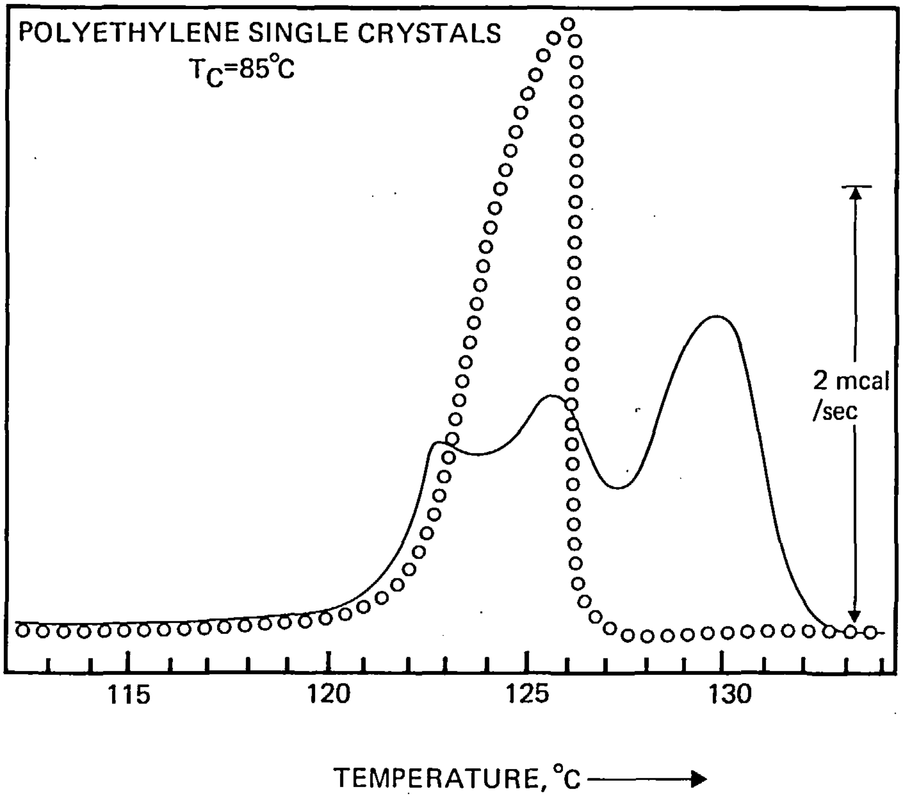


Figure 51. DSC melting curves for unirradiated, – , and irradiated, oooo, polyethylene crystals.[3]

TMA given appropriate penetrometer foot design. A simple method for determining Young's Modulus, which requires only a small specimen, consists of measuring the depth of penetration of a rigid sphere under a normal force, F, into a rubber system. The modulus, E is given by

$$F = \frac{16}{9} E R^{1/2} P^{3/2}$$

where R is the radius of the sphere and P is the depth of penetration. The slope of a plot of load on the probe vs. $P^{3/2}$ is F and the above equation may be solved by substitution. The units are chosen to give E in dynes/cm^2 (multiplied by 980). Additional applications will become apparent as instrument availability increases. For example, swelling of rubbers, membranes, and biological materials in various solvents, vapors and humidities by this simple technique have not been explored in the literature to date. With little difficulty it should be possible to automate the whole group of ASTM tests relating to cone penetration, spherical ball penetration, and surface flow.

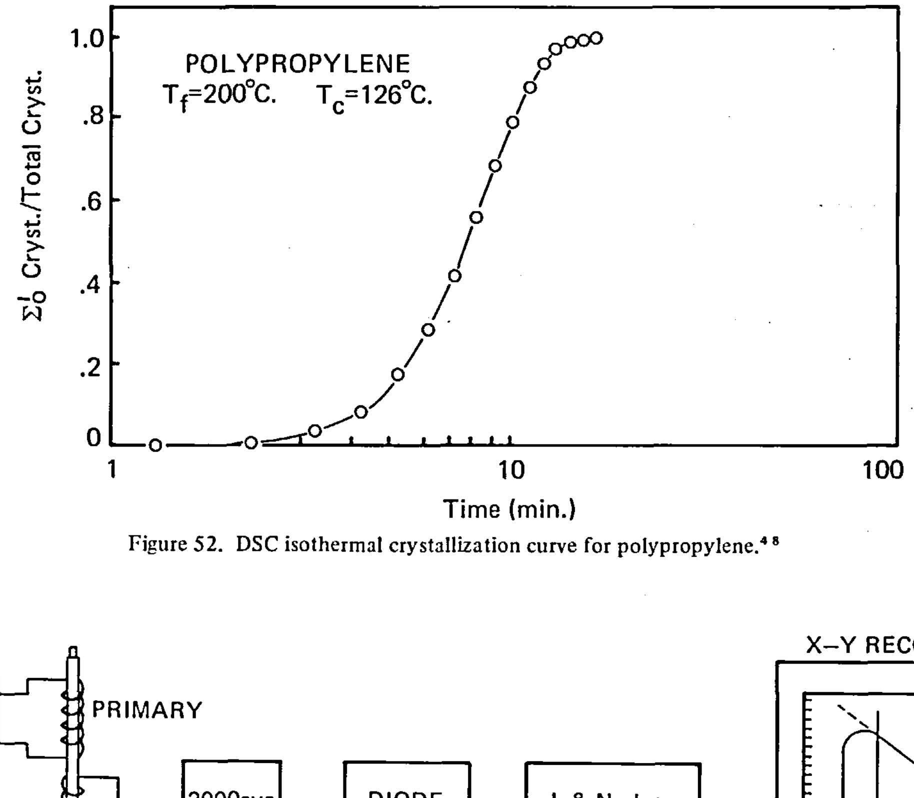


Figure 52. DSC isothermal crystallization curve for polypropylene.[48]

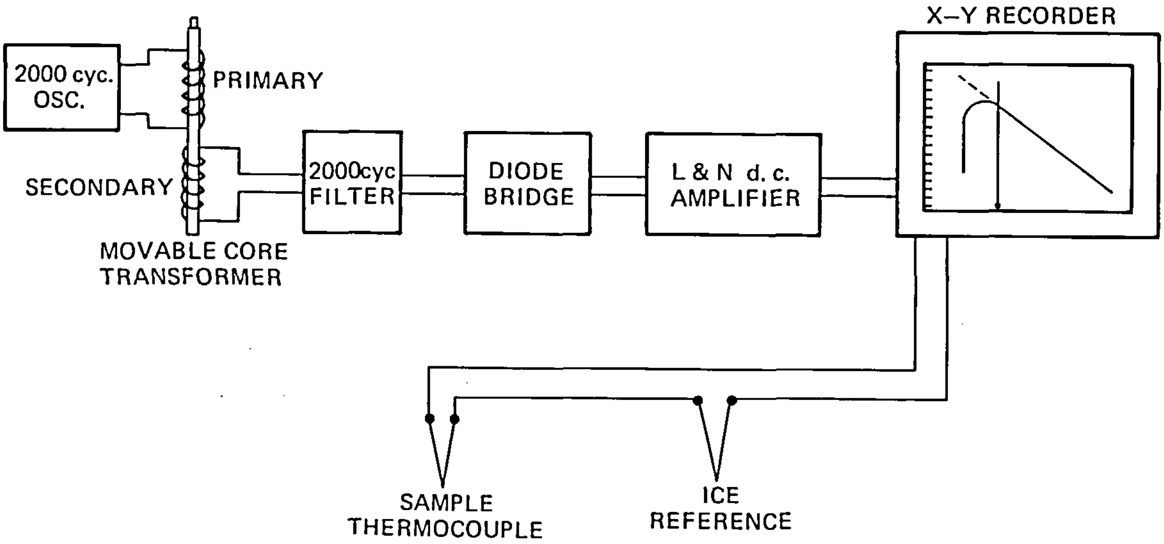


Figure 53. Schematic of a typical thermomechanical apparatus.[6]

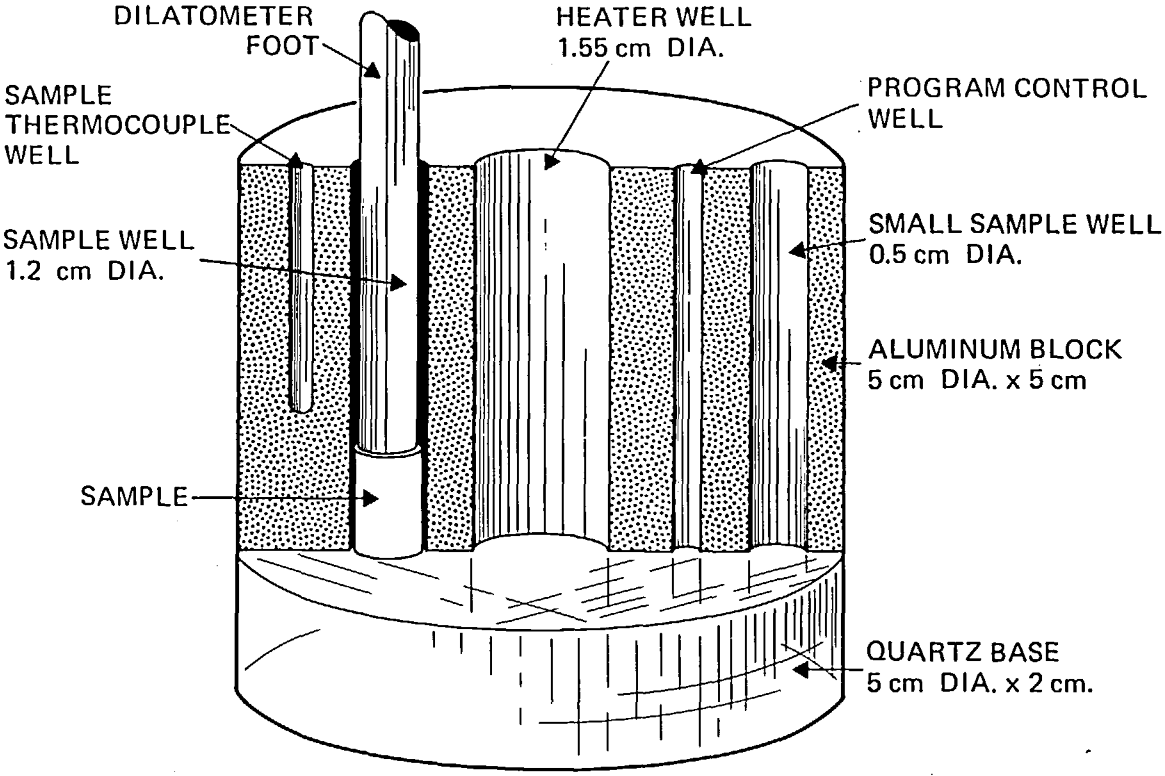


Figure 54. Aluminum sample block for thermomechanical apparatus.[6]

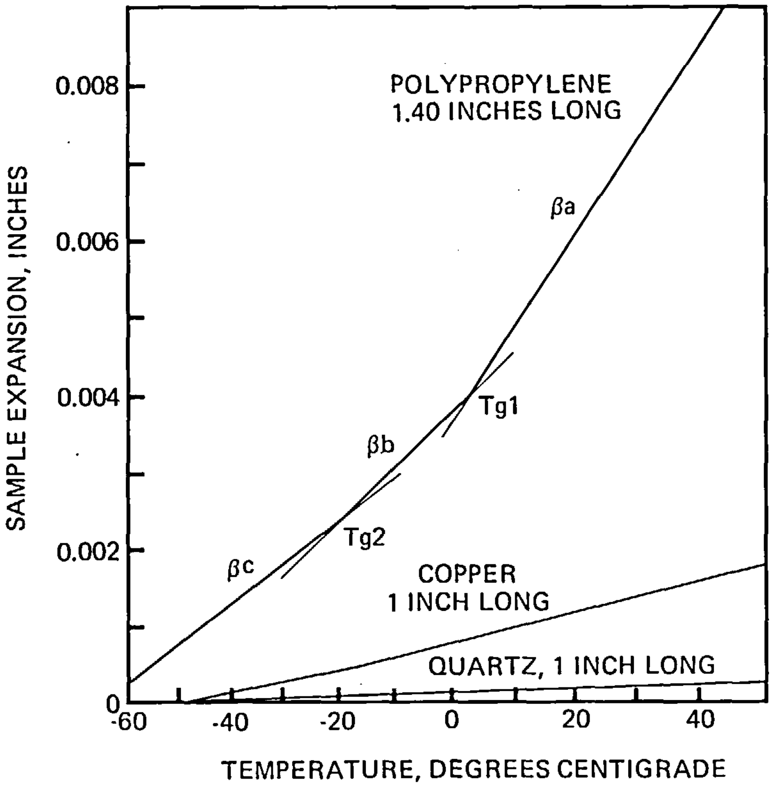


Figure 55. Thermal expansion curve for polypropylene, copper, and quartz.[6]

IV. SUMMARY

It is safe to conclude that the application of DTA, DSC, and TMA to problems in polymer characterization are principally limited by the imagination of the scientist. Modern instrumentation has the required sensitivity to measure almost any thermodynamic property of a polymer system given proper experiment design. The major areas for improvement lie not so much in instrument design but in data reduction and interpretation. The information contained in a well run DTA, DSC, or TMA curve far exceeds the information deduced by modern techniques. We are now at the point that mass spectrometry reached in the early 1960's. We are flooded with recorder charts. Progress in thermal analysis lies in removing the recorder from the data reduction link and introducing the advanced means of data acquisition already in service in mass spectrometry, gel and gas chromatography, x-ray diffraction, and transform spectrometry. There is no instrumental reason why a single DTA or DSC scan should not give in neatly printed form the specific heat, transition heat, and heat of reaction or decomposition as a function of temperature.

The thermal analysis of polymers reaches its greatest power in conjunction with other methods of characterization such as chromatography and x-ray diffraction. Because of the dynamic nature of most thermal methods, processes which reach

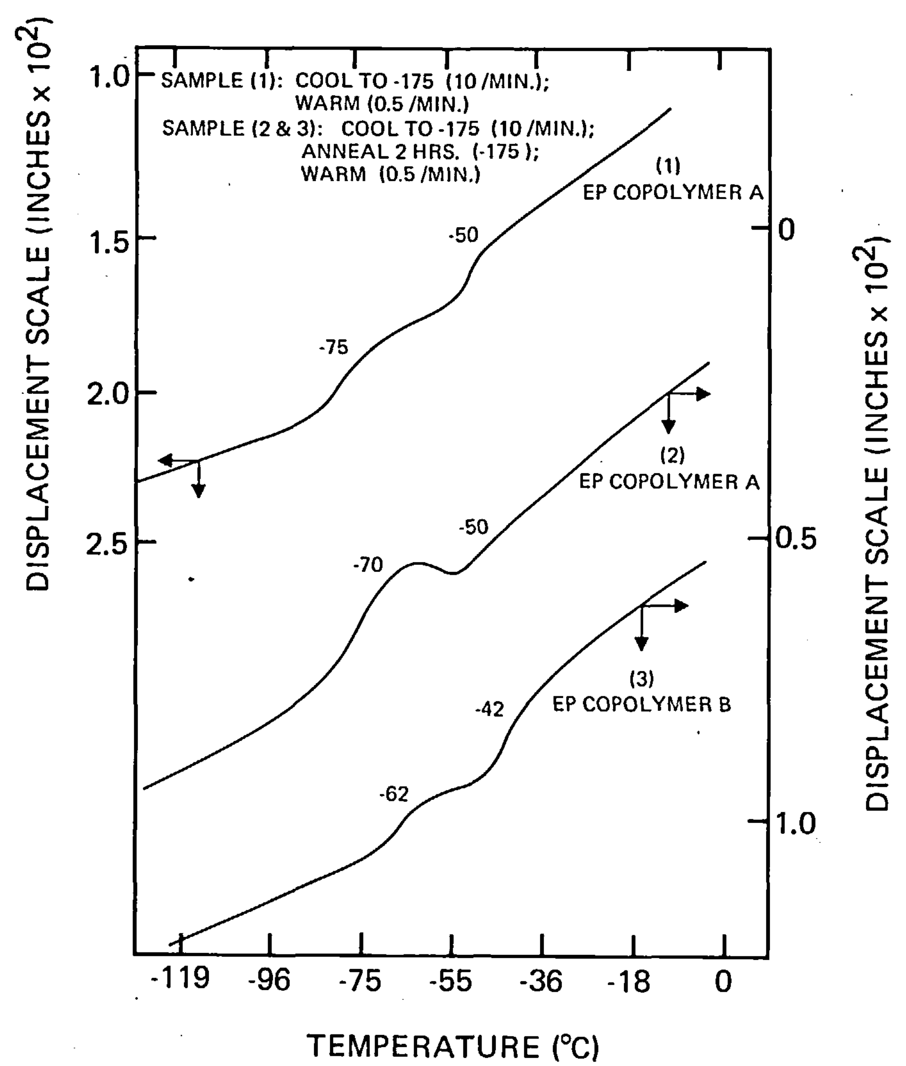


Figure 56. Thermal expansion of ethylene-propylene copolymer.[61]

equilibrium quickly have been the most frequently studied. However, as discussed earlier, less rapid equilibrium studies can be treated isothermally with much the same equipment, given a knowledge of the critical parameters.

A critical review of a rapidly moving area of analytical science can remain current but a short time. However, it is hoped that the partial bibliography and references to current texts will furnish an introduction to modern developments some time after the currency of this text has vanished. The development of specific journals in the field, *Journal of Thermal Analysis* and *Thermochemica Acta*, should encourage a concentration of thermal data in the future which has been lacking in the past. The frequent symposia sponsored by the American Chemical Society and other agencies also furnish an opportunity for coherence in the field.

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Journal or Book and Publisher	Figures
Analytical Chemistry	1, 8, 9, 10, 13, 23, 24, 27, 35, 53, 54, 55
Thermal Analysis, Academic Press	2, 3, 5, 6, 7, 12, 16, 17, 18, 19, 20, 21, 22, 25, 26
Journal of the American Ceramic Society	4
Journal of Polymer Science	8, 28, 31, 32, 36, 37, 38, 39, 40, 41
Journal of Applied Polymer Science	8, 42, 45, 46, 47, 49
Analyst	9
Journal of Thermal Analysis	10, 11
Techniques and Methods of Polymer Evaluation, M. Dekker	33, 34
Analytical Calorimetry, Plenum Press	14, 15, 43, 44, 48, 50, 51, 52, 56
Applied Polymer Symposia	29, 30
Journal of Applied Physics	36

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