

# Comparison of Thermal Techniques for Glass Transition Measurements of Polystyrene and Cross-linked Acrylic Polyurethane Films\*

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## SYNOPSIS

There are few quantitative comparisons in the literature between glass transitions ( $T_g$ ) measured by differential scanning calorimetry (DSC) and by dynamic mechanical analysis (DMA). Also, in the case of DMA, two different operational definitions have been used to obtain the glass transition, namely, the loss modulus ( $E''$ ) and damping ( $\tan \delta$ ) peak temperatures. We propose a new DMA definition of  $T_g$  and demonstrate that it agrees with DSC  $T_g$  measurements within  $\pm 2^\circ\text{C}$  for both thermoplastic polystyrene and thermoset cross-linked acrylic polyurethane films with measurable  $\tan \delta$  peaks. The glass transitions for a single polystyrene standard and several cross-linked acrylic polyurethane films were measured by DSC. Additionally,  $E''$  and  $\tan \delta$  peak temperatures were measured by DMA as a function of frequency and temperature. Empirically, it was determined that the average of the  $E''$  and  $\tan \delta$  peak temperatures measured at 1 rad/s oscillation frequency corresponds to the glass transition measured by the ASTM E1356 DSC test method. © 1994 John Wiley & Sons, Inc.

## INTRODUCTION

The glass transition ( $T_g$ ) of a polymer can be determined by observing the temperature range over which a significant change takes place in some specific electrical, mechanical, thermal, or other physical property. This temperature range can vary significantly depending on the property chosen for observation and on details of the experimental technique (e.g., heating rate, test frequency). In this study, glass transitions measured by differential scanning calorimetry (DSC) and dynamic mechanical analysis (DMA) are compared.

In the literature, there are few quantitative comparisons between glass transitions measured by DSC and DMA. In part, quantitative comparisons are difficult because reported results vary with instrument

calibration and experimental heating rate. For example, DSC measurements have been reported to vary with heating rate; therefore, the instrument has to be properly temperature-calibrated for a particular heating rate to compensate for thermal lag.<sup>1</sup> Furthermore, there is no universally accepted operational definition of DSC  $T_g$ . Whereas some investigators use the midpoint of the heat-capacity shift,<sup>2-4</sup> others use the extrapolated onset temperature<sup>5,6</sup> to define  $T_g$ . The Precision and Bias Section in ASTM E1356<sup>1</sup> demonstrates that the midpoint is preferred over the onset temperature, because it can be measured with greater analytical precision.

Like DSC, DMA literature has no universally accepted operational definition of  $T_g$ . Some investigators use the loss tangent ( $\tan \delta$ ) peak and others use the loss modulus ( $E''$ ) peak or the elastic modulus ( $E'$ ) decrease onset to define  $T_g$ .<sup>7a,b</sup> The results of DMA measurements are inherently frequency-dependent and peak temperatures increase 6–8°C for every decade increase in test frequency. Sichina<sup>4</sup> recognized this fact and developed an Arrhenius expression to relate DMA  $T_g$  (based on the loss modulus peak) and DSC  $T_g$  measurements by as-

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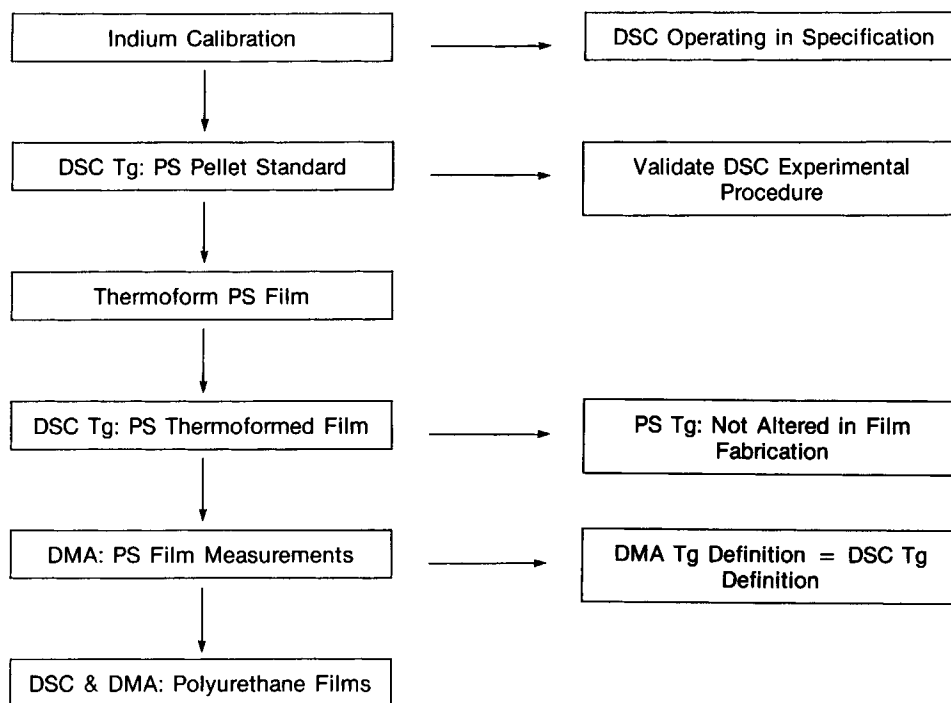


Figure 1 Schematic diagram of experimental strategy.

signing an apparent low frequency to DSC measurements (0.0001 Hz or 0.00063 rad/s). Using an empirical approach, Cassel et al.<sup>7a,b</sup> compared glass transitions for a single-epoxy composite material as measured by DSC, DMA, and thermomechanical analysis (TMA). These authors found the best agreement among  $T_g$  values for the DSC heat flow midpoint, the onset of DMA elastic modulus decrease measured at 0.1 Hz (0.7 rad/s), and the onset of TMA expansion. In the literature, generally, DMA  $T_g$ 's, defined by the  $\tan \delta$  peak, are reported to be 10–30°C higher than  $T_g$ 's measured by DSC, but the effect of frequency is usually not considered in detail.<sup>2–7</sup>

The aim of the present study was to develop a DMA method for measuring  $T_g$  that agrees with DSC glass transition measurements. In this study, a new, quantitative relationship between DSC and DMA  $T_g$  measurements is reported. The experimental strategy, shown schematically in Figure 1, was to (i) demonstrate that the DSC instrumentation was operating within specification, (ii) determine the  $T_g$  of a well-characterized polystyrene (PS) pellet standard by DSC, (iii) establish the effect of polymer thermal history on the  $T_g$  for the PS standard and validate the DSC experimental procedure, (iv) thermoform film from the PS pellet standard for DMA measurements, (v) demonstrate that thermoforming did not alter the DSC  $T_g$  of the PS standard, (vi)

determine the DMA  $T_g$  of PS standard film, and (vii) compare the DSC  $T_g$  and DMA  $T_g$  results for the thermoformed film. After validating the DSC and DMA analysis techniques, these techniques were applied to the study of experimental cross-linked acrylic polyurethane films.

For the PS film and cross-linked acrylic polyurethane films, DMA  $T_g$ , defined as the average of the loss modulus and  $\tan \delta$  peak temperatures measured at 1 rad/s, corresponds to the DSC  $T_g$  within  $\pm 2^\circ\text{C}$  for both thermoplastic PS and thermoset cross-linked acrylic polyurethane films. This definition, however, is not universal in that it cannot be applied to thermoplastic films that do not have a measurable  $\tan \delta$  peak.

## EXPERIMENTAL

### Materials

A sample of 99.999% pure indium, used to calibrate the temperature axis of the DSC, was supplied by Mettler Instrument Corp. (Part #ME-29749).

The polystyrene pellet standard was GM-754 ICTA Certified Reference Material.<sup>8</sup> A miniplaten press was used to fabricate film from the PS pellet standard. Thermoformed film, 0.27 mm thick, was made by pressing the pellets at 275°C between Tef-

lon® sheets reinforced with glass fabric for 30–45 min.

Cross-linked acrylic polyurethane paint films were made using a release agent to cast, bake, and remove the coating from steel panels as free films. Both solvent-cast and powder paint coatings were prepared and studied.

## Differential Scanning Calorimetry (DSC) Method

### General

The indium temperature calibrant, PS standard, and cross-linked acrylic polyurethane films were encapsulated in aluminum pans in a dry nitrogen-purged glove box. Samples were run on both a Mettler TA-3300 DSC and a Mettler TA-4300 DSC to eliminate any instrument bias. Dry nitrogen (liquid nitrogen boil-off) purged the DSC instruments at 25 mL/min during heating and cooling cycles.

Encapsulated samples were reweighed at the completion of the series of DSC experiments; no weight loss had occurred in any sample. Although the specimen mass is not used in the  $T_g$  calculation, weight loss could indicate that volatilization, an unwanted thermal process, is occurring within the range of the  $T_g$  measurement.

Data files obtained from the Mettler TA-3300 DSC were electronically transferred to the Mettler TA-4300 system. These files and data files generated directly with the Mettler TA-4300 were analyzed with the Mettler GraphWare® software package.

### Temperature Calibration

All samples and standards were heated at 10°C/min. The experimentally determined melting point ( $T_m$ ) and heat of fusion ( $\Delta H_f$ ) for indium were compared with the corresponding literature values, i.e., 156.6°C and  $28.42 \pm 0.36$  J/g, respectively.<sup>9</sup> Results are shown in Table I.

### Sample Heating Cycle

In general, DSC data from the first heating cycle reflect both polymer properties and sample thermal

**Table I Indium Standard: 10°C/Min**

Instrument	Temperature Range (°C)	$T_m$ (°C)	Peak (°C)	$\Delta H_f$ (J/g)
TA-3300 DSC	100–180	156.7	156.8	28.3
TA-4300 DSC	100–180	156.4	156.8	28.9

$T_m$  = melting point.

**Table II Polystyrene Standard: 10°C/Min**

Instrument	Wt (mg)	Form	Temperature Range (°C)	$T_g$ (°C)
TA-3300 DSC	13.39	Pellet	30–150	104.9
TA-4300 DSC	13.39	Pellet	30–150	104.3
TA-3300 DSC	24.27	Pellet	30–150	105.7
TA-4300 DSC	24.27	Pellet	30–150	105.0
TA-3300 DSC	19.28	Film	30–150	105.7
TA-3300 DSC	19.28	Film	30–150	106.6
TA-4300 DSC	19.28	Film	30–160	104.8
TA-4300 DSC	19.28	Film	30–150	105.5

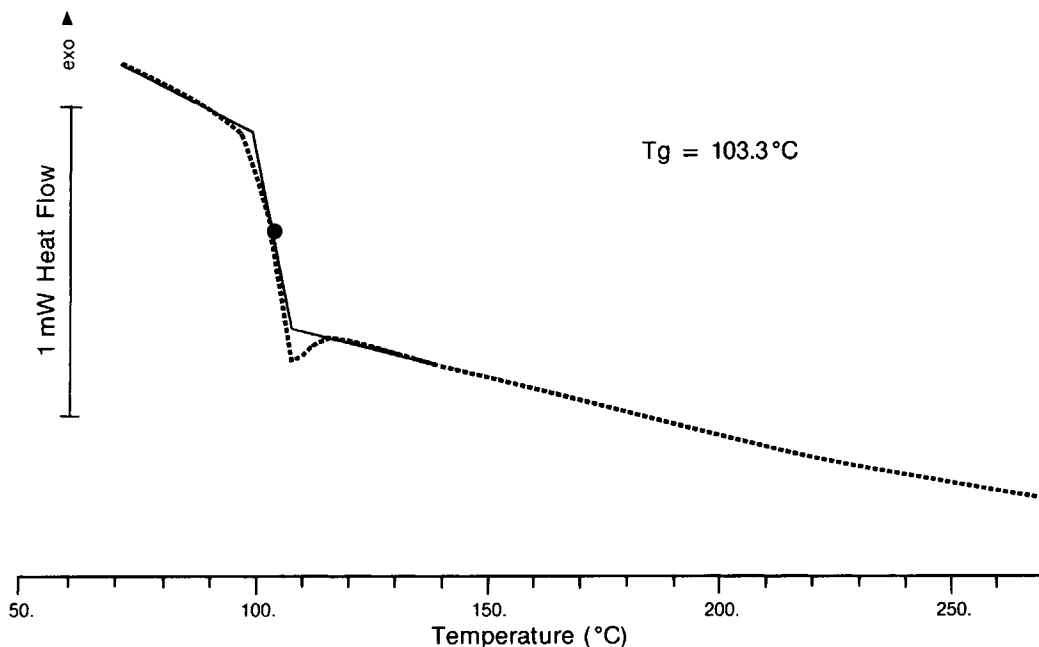
history. By heating the polymer above its  $T_g$ , the “memory” of this thermal history is erased. Therefore, the second heating cycle results are more indicative of the  $T_g$  of the polymer matrix. Consequently, all polymer samples were subjected to two heating cycles and quench-cooled between heating cycles unless stated otherwise.

To illustrate thermal history effects, e.g., the effects imposed on PS during an annealing process, the following thermal history was imparted to a PS pellet sample: (i) heat from 30–280°C at 10°C/min to determine whether the material was crystalline, (ii) quench-cool to 30°C, (iii) heat from 30 to 150°C at 10°C/min, (iv) anneal at 150°C for 30 min, (v) quench-cool to 30°C, (vi) heat from 30 to 150°C at 10°C/min, (vii) quench-cool to 30°C, (viii) heat from 30 to 150°C at 10°C/min, and (ix) quench-cool to 30°C. The consequences of this thermal history effect study are discussed in the Results section.

DSC results for the PS standard established the validity of the requirement to erase the polymer's thermal history. Therefore, PS standard film and the cross-linked acrylic polyurethane films were analyzed after their second heating cycles.

### Dynamic Mechanical Analysis (DMA) Method

Dynamic mechanical properties of the PS and cross-linked acrylic polyurethane films were measured in tension as a step-function of temperature (25–137°C) and frequency (0.4–63 rad/s) using a Rheometrics RSA II instrument. Strain was adjusted so as to be in the linear viscoelastic range for each sample. Film samples were prepared as described and die cut to uniform 6 mm width. For each sample, the experimental protocol consisted of step-heating with isothermal frequency sweep data taken every 5°C. DMA experiments were performed in this way



**Figure 2** DSC thermal curve for PS pellets as received, 0–270°C at 10°C/min, nitrogen.

to study the frequency dependence of both  $E''$  and  $\tan \delta$  and to avoid temperature lag problems.  $E''$  and  $\tan \delta$  peak temperatures vs. logarithm frequency data were fit by linear regression for each sample. By taking the logarithm of the frequency and plotting it on a linear abscissa scale, the ordinate intercepts are effectively  $E''$  and  $\tan \delta$  peak temperatures measured at 1 rad/s. Preliminary studies indicated that for each sample the average of the  $E''$  and  $\tan \delta$  intercepts closely approximated the DSC  $T_g$ .

## RESULTS

### DSC

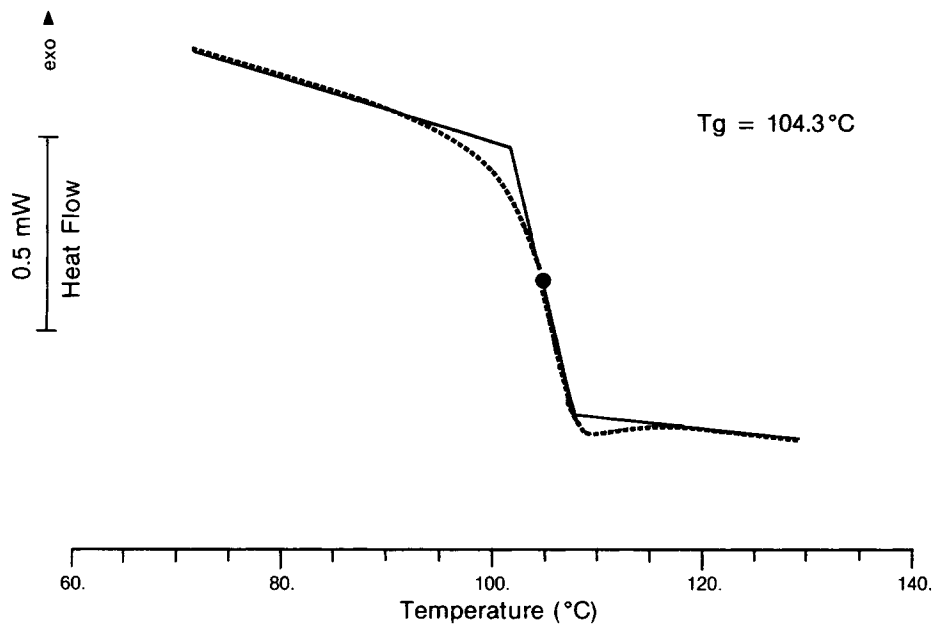
DSC  $T_g$  results for the PS pellet and PS film samples are shown in Table II. The characteristic DSC thermal curve for the PS pellet standard is shown in Figure 2. The glass transition is the only thermal event observed up to 270°C. Representative thermal curves for the pellets and the film thermoformed from the pellets are presented as Figures 3 and 4. A comparison of these curves shows that thermoforming had no effect on the PS glass transition within the experimental precision of the method.

The effect of thermal history imposed on one PS pellet sample by annealing is shown in Table III. Representative thermal curves are presented as Figures 5–7. Figure 5 shows the  $T_g$  as the only thermal event in the 30–150°C temperature range; no ther-

mal events are observed during the isothermal annealing at 150°C. In Figure 6, a thermal event is superimposed on the  $T_g$  as a result of annealing. Even for this well-characterized polymer standard, it is possible to alter the curve shape by prior thermal history. As shown in Figure 7, after heating the annealed sample above its  $T_g$  and quench-cooling, this stress is dissipated, i.e., memory of the thermal history has been removed. This results in a  $T_g$  equivalent to the initial  $T_g$ . Therefore, this series of experiments validates the experimental technique of subjecting each polymer sample to two heating cycles and quench-cooling between the heating cycles to yield a  $T_g$  representative of the polymer matrix itself.

### DMA

Based on preliminary DMA experiments, a parameter called a DSC-equivalent  $T_g$  is defined. It is the average of the  $E''$  and  $\tan \delta$  peak temperatures at 1 rad/s. This definition will be discussed later. DMA  $T_g$  results are shown in Table IV. A representative thermal curve is shown in Figure 8. Following accepted conventions regarding data analyses, rounding off of results to the proper number of significant figures is carried out at the last step. DSC and DMA  $T_g$  results are compared in Table V. This comparison shows that the  $T_g$  measurements from both techniques agree within  $\pm 2^\circ\text{C}$ . Representative DSC and DMA thermal curves are presented as Figures 9 and 10, respectively.

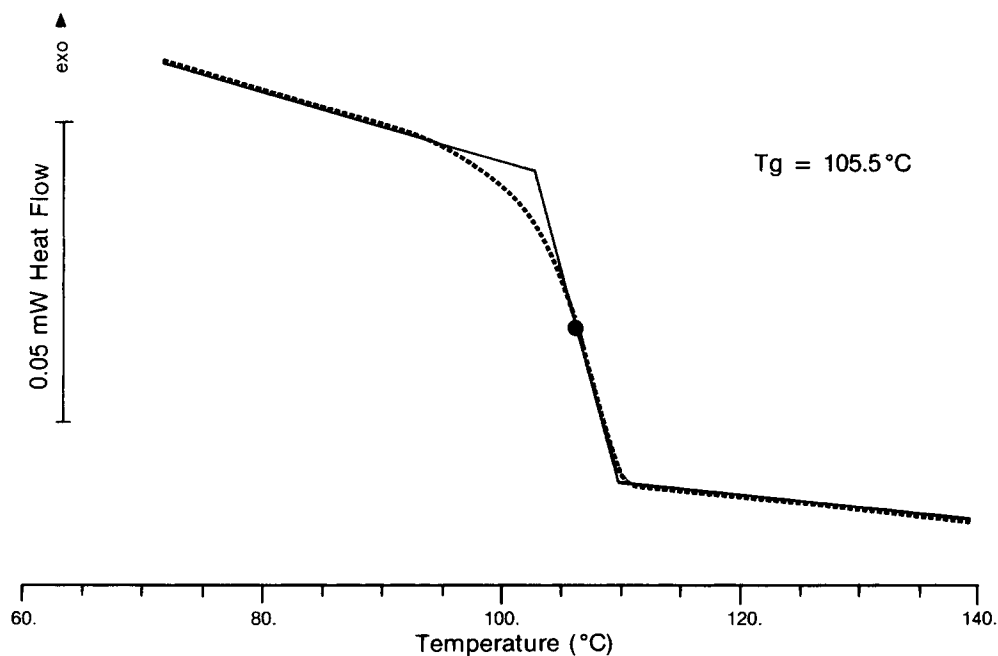


**Figure 3** DSC thermal curve for PS pellets, 0–150°C at 10°C/min, nitrogen.

To show the consistency of the DMA data, time-temperature superposition of  $E'$ ,  $E''$ , and  $\tan \delta$  for a representative cross-linked acrylic polyurethane film is shown in Figure 11. For all cross-linked films, time-temperature superposition did not fit the WLF equation,<sup>10</sup> but, rather, followed simple Arrhenius behavior. In Figure 11, data were shifted along the frequency axis using the shift factor ( $a$ ) defined by

$$\log a = -(T - T_g)/7 \quad (1)$$

In effect, this procedure creates a master curve of the frequency dependence of film dynamic mechanical properties at its  $T_g$ . It takes data measured at many temperatures, but limited to 2 decades of frequency, and transforms it to show behavior at one temperature,  $T_g$ , and over 12 decades of frequency.



**Figure 4** DSC thermal curve for PS film, 0–150°C at 10°C/min, nitrogen.

**Table III Polystyrene Standard<sup>a</sup>: Annealing**

Step	$T_g$ (°C)		Peak (°C)		$\Delta H$ (J/g)	
	TA-3300	TA-4300	TA-3300	TA-4300	TA-3300	TA-4300
1	103.6	103.3				
3	104.9	104.4				
6 <sup>b</sup>	104.9	104.3	108.5	108.5	1.1	1.2
8	106.0	104.7				

<sup>a</sup> Pellet (13.39 mg) heated at 10°C/min.

<sup>b</sup> Thermal event superimposed on  $T_g$ .

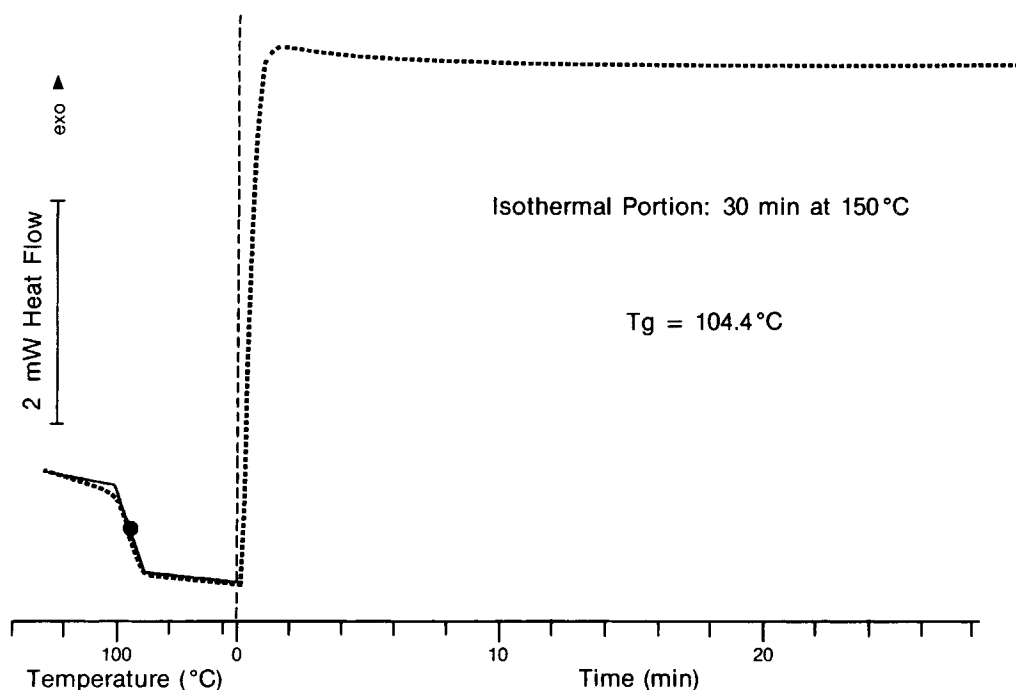
In Figure 12, the  $E''$  and  $\tan \delta$  peaks are marked and the  $T_g$  is indicated, by definition, halfway between.

## DISCUSSION

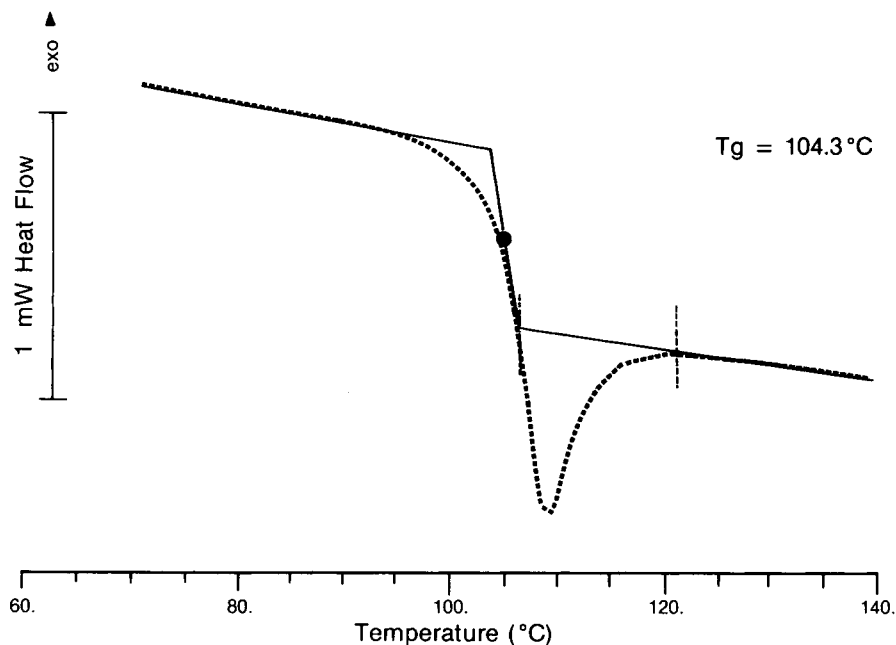
Figure 12(A) demonstrates the ASTM<sup>1</sup> DSC method for measuring glass transitions. ASTM interlaboratory round-robin results have shown that the heat-capacity transition midpoint can be determined with better analytical precision than either the extrapolated onset or extrapolated end temperature. Therefore, because of this better precision, the midpoint is used to characterize the  $T_g$  of the PS standard and the cross-linked acrylic polyurethane films. The aim is analytical precision in comparing DSC and DMA measurements of  $T_g$ .

Figure 12(B) shows corresponding dynamic mechanical data over the same temperature range. The DMA elastic modulus ( $E'$ ) decreases logarithmically with increasing temperature by 2–3 decades from a high value characteristic of a glass to a lower value corresponding to a rubber. However, because of the logarithmic scale, linear base-line extrapolations cannot be used as in the case of DSC measurements.

Characteristically, the loss modulus ( $E''$ ) shows a maximum near the beginning of the transition and  $\tan \delta$  shows a maximum near its end. By convention, some investigators identify the  $\tan \delta$  peak temperature as the  $T_g$ ; others use the  $E''$  peak temperature. We propose that the average of those two peak temperatures, measured at 1 rad/s, defines the same  $T_g$  as measured by DSC. We clearly recognize that, at



**Figure 5** Effect of annealing PS pellets, 10°C/min, nitrogen.

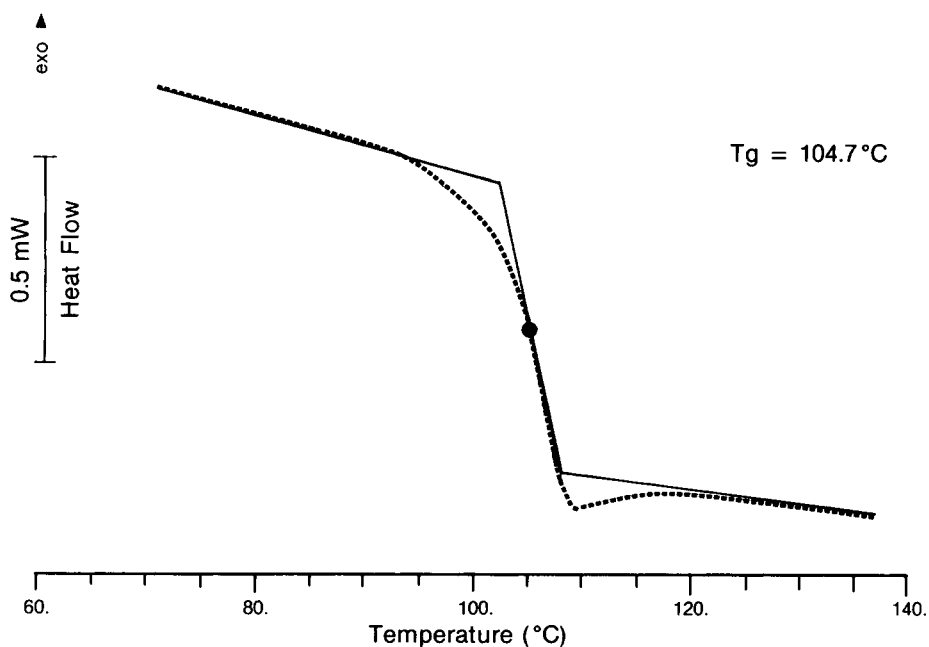


**Figure 6** First heating cycle after annealing PS pellets, 10°C/min, nitrogen.

present, this definition is empirical, based on the limited experimental data, and does not have a theoretical foundation.

By analogy with DSC  $T_g$  measurements, an average or midpoint value will have greater precision than either single value alone. Also, this strategy allows for comparing materials in which the breadth

of the  $T_g$  range varies. Additionally, a low frequency such as 1 rad/s is consistent with the general observation that low-frequency dynamic mechanical (and dielectric) data more closely approach  $T_g$  as measured by DSC. In Table V, DSC and DMA  $T_g$ 's for a series of cross-linked acrylic polyurethane films agree within  $\pm 2^\circ\text{C}$  on average. Clearly, three indi-



**Figure 7** Second heating cycle after annealing PS pellets, 10°C/min, nitrogen.

**Table IV**  $T_g$  of Polystyrene Film (PSF):  
DSC vs. DMA

DSC $T_g$ (°C)	$E''^a$ (°C)	Tan $\delta^a$ (°C)	DMA $T_g$ (°C)
104	103.7	114.9	109
108	103.8	111.6	108
	100.9	113.7	107
	103.8	112.6	108

<sup>a</sup> Read at peak maximum.

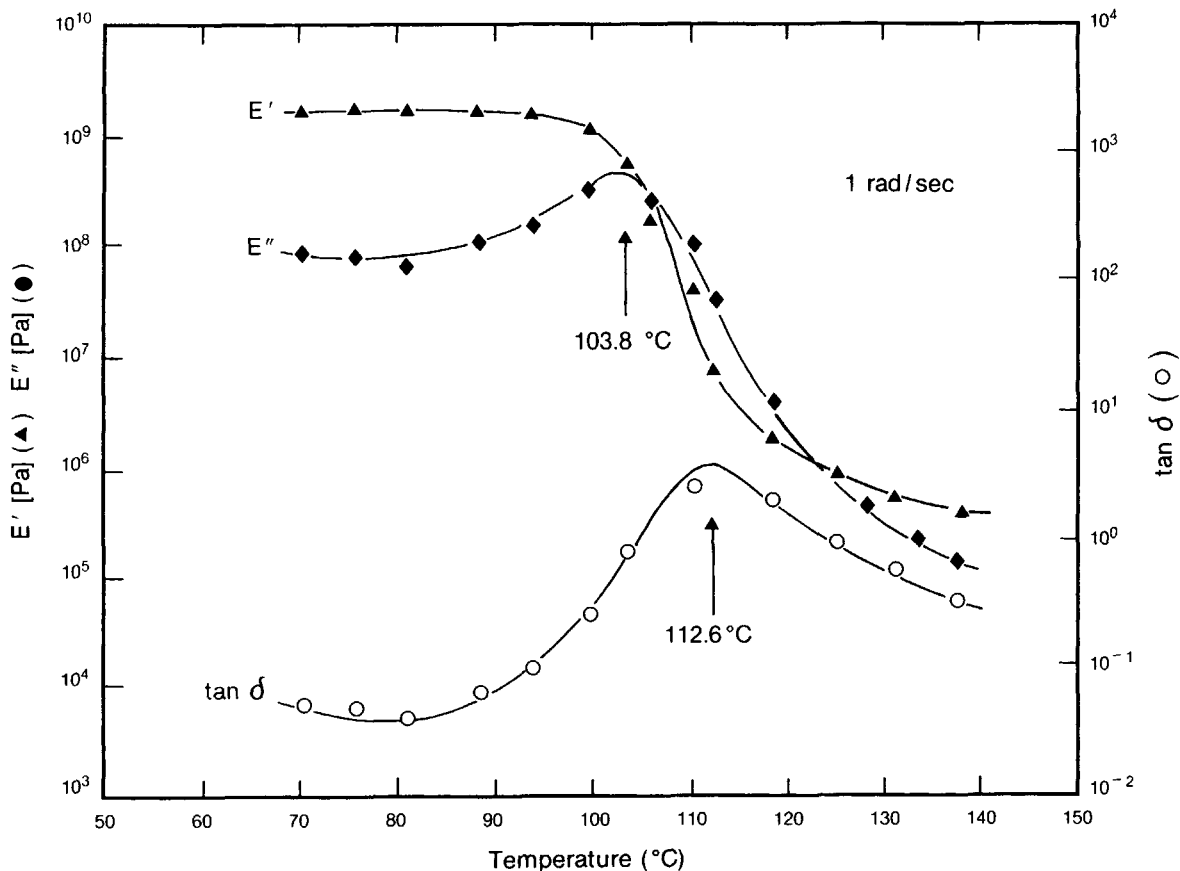
vidual analyses lie outside these limits, namely, samples A, F, and L. These outliers reflect a combination of the DSC  $T_g$  measurement precision of  $\pm 2^\circ\text{C}$  (Ref. 1) and possible sample inhomogeneity. An example of sample inhomogeneity is sample L, where replicate 10 mg samples show an  $8^\circ\text{C}$  difference in the DSC  $T_g$ . Overall, there appears to be no bias between the DSC  $T_g$  and DMA  $T_g$  methods, as the sum of the  $\Delta T_g$ 's in Table V is  $0.3^\circ\text{C}$ . This same agreement between methods is observed for the PS standard.

**Table V** Crosslinked Acrylic Polyurethane Film

Sample	DSC $T_g$ (°C)	DMA $T_g$ (°C)	$\Delta T_g$ (°C)
A	70 74	74 75	-2.5
B	70 72	70 73	-0.5
C	66 64	64 63	1.5
D	59 61	60 59 59	0.7
E	66 68	67 67	0.0
F	75 77	72	4.0
G	71 73	70	2.0
H	71 73	70	2.0
I	57 59	60	-2.0
J	66 68	65	2.0
K	67 69	67 67	1.0
L	48 56	57	-5.0
M	64 68	65	1.0

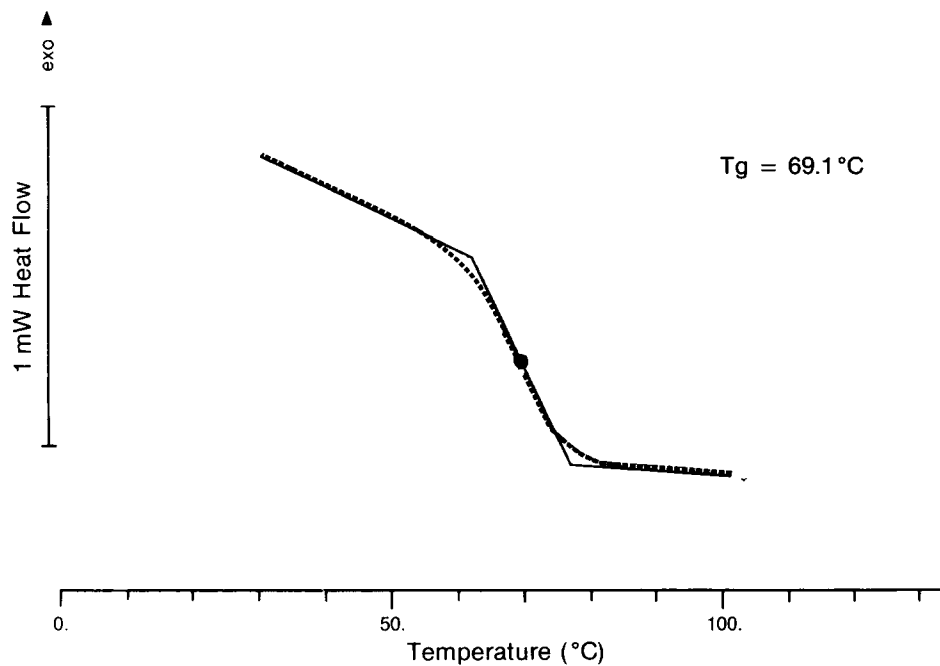
**CONCLUSION**

A dynamic mechanical analysis glass transition (DMA  $T_g$ ) defined as the average of the loss modulus ( $E''$ ) and loss tangent ( $\tan \delta$ ) peak temperatures

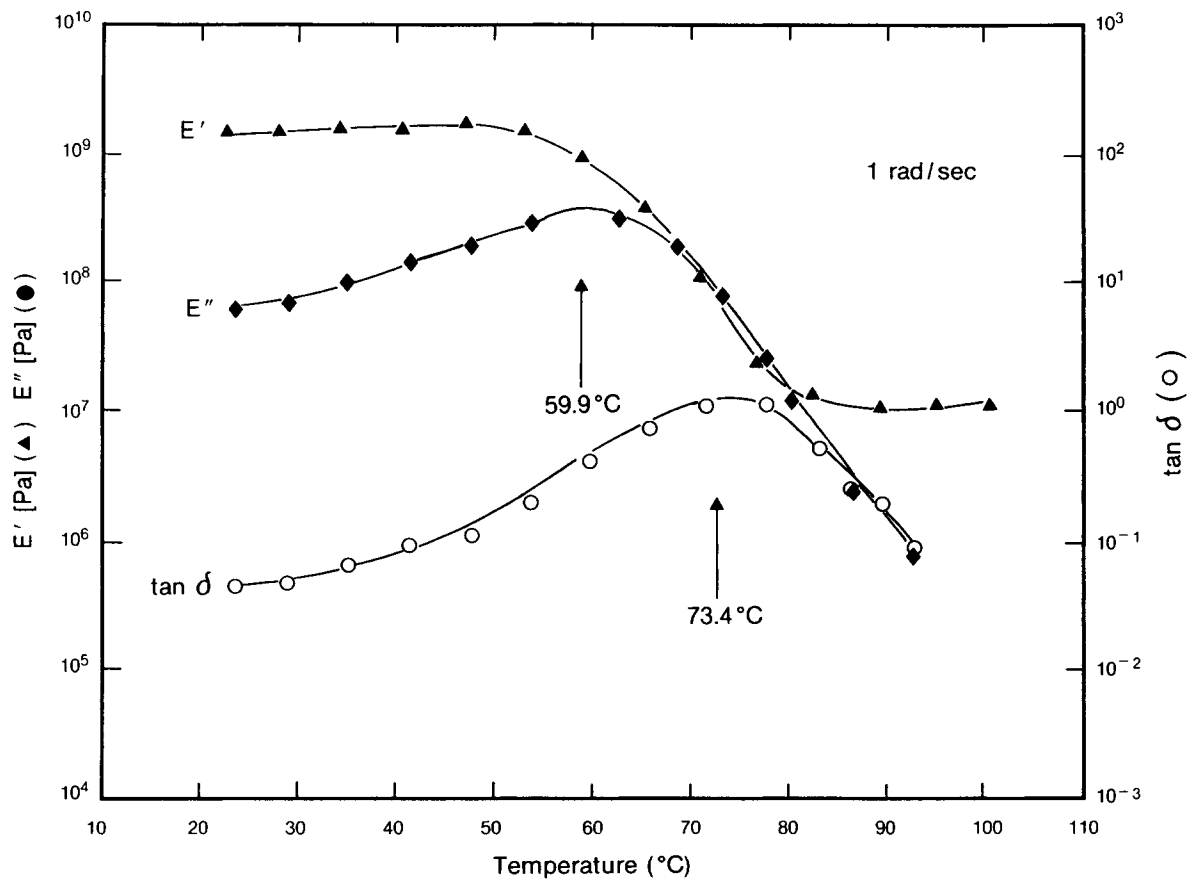


**Figure 8** DMA thermal curve for PS film, step heating with isothermal frequency sweep every  $5^\circ\text{C}$ , nitrogen.





**Figure 9** DSC thermal curve for cross-linked acrylic polyurethane film, 10°C/min, nitrogen.



**Figure 10** DMA thermal curve for cross-linked acrylic polyurethane film, step heating with isothermal frequency sweep every 5°C, nitrogen.

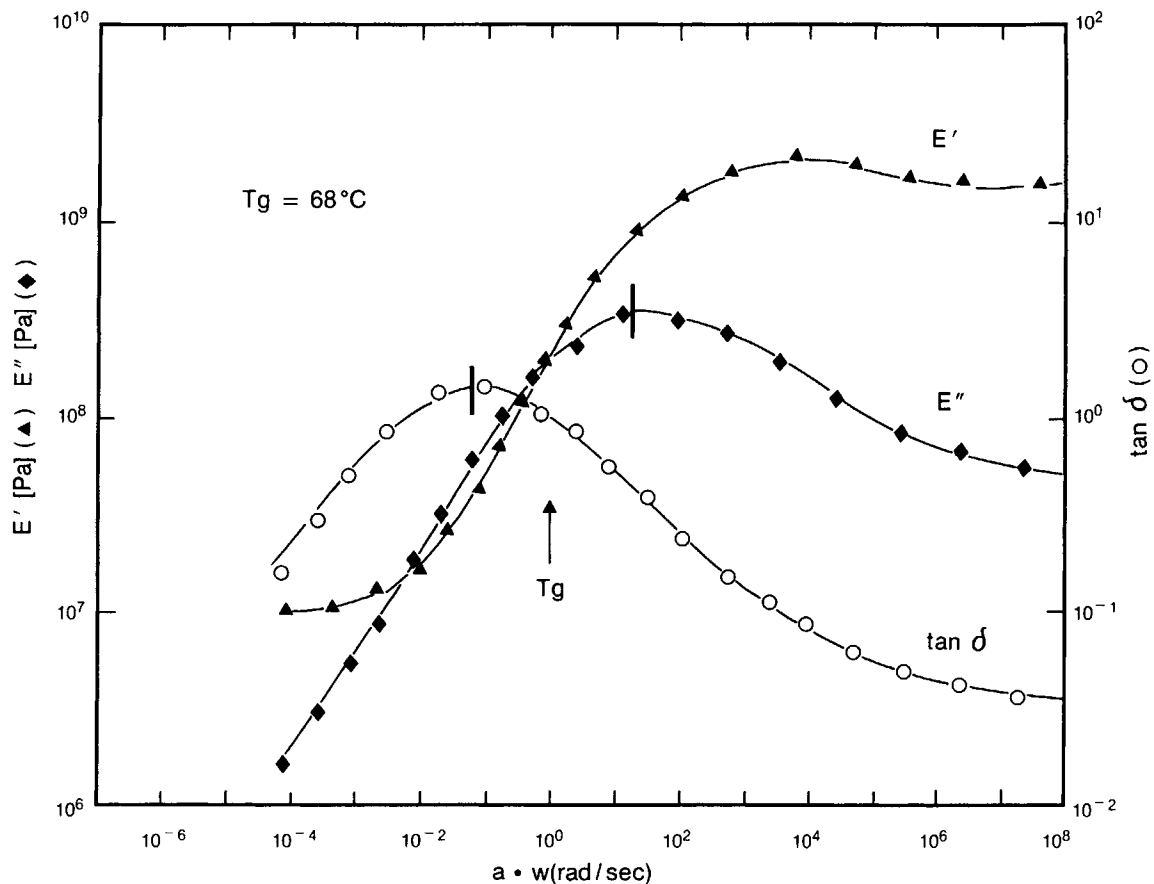


Figure 11 DMA time/temperature superposition—cross-linked polyurethane film.

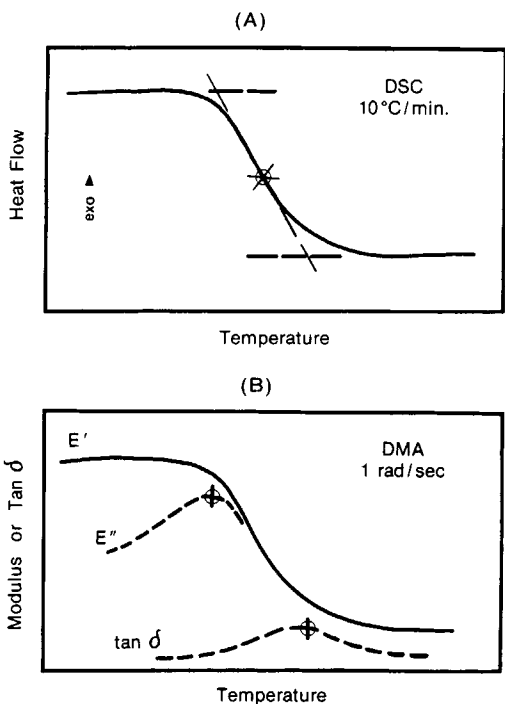


Figure 12 DSC/DMA analogy.

measured at 1 rad/s oscillation frequency agrees with the differential scanning calorimetry (DSC  $T_g$ ) within  $\pm 2^\circ\text{C}$ . We recommend that these techniques be used to measure the  $T_g$  of thermoset and thermoplastic films for which  $E''$  and  $\tan \delta$  peak temperatures can be measured.

**DEFINITIONS OF TERMS**

The terms below are used in this investigation and generally follow ASTM definitions<sup>11,12</sup>:

DSC: Differential scanning calorimetry. A technique in which the difference in energy inputs into a substance and a reference material is measured as a function of temperature while the substance and reference material are subjected to a controlled-temperature program.

DMA: Dynamic mechanical analysis. A technique in which the storage modulus (elastic response) and loss modulus (viscous response)

of a substance under oscillatory load is measured as a function of temperature, time or oscillation frequency while subjected to a controlled-temperature program.

$E'$ : Storage (elastic) modulus in tension. A measure of energy stored, defined as the ratio of stress (in phase with the oscillating strain) to the magnitude of the strain.

$E''$ : Loss modulus measure in tension. A quantitative measure of energy dissipation, defined as the ratio of stress ( $90^\circ$  out of phase with oscillating strain) to the magnitude of the strain.

Tan  $\delta$ : Loss tangent. Ratio of loss modulus to storage modulus,  $E''/E'$ .

$T_g$ : Glass transition. Reversible change in an amorphous material or in amorphous regions of a partially crystalline material, from (or to) a viscous or rubbery condition to (or from) a hard and relatively brittle one. The glass transition generally occurs over a temperature region.

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