

Thermal Analyses of Polymers. VII. Calorimetric and Dilatometric Aspects of the Glass Transition

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Synopsis

For the determination of T_g by DTA with the use of small samples, slow heating rates, and extrasensitive amplification, it can be shown that the previously reported baseline changes for polystyrene, polychloroprene, poly(methyl methacrylate), and polycarbonate can be resolved as endotherms. Measurements with small samples more accurately determine the calorimetric changes than with large samples, even at slow heating rates. The use of large samples for DSC or DTA measurements may be the reason for apparent heating rate dependence. The measurements of this study indicate little heating rate dependence if very small samples are used. Moreover, the slower the cooling from the melt, the sharper the endotherms, indicating the importance of thermal history. The data raise the question about the validity of assuming that a baseline or abrupt change in C_p via a DTA measurement is necessarily that of a real second-order change or T_g . Preliminary dilatometric results tend to show that the changes for polystyrene, polychloroprene, poly(methyl methacrylate), and polycarbonate may be first order at 94°, 32°, 114°, and 156°C, respectively. Only the change at 75°C for polystyrene appears second order by volume-temperature data.

INTRODUCTION

One of the major areas of study in polymer science is that of the glass transition phenomenon usually found in high molecular weight macromolecules. The glass transition has been observed to occur in discrete temperature ranges by a number of modes of measurement. While dilatometry is the standard technique used in identifying the occurrence of the glass transition, many people have used differential thermal analysis or differential scanning calorimetry for the identification of T_g . Numerous authors have reported a step change in the baseline during DTA or DSC measurements occurring at the temperature of the glass transition,¹⁻³ and still others have shown the baseline to have a small endothermic peak associated with it which is dependent upon the conditions of the experiment.^{4,5} Wunderlich et al.⁶ have claimed that at the glass transition, a baseline or step change in heat capacity does occur and that the endothermic peak associated with this change in heat capacity is due to a metastable state, induced by differences between the heating and cooling

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programs to which the sample is subjected. Wunderlich⁶ has restated the postulate of Tool and Eichlin⁷ that on slow cooling few holes are frozen in and that on fast heating the equilibrium number of holes is overshot. The glass structure returns to equilibrium via an apparent endothermic peak. On fast cooling, a large number of holes are frozen in the lattice structure, and on slow heating, equilibrium is reached near the T_g . Figure 3 in ref. 6 indicates that slow cooling (1.4×10^{-4} °C/sec) produces an endotherm on reheating, whereas cooling at 0.5°C/sec does not when both samples are measured at the same heating rate (0.09°C/sec).

McKinney and Foltz⁸ have shown that the step change in the baseline could be developed to produce an endotherm at the same temperature by annealing. With the annealing of PVC, it was hypothesized that the annealing time enabled the polymer chains to relax rather than being frozen in their state by rapid cooling. If this is viewed in another manner, the long annealing and relaxation times may promote the formation of a greater degree of molecular order by segmental diffusion and alignment, and the expected DSC response would be an endotherm such as that of McKinney and Foltz. A number of other reports,⁴ particularly that of Ueberreiter,⁹ have alluded to the fact that the step change in the baseline may indeed have first-order character, particularly if annealing tends to produce an endotherm.

It has been assumed by many investigators that T_g can be readily identified as a step change in the baseline of a DTA or DSC scan, and under ideal thermodynamic circumstances this is true. The present study was undertaken to illustrate effects which will influence the shape of the DSC response at T_g and to confirm these results with dilatometric data. Because of the disparity among the calorimeter responses, as well as the differences in their temperature-sensing techniques, linear programming capability, and modes of heat transfer and individual interpretations, errors in data determination can occur. Moreover, in many studies where the standard DTA cell is used, i.e., the measurement of thermal differences is carried out with one thermocouple in the sample and one in a reference material, the heat capacity changes are indeed accompanied by a very sharp endotherm. The thermal resistance of a scanning calorimeter is purposely higher than that of the DTA cell in which the thermocouple is immersed directly in the sample. This DTA cell provides the highest degree of temperature accuracy, whereas the DSC cell accurately quantifies the heat capacity and enthalpy changes. In this work, the responses of four polymers to a differential scanning calorimeter whose amplification is at least ten times that of other commercial calorimeters were determined.

EXPERIMENTAL

Materials

The samples of polystyrene and poly(methyl methacrylate) were purchased from the Polymer Bank, Brooklyn Polytechnic Institute. The

polycarbonate sample, an M-60 Merlon, was obtained from the Mobay Chemical Company. The Neoprene W was obtained from the Elastomers Department, du Pont Company.

DSC Measurements

A du Pont 900/600 DSC cell was used in the usual manner. The ΔT amplifier of the 900 Thermal Analyzer had been converted to ten times the sensitivity of the standard model by replacement of a part of the feedback circuit. This is a special change within the instrument which can be carried out on special order by the Service Section of the Instrument Products Division of the du Pont Company. However, on increasing the gain of the ΔT amplifier ten times, the noise level was also increased. As can be seen in these studies, the noise level was tolerable for the measurements reported here.

Dilatometer Measurements

A du Pont 941 TMA equipped with the dilatometric attachment was used for the determination of the volume expansivities as a function of temperature. The volume measurements were carried out at a heating rate of 2°C/min.

941 TMA

The basic du Pont 941 Thermomechanical Analyzer consists of a probe connected mechanically to the core of a linear variable differential transformer (LVDT). Samples to be examined are placed on a support which is stationary with respect to the coil of the LVDT, so that displacement of the sample results in a net displacement of the transducer core relative to the transducer coil. The resulting transducer output is a d.c. signal whose magnitude is proportional to the amount of displacement and whose sign is dependent upon the direction of displacement from the transducer zero. The use of fused silica for sample holder and probe, along with careful isolation of the transducer from the sample temperature zone, results in a baseline which is essentially flat over the range -190° to $+700^{\circ}\text{C}$. Sample temperature is maintained by a coaxial heater which surrounds the sample support and probe assembly and which is controlled by the programming capability of a du Pont 900 Thermal Analyzer. Amplification and recording of transducer output, as well as sample temperature as detected by a thermocouple in close proximity to the sample, are also provided by the 900 Thermal Analyzer, resulting in a plot of sample displacement versus sample temperature.

The weight of the probe/transducer core assembly is small and is counter-balanced by a coil spring, so that the effective stress upon the sample may be set at zero for expansion measurements. For measurements in compression, a given stress is applied by loading the probe by means of the weight pan attached to its top.

The Dilatometric Attachment

This new assembly consists of a shaft, LVDT core, and a fused-quartz piston-like probe which fits in a cylindrical vial of the same material; the probe assembly moves vertically within the LVDT. The vial is about 0.250 in. in diameter and 1.0 in height, while the probe tip has a diameter of about 0.245 in. (Fig. 1). This clearance of 0.005 in. and the lack of fluffing of the filling material ensure against wall friction by the probe. The filling medium is ellipsoidal silica which mechanically exhibits behavior similar to that of a fluid. Fused silica beads with a distribution of particle size ranges can have the same apparent mechanical behavior as a fluid. Measurement of solid-state transitions can be easily measured by this technique, but solid-liquid changes can only be measured with certain material systems. It should be emphasized that this filling medium works only with solids or liquids whose viscosity exceeds 15,000 poises. This

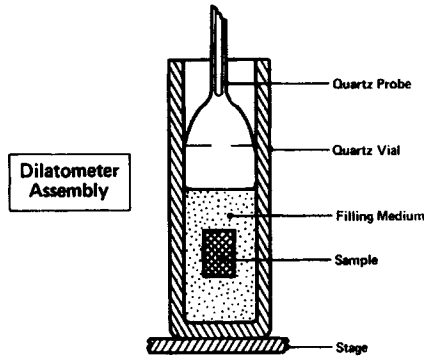


Fig. 1. Dilatometric assembly for TMA.

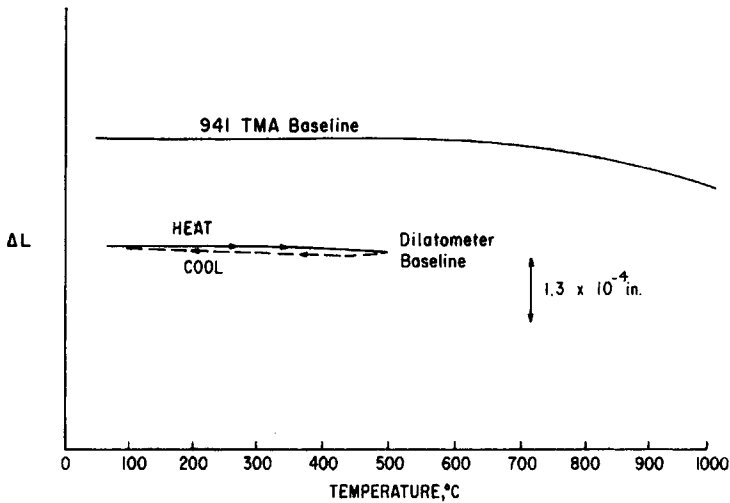


Fig. 2. Baseline of dilatometer filling medium.

allows the measurement of volume changes for some polymer melts, gum rubbers, adhesives, and any type of solid material, but solvents, oils, solutions, and other materials of low viscosity may only be examined when cooled to their solid states or to viscosities above 15,000 poises. This latter aspect allows the easy volume determination of the low-temperature properties of many liquids whose viscosity at room temperature is low.

The use of this solid, nonexpansive filling medium makes it possible to examine the volumetric behavior of a material from -200° to $+700^{\circ}\text{C}$, and for less sensitive measurements to $+1000^{\circ}\text{C}$. The baseline characteristics for heating and cooling are shown in Figure 2 for the summation of movement of the quartz parts and the filling medium to 500°C . While the TMA baseline is insensitive to change up to 700°C , even at the most sensitive setting ($1.3 \times 10^{-4}\text{in./in. C.P.}$) a change of only 2 in. of chart paper ($2.6 \times 10^{-4}\text{in.}$) occurs *above* 700°C .

A weight of 5 g is placed on the probe during a dilatometric scan to ensure complete contact of the probe with the surface of the silica filling medium. The vial is packed so that the material under study is completely surrounded by a sufficient quantity of the filling medium; in this fashion the sample does not contact the sides of the vial nor the face of the probe.

Calibration of the Dilatometer

Since it is impossible to produce numerous vials and probes of identical dimension and since the filling medium is not an ideal fluid, the vial must be calibrated with a given probe to elucidate the average vial diameter and probe response. The dilatometer is calibrated by using spheres of aluminum or lead completely immersed in the silica filling medium. The medium should fill the tube with the sample to about $\frac{2}{3}$ of its volume, but not less than $\frac{1}{2}$ its volume. The calibration is unaffected by sample size and level of filling medium as long as it is $\frac{1}{2}$ to $\frac{3}{4}$ full and the sample is completely encapsuled by the filling medium, but the calibration should be determined at the same heating rate as that of the sample. The filling medium should be kept desiccated, and may be dried at 300°C for 4 hr. The adsorption of moisture by the silica filling medium is the major source of inaccurate results for α_c . The cubical coefficient of expansion can be obtained from the following equations:

$$\alpha_c = \frac{1}{V} \frac{dV}{dT} \quad (1)$$

where α_c is the cubical coefficient of expansion, V is the volume of the sample under investigation, and dV/dT is the volume change per unit temperature.

Since the change in volume is measured linearly, dV/dT must be converted to dL/dT . Hence,

$$\alpha_c = \frac{1}{V} \frac{dL}{dT} K \quad (2)$$

where K is a constant for the cross-sectional area of the vial times a factor for the mechanical efficiency of the vial, probe, and filling medium, multiplied by the conversion of dL from inches to centimeters. K is then expressed as

$$K = \alpha_c V \frac{dT}{dL} \text{ cc/in.} \quad (3)$$

For α_c of aluminum of 72.3×10^{-6} at 77°C , K is usually in the range of 0.75 to 0.85. In some cases, glass beads or other compositions of silica spheres or ellipsoids may be used as the filling medium. The use of these more expansive materials will provide a baseline which will not be flat at maximum sensitivity, which will tend to decrease the intensity of the transition and in some cases eliminate it, and which will produce a low value for K (0.2 to 0.5).

Calculation of α_c

Ideally, for a volume movement across a 0.250-in. diameter surface, the area would be 0.049 in.^2 . Then,

$$K = 0.049 \text{ in.}^2 \times 16.39 \text{ cc/in.}^3 \times f = 0.803f \quad (4)$$

where f is a factor for the movement of the filling medium and 16.39 is a conversion factor. Where the medium is behaving mechanically similar to a fluid, f has a value of 1.0. However, with improper technique, rapid heating rates, poor packing of the vial, wet filling medium, or a filling medium whose expansivity is greater than fused quartz whose bulk density is very low, f will decrease and cause K to approach values from 0.15 to 0.6.

Example of Calculation. A typical example may be cited for polystyrene, whose linear coefficient of expansion (α_L) from 40° to 60° was 6.2×10^{-5} in./in./ $^\circ\text{C}$. From a knowledge of the linear displacement sensitivity S and the value of K , a volume sensitivity may be determined to calculate the volume change per inch of chart as

$$S \times K = \Delta v$$

where S is linear displacement sensitivity of the LVDT. Hence, for $K = 0.74$ and $S = 1.40 \times 10^{-4}$ in./in.,

$$\Delta v = 1.036 \times 10^{-4} \text{ cc/in. chart.}$$

Then, for a 13.2-mg sample of polystyrene which produces a linear displacement of 0.35 in. from 40° to 60°C , the cubical coefficient of expansion α_c may be calculated as

$$\alpha_c = \frac{1}{v} \frac{dL}{dT} \Delta v \quad (5)$$

where Δv is the volume sensitivity. Hence, from eq. (5),

$$\begin{aligned}\alpha_c &= \frac{1}{0.0126 \text{ cc}} (0.35 \text{ in./}20^\circ\text{C}) 10.36 \times 10^{-5} \text{ cc/in.} \\ &= 18.5 \times 10^{-5} \text{ cc/cc/}^\circ\text{C.}\end{aligned}$$

From the measurement of linear expansion as 6.2×10^{-5} , and if $3\alpha_L = \alpha_c$, α_c should equal 18.6×10^{-5} , in good agreement with the volume measurement. The literature yields values of 6 to 8×10^{-5} for α_L ,¹⁰ and 17 to 21×10^{-5} for α_c for α_c ,¹¹ and these values may be altered considerably by variations in composition, morphology, and thermal history.

Similarly, for poly(methyl methacrylate), a value of α_L at 40°C is $6.1 \times 10^{-5}/^\circ\text{C}$ and at 80°C , $9.2 \times 10^{-5}/^\circ\text{C}$. The values of α_c at these temperatures are 21.9×10^{-5} and $30.2 \times 10^{-5}/^\circ\text{C}$, respectively. The two values of α_c at 40° and 60°C are taken from the V - T slopes before and after the 60°C transition. The linear coefficients of expansion of a PMMA cube at 40°C , determined by measuring α_L in the x , y , and z directions, yielded values of 6.9, 8.1, and $9.1 \times 10^{-5}/^\circ\text{C}$, totalling 24.1×10^{-5} for α_c . The ratio of α_c/α_L at 40°C is 3.59, and α_c/α_L is 3.28 at 80°C . Loshaek¹³ had reported α_c to be $19 \times 10^{-5}/^\circ\text{C}$ at temperatures below 105°C .

Major Sources of Error

The major sources of error in measurement are poor technique in packing the vial, too rapid heating rates, improper setting of the probe for zero-point expansion, improper calibration constant, and, most importantly, a wet filling medium.

The packing of the filling medium in the vial with either the probe, a steel rod, or with a vibrator is desirable. The filling medium will pack adequately by tapping the vial on the table top several times and gently packing with the probe after the vial has been placed on the dilatometer stage. Several taps on the probe will pack the vial sufficiently. Poor packing of the sample and filling medium can manifest itself as a stepping of the expansion curve as well as a smaller α_c for polymer melts and some liquids.

Rapid heating rates, that is, greater than $3^\circ\text{C}/\text{min}$, reflect drastic changes in α_c and the transition temperatures. Ideally, samples should be heated at $0.5 \rightarrow 2^\circ\text{C}/\text{min}$.

The proper setting of the probe on the surface of the filling medium was achieved by weighting the probe with the sample pan and 5 g. The calibration constant K should be determined several times initially for each vial to ensure the proper constant value at the same heating rate as the sample under investigation. K should then be checked periodically, i.e., every few weeks, depending on the frequency of use and the types of materials used.

RESULTS AND DISCUSSION

Normally, sample weights upward of 10 mg in quantity are used for routine measurements of differential thermal analysis. Naturally, the larger the sample, the slower the heating rate for thermal equilibrium to occur within the sample; for the sample, which is usually a thermal insulator, may not be uniformly changed in temperature as the programmer dictates. On the other hand, the use of extremely small samples enables one to use faster programming rates because of rapid temperature equilibrium within the sample. This effect of temperature equilibration is often shown by measuring the area of an endothermic transition or heat capacity change of a material as a function of heating rate, noting that the transition temperature and peak height usually increase as one progresses to higher heating rates. Usually there is a heating rate range in which the change in C_p with temperature is constant.

Heating Rate Effects

Using very small samples (2–5 mg) on a calorimeter under standard conditions of calorimetric sensitivity (0.1°C), at a heating rate of $10^\circ\text{C}/\text{min}$, produces DSC traces such as those in Figure 3 for Neoprene, polystyrene, polycarbonate, and poly(methyl methacrylate), showing heat capacity changes of -39° , 90° , 150° , and 114°C , respectively. Even at this highest sensitivity setting of the commercial calorimeter, these small amounts of materials produce a very small endothermic effect which will usually appear as a small baseline shift at higher heating rates.

If the sensitivity of the instrument is increased tenfold and a very small sample of polystyrene is examined at various heating rates, curves such as

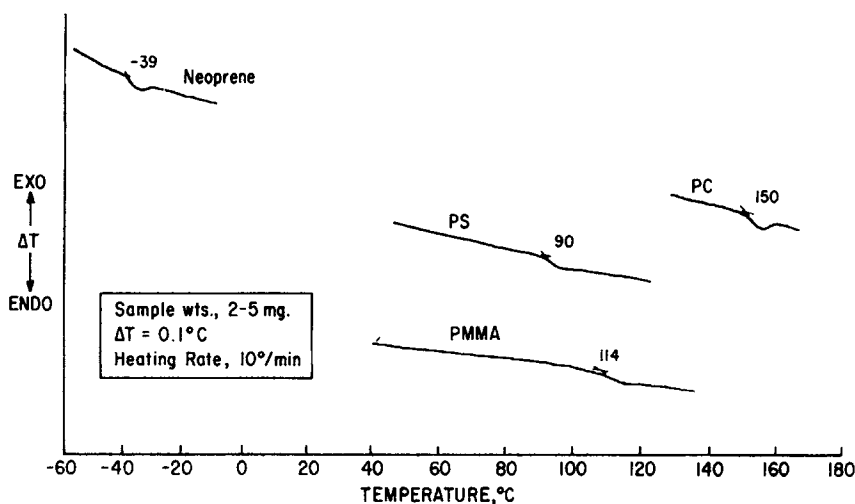


Fig. 3. Usual DSC response of small samples of Neoprene, polystyrene, poly(methyl methacrylate), and polycarbonate (heating rate, $10^\circ/\text{min}$).

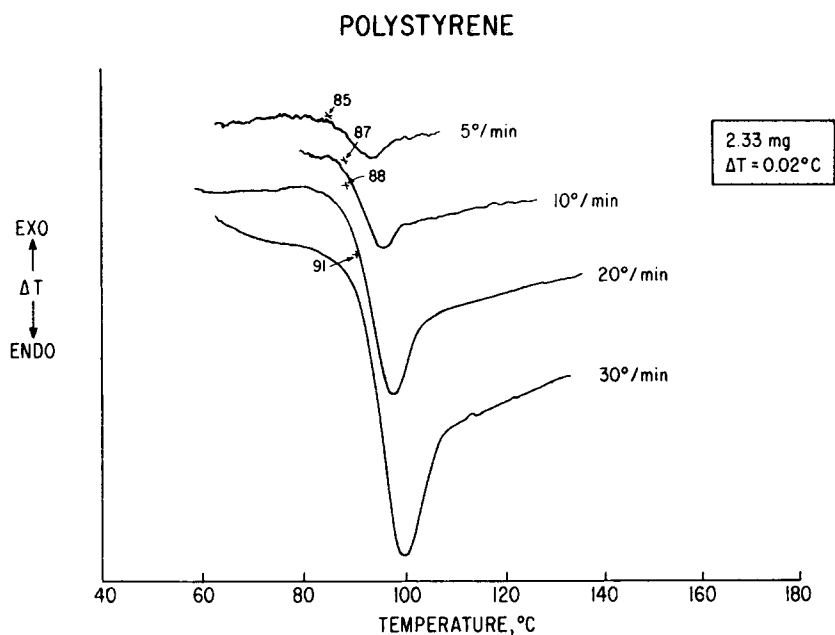


Fig. 4. Effect of heating rate on the response of a small sample of polystyrene (2.33 mg).

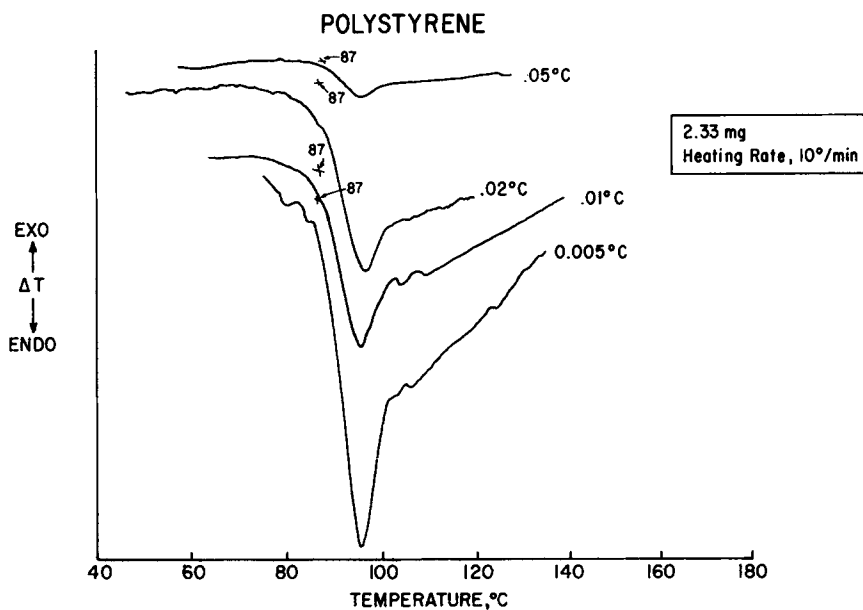


Fig. 5. Endothermal response of polystyrene at various ΔT sensitivities.

those in Figure 4 result at heating rates of 5°, 10°, 20°, and 30°C per minute on a 2.33-mg sample of polystyrene at a ΔT setting of 0.02°C/in. The temperature of onset of the endotherm increases as the heating rate increases, and naturally the magnitude of the endotherm increases as well. The same behavior can be shown for polycarbonate. Ideally, slow heating rates are necessary for accurate temperature determination with a DSC cell, even with the accompanying decrease in signal intensity.

Accurate temperature readings resulting from slow heating rates may only be obtained at very high sensitivities with very small amounts of material, as shown in Figure 5, wherein 2.33 mg polystyrene at a heating rate of 10°C/min showed a variation in the depth of the endotherm as a function of the sensitivity. These curves leave no doubt that a calorimeter of increased sensitivity employing small samples produces endotherms of much better resolution. The same presence of an endothermic peak has been observed at the reported glass transitions for polycarbonate, poly(methyl methacrylate), and Neoprene. On increasing the sensitivity of the ΔT amplifier, use of very small sample sizes and slow heating rates illustrate that the T_g of the polymer need not be identified solely by a baseline change.

Thermal History Effects

The glass transition has been reported to be affected by changes in the thermal history of the sample. To assess the effect of thermal history on

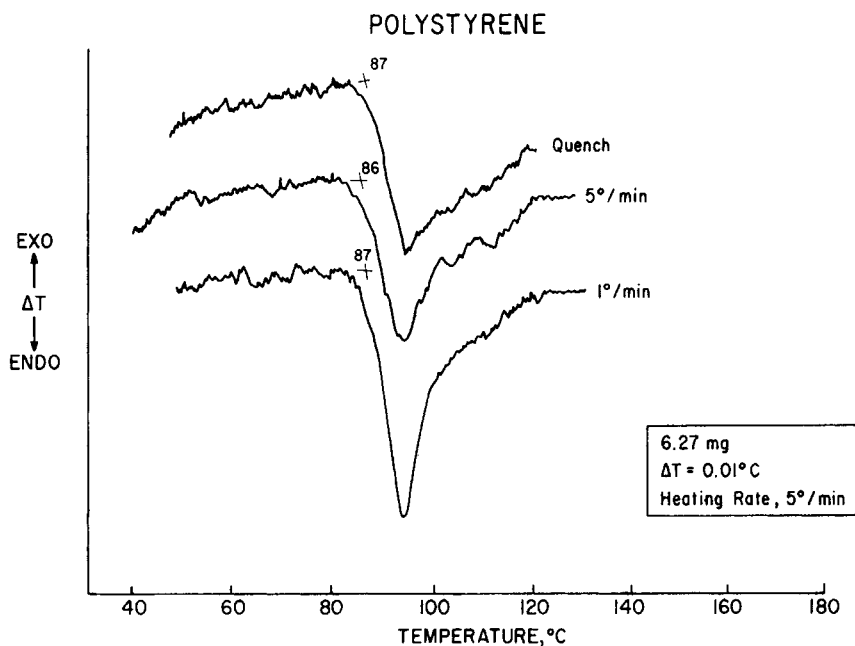


Fig. 6. Thermal history effects on the endothermal character of polystyrene.

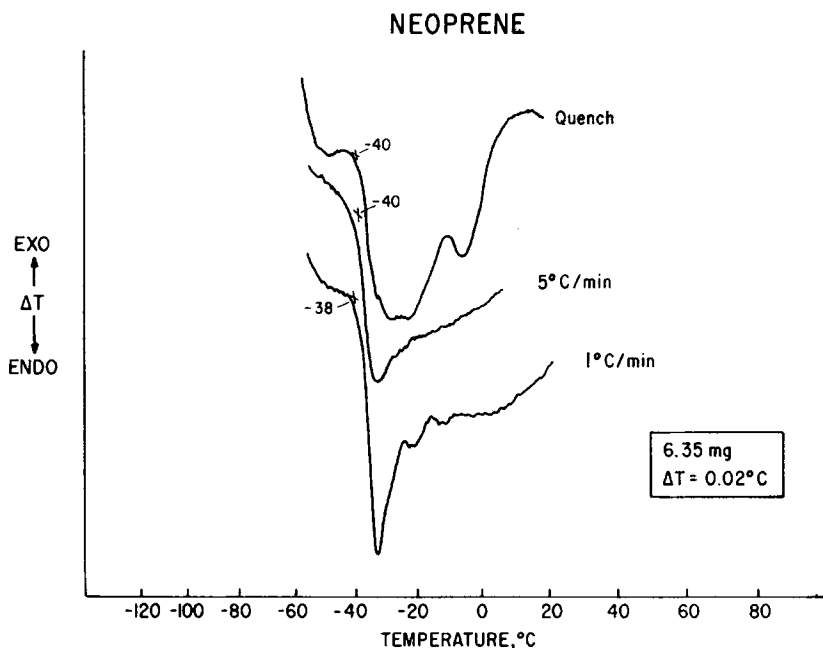


Fig. 7. Thermal history effects on the endothermal character of Neoprene.

the DSC response, three DSC curves are shown in Figure 6 of polystyrene which had been heated to 160° followed by (a) quenching with liquid nitrogen to subambient temperatures; (b) cooling at 5°C/min; (c) cooling at 1°C/min. These data show that cooling at 1°C/min imparts an endotherm which is very sharp; cooling at 5°C/min decreases the sharpness with which the endothermal transition occurs; and quenching from the melt widens the endotherm even further. It is possible that the increasing baseline prior to the endotherms in Figure 6 may be the exhibition of a very small amount of exothermic activity prior to endothermal melting, and the quenched sample appears to have more premelting character than the slowly cooled samples. This premelting behavior is not observed with Neoprene, which is shown in Figure 7 under the same conditions. Quenching apparently introduces a randomness about the transition in that there are three peaks spreading over some 40°, whereas cooling at 1°C/min produces a very sharp endotherm. The temperatures at the onset of the transition are almost identical at heating rates of 5°C/min. The curvature of the DSC onset can change at higher heating rates, eliminating the premelting exotherm. Annealing of PVC not only has been shown to cause a sharpening of the endotherm at the reported T_g , but the degree of exothermic behavior prior to the reported T_g increases with annealing times. Hence, the premelting exotherm seen in this work and that reported by Wunderlich et al.⁶ are different from the annealing of PVC. With polystyrene, rapid quenching causes a preme-

ing exotherm, whereas quenching PVC or Neoprene does not cause an observed premelting exotherm.⁸

Dilatometric Behavior

All of the endothermal processes reported thus far in this study have been those which normally are attributed to the glass transition of the four polymers in this study. We have shown that it is erroneous to conclude that a baseline change via DTA or DSC must be a glass transition. It can appear that with the proper circumstances of heating rate, sensitivity, and thermal history, an endotherm occurs rather than merely a step change in the heat capacity. Thermodynamically, real second-order changes occur as step changes in the heat capacity, but the presence of a first-order change following several degrees after a second-order change or the presence of a small

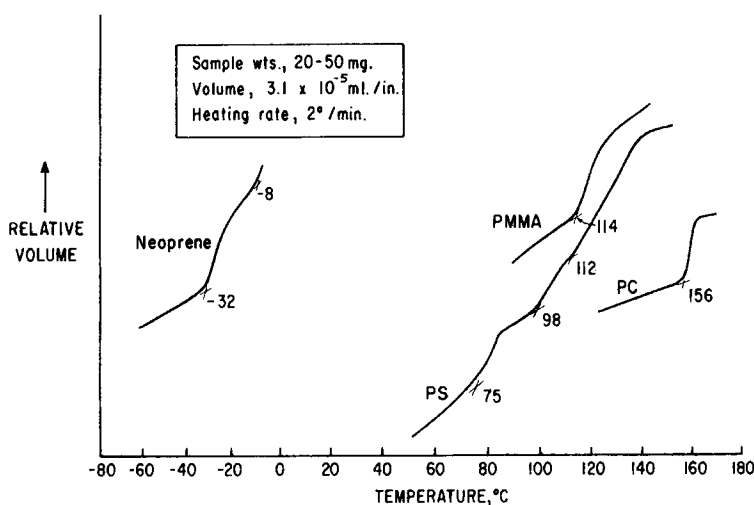


Fig. 8. Dilatometric response of Neoprene, polystyrene, polycarbonate, and poly(methyl methacrylate).

first-order phenomenon could easily occur as a partial endotherm. Consideration must also be made for the time constant of the DSC cell and circuit in that a smaller time constant will aid in the resolution of an endotherm from a baseline change. Slow heating rates minimize the effect of the time constant.

The identification of a first- or second-order change in the thermodynamic sense may be shown by the data of Bekkedahl.¹⁴ A second-order change is shown by a change in slope of a $V-T$ plot or an abrupt change in the plot dV/dT versus T . A first-order change may be identified by the abrupt change or discontinuity in volume at a given temperature. This behavior has been shown for metals and inorganic salts, which exhibit typically crystalline fusion.¹⁵

To clarify this effect further, we examined, as shown in Figure 8, the volumetric response of these four polymers at heating rates of $2^{\circ}\text{C}/\text{min}$. The thermal histories of these samples resulted from cooling rates of approximately $1^{\circ}\text{C}/\text{min}$ from temperatures 100° above the transition. The volumetric change at -32°C for neoprene is rather sharp, and its profile corresponds well with the volumetric response of the fusion of crystallized natural rubber near -11°C .¹⁴ The volume response of PMMA shows the same characteristic change at 114°C as Neoprene, and continued experiments with PMMA illustrating its apparent first-order character near 114°C will be reported elsewhere. The three volume changes for polystyrene at 75° , 98° , and 112°C correspond to the T_g (change in coefficient of expansion) and two abrupt changes in volume. By proper annealing near 94°C , those changes at 98° and 112°C will become sharper in their volume discontinuity. The nature of these changes as a function of molecular weight and molecular weight distribution will be reported elsewhere.

The apparent leveling near the end of the volume curve of polystyrene is due to the filling of the interstices of the dilatometric filling medium by the polymer melt, illustrating an undesirable feature of a mechanical filling medium. As long as the polymer maintains its integrity and will not flow, the volume response will be normal. This same effect holds also for the abrupt volume change in polycarbonate at 156°C .

Since calorimetry is a heat-averaging technique, the endotherm occurring in the region of 87°C may be the composite of the 75°C glass transition and the 98°C first-order change in the specific volume, or it could represent the real onset of the 98°C first-order transition beginning as low as 87° or 88°C . This behavior is easy to rationalize looking at the definite change in slope at 75°C on the volumetric curve for polystyrene. More recent data have shown that a second-order change for poly(methyl methacrylate) occurs near 10°C , coincident with the beta-maximum in dynamic mechanical loss studies.¹² A second-order change in the volume of polycarbonate occurs at -137°C .¹² The first-order change for Neoprene near -32°C is influenced by the crystallinity of the sample, and when the Neoprene sample is quenched from the melt to liquid nitrogen temperatures, the transition near -32°C appears to be the fusion temperature, with no crystallization response occurring at temperatures above 0°C .

CONCLUSIONS

Reported step changes in the heat capacity from differential scanning-calorimetric measurements were resolved to show discrete and resolute endothermal character when examined on a very sensitive calorimeter at slow heating rates and with small sample sizes. In these cases, the transition did not appear as heating-rate dependent as previously published studies have indicated. A transition should not be classified as a glass transition merely by its identification as a step change in the heat capacity, though this may accompany the T_g . In some cases, such as those shown in this study, this reported change in heat capacity is, in essence, an endo-

thermal change as well as a first-order volume change. These results raise the question of whether T_g has some first-order character or whether these volume changes coincident with endothermal phenomena may be real first-order phenomena.

Heat averaging by DTA or DSC measurements may not separate two proximate transitions, but the additional data from volume measurements can aid in resolving these transitional changes. Several specific modes of thermal characterization should be used to determine the identity of the glass transition temperatures with careful control of thermal history.

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