Thermomechanical Analysis of T_g and $T > T_g$ Transitions in Polystyrene

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Synopsis

Phenomenological softening points were measured on a series of 13 anionic, nearly monodisperse, atactic polystyrenes using a DuPont 943 thermomechanical analyzer (TMA) in a penetration mode. Although TMA cannot identify the nature of the "transition" observed as such, the results obtained support the evidence for the T_g, T_{ll}, and T'_{ll} transitions in polystyrene discussed in recent literature. T_g and T_{ll} were found to vary with molecular weight in a systematic manner, while T'_{ll} could only be observed at very high molecular weight. The technique appears to be quite useful in offering rapid and reproducible information on the various transitions in the liquid state of polystyrene.

INTRODUCTION

Thermomechanical analysis (TMA) is gaining popularity as a quick characterization method for studying thermosets[1] and elastomers.[2-4] In many of these studies, the primary interest has been in measuring changes in sample dimensions (e.g., linear expansion) with increasing temperature. However, the TMA technique is also very useful, in a penetration mode, in studying the softening temperatures of thermoplastics. In this paper, we report some of the work being done using TMA to study various transitions, T_g and transitions above T_g, in atactic polystyrene.

The first thermomechanical analysis work reported in the literature dates back to the early 1950s.[5] In two reports, Kargin and Malinski discuss the results of experiments carried out on fractions of poly(vinyl chloride) and polystyrene. They measured the relative penetration of a weighted probe into a sample after a 10-sec penetration time. Two transitions were observed and designated as T_g (glass transition temperature) and T_f (flow temperature). Both T_g and T_f were characterized with respect to molecular weight dependency over the range of molecular weight fractions studied.

After careful analysis of these early results and based upon our own experience with the TMA technique, we believe the T_f transition may be associated with the liquid–liquid transition temperature (T_{ll}). A good historical discussion and chronological listing of the T_{ll} related literature has been compiled by Boyer.[6]

EXPERIMENTAL

The thermomechanical analyzer used in this work was the DuPont 943 TMA; this is a plug-in module used in conjunction with the DuPont 990 thermal analyzer temperature programming and recording unit. Detailed descriptions of the instrument are available in the literature.[2,3,7] All measurements reported were collected using the TMA in a penetration mode by observing the penetration

of a weighted (2 g), flat-tipped probe (2.54-mm diam) through a sample at a constant heating rate (5°C/min).

A homologous molecular weight series of 13 well-characterized, nearly monodisperse, anionically prepared, atactic polystyrene standards from nominal molecular weight 2,200 to 7,200,000 was studied. The samples were obtained from three sources: Pressure Chemical Co., Polymer Laboratories, and Waters Associates. The physical nature of the samples as received ranged from coarse, crumbly powder to fine grained powder to fluffy, fibrous material as molecular weight increased. Values of nominal molecular weight, number average molecular weight ($\overline{M}_n$), weight average molecular weight ($\overline{M}_w$), and polydispersity ($\overline{M}_w/\overline{M}_n$) are given in Table I; source and batch number are also tabulated.

All results reported are for transitions observed on clear, fused melts of the as-received powdered materials. The melt samples were prepared by one of two methods: (1) molecular weight 2,200 to 110,000—small portions of a powdered sample were placed into DSC sample pans and fused in the open air on a laboratory hotplate at a temperature above the expected T_{ll} temperature for a period of up to 20 sec; (2) molecular weight 275,000 and 7,200,000—small portions of compressed powder were placed into DSC sample pans and placed into an evacuated vacuum oven at 190°C for a period of 12–24 hr. The vacuum oven procedure was used for the higher-molecular-weight members to avoid thermal decomposition during the extended heating times required for the powders to fuse into clear glasses. Sample thickness ranged between 0.5 and 1.0 mm for the smooth glasses. Typical instrumental sensitivity settings ranged from 50–100 μm/cm of vertical chart displacement.

RESULTS

Figures 1–3 show typical penetration thermograms for samples of nominal molecular weight 4,000, 110,000, and 1,800,000, respectively. The upper traces correspond to the vertical displacement of the TMA probe as it penetrates through the sample. The lower traces are first derivatives of the penetration traces. In all cases, clear evidence for two "softening" points is observed in scanning from low to high temperatures, and in some cases (at very high molecular weights) evidence for three softening points.

Transition temperatures are assigned either as the intersection of two straight line segments for the lower transition(s) or as the onset point of increasing penetration rate for the uppermost transition (see Figs. 1–3 for clarification). Peak temperatures of the derivative trace have no direct correspondence with the transition temperatures and should not be used to assign transition temperature values. The utility of the derivative trace lies in its ability to clarify the number of transitions occurring in the thermogram and the region in which they appear.

The very first penetration of the TMA probe occurs at the glass transition temperature. Below T_g, penetration into the glassy sample is impossible and a level plateau region leading up to T_g is observed. If a temperature scan is stopped several degrees above T_g, the weighted probe continues to penetrate through the viscoelastic medium, albeit quite slowly.

Interestingly though, if one continues to scan up in temperature beyond the T_g region, a second softening point is observed that likely reflects the liquid–

TABLE I
Molecular Weights of Anionic Polystyrenes[a]

Nominal molecular weight	$\bar{M}_n$	$\bar{M}_w$	$\bar{M}_w/\bar{M}_n$	Source[b]	Batch no.
2,200	2,220[c]	—	≤1.06[d]	Pressure Chem.	12c
4,000	3,100[c]	—	≤1.10[e]	Pressure Chem.	11b
9,000	9,168[c]	—	≤1.06[d]	Pressure Chem.	60422
17,500	15,100[f]	20,400[g]	≤1.06[d]	Pressure Chem.	41220
37,000	36,300[f]	32,600[g]	≤1.06[d]	Pressure Chem.	7b
50,000	51,150[f]	53,700[g]	≤1.06[d]	Pressure Chem.	60917
110,000	111,000[f]	111,000[g]	≤1.06[d]	Pressure Chem.	4b
275,000	275,000[f]	—	<1.05[e]	Polymer Labs.	—
470,000	350,000[f]	392,000[g]	≤1.06[d]	Waters Assoc.	3b
1,010,000	1,010,000[f]	—	<1.10[e]	Polymer Labs.	—
1,800,000	—	1,790,000[g]	≤1.30[d]	Pressure Chem.	61124
2,000,000	1,990,000[h]	2,050,000[g]	≤1.30[h]	Pressure Chem.	14b
7,200,000	7,200,000[f]	—	<1.30[e]	Polymer Labs.	—

[a] Molecular weight and polydispersity characterization provided by the source.
[b] Pressure Chemical Co., Pittsburgh, Pennsylvania 15201; Polymer Laboratories, Stow, Ohio 44224; Waters Associates, Milford, Massachusetts 01757.
[c] Vapor phase osmometry.
[d] Gel permeation chromatography.
[e] Characterization technique not provided by the source.
[f] Membrane osmometry.
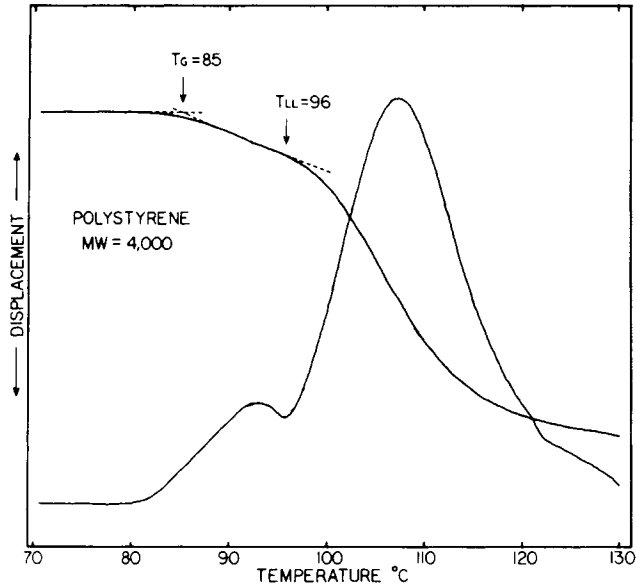[g] Light scattering.
[h] Fractionation.

Fig. 1. TMA thermogram of 4,000 molecular weight polystyrene. In this and all other thermograms, upper trace is penetration trace, lower trace is first derivative display of the penetration trace. Note only T_g and T_{ll} transitions present at low molecular weight.

liquid transition temperature (T_{ll}) spoken of in the literature.[6] Above T_{ll} the probe encounters a quite less viscous, more fluid medium and quickly penetrates through the sample, the increased rate of penetration showing up on the thermogram as the large second "step" into the sample.

In some cases, at very high molecular weights, even above T_{ll} the probe does
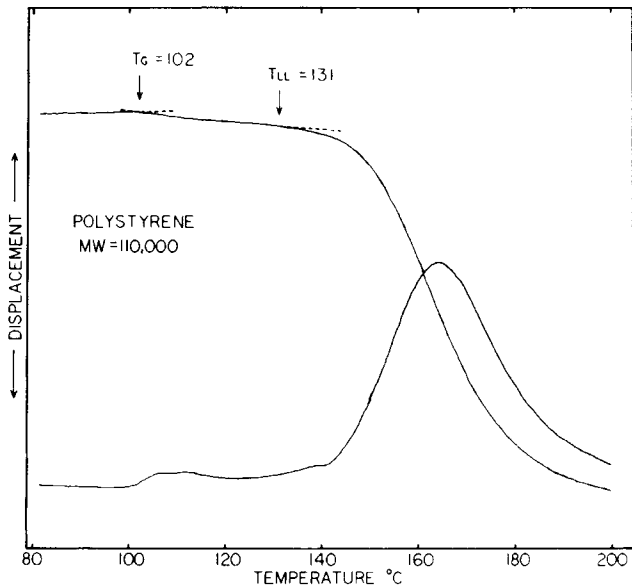

Fig. 2. TMA thermogram of 110,000 molecular weight polystyrene. Note only T_g and T_{ll} transitions present at intermediate molecular weight.
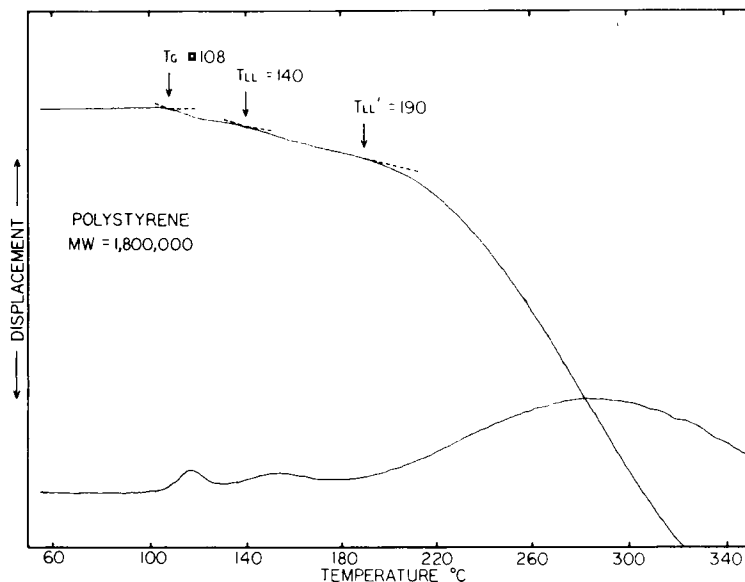
Fig. 3. TMA thermogram of 1,800,000 molecular weight polystyrene. Note all three transitions, T_g, T_{ll}, and T'_{ll}, present at high molecular weight.

not quickly penetrate through the more fluid sample because of the increased viscoelastic integrity of the material imparted by an increasing number of intermolecular entanglements as molecular weight increases. Figure 3 (molecular weight 1,800,000) shows an example of this case. After traversing T_g at 108°C and T_{ll} at 140°C the weighted probe is still encountering sufficient resistance against complete and rapid penetration until around 190°C when suddenly the material appears to become significantly more fluid and a final abrupt penetration step into the sample is observed. We feel this final step may be the T'_{ll} transition recently clarified.[8]

Both T_g and T_{ll} transitions show a clear and systematic dependence on molecular weight. Table II summarizes the transition temperature values obtained on the fused melt samples over the entire molecular weight range from 2,200 to 7,200,000. All transition temperatures reported are averaged values of from two to six runs and were obtained under the conditions of a 2-g loading weight and a 5°C/min heating rate. Figure 4 shows a plot of the data as log molecular weight vs. temperature. The vertical bars indicate the range of transition temperatures observed over repeated runs.

The degree of reproducibility is greatest for the T_g transition; the T_{ll} transition is somewhat less reproducible and the T'_{ll} transition temperature shows the most scatter in the data. Standard deviations were calculated for the three transitions to get a quantitative feel for their reproducibility. Measurements of T_g, T_{ll}, and T'_{ll} exhibited standard deviations of 1.4, 3.0, and 4.3°C, respectively.

Table II also lists the values of the T_{ll}/T_g ratio for each member of the molecular weight series. The ratio was observed to increase with increasing molecular weight and ranged from 1.02 for molecular weight 2,200 up to a maximum value of 1.12. These T_{ll}/T_g ratios are somewhat lower than those reported by others using different techniques.[9-11]

TABLE II
Effect of Molecular Weight on T_g, T_{ll}, and T'_{ll} Transitions of Polystyrene

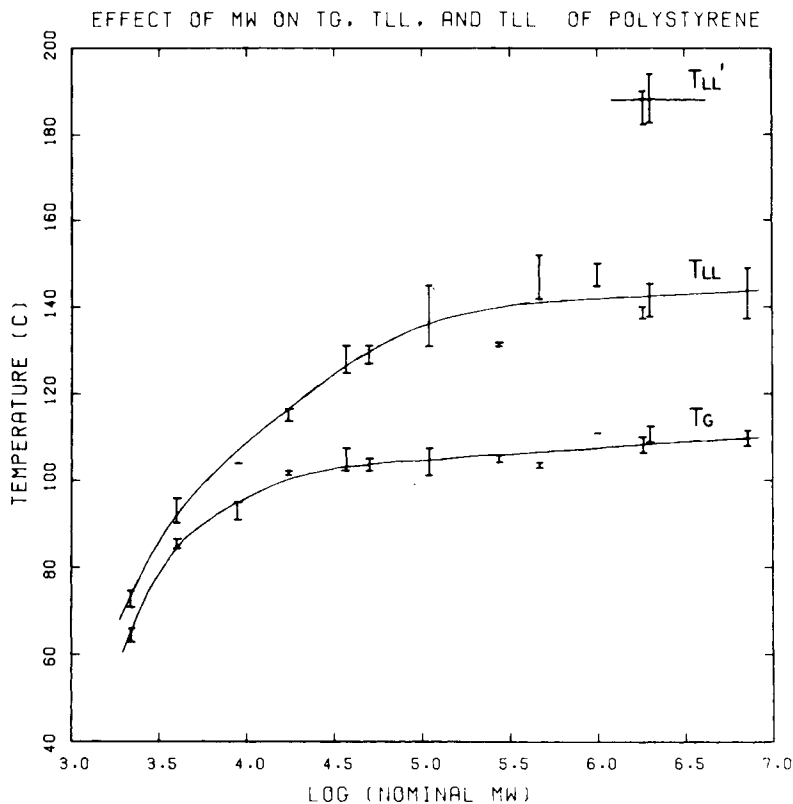| Nominal molecular weight	Log molecular weight	Number of runs	T_g		T_{ll}		T_{ll}/T_g	T'_{ll}	
			(°C)	(K)	(°C)	(K)	(K/K)	(°C)	(K)
2,200	3.34	3	64.5	337.5	72.7	345.7	1.02	—	—
4,000	3.60	4	85.1	358.1	94.4	367.4	1.03	—	—
9,000	3.95	2	93.0	366.0	104.0	377.0	1.03	—	—
17,500	4.24	2	101.8	374.8	115.3	388.3	1.04	—	—
37,000	4.57	4	104.6	377.6	128.8	401.8	1.06	—	—
50,000	4.70	3	103.8	376.8	129.5	402.5	1.07	—	—
110,000	5.04	5	104.3	377.3	139.1	412.1	1.09	—	—
275,000	5.44	2	105.3	378.3	131.5	404.5	1.07	—	—
470,000	5.67	2	103.5	376.5	147.0	420.0	1.12	—	—
1,010,000	6.00	2	111.0	384.0	147.5	420.5	1.10	—	—
1,800,000	6.26	3	108.2	381.2	138.8	411.8	1.08	186.3	459.3
2,000,000	6.30	6	110.3	383.3	140.2	413.2	1.08	188.8	461.8
7,200,000	6.86	3	109.5	382.5	141.8	414.8	1.08	—	—

Fig. 4. Molecular weight dependence of T_g, T_{ll}, and T'_{ll} transitions of polystyrene by TMA. Note that T'_{ll} is only observed at very high molecular weight. Vertical bars indicate range of transition values obtained over two to six runs.

DISCUSSION

A general qualitative discussion of the phenomenological behavior we observe has appeared in the *Encyclopedia of Polymer Science and Technology*.[12]   In that report the authors discuss the molecular weight effect on the glass transition temperature (T_g) and on a higher temperature transition referred to as the flow temperature (T_f).   For the discussion at hand one may think of T_{ll} in the sense of a flow temperature inasmuch as T_{ll} is the point where the sample experiences increased fluidity.

We have been able to observe the T_{ll} transition in even the very lowest-molecular-weight material (molecular weight 2,200) whereas the earlier thermomechanical studies[5] did not observe a separate flow temperature transition until reaching a molecular weight in the range of 10^5; the increased sensitivity of the commercial TMA instrument is probably the reason for this.

TMA observed T_g values tend to run several degrees above literature differential scanning calorimetry (DSC) data[10,11,14] and several degrees below literature torsional braid analysis (TBA) and differential thermal analysis (DTA) data.[9] However, the TMA observed T_{ll} transition temperatures fall consistently some 10–15°C lower than similar values in the literature arising from melt viscosity,[8] DTA,[9] TBA,[9] and DSC[10,14] measurements.   Part of the reason for this discrepancy lies in the difference in scan speeds used in the various techniques.   In this

work, we have used a relatively slow scan speed (5°C/min) in comparison to that used in either the DTA[9] (30°C/min) or DSC[10,11] work (40°C/min). In some preliminary studies on the effect of scan speed we do find a dependence of transition temperatures on scan speed. Loading weight also plays a role in lowering especially the T_{ll} transition. In some work in progress in studying the effect of loading weight on the observed transition temperatures, we have found that even a 2-g weight on the TMA probe may significantly lower the observed T_{ll} transition, while showing relatively little effect on the T_g transition. The principal reason the T_{ll}/T_g ratios we report are somewhat low is due to the fact that the observed T_{ll} transitions fall somewhat low.

Gillham's results using TBA[9,13] indicate two distinct regions of T_{ll} behavior with increasing molecular weight—below and above the critical entanglement molecular weight (M_c). Below M_c, T_{ll} increases in a curvilinear fashion with increasing molecular weight; above M_c, T_{ll} increases more rapidly with molecular weight in a linear manner. The TBA technique measures a sample under a certain finite shear rate. In static, nonshear test methods, as in zero shear melt viscosity,[8] DTA,[9] or DSC[10,11] techniques the value of T_{ll} tends to reach a limiting value somewhere around 160°C leveling off at high molecular weight in a fashion quite similar to the familiar T_g–molecular weight dependence.

One reason to identify the uppermost TMA transition by the point of departure from an initial baseline, as such, was to avoid obtaining transition temperatures at some unknown shear rate. In the region above the onset point, the TMA probe, encountering an increasingly more fluid medium, penetrates through the sample more quickly at unknown and increasing finite shear rates. The TMA probe experiences infinitesimally small or zero shear at the onset point. The behavior of T_{ll} with molecular weight we observe (see Fig. 4) is quite to be expected; in our case though, a limiting T_{ll} value of around 145°C is obtained.

It has been claimed[15–17] that the T_{ll} transition observed by TBA[9,13] is an artifact caused by the interaction between the glass braid and molten polymer. In view of both qualitative and quantitative similarities between TBA and TMA results, any artifact effect ascribed to TBA is either missing or very minimal.

Gillham et al.[13] reported the existence of a transition above T_{ll} denoted as T'_{ll} using TBA. Enns et al.[18] independently discovered this same transition using a DSC technique. Enns et al.[19] further went on to identify the T'_{ll} transition based on Fourier transform infrared (FTIR) analysis. Recently, clear evidence for distinguishing between T_{ll} and T'_{ll} transitions from zero shear melt viscosity data has appeared.[8] The transition observed by TMA around 190°C supports the existence of the T'_{ll} transition proposed in those earlier studies. In using the TMA technique alone to characterize a polymer sample, one would be hard pressed to identify definitively a T_{ll} or T'_{ll} transition as such, since the TMA method does not give direct evidence or clues about the types of molecular motion involved with the softening points observed. The TMA results do, however, complement a growing body of literature supporting the existence of T_{ll} and T'_{ll} transitions in the liquid state of polystyrene.

Sillescu et al.[20,21] have proposed, from NMR evidence on deuterated polystyrene, that around 200°C main chain polymer backbone motion becomes as facile as rotation of the phenyl substituent. This observation gives credence to the concept of an intramolecular relaxation ascribed as T'_{ll}. In terms of TMA results, the greater the number of molecular entanglements at very high molec-

ular weight the greater the resistance to complete and rapid penetration of the probe through the sample above T_{ll}; it may take this extra amount of intramolecular wriggling motion to allow the probe to continue less hindered passage through the material.

CONCLUSIONS

The TMA method is a technique that gives direct information about phenomenological softening points in the polymer liquid state. Although one cannot obtain information as to the type of molecular motion responsible for the relaxation observed, TMA results corroborate the existence of processes in the polymer melt where abrupt increases in fluidity become apparent.

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