The T_{ll} ($> T_g$) Transition of Atactic Polystyrene

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Synopsis

Torsional braid analysis (TBA) (~0.3 Hz) and differential thermal analysis (DTA) data are presented for the temperature region 0–200°C for two series of atactic polystyrenes with narrow molecular weight distributions: (a) anionic series, $\bar{M}_n$ = 600–2×10⁶, $\bar{M}_w/\bar{M}_n \simeq$ 1.1; (b) fractionated thermal series, $\bar{M}_n$ = 2,000–1.1×10⁵, $\bar{M}_w/\bar{M}_n$ ≲1.25. Preliminary results on bimodal blends are also reported. Heating and cooling cycles were employed with TBA; only the heating mode was used with DTA. In addition to a dynamic mechanical loss peak at T_g, a higher temperature loss peak was also found. Designated the T_{ll} or liquid–liquid transition (relaxation), its temperature is 1.1 to 1.2 T_g (°K) for polymers with molecular weight below the critical molecular weight (M_c) for chain entanglements. Above $M_c \simeq$ 35,000, it rises steeply, being ≃200°C for $\bar{M}_n$ = 110,000. The common dependence of T_g and T_{ll} on $\bar{M}_n^{-1}$ below M_c suggests a common molecular origin. The two facts, (a) that $T_{ll} > T_g$ and (b) that T_{ll} reflects chain entanglements, further suggest that T_{ll} involves a longer chain segment length and possibly the entire molecule. Comparison of T_{ll} versus log M plots with T versus log M isoviscous state plots based on zero-shear melt viscosity data from the literature implies that T_{ll} as measured by the TBA technique corresponds to an isoviscous state of 10⁴–10⁵ poises. The employment of narrow molecular weight polymers is presumably responsible for both the linear variation of the T_{ll} transition with $\bar{M}_n^{-1}$ (which suggests a free volume basis for the relaxation) and the form of the variation of the T_{ll} transition with log M (which suggests an isoviscous basis for the relaxation). The sharpness of the T_{ll} loss peak by TBA decreases with increasing molecular weight and dispersity. The DTA endothermic event corresponding to T_{ll} is clearly related to the occurrence of flow since the fused films which result from heating granules to 200°C and cooling to R.T. do not reveal a T_{ll} on reheating. If a fused film is crushed, a T_{ll} event is observed on heating. For bimodal blends with $\bar{M}_n < M_c$ for both components, the T_{ll} transition was averaged; with one component less than and one greater than M_c, the T_{ll} transitions of the components appeared to occur independently at temperatures corresponding to those of the isolated components. In accordance with Ueberreiter and Orthmann, T_g appears to separate a glassy state from a fixed liquid state, whereas T_{ll} separates the fixed liquid from a true liquid state. Possible molecular interpretations for the T_{ll} process are discussed. Systematic bodies of data from the literature which indicate the presence of the T_{ll} process in other polymers are summarized.

INTRODUCTION

The existence of a transition located above the temperature of the glass transition in amorphous polymers is a subject of controversy. Evidence for such a transition and the main features of its behavior have been summa-

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rized.[1-3] Its temperature of occurrence increases with frequency and with molecular weight, and it is suppressed by crosslinking. Since the transformation involves a change from one liquid state to another, it has been designated T_{ll}.[1,3] In particular, for atactic polystyrene, a high-temperature ($T > T_g$) amorphous transition has been observed using such diverse techniques as thermal expansion,[4-7] heat capacity,[8] differential thermal analysis,[1] x-ray,[9] deformation-temperature,[10,11] dynamic mechanical loss,[12] stress relaxation,[13] diffusion,[14] and melt viscosity.[1,15] The nature of the transformation has been attributed to the onset of flow,[2,10,11,16] changes in the state of localized order,[17,18] chain entanglements and chain ends,[19] and the onset of motion of entire polymer chains.[1,2]

Preliminary published work using differential thermal analysis (DTA) appeared to reveal the existence of a transition or relaxation anomaly in the region of 160°C in polystyrene with an average molecular weight of 82,000 (see ref. 1, Fig. 3).

Thermomechanical experiments above T_g for amorphous polymers are facilitated by using supported samples. One method employs a mixture of low molecular weight polymer in a matrix of the same polymer having high molecular weight. In this way, the dependency of a $T > T_g$ relaxation on molecular weight has been studied for 1,4-polybutadiene (with approximately equal amounts of cis and trans repeat units).[2] The dynamic mechanical experiment (~50 Hz) revealed the transition by a loss peak. Another approach investigates a composite specimen consisting of polymer and inert glass substrate. In torsional braid analysis (TBA), a multifilamented heat-cleaned glass braid acts as the support for a specimen in a freely damped torsional pendulum experiment operating at about 1 Hz.[20,21] Although the T_{ll} transition in amorphous polystyrene, as determined by mechanical loss, has been alluded to in the literature,[1] no published data appear to exist. TBA experiments performed herein cover the temperature sequence 200° → −190° → 200°C with a programmed cooling and heating cycle. The present report is concerned only with T_g and T_{ll} data. Analysis of loss peaks in the β and γ regions of polystyrene will be presented on a later occasion.

The two series of polystyrenes, each with varying molecular weight, which were studied in this present work were "monodisperse" anionic polystyrenes and narrow molecular weight fractions from a batch of thermally polymerized styrene. The present research with DTA establishes the existence, the origin (on a macroscopic basis), and the conditions for observing the transition by DTA, and also demonstrates its dependence on molecular weight. The TBA experiments clearly show the existence of the T_{ll} transition in amorphous polystyrene, the reversibility with respect to temperature, and also the dependence on molecular weight. The transitions as measured by TBA agree with determinations made by DTA.

Investigations of a bimodal blend of low molecular weight polymers by DTA and TBA show that the T_{ll} transition, like the glass transition, is an average value of the two constituents. However, a blend of a high molecular weight polymer with a low molecular weight polymer shows a T_{ll} loss peak corresponding to the low molecular weight polymer.

The present manuscript follows up a preliminary report by the authors.[22]

EXPERIMENTAL

Materials

A series of polystyrene samples, obtained from the Pressure Chemical Co., Pittsburgh, Pa., was synthesized by an anionic polymerization procedure which produces "monodisperse" material, $\bar{M}_w/\bar{M}_n \simeq 1.1$ (see Table I). The reaction of styrene is initiated in benzene with an n-butyllithium/tetrahydrofuran complex and terminated by addition of methanol. This results in n-butyl and hydrogen ends for each polystyrene chain. Following termination, the polymer solution is diluted with benzene to a concentration of 2.5%. Boiling distilled water is used to flash off the solvent, producing polymer "popcorn" or "lollipop"[23] which is then chopped in a stainless-steel grinder and dried as outlined in Table I. The difference in the physical appearance (morphology) of the polystyrene samples (from granular to fibrous form with increasing molecular weight) results in part from the fact that the higher molecular weight samples have glass transition temperatures above the flash temperature ($\sim100°C$).

Another series of polystyrene samples (see Table II) was prepared in the following manner: A thermally polymerized polystyrene ($\bar{M}_n$ = 1,532, $\bar{M}_w/\bar{M}_n$ = 20.5) designated PS-1 (Dow Chemical Company, see Table II), was fractionated by a preparative gel permeation chromatography (GPC) unit (Waters Company Anaprep) into 19 fractions and isolated by methanol precipitation from methylene chloride and then vacuum dried at 60°C.[24] The molecular weight distributions of all fractions were characterized by GPC and had polydispersities ($\bar{M}_w/\bar{M}_n$) in the 1.1–1.3 range.[24] Vapor-pressure os-

TABLE I
Molecular Weights of Anionic Polystyrenes[a]

Sample no.	Batch no.	$\bar{M}_n$	$\bar{M}_w$[b]	$\bar{M}_v$[c]	$\bar{M}_w/\bar{M}_n$	"As received" prehistory[d]	
						Max T, °C	Press., in. Hg
1	14b	1,990,000[e]	2,050,000	2,340,000	<1.30	40	28
2	13a	640,000[e]	670,000	678,000	<1.10	80	20
3	3b	355,000[e]	392,000	388,000	<1.10	80	20
4	1c	193,000[e]	200,000	186,000	<1.06	80	20
5	4b	111,000[e]	111,000	111,000	<1.06	80	20
6	7b	36,000[e]	33,000	38,000	<1.06	80	20
7	2b	20,200[e]	20,800	20,400	<1.06	80	20
8	8b	9,600[f]	—	9,300	<1.10	40	28
9	11b	3,100[f]	—	3,600	<1.10	40	28
10	12b	2,050[f]	—	2,120	<1.10	40	28
11	16a	585[f]	—	578	<1.10	80	20

[a] Polymers and characterization: Pressure Chemical Co., Pittsburgh, Pa.
[b] Light scattering.
[c] Intrinsic viscosity.
[d] Dried to constant weight.
[e] Membrane osmometry.
[f] Vapor-pressure osmometry.

mometry and osmotic pressure were used to further characterize the low and high molecular weight fractions, respectively.[24]

Assignments of tacticity were obtained on a few samples from 20-MHz C^{13} NMR spectra using the resonances of the C-1 aromatic carbon atom.[25] Although the backbone methylene carbon also showed tacticity effects, this resonance area was obscured by the backbone methine carbon and therefore was not used in estimating values. For anionic polystyrene the tacticity was estimated to be 19/28/53 and 18/26/56 for the iso/hetero/syndio percentages for $\bar{M}_n = 20,200$ and $\bar{M}_n = 1,990,000$, respectively. For the unfractionated thermal polystyrene, the corresponding percentages were 17/25/58. The values were based upon the best computer fit using ten peaks associated with pentad sequences and triad assignments according to published procedures.[26,27] The estimate of accuracy was 10% based on a change in computer parameters.[25]

Differential Thermal Analysis (DTA)

Unless otherwise noted, the samples were examined "as received" under the following conditions.

A differential thermal analyzer (du Pont Model 900 with a du Pont Model 900-600 DSC cell) was used to examine the thermal behavior of the polystyrene samples from room temperature to 500°C. Specimens were contained in open aluminum sample pans (du Pont Model 900-656) and heated in an at-

TABLE II
Molecular Weights of Thermal Polystyrene Fractions[a]

Fraction no.	$\bar{M}_w$[b]	$\bar{M}_n$[b]	$\bar{M}_n$[c]	$\bar{M}_w/\bar{M}_n$[b]
1	2,470	2,200	—	1.11
2	2,720	2,490	1,880	1.09
3	3,100	2,470	2,130	1.25
4	3,890	2,370	2,690	1.15
5	5,030	4,430	3,600	1.14
6	6,660	5,810	5,380	1.15
7	8,360	7,350	6,270	1.14
8	10,800	9,330	8,180	1.15
9	13,600	11,700	11,800	1.16
10	15,500	13,300	13,400	1.16
11	23,400	19,800	23,500	1.18
12	30,500	25,200	35,400	1.21
13	39,400	32,800	47,200	1.20
14	49,500	41,200	56,700	1.20
15	66,100	54,500	70,800	1.21
16	95,000	75,100	94,400	1.26
17	134,000	107,000	111,000	1.25
18	208,000	163,000	182,000	1.28
19	294,000	229,000	—	1.29

[a] Material was fractionated from PS-1, sample no. Lot SL-10402 which had been prepared in a semicommercial unit of the Dow Chemical Company at temperatures in excess of 250°C. This specimen had a 10% by weight solution viscosity in toluene of about 1.0 cp at 20°C.

[b] GPC.

[c] Vapor-pressure osmometry for fractions 1–10. Membrane osmometry for fractions 11–18.
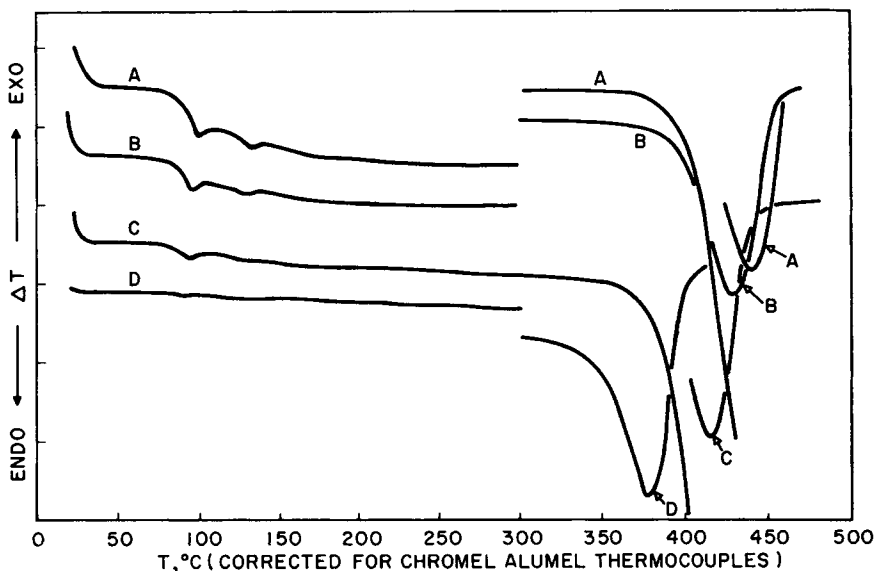
Fig. 1. DTA. Anionic polystyrene ($\bar{M}_n$ = 9,600): effect of heating rate. Sample size = 11 mg; ΔT (y-axis) = 0.5°C/division; heating rates: (A) = 30°, (B) = 20°, (C) = 10°, (D) = 1.5°C/min; samples, "as received."

mosphere of flowing nitrogen (Liquid Carbonic, 99.996% pure) at a rate of 30°C/min. An empty aluminum pan was used for a temperature reference.

Low molecular weight specimens which are designated "crushed" were prepared in the following manner. The "as received" sample was heated to 200°C at 2°C/min and then "quenched" over 18 min to room temperature (free cooling to room temperature made no difference). The resulting clear film was then granulated by applying pressure to the sides of the sample pan with a pair of forceps. This procedure produced particles which were approximately the size of common table salt.

Torsional Braid Analysis (TBA)

Specimens were prepared using 2-in. braids, from 10% solutions (g polymer/ml toluene). The solvent was removed from the mounted specimen by heating to 200°C at 2°C/min in a fast-flowing nitrogen atmosphere. Freely damped torsional oscillations were induced in the specimen intermittently during cooling to −195°C at 1.5°C/min and then heating to 200°C at 1.5°C/min in a slow-flowing, dry helium atmosphere. The experiment was controlled and data were acquired and processed using an automated system.[21,28] The analyzer provides digital printout on paper tape of the period (P = period of oscillations in seconds), logarithmic decrement ($\Delta \equiv \log_e A_i/A_{i+1}$, where A_i is the amplitude of the ith oscillation), and thermocouple voltage (mV). Thermomechanical plots of relative rigidity ($1/P^2$) and logarithmic decrement versus temperature (°C), were obtained from a computer-driven plotter (Calcomp Model 565) using punched cards as input. Use of the logarithmic decrement rather than the out-of-phase shear modulus (G'') results in amplification of the loss peaks at higher temperatures (since $G'' \simeq \Delta/\pi P^2$
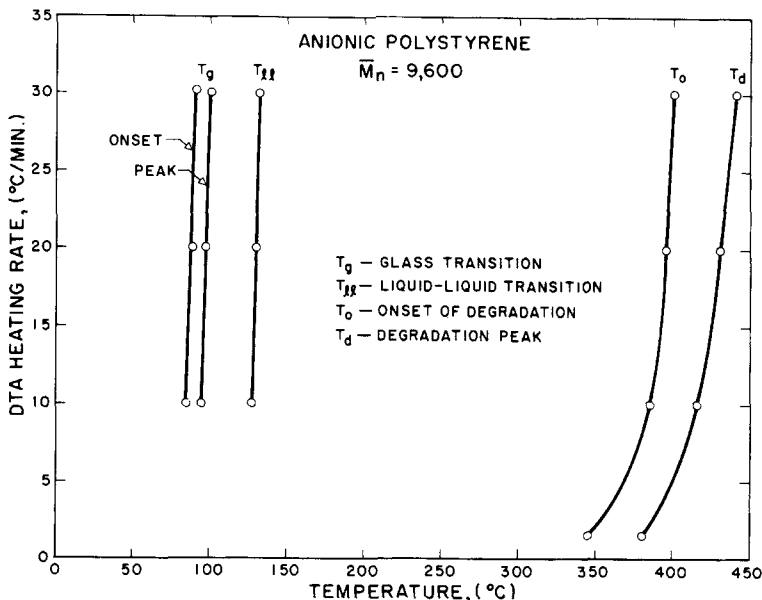
Fig. 2. DTA. Anionic polystyrene ($\bar{M}_n$ = 9,600): dependence of transition and degradation temperatures on heating rate (see Fig. 1).

and the period generally increases with temperature).[29,30] In this report, only the T_g and T_{ll} transitions are discussed; data obtained below T_g will form the basis of a future communication.

RESULTS

DTA

Investigation of the effect of heating rate on particulate anionic polystyrene ($\bar{M}_n$ = 9,600), from 1.5° to 30°C/min, indicates that a rapid heating rate (>10°C/min) is necessary for the clear observation of a T_{ll} transition (Fig. 1). A plot of transition and degradation temperatures as a function of heating rate shows an especially strong heating rate effect on the degradation temperature T_d (Fig. 2). (A study of the degradation of the anionic and thermal polystyrenes as a function of molecular weight by pyrolysis–molecular weight chromatography is under way.[31]) The temperatures for the onset of T_g and T_d are included in Figure 2; these were determined from the intersection of linear extrapolations of the initial baseline and the left side of the endotherm. The assigned temperatures for the T_g and T_{ll} transitions found at 30°C/min are 7° to 8°C higher than values obtained by linear extrapolation to low rates of heating (e.g., 1.5°C/min).

The effect of physical form of the DTA specimen is shown in Figure 3 (curves A, B, C, D, and E) for a sample of anionic polystyrene with a number average molecular weight of 3,100. Curve A is the result obtained during heating the "as received" particulate sample to 200°C at 30°C/min. (Information supplied with the anionic polystyrene samples from the Pressure Chemical Company indicates that the size of the particles is minus 6 mesh.)
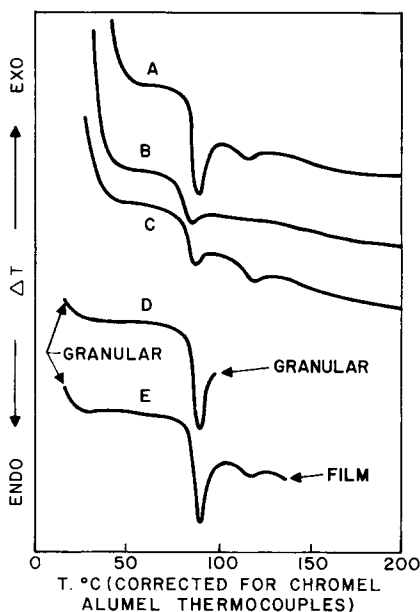
Fig. 3. Influence of physical form of anionic polystyrene ($\bar{M}_n$ = 3,100) on T_{ll}: $\Delta T/\Delta t$ = 30°C/min; (A) "as received"; (B) prehistory: "as received" sample heated to 200°C at 2°C/min followed by free cooling; (C) prehistory: same as (B) with the sample crushed to granular form; (D) "as received" heated to 100°C (see Fig. 4, top); (E) "as received" heated to 135°C (see Fig. 4, bottom).

The T_g and T_{ll} transitions are clearly observed. Curve B is the result of heating to 200°C at 30°C/min the film formed in experiment A. In this case, the glass transition is observed but the T_{ll} transition is not. The character of the DTA response through the glass transition region has been altered from a sharp endothermic peak to a baseline shift. This is presumably due to differences in prehistory. When the polymer film from experiment B is granulated and heated to 200°C at 30°C/min, both the T_g and T_{ll} endothermic peaks are once again observed (curve C). Curves D and E define the temperature prehistories used for the visual examination of the changes in physical form through the T_{ll} transition. In experiments D and E, "as received" sample was heated to 100° and 135°C, respectively, and then quenched to room temperature. The photographs (×100, Fig. 4) were obtained using a research microscope (Carl Zeiss). Granules are still observed (Fig. 4, top) after heating to above the T_g but below the T_{ll} transition (the black area with striations is the specimen container). However, a clear film (Fig. 4, bottom) formed (having cracks and concave dimple formations presumably due to escaping air bubbles) on heating to above the T_{ll} transition.

The effect of both molecular weight and physical form for the anionic and fractionated thermal polystyrene series on T_g and T_{ll} are shown in Figures 5 and 8, respectively. Numerical data are summarized in Tables III, IV, and V. The heating rate for all experimental runs was 30°C/min. For the "as received" particulate anionic polystyrene specimens (Fig. 5, left), a T_{ll} transition is observable for $\bar{M}_n < 111,000$ under the experimental conditions. Smaller amounts of polymer were used for specimens with $\bar{M}_n > 111,000$
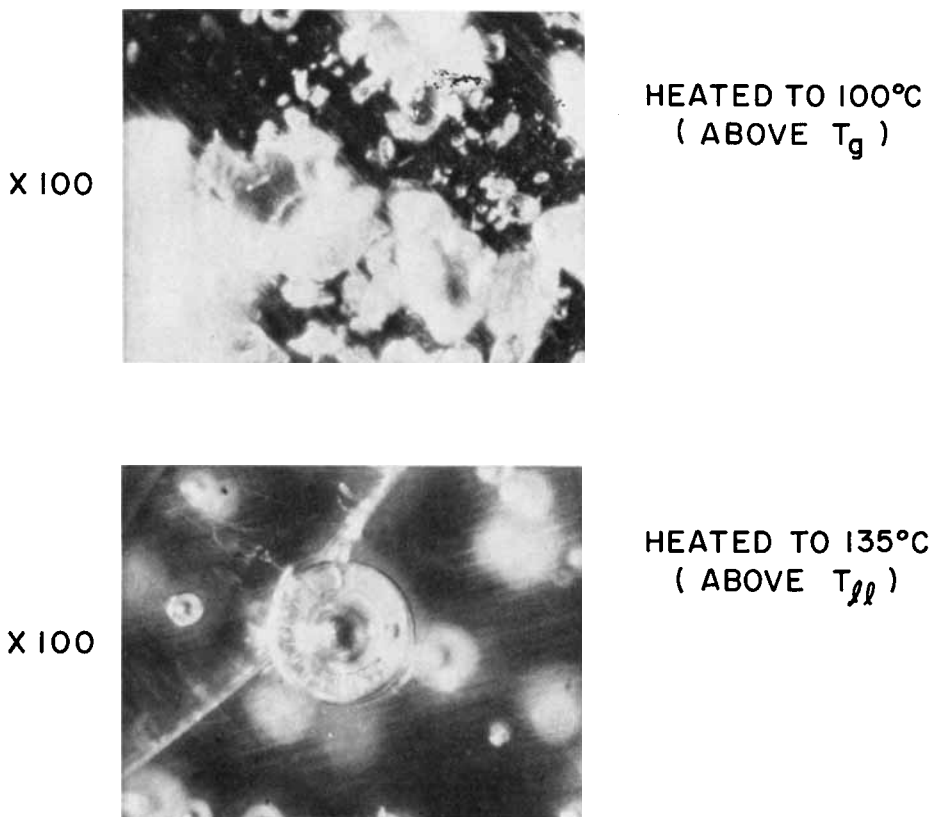
HEATED TO 100°C
(ABOVE T_g)

X 100

HEATED TO 135°C
(ABOVE T_{ll})

X 100

Fig. 4. Visual observations (×100) on granular anionic polystyrene ($\bar{M}_n$ = 3,100) after heating: top, results of prehistory shown in Fig. 3D; granules (black area is the sample container); bottom, results of prehistory shown in Fig. 3E; film (with crack and dimples).

which have lower bulk densities due to the method of isolation. Efforts were made to increase the amount of sample in the container by first making films from the bulky fibrous material by heating to 200°C at 2°C/min and then cutting them into smaller pieces. No change in the results was noted. Heating the higher molecular weight samples above 200°C did not reveal any information on T_{ll}. Anionic polystyrene specimens with a prehistory of heating to 200°C at 2°C/min (i.e., formed into a film for $\bar{M}_n$ < 111,000) showed no T_{ll} endothermic transition for all molecular weights (Fig. 5, right).

The T_g and T_{ll} transition temperatures for anionic polystyrene are plotted versus $1/\bar{M}_n$ (Fig. 6), as is customary in investigating the effect of free volume.[4] The curves were drawn using TBA data (see below), and the DTA results on "as received" polymers were added. The T_g plot shows two linear regions, each of which follows the relationship $T_g = T_g^\infty - K_g \bar{M}_n^{-1}$, with K_g = 20 × 10^4 and T_g^∞ = 386°K for $\bar{M}_n$ > 6.6 × 10^4, and K_g = 7 × 10^4 and T_g^∞ = 384°K for 10^3 < $\bar{M}_n$ < 6.6 × 10^4. These values agree fairly well with the literature[32]; for a number of polymers, K_g = 20 × 10^4 for M > 10^4 and $K_g \simeq 8$ × 10^4 for 10^3 < M < 10^4. For M < 10^3, K_g is reported to change to a smaller value[32]: this agrees with the present datum for $\bar{M}_n$ = 585 (see Table III). K_g parameters were determined from plots of log $\bar{M}_n$ versus log $(T_g^\infty - T_g)$
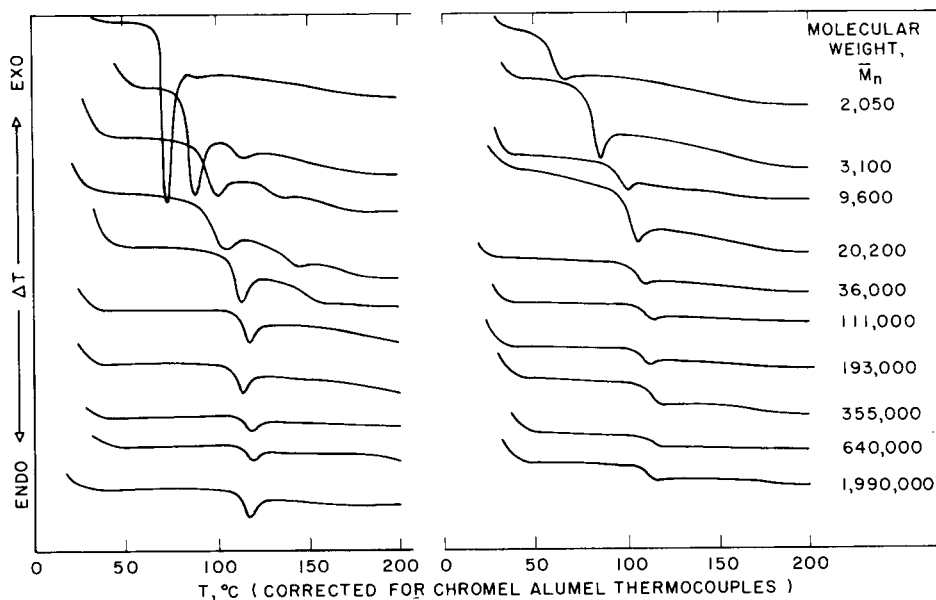
Fig. 5. DTA. Anionic polystyrene: effect of molecular weight and prehistory on T_g and T_{ll}: $\Delta T/\Delta t = 30°C/min$; left, "as received"; right, prehistory: films made by heating to 200°C at 2°C/min and free cooling.
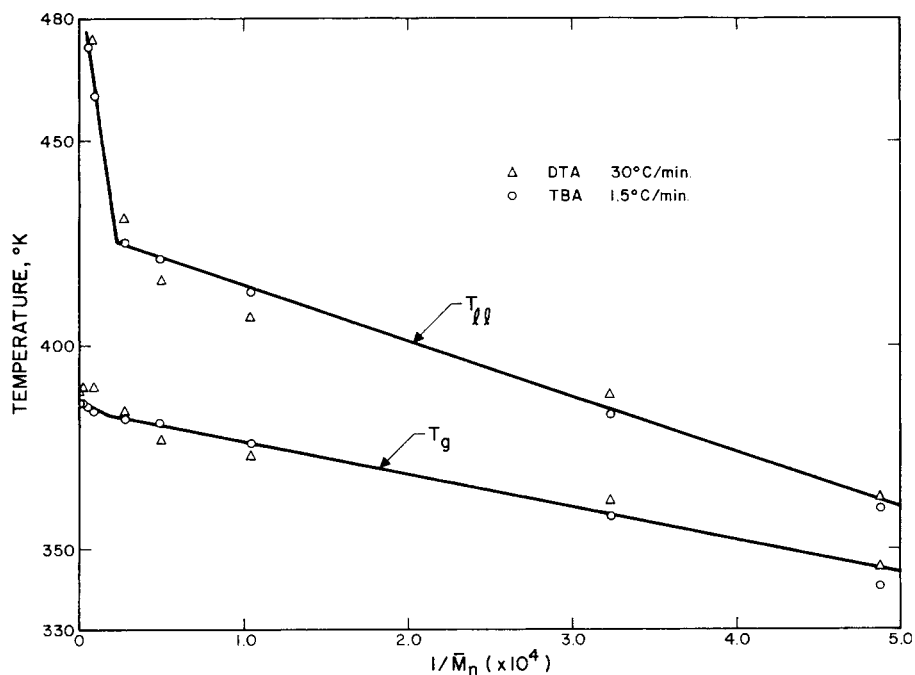

Fig. 6. DTA and TBA. Anionic polystyrene: T_g and T_{ll} vs. $1/\bar{M}_n$. (For DTA, T_g was defined as the peak of the endotherm.)

TABLE III
DTA. Anionic Polystyrene: Effect of Molecular Weight on T_g and T_{ll}

Monodisperse

| | | Granules[a] | | | | | | | | | Film[b] | | | |
| | | | | T_g, °K | | | | T_d, °K | | | | | T_g, °K | |
$\bar{M}_n$	$1/\bar{M}_n$ (× 10⁴)	Wt, mg	ΔT, °C/in.	Onset	Peak	T_{ll}, °K	T_g/T_{ll}, °K/°K	Onset	Peak	Wt, mg	ΔT, °C/in.	Onset	Peak
585	17.1	13	0.5	256	269	313	0.86	N	N	N	N	N	N
2,050	4.87	11	0.5	343	346	363	0.95	665	721	11	0.5	327	338
3,100	3.24	13	0.5	356	362	388	0.93	665	718	13	0.5	351	358
9,600	1.04	13	0.5	362	373	407	0.92	668	712	10	0.5	365	373
20,200	0.495	13	0.5	365	377	416	0.91	668	713	13	0.5	370	378
36,000	0.277	10	0.5	378	384	431	0.89	676	713	10	0.5	373	381
111,000	0.090	5	0.5	385	390	475	0.82	678	711	5	0.5	379	385
193,000	0.0518	5	0.5	381	386	—	—	669	710	5	0.5	376	383
355,000	0.0274	3	0.5	384	390	—	—	N	N	8	0.5	380	388
640,000	0.0156	6	0.5	385	390	—	—	680	711	5	0.5	381	388
1,990,000	0.0050	5	0.5	383	389	—	—	N	N	5	0.5	378	386

Bimodal Blend

(3,100 + 20,200; 1/1 Blend by Weight)	Wt, mg	ΔT, °C/in.	T_{g1}, °K	T_{g2}, °K	T_{ll}, °K	T_g/T_{ll}, °K/°K
Dry Mixture	13	0.5	361	373	403	—
Film formed from solution and crushed to granules	8	0.2	367	—	410	0.90

[a] "As received."

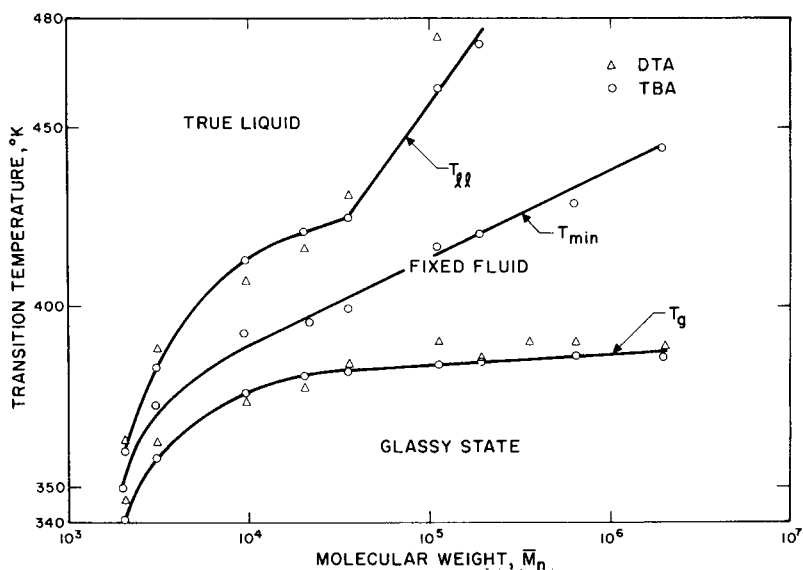[b] Prehistory: film formed by heating to 200° C at 2° C/min and free cooling; N, not determined.

Fig. 7. DTA and TBA. Anionic polystyrene: T_g, T_{min}, and T_{ll} vs. log $\bar{M}_n$. The designations of the three regions shown were adapted from ref. 16. A fixed fluid is considered to exist between T_g and T_{ll}.

with the data fitted to slopes of -1.[32] The values obtained by this method agreed with those determined from plots of T_g versus $1/\bar{M}_n$. [The same technique was used to determine corresponding K_{ll} values for $M < M_c$ (see below).] The plot of the T_{ll} transition temperatures versus $1/\bar{M}_n$ also has two regions (for $\bar{M}_n \geq 2,050$) which intersect at $\bar{M}_n \simeq 4 \times 10^4$. The region below $\bar{M}_n = 4 \times 10^4$ has a slightly higher negative slope than the T_g-versus-$1/\bar{M}_n$ plot with the ratio of T_g/T_{ll} (°K/°K) decreasing from 0.95 ($\bar{M}_n = 2,050$) to 0.90 ($\bar{M}_n = 36,000$) with increasing molecular weight (TBA data, Table VI). The higher molecular weight region of the T_{ll}-versus-$1/\bar{M}_n$ plot has a steep negative slope: in this region, the T_{ll} transition varies linearly with the logarithm of $\bar{M}_n$[10,11,16] (Fig. 7). For $M \gg M_c$, T_{ll} may be above the onset of thermal degradation. Table IV defines and summarizes the various constants for the T_g and T_{ll} transitions-versus-$1/\bar{M}_n$ relationships for the anionic samples.

Figures 8, 9, and 10 present corresponding results (T_g and T_{ll} transition data) for the series of samples of fractionated thermal polystyrene. Numerical data are summarized in Table IV and Table V. The T_{ll} transition is observed (Fig. 8, left) for all fractions examined ($\bar{M}_n = 1,880–111,000$). (It should be noted that T_{ll} data determined by TBA are about 10°C lower than values determined by DTA for the two thermal specimens examined by TBA.) These specimens for DTA were first heated to 200°C at 2°C/min to remove the diluent used in fractionation and were then crushed to granules. Fractionated thermal polystyrene specimens with a prehistory of heating to 200°C at 2°C/min (to form a film) showed no T_{ll} endothermic transition for all molecular weights (Fig. 8, right). The plots of T_{ll} and T_g versus $1/\bar{M}_n$ (Fig. 9) are similar to those for the anionic polystyrene series. The intersections of the two regions of the T_g and T_{ll} plots occur at $\bar{M}_n = 4 \times 10^4$ and $\bar{M}_n = 3.3 \times 10^4$, respectively. The parameters determined from the T_g peak data

TABLE IV
Anionic and Thermal Polystyrene: T_g and T_{ll} Parameters
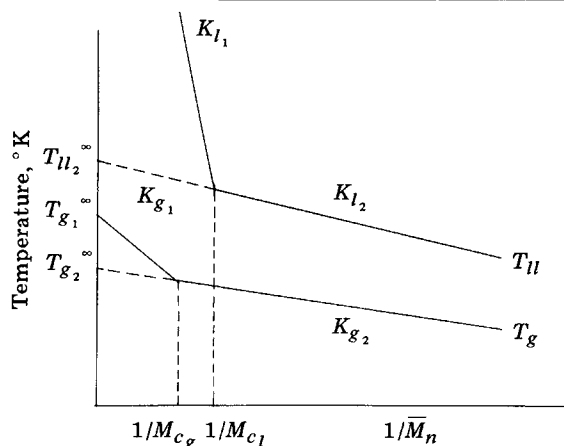
$$T_g = T_{g_1}^{\infty} - K_{g_1} \bar{M}_n^{-1} \qquad\qquad \bar{M}_n > M_{c_g}$$
$$T_g = T_{g_2}^{\infty} - K_{g_2} \bar{M}_n^{-1} \qquad\qquad \bar{M}_n < M_{c_g}$$
$$T_{ll} = T_{ll_1}^{\infty} - K_{l_1} \bar{M}_n^{-1} \qquad\qquad \bar{M}_n > M_{c_l}$$
$$T_{ll} = T_{ll_2}^{\infty} - K_{l_2} \bar{M}_n^{-1} \qquad\qquad \bar{M}_n < M_{c_l}$$

	Anionic (TBA data)	Thermal (DTA data)
$T_{g_1}^{\infty}$, °K	386	394
$T_{g_2}^{\infty}$, °K	384	386
M_{c_g}	6.6×10^4	4×10^4
K_{g_1} [a]	20×10^4	35×10^4
K_{g_2} [a]	7×10^4	8×10^4
$T_{ll_2}^{\infty}$	429	435
M_{c_l}	4×10^4	3.3×10^4
K_{l_1}	272×10^4	228×10^4
K_{l_2} [a]	15×10^4	11×10^4

[a] Values obtained from intercept of plots of log $(T_g^{\infty} - T_g)$ and log $(T_{ll}^{\infty} - T_{ll})$ vs. log $\bar{M}_n$ with the data fitted to slopes of -1.

(DTA) are $K_g \simeq 35 \times 10^4$ and $T_g^{\infty} = 394°K$ for $\bar{M}_n > 4 \times 10^4$, and $K_g = 8 \times 10^4$ and $T_g^{\infty} = 386°K$ for $1{,}880 < \bar{M}_n < 4.0 \times 10^4$. T_g and T_{ll} parameters are summarized in Table IV. Also included in Fig. 9 is the dependence of the onset of the glass transition temperature (measured by DTA) versus $1/\bar{M}_n$. The ratio of T_g/T_{ll} (°K/°K) decreased from 0.91 ($\bar{M}_n = 1{,}880$) to <0.88 ($\bar{M}_n > 23{,}000$) with increasing molecular weight (DTA, Table V).

The effect of blending two "monodisperse" anionic polystyrene samples to form a bimodal mixture on the T_g and T_{ll} transitions is illustrated in Figure 11. Experiments A and B show the result of heating "as received" samples with $\bar{M}_n = 20{,}200$ and $3{,}100$ to 200°C at 30°C/min. The T_g and T_{ll} transitions are observable for each sample. Curve C resulted from the 1/1 (by weight) dry blending of the polymer samples used in experiments A and B.

The blend was made by vigorously shaking a bottle containing small amounts of the polymer granules. Each glass transition is observable but only one intermediate T_{ll} endotherm is present (see Table III). The sample used for experiment C was dissolved in toluene, formed into a film by drying to 200°C at
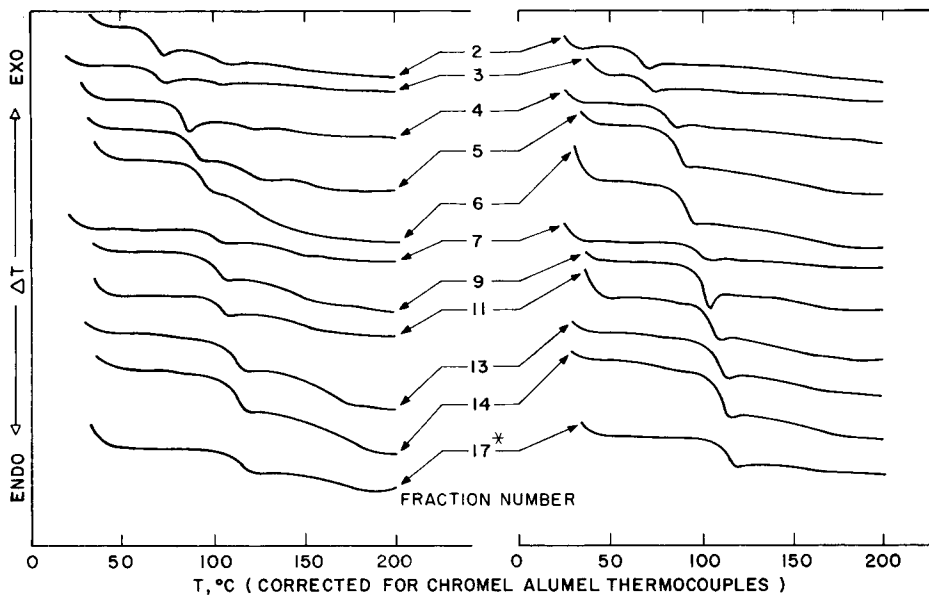
Fig. 8. DTA. Thermal polystyrene fractions: effect of molecular weight and prehistory on T_g and T_{ll}: $\Delta T/\Delta t = 30°C/min$; numbers identify fractions (Table II); left, prehistory: R.T. → 200°C at 2°C/min, free cooling and then crushed to granules; right, prehistory: films from DTA experiments on left. *Film only cut into pieces because of toughness.
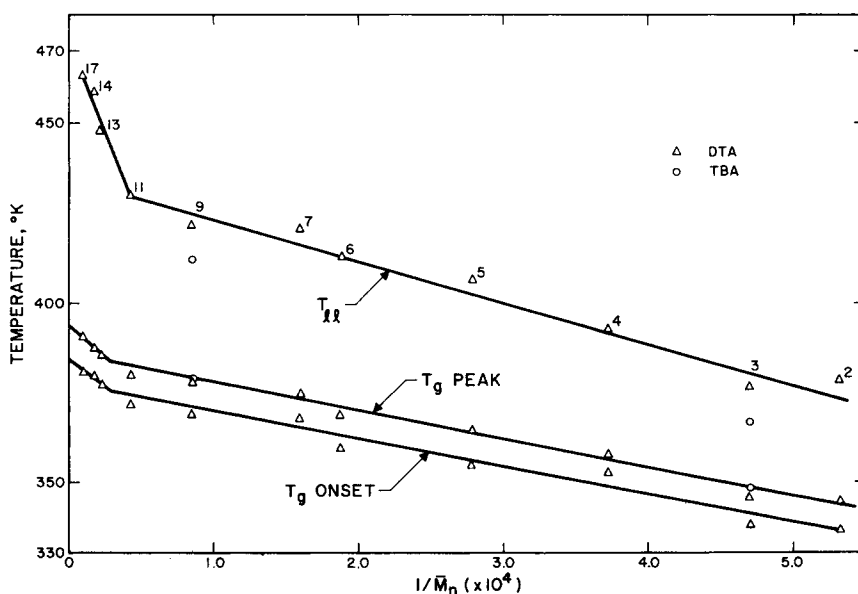
Fig. 9. DTA and TBA. Thermal polystyrene fractions: T_g and T_{ll} vs. $1/\bar{M}_n$. Numbers identify fractions (Table II).
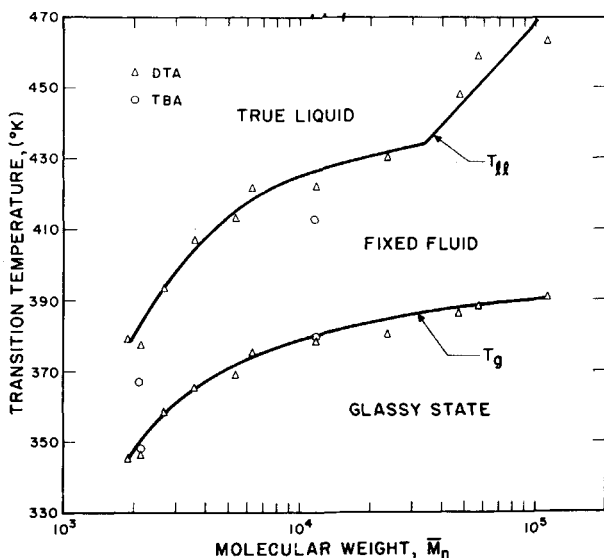
Fig. 10. DTA and TBA. Thermal polystyrene fractions: T_g and T_{ll} vs. log $\bar{M}_n$. Compare with Fig. 7.

$2°C/min$ and crushed into granules before being heated to 200°C at 30°C/min (experiment D). Single T_g and T_{ll} transitions are present which occur at temperatures between those of the components. If the film formed from solution is not crushed, no T_{ll} transition is observable (experiment E). Blending results obtained by TBA are given below.

TBA

Typical results for a torsional braid analysis (TBA) experiment are shown in Figure 12. A solution-impregnated braid of anionic polystyrene ($\bar{M}_n$ = 20,200) was mounted in the TBA apparatus and heated to 200°C at 1.5°C/min in an environment of fast-flowing helium to remove solvent. The experimental run involved immediately cooling to liquid nitrogen temperature at 1.5°C/min and then heating to 200°C at 1.5°C/min in a slow-flowing, dried helium atmosphere (Helium—M. G. Scientific, Grade 5.5 with Oxisorb Purification System). Data shown are for 200° → 80°C (△) and 80° → 200°C (+). The TBA dynamic mechanical spectra, logarithmic decrement (△) and relative rigidity $(1/P^2)$ versus temperature (°K), show that the glass transition (108°C, 0.6 Hz) and the T_{ll} transition (148°C, 0.3 Hz) are discernible and reversible with heating and cooling.

Figure 13 shows corresponding results for a fractionated thermal polystyrene specimen ($\bar{M}_n$ = 11,800, fraction number 9) with T_g (106°C, 0.6 Hz) and T_{ll} (139°C, 0.3 Hz) being discernible and reversible (Table VII).

A composite figure illustrating TBA results (logarithmic decrement versus T, °C) for ten anionic polystyrene samples varying in molecular weight from $\bar{M}_n$ = 585 to 1,990,000 is shown in Figure 14. The corresponding rigidity results are presented separately in Figure 15. The curves presented are for the decreasing temperature programming mode and have been displaced vertically by arbitrary amounts for the purpose of clarity. The T_{ll} transition is ob-

TABLE V
DTA. Thermal Polystyrene Fractions: Effect of Molecular Weight on T_g and T_{ll}

Fraction no.	$\overline{M}_n$	$(1/\overline{M}_n)$ $\times 10^4$	Weight, mg	ΔT, °C/in.	Granules[a] T_g, °K Onset	Peak	T_{ll}, °K	$(1/T_{ll})$ $\times 10^3$	T_g/T_{ll} °K/°K	Film[b] T_g, °K Onset	Peak
2	1,880	5.32	9	0.5	337	345	379	2.64	0.91	334	343
3	2,130	4.69	7	0.5	338	346	377	2.65	0.92	340	346
4	2,690	3.72	6	0.5	353	358	393	2.54	0.91	348	358
5	3,600	2.78	11	0.5	355	365	407	2.46	0.90	355	365
6	5,380	1.86	15	0.5	360	369	413	2.42	0.90	358	368
7	6,270	1.59	5	0.5	368	375	421	2.38	0.89	367	373
9	11,800	0.848	9	0.5	369	378	422	2.37	0.89	369	376
11	23,500	0.425	7	0.5	372	380	430	2.33	0.88	371	380
13	47,200	0.212	11	0.5	378	386	448	2.23	0.86	376	385
14	56,700	0.176	14	0.5	380	388	459	2.18	0.85	379	386
17	111,000	0.090	8	0.5	381	391	463	2.16	0.84	381	391

[a] Prehistory: heat to 200°C at 2°C/min. Crush resulting film into granules at room temperature by applying pressure to the outside of sample pan with forceps.
[b] Prehistory: film formed as the result of experiment (a).

TABLE VI

TBA. Anionic Polystyrene: Effect of Molecular Weight on T_g and T_{ll}[a]

$\bar{M}_n$	T_g, °K (Hz)	T_{min}, °K (Hz)	T_{ll}, °K (Hz)	$(1/T_{ll}) \times 10^3$	T_g/T_{ll}, °K/°K
"Monodisperse"					
585	269 (.56)	281 (.35)	290 (.31)	3.45	0.93
2,050	341 (.57)	350 (.35)	360 (.28)	2.78	0.95
3,100	358 (.63)	373 (.40)	383 (.36)	2.61	0.93
9,600	376 (.65)	393 (.35)	413 (.30)	2.42	0.91
20,200	381 (.63)	396 (.36)	421 (.30)	2.37	0.90
36,000	382 (.63)	398 (.34)	425 (.29)	2.35	0.90
111,000	384 (.63)	417 (.33)	461 (.28)	2.17	0.83
193,000	385 (.63)	421 (.35)	>473 (.29)	<2.11	0.81
640,000	386 (.70)	429 (.34)	—	—	—
1,990,000	386 (.71)	443 (.37)	—	—	—
Bimodal Blend					
3,100 and 20,200; 1/1 Blend by weight	368 (.63)	383 (.36)	405 (.30)	2.47	0.91
20,200 and 1,990,000; 1/1 Blend by weight	381 (.64)	401 (.34)	408 (.32)	2.45	0.93

[a] Transition temperatures: determined from TBA logarithmic decrement data in the decreasing temperature mode using 2-in. braids. Specimen preparation: 10% (g/ml) of polystyrene in toluene. Temperature prehistory: drying; R.T. → 200° C at 2° C/min to remove solvent. Environmental gas:helium.

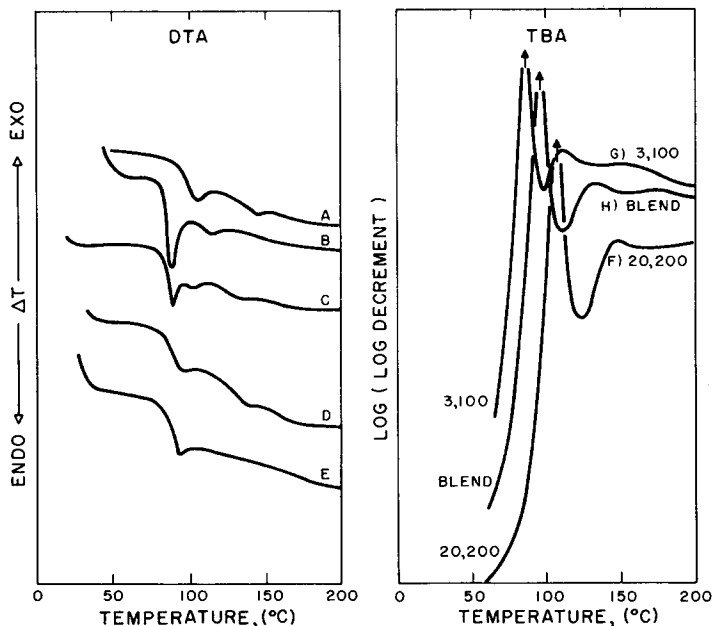Fig. 11. Left, DTA. Blending of anionic polystyrene: effect on T_g and T_{ll}; $\Delta T/\Delta t = 30°C/$ min; (A) $\bar{M}_n = 20,200$, "as received"; (B) $\bar{M}_n = 3,100$, "as received"; (C) 1/1 dry mixture of "as received" polymers used in experiments A and B; (D) prehistory: film formed from toluene solution of polymers used in experiment C, dried to 200°C at 2°C/min, and then crushed to granules; (E) prehistory: film formed from DTA experiment D.

Right, TBA. Blending of anionic polystyrene: effect on T_{ll}; (F) $\bar{M}_n = 20,200$; (G) $\bar{M}_n = 3,100$; (H) 1/1 blend of A and B. Compare with Fig. 16.

servable in the loss curves for all specimens with $\bar{M}_n \leq 111,000$. In addition, a T_{ll} transition above 200°C for $\bar{M}_n = 193,000$ is indicated. Numerical data from these curves are tabulated in Table VI. Plots of the T_g and T_{ll} transition temperatures determined by TBA for anionic polystyrene versus $1/\bar{M}_n$ are presented in Figure 6 and versus log $\bar{M}_n$ in Figure 7. The results are similar to those determined using DTA (Figs. 6 and 7).

$T_{\min}$ is defined as the temperature of minimum damping between the T_g and T_{ll} transitions (Tables VI and VII). The temperature and breadth of the damping minimum increase while the damping level decreases (not shown) with increasing molecular weight. The damping level at $T_{\min}$ gives an indication of the elastic effects in the polymer. The lower the damping level, the greater the melt elasticity which for high molecular weights may result in part from chain entanglements. The possibility of using the $T_{\min}$ temperature as a means for determining the molecular weight of a specimen, and the breadth of the minimum as a measure of the molecular weight distribution has been discussed by others.[2,33,34,35] Included in Figure 7 is a plot of the values of $T_{\min}$ versus log $\bar{M}_n$. The linearity at higher molecular weight concurs with unpublished results.[36]

The effect of blending (1/1 by weight) two "monodisperse" anionic polystyrene samples ($\bar{M}_n = 20,200$ and 3,100) on the T_g and T_{ll} transitions is illustrated in Figure 11 (right). Specimens were prepared from 10% toluene solution (g polymer/ml solvent) by drying to 200°C. The logarithmic decrement
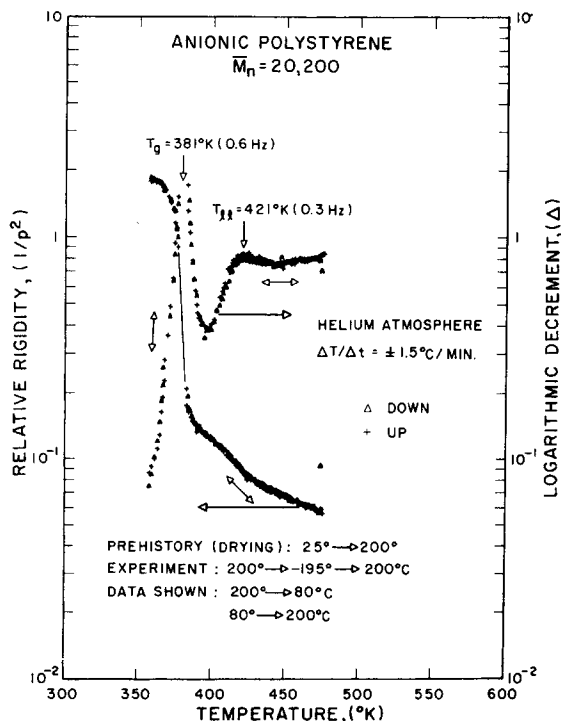
Fig. 12. TBA. Thermomechanical spectra [relative rigidity and logarithmic decrement vs. temperature (°K)] of anionic polystyrene, $\bar{M}_n$ = 20,200.

for both of the "monodisperse" samples and the bimodal blend are plotted versus temperature, °C. The data presented are for the decreasing temperature programming mode with the curves displaced vertically for clarity. As in the DTA results, the T_g and T_{ll} transitions for the blend of two low molecular weight species are between those of the components (Table VI). Using the transition temperature-versus-structure equation,[37] generalized to include the T_{ll} transition, i.e.,

$$1/T_{ll} = W_1/{_1}T_{ll} + W_2/{_2}T_{ll}$$

where ${_1}T_{ll}$, ${_2}T_{ll}$, and T_{ll} are the values of the T_{ll} (°K) transition for polymer 1, polymer 2, and the blend of 1 and 2, and W_1 and W_2 are the respective weight fractions of polymers 1 and 2, the value calculated for the blend (i.e., 401°K) is close to that determined experimentally (i.e., 405°K). This suggests further that chain ends (free volume) determine the T_{ll} transition temperature.

Examination of another solution-formed blend (1/1 by weight) of two anionic polystyrene samples with $\bar{M}_n$ of the components on either side of the critical molecular weight M_c = 40,000 (low molecular weight component, $\bar{M}_n$ = 20,200; high molecular weight component, $\bar{M}_n$ = 1,990,000) indicates that the thermomechanical loss above T_g is a summation of the components (Fig. 16). The overall thermomechanical behavior ($T > T_g$) of the blend resembles the higher molecular weight component but there is a small damping peak at 135°C which is due to the influence of the lower molecular weight component. (The glass transition temperatures of the components of the
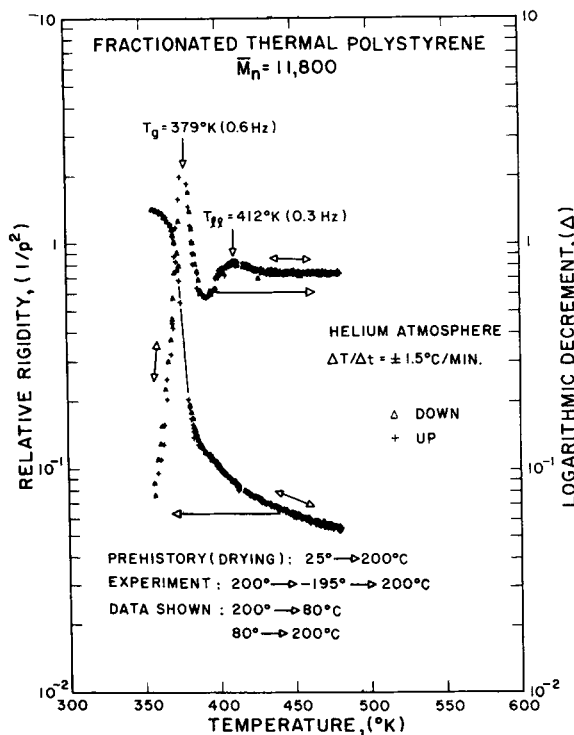
Fig. 13. TBA. Thermomechanical spectra [relative rigidity and logarithmic decrement vs. temperature (°K)] of fractionated thermal polystyrene, $\bar{M}_n = 11,800$.

blend are too close together to test their resolution.)   The apparent shift in the T_{ll} transition of the lower molecular weight component (from 148°C to 135°C) results from addition of the shoulder on the loss peak due to the glass transition of the high molecular weight component to the loss region of the lower molecular weight component.

DISCUSSION

Three conditions aid the observation of the T_{ll} transition in amorphous polystyrene using DTA: (1) high heating rate (i.e., $\Delta T/\Delta t > 10°C/min$); (2)

TABLE VII
TBA. Thermal Polystyrene Fractions: Effect of Molecular Weight on T_g and T_{ll}[a]

Fraction no.	$\bar{M}_n$	T_g, °K (Hz)	T_{min}, °K (Hz)	T_{ll}, °K (Hz)	T_g/T_{ll}, °K/°K
3	2,130	348 (.50)	358 (.33)	367 (.30)	0.95
9	11,800	379 (.57)	393 (.34)	412 (.29)	0.92
Unfractionated polymer	1,532	360 (.59)	384 (.34)	$\simeq 398$[b] (.32)	0.90

[a] Transition temperatures: determined from TBA logarithmic decrement data in the decreasing temperature mode using 2-in. braids. Specimen preparation: 10% (g/ml) of polystyrene in toluene. Temperature prehistory: drying; R.T. → 200°C at 2° C/min to remove solvent. Environmental gas: helium.

[b] Broad.

TABLE VIII
Summary of Some Systematic Studies[a] of T_{ll} Transitions in Homopolymers and Copolymers

No.	Polymer	Method	Type of specimen	Mol. wt/composition range	Evidence for M_c[b]	Year	Authors and References
1	Poly(vinyl chloride)	penetrometer	PF[c]	10^3–10^5	yes	1950	Kargin and Malinsky [10,11]
2	Polystyrene	penetrometer	PF[c]	10^3–10^5	yes	1950	Kargin and Malinsky [10,11]
3	Polystyrene and hexachlorodiphenyl	thermal diffusivity	PF[c]	2300 and 23000/ 0–100% diluent	N.A.	1955	Ueberreiter and Purucker [56]
4	Polystyrene and plasticizer	falling-ball viscosity	H[d]	0.085–0.5 wt fraction tritolyl phosphate and dioctyl-phthalate	N.A.	1967	Colborne [57]
5	Polybutadiene (~50% cis, 50% trans, $T_g \sim -60°C$)	dynamic mechanical[e] (50 Hz)	H[d]	10,000 to 305,000	no[f]	1970	Sidorovich et al. [2]
6	Polystyrene	NMR: T_1 and $T_{1\rho}$[g]	A[h]	900 to 1.8×10^6	no	1970	Connor [47]
7	Butadiene-co-acrylonitrile	creep, DTA, gas permeation[i]	H[d]	29, 31, and 35% acrylonitrile	no	1970	Geiszler et al. [58]
8	Poly(methyl-methacrylate)	thermal diffusivity[j]	PF[c]	200 to 4.5×10^6	no	1972	Ueberreiter and Naghizadeh [53]

9	Polystyrene	DTA	A^h	6,400 to 694,000	no	1974	Utracki[59]
10	Plasticized PVC	melt viscosity[k]	H^d	3—60 wt-% plasticizer	N.A.	1974	Utracki[59]
11	Polystyrene	DTA and TBA	A^h, PF[c]	600 to 2 × 10⁶	yes	current	Stadnicki et al. (this paper)
12	Polystyrene bimodal blends	TBA	H^d	2,000–110,000	yes	current	Glandt et al. (following paper)

[a] "Systematic studies" implies the use of one or more experimental techniques on a series of polymers of known molecular weight or on co-polymers or blends covering a known range of composition. Omitted from this tabulation are the polystyrene results of refs. 4, 7, and 63, which are conflicting.

[b] M_c = Critical molecular weight for chain entanglement; N.A. = Not applicable

[c] PF = Precipitated fractions.

[d] H = Heterogeneous, either "as polymerized" or by blending.

[e] Polybutadiene of 10,000 to 305,000 MW dispersed in polybutadiene of 10⁶ MW.

[f] All specimens and blends were above M_c in molecular weight.

[g] Nonexponential decay of $T_{1\rho}$ on high-temperature side of T_g was indicative of (1) a second process, (2) crystallinity, or (3) broad molecular weight distribution. Since (2) and (3) could be eliminated, the author suggested a T_{ll} process.

[h] A = Anionic, narrow molecular weight distribution.

[i] The authors suggest some degree of ordering or some low-grade crystallinity in the butadiene parts of the chain.

[j] Prof. Ueberreiter supplied us with a fraction of PMMA of 25,000 MW. By TBA at 2°C/min (heating and cooling), it shows a T_g loss peak at 110°C (~1 Hz) compared with the static value of 103°C and a T_{ll} peak at 173°C (≃0.3 Hz) compared with the upper temperature break of 161°C. The strong β-peak observed at 30°C by TBA indicates that this fraction is highly syndiotactic (see Fig. 5 of ref. 21).
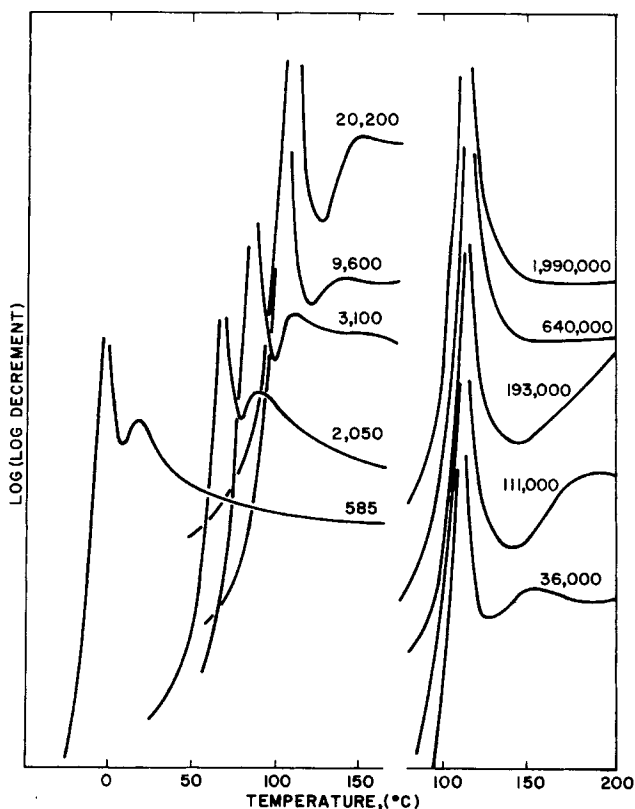
[k] Change in slope of log η-vs.-$1/T$ plots.

Fig. 14. TBA. Thermomechanical spectra [logarithmic decrement vs. temperature (°C)] of anionic polystyrene: effect of molecular weight on T_g and T_{ll}. Curves have been displaced vertically by arbitrary amounts for purposes of clarification. Line drawings are shown for the decreasing temperature mode.

low molecular weight (i.e., $\bar{M}_n < 111,000$); and (3) particulate form for the sample. On the basis of visual observations, the DTA response is due to flow. The "endothermic" peak is a consequence of an increase in heat transfer surface area as the geometry of the specimen changes with respect to its container. As such, no changes in thermal properties (such as heat capacity) of the polymeric material are necessary for the observation of the T_{ll} "transition" by DTA. Observation of the transition is suppressed by low heating rates which do not allow discrete changes in the geometry of the specimen, by high molecular weights for which the specimens do not flow in the time/temperature scale under the low (gravitational) stress level of the experiment, and by use of a specimen in film form for which the surface area for heat transfer has been established. In order to assign a temperature to the transition by DTA, a compromise is made between a rapid heating rate required for the clear observation of an "endotherm" and the period of time required for flow. Although only a macroscopic response is observed by DTA, it must have its origin at the molecular level.

The other approach used in this work for examining the T_{ll} transition involved torsional pendulum experiments performed above the glass transition
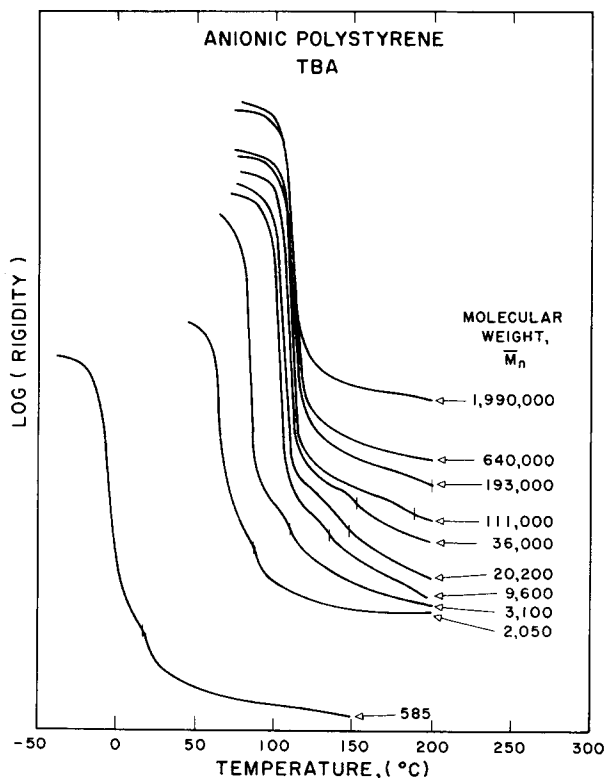
Fig. 15. TBA. Thermomechanical spectra [rigidity vs. temperature (°C)] of anionic polysty-rene (see caption for Fig. 14). Vertical tick marks designate the location of the T_{ll} peaks (loga-rithmic decrement). See caption of Fig. 14.

temperature. In these the polymer was supported as a continuous film on glass fibers (TBA), and measures of the storage $(1/P^2)$ and loss (logarithmic decrement) moduli were obtained at about 1 Hz as a function of temperature. For the same two series of polystyrenes examined by DTA, distinct maxima in loss were observed above the glass transition temperature with both in-creasing and decreasing modes of temperature change. The temperature of the transitions corresponded with the results obtained using DTA.

What then is the molecular basis of the T_{ll} transition? A summary of rele-vant facts follows:

1. The reversibility of the data for the T_{ll} loss peak with respect to tem-perature indicates that the transition as observed by TBA is not due to an order/disorder process unless the ordering occurs rapidly on cooling. In this respect, it behaves like the glass transition. (In a TBA experiment in which a crystallizable specimen is cooled from the fluid state through the solid state and heated back to the fluid state, crystallization often occurs at a lower tem-perature than melting and gives rise to thermohysteresis.[20,21])

2. The linear dependence of the T_{ll} and T_g transition temperatures on re-ciprocal number-average molecular weight for $2,000 < \bar{M}_n < 30,000$ indicates that free volume plays a critical role for their occurrence. The type of aver-aging of the T_{ll} transition data for the anionic polystyrene blend (both com-ponents with $\bar{M}_n$ below 40,000) appears to support this observation.
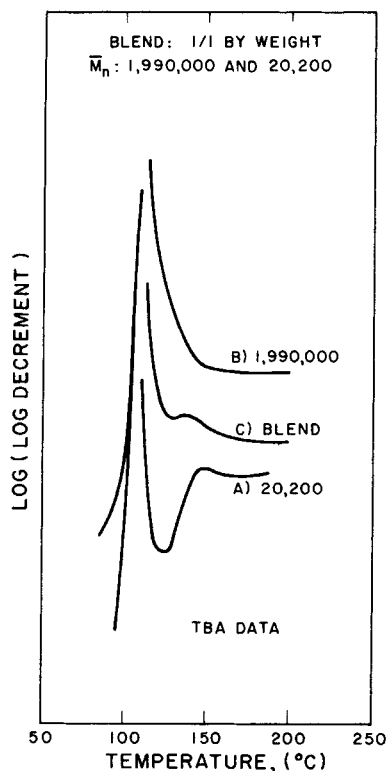
Fig. 16. TBA. Blending of anionic polystyrene: effect on T_{ll}: (A) $\bar{M}_n = 20,200$; (B) $\bar{M}_n = 1,990,000$; (C) 1/1 blend of A and B. Compare with Fig. 11.

3.   The particular molecular motion in question involves a modified mechanism above a critical molecular weight.   From stress relaxation and other measurements, a molecular weight of the same order of magnitude has been reported for the onset of chain entanglements.[38,39,40,41]   It appears that the presence of chain entanglements at high molecular weights interferes with the basic relaxation process, and is responsible for the different functional relationship of the T_{ll} transition (see Figs. 6, 7, 9, and 10).   Added support for this is found in the disappearance of the T_{ll} transition (by DTA) for high molecular weight polystyrene specimens and its reported diminishment with crosslinking for polybutadiene[2] and other rubbers.[3]

The temperature of the T_{ll} transition for any given molecular weight ($\bar{M}_n < \sim 40,000$) is somewhat lower, and the critical molecular weight M_c is slightly higher for the anionic series than for the fractionated thermal polystyrene series.   This may be due to the n-butyl chain ends acting as an internal plasticizer allowing this transition to occur more readily.   Since the tacticity assignments for the anionic and the thermal polystyrenes are similar, tacticity itself is probably not a factor.   It is interesting to note that the type of chain end appears to have a small influence on T_g since T_g^{∞} (thermal) $> T_g^{\infty}$ (anionic) [T_g^{∞} (thermal) $= 394°K$ (DTA), T_g^{∞} (anionic) $= 386°K$ (TBA)].   However, the exact temperature of the transitions observed by DTA at a constant heating rate will depend on the surface area available for heat transfer,
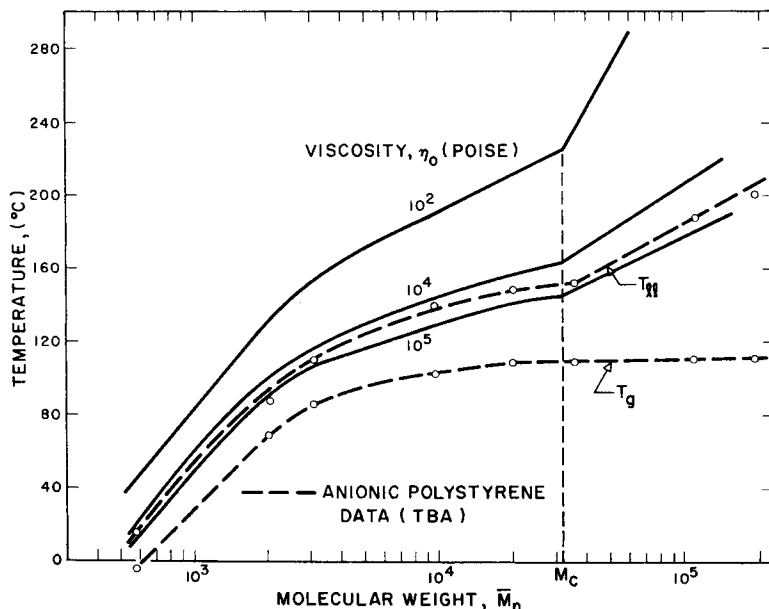
Fig. 17. Polystyrene. Zero-shear melt viscosity data. Temperature (°C) vs. log $\bar{M}$ for different isoviscous levels, following Fig. 15 of ref. 41 and using data replotted from ref. 44 (solid lines). Data points and dashed lines are for the T_{ll} and T_g transitions of anionic polystyrene vs. $\bar{M}_n$ of the present work (see Fig. 7). Note that $\bar{M}_n$ is used for the abscissa rather than $\bar{M}_w$ inspite of the dependence of η_0 on the latter. This mode of presentation is valid when $\bar{M}_w/\bar{M}_n$ is constant (as for the fractions of ref. 44 and for the anionic polymers of the present work). Further research has established that the T_{ll} transition depends uniquely on $\bar{M}_n$ and not on $\bar{M}_w$.[51]

i.e., the shapes, sizes, and arrangement of the particles in the sample pan. The higher value of the critical molecular weight for the glass transition of the anionic vis à vis the thermal polystyrenes may also be a reflection of the plasticizing n-butyl endgroups.

Although experimental results (TBA and DTA) on a blend of anionic polystyrene samples, each with a molecular weight below M_c, show that both the T_g and T_{ll} transitions occur at temperatures between those of the components, when a low molecular weight sample was blended with a high molecular weight material, a different effect was observed (by TBA) in that mechanical loss in the T_{ll} region appeared to be a summation of the individual species. The latter result is similar to that reported using bimodal blends of polybutadiene[2] where the high molecular weight material acts as a supporting matrix for the study of the low molecular weight component. It appears that the short chains of the low molecular weight component exhibit molecular motion without interference from the entangled network of the high molecular weight matrix. The possibility also exists that the two components separate into domains.

4. Under the experimental conditions, the T_{ll} transition is found to correspond visually to the flow temperature by DTA. In the temperature region between T_g and T_{ll} the polystyrene specimen is a fixed fluid (as defined in ref. 16) under the experimental conditions. Above T_{ll}, the molecular motion

is such that the specimen is a true liquid capable of flow. The T_{ll} transition temperature separates two regimes of flow and would presumably decrease in value with a prolonged experimental time scale. As such, the temperature interval $T_g < T < T_{ll}$ would correspond to the rubbery plateau region determined from stress relaxation measurements.[42,43] The T_{ll} transition temperature would then approximately represent the inflection point in the modulus curve above the plateau region (see also Fig. 15).

From dilatometric studies of anionic polystyrene ($\bar{M}_n$ = 51,000), it has been suggested[7] that there is a departure from equilibrium below 170°C and that full attainment of equilibrium below ~170°C is prevented by a freezing-in process. This conclusion agrees with the concept that a fixed fluid exists between the T_g and T_{ll} transitions. Equilibrium (in the time scale of the TBA and DTA experiments) is only established above the T_{ll} transition.

Plots of log viscosity (η) versus $1/T°K$ (which are linear for simple liquids) show complex behavior for high molecular weight molecules above T_g. For polystyrene at fixed shear rates the log η versus $1/T°K$ relationship has been interpreted to show two approximately linear regions whose point of intersection depends on the molecular weight.[1] This intersection point has been associated with the T_{ll} transition.[1] Others have concluded that log η follows a $1/T^6$ relationship and do not invoke the idea of a T_{ll} transition.[4]

Since viscosity is directly related to the time required for flow under defined conditions, the viscosity in a sense can be regarded as the time scale of an experiment to determine flow. For a fixed stress level (e.g., gravity), there is a particular viscosity for which flow will occur in a time scale of about 1 sec. This viscosity is around 10^4 poises (say). The heat transfer parameters which would affect the results in an actual experiment (e.g., heat capacity, density, thermal conductivity) are essentially independent of molecular weight. If temperature versus log M for a fixed viscosity ($\eta = 10^4$ poises) is plotted, a curve displaying the same character as Figures 7 and 10 results, with a change in the functional relationship occurring around $\bar{M}_n$ = 35,000.[41]

It has been suggested that this break corresponds to the onset of chain entanglements.[41] It might appear to be only fortuitous that the choice of a viscosity of 10^4 poises led to a M_c of 35,000. The choice of a different isoviscous level (e.g., $\eta = 10^5$ poises) would represent flow behavior under a different (longer) time scale which might be expected to give rise to a different critical molecular weight. Further analysis of the original literature[44] shows that this is not so (Fig. 17). This is due to the fact that all data reported are for zero-shear melt viscosity. This does not preclude the possibility of a different M_c at different time scales. However, shear rate studies indicate that M_c is not frequency dependent.[40] The decreasing slope of the T-versus-log M plot above M_c with higher isoviscous levels indicates that the effect of chain entanglements will not be significant at long time scales. The T_{ll} and T_g-versus-molecular weight curves would be expected to coincide at long time scales. This extrapolation supports the hypothesis of the isoviscous state for the glass transition and implies that, while there is sufficient thermal energy for flow just above T_g, the flow process will take a long time. The effect of chain entanglements on T_g is alluded to later. The level of isoviscosity for the T_{ll} transition for anionic polystyrene of the present work (TBA data) is interpolated from Figure 17 to be between 10^4 and 10^5 poises. An empirical

equation for polystyrene relating viscosity to temperature and carbon chain length (Z = number of atoms in the backbone of a polymer chain) is

$$\log \eta = 3.4 \log Z + 2.7 \times 10^{16}/T^6 - 9.51 \text{ for } Z > Z_c$$

where Z_c is the critical carbon chain length for entanglements.[45] Assuming an isoviscous level, this equation indicates that the viscosity for the T_{ll} transition observed by TBA is 8.9×10^4 poises for the anionic series above M_c, which is in accord with the interpolation made above using isoviscosity data from the literature (Fig. 17).

The elementary process for viscous flow in polymer melts consists of the displacement or jump of small segments of the molecules rather than the displacement of the entire molecule as a unit. Because these moving segments are attached by primary valence bonds to the polymer backbone, there must be an intramolecular cooperation of the moving segments for flow to progress. For high molecular weight polymers, additional intermolecular restrictions (entanglements) must be overcome.

The T_{ll} transition is considered to represent the onset of chain slippage which facilitates irreversible, nonrubbery flow. Although considerable cooperative segmental motion would be necessary for occurrence of the T_{ll} transition and flow, the entire polymer chain need not move as a unit. However, the latter mechanism for flow probably does occur at low molecular weights. If dynamic mechanical transitions are interpreted as the breakdown of different types of secondary bonding, thus allowing a particular molecular motion,[46] then the T_{ll} transition would correspond to the point where interchain (van der Waals) forces are overcome. In a sense, the T_{ll} transition might thus be regarded as the "melting point" of the polymer under external stress, which, being amorphous, does not have a true first-order transition.[47]

For many polymers a crystalline phase, premelting transition, designated α_c, occurs at a temperature T_{α_c} where T_{α_c} (100 Hz) $\simeq 0.83\ T_M$.[48] Moreover, the rate of isothermal crystallization for many polymers is a maximum at a temperature $T_{\max} \simeq 0.83\ T_M$.[49,50] Since $T_{ll} \simeq 1.2\ T_g$ and $T_g \simeq \frac{2}{3} T_M$, then $T_{ll} \simeq 0.8\ T_M$. These numerical similarities may or may not represent a coincidence. A maximum in rate of crystallization arises from competition between the number of nuclei which increases with $T_M - T$ and molecular mobility which depends on $T - T_g$. Since the polymer chains are not completely free until T_{ll} is reached, there may be a causal relationship between T_{ll} in the amorphous phase of the semicrystalline polymer and $T_{\max}$.

It is necessary to question whether the T_{ll} transition might be an artefact arising from some impurity such as water or residual monomer. Several lines of evidence from these laboratories provide support for the inherent presence of the relaxation:

a. Identical values for the temperature of the T_{ll} transition are obtained by TBA on cooling from 250°C and reheating, and after any number of consecutive heating and cooling cycles below degradation temperatures.

b. The systematic variation of the T_{ll} transition with $\bar{M}_n^{-1}$ below M_c.

c. Results on bimodal blends which are to be reported.[51]

d. Preliminary unpublished results on the addition of known amounts of diluents which lower the temperatures of both T_g and T_{ll} in proportion to the amount of diluent.

e.   The return to normal values for the T_g and T_{ll} transitions after removal of volatile diluents.

CONCLUSIONS

The T_{ll} transition for polystyrene is considered to separate two regions which are designated as "fixed fluid" and "true liquid" on the basis of their rheological behavior under the experimental conditions.[16] The transition temperature depends on the molecular weight and the time scale of the experiment.   The T_g and T_{ll} transition temperatures-versus-$1/\bar{M}_n$ relationships, each of which show two regions, indicate a change in the underlying molecular mechanism at their points of intersection.   This change is probably caused by the restriction of segmental motion and chain slippage due to entanglements at high molecular weights.   In addition, the further change in T_g and T_{ll}-versus-$1/\bar{M}_n$ relationships at $\bar{M}_n \simeq 10^3$ may be the point above which motion of the entire polymer molecule as a unit is no longer possible.   Entanglements become influential at lower molecular weights for the T_{ll} transition process than for the glass transition process (Table IV).   This indicates that the T_{ll} transition mechanism involves a longer range motion than the glass transition.   The linear relationships between the T_{ll} and T_g transition temperatures and reciprocal number-average molecular weight suggest a free-volume basis for both transitions.

In the dynamic mechanical TBA experiment, the time scale is about 1 sec (the T_{ll} loss peaks occur at about 0.3 Hz); in the DTA experiment, flow occurs in about the same time scale to give a pseudoendothermic change.   The transition temperature assignments were about the same for TBA and DTA.   Flow occurs for any molecular weight in a given time scale under set experimental conditions when the viscosity reaches a certain isoviscous level.   Isoviscosity data from the literature show two regions of flow separated by a transition with a molecular weight dependence which parallels the results reported herein.   The data of Figure 17 demonstrates indirectly the effect of time scale.

A further study of blends which aims to distinguish between an isofree-volume and isoviscous basis for the T_{ll} transition is in progress.[51]

This work clearly establishes the existence and molecular weight dependence of the T_{ll} process in anionic and thermal polystyrene fractions and blends.   The phenomenon has likewise been defined for 1,4-polybutadiene.[2] Thermomechanical data (TBA) on syndiotactic and atactic poly(methyl methacrylates) (PMMAs) also indicate the presence of a T_{ll} transition at temperatures greater than 200°C for $\bar{M}_n$ = 62,700 and 48,000, respectively.[52] Measurements of thermal diffusivity on a series of poly(methyl methacrylate) fractions have been reported to show a normal variation of T_g with molecular weight and a second transition at 30° to 70°C above T_g which appears to level off at 434°K at molecular weights >11,700.[53] An examination in this laboratory[54] of one of these fractions of poly(methyl methacrylate) by TBA revealed a peak in logarithmic decrement (and G'') at a temperature which corresponds with the published thermal diffusivity experiment (see Table VIII). A further study of thermal diffusivity on single specimens of amorphous polystyrene, PMMA, and nylon 6 shows a T_{ll}-type of behavior in each case

some 50°C above T_g, i.e., at 160°, 140°, and 98°C, respectively.[55] The T_{ll} process in nylon 6 is reportedly best seen in a quenched specimen, but it then disappears on annealing. There is also evidence for a T_{ll} transition in an amorphous ethylene–propylene copolymer which is diminished in intensity with vulcanization.[3]

Table VIII is a compilation of systematic studies of the T_{ll} region.

The phenomena and interpretation of the T_{ll} transition must be considered to be general for all amorphous polymers and have implications for the behavior of semicrystalline polymers. The relationship between the T_{ll} transition and molecular weight described herein should be of practical importance in polymer processing steps which involve flow (e.g., extrusion, molding), diffusion (e.g., mixing of plasticizers and/or additives), and dimensional stability (e.g., processing film). A specific example relating to end effects in capillary flow has been reported.[60] Operating conditions which will have an effect on the T_{ll} transition include shear stress and shear rate.

Additional bodies of systematic data with regard to the influence of molecular weight and heterogeneity on the response of various techniques to various polymer systems are needed in the immediate future. At the same time, clarification is required in two key problem areas which are concerned mostly with polystyrene data. These are:

1. The seemingly elusive nature of the phenomenon in the literature. Whereas some workers have observed a $T > T_g$ transition in volume–temperature plots,[4,61,62] others performing seemingly identical experiments do not verify these results.[7,63]

2. The T_{ll}-type transition has been observed by both dynamic (e.g., TBA, melt flow, and DTA) and pseudoequilibrium (e.g., thermal expansion, thermal diffusivity, x-ray scattering, solubility, and steady-state diffusion) methods.

The present report sets the stage for further studies of the T_{ll} transition.

References

1. R. F. Boyer, *J. Polym. Sci.*, **C14**, 267 (1966).

2. E. A. Sidorovich, A. I. Marei, and N. S. Gashtol'd, *Rubber Chem. Technol.*, **44**, 166 (1971); translated from *Visokomol. Soedin.*, **(A)12**, No. 6, 1333 (1970).

3. R. F. Boyer, *Rubber Chem. Technol.*, **36**, 1303 (1963).

4. T. G. Fox, Jr., and P. J. Flory, *J. Appl. Phys.*, **21**, 581 (1950).

5. T. Holt and D. Edwards, *J. Appl. Chem.*, **15**, 223 (1965).

6. G. Natta, F. Danusso, and G. Moraglio, *Makromol. Chem.*, **28**, 166 (1958).

7. H. Höcker, G. J. Blake, and P. J. Flory, *Trans. Faraday Soc.*, **67**, 8, 2251 (1971).

8. D. R. Stull, The Dow Chemical Co., Midland, Mich., personal communication to R. F. Boyer (see Fig. 3 of R. F. Boyer and R. S. Spencer, *J. Appl. Phys.*, **15**, 402 (1944)).

9. S. Krimm and A. V. Tobolsky, *J. Polym. Sci.*, **6**, 667 (1951).

10. V. A. Kargin and U. M. Malinskii, *Doklady Akad. Nauk SSSR*, **72**, 4, 725 (1950).

11. V. A. Kargin and U. M. Malinskii, *Doklady Akad. Nauk SSSR*, **72**, 5, 915 (1950).

12. S. G. Turley, A. A. Pettis, and J. A. Fritz, The Dow Chemical Co., Midland, Michigan, private communication to R. F. Boyer.

13. A. V. Tobolsky, J. J. Aklonis, and G. Akovali, *J. Chem. Phys.*, **42**, 723 (1965).

14. J. L. Duda and J. S. Vrentas, *J. Polym. Sci. A-2*, **6**, 675 (1968).

15. R. S. Spencer and R. E. Dillon, *J. Colloid Sci.*, **4**, 241 (1949).

16. K. Ueberreiter and H-J. Orthmann, *Kunststoffe*, **48**, 525 (1958).

17. G. S. Y. Yeh, *J. Macromol. Sci.-Phys.*, **B6**(3), 465 (1972).

18. R. F. Boyer, *J. Macromol. Sci.-Phys.*, **B8**(3–4), 503 (1973).

19. E. Maekawa, R. G. Mancke, and J. D. Ferry, *J. Phys. Chem.*, **69**, 2811 (1965).

20. J. K. Gillham, *CRC Crit. Rev. Macromol. Sci.*, **1**, 83 (1972).

21. J. K. Gillham, *A.I.Ch.E. J.*, **20**(6), 1066 (1974).

22. S. J. Stadnicki, J. K. Gillham, and R. F. Boyer, *Amer. Chem. Soc., Polym. Prepr.*, **16**(1), 559 (1975); S. J. Stadnicki, Ph.D. Thesis, Department of Chemical Engineering, Princeton University, Princeton, N.J., 1975.

23. T. Altares and E. L. Clark, *Ind. Eng. Chem., Prod. Res. Develop.*, **9**, 2, 168 (1970).

24. DeBell & Richardson Testing Institute, Enfield, Conn., Project Number 236.28. Letters dated June 21, 1974, July 8, 1974, and July 18, 1974 to R. F. Boyer. We are indebted to Meyer Ezrin for performing the fractionation and determining the molecular characteristics.

25. Institute of Polymer Science, University of Akron, Akron, Ohio. Letter dated November 25, 1974 to J. K. Gillham. We are indebted to Everett R. Santee, Jr., for performing the NMR analyses.

26. L. F. Johnson, F. Heatley, and F. A. Bovey, *Macromolecules*, **3**(2), 175 (1970).

27. K. Matsuzaki, T. Uryu, K. Osada, and T. Kawamura, *Macromolecules*, **5**(6), 816 (1972).

28. C. L. M. Bell, J. K. Gillham, and J. A. Benci, *Amer. Chem. Soc., Polym. Prepr.*, **15**(1), 542 (1974).

29. Y. Hazony, S. J. Stadnicki, and J. K. Gillham, *Amer. Chem. Soc., Polym. Prepr.*, **15**(1), 549 (1974).

30. T. M. Connelly and J. K. Gillham, *J. Appl. Polym. Sci.*, **20**, 473 (1976).

31. H. H. Kuo, H. A. Pfeffer, and J. K. Gillham, *Amer. Chem. Soc., Coat. Plast. Prepr.*, **35**(1), 434 (1975).

32. R. F. Boyer, *Macromolecules*, **7**, 142 (1974).

33. T. P. Yin, S. E. Lovell, and J. D. Ferry, *J. Phys. Chem.*, **65**, 534 (1961).

34. R. Marvin, *Viscoelasticity: Phenomenological Aspects*, J. T. Bergen, Ed., Academic Press, New York, 1960, Chap. 2.

35. W. P. Cox, R. A. Isaksen, and E. H. Merz, *J. Polym. Sci.*, **44**, 149 (1960).

36. C. A. Arends, unpublished data, Dow Chemical Company.

37. M. C. Shen and A. V. Tobolsky, *Advan. Chem. Ser.*, **48**, 27 (1965).

38. F. Bueche, *J. Appl. Phys.*, **26**, 738 (1955).

39. G. C. Berry and T. G. Fox, *Advan. Polym. Sci.*, **5**, 261 (1968).

40. R. S. Porter and J. F. Johnson, *Chem. Rev.*, **66**, 1 (1966).

41. K. S. Hyun and R. F. Boyer, *Encyclopedia of Polymer Science & Technology*, H. F. Mark, N. G. Gaylord, and N. M. Bikales, Eds., Vol. 13, Wiley, New York, 1970, p. 370.

42. A. V. Tobolsky, *Properties and Structure of Polymers*, Wiley, New York, 1962, Chap. 4.

43. J. D. Ferry, *Viscoelastic Properties of Polymers*, Wiley, New York, 1961.

44. V. R. Allen and T. G. Fox, *J. Chem. Phys.*, **41**(2), 337 (1964).

45. L. E. Nielsen, *Mechanical Properties of Polymers*, Reinhold, New York, 1962, p. 58.

46. R. D. Andrews, *J. Polym. Sci.*, **C14**, 261 (1966).

47. T. M. Connor, *J. Polym. Sci. A-2*, **8**, 191 (1970).

48. R. F. Boyer, *Multiple Transitions in Semi-Crystalline Polymers*, 7th Swinburne Award Address, The Plastics Institute, London, 1972.

49. Y. K. Godovoskii, *Polym. Sci. USSR*, **11**, 9, 2423 (1970).

50. L. Mandelkern, *Crystallization of Polymers*, McGraw Hill, New York, 1964, p. 264.

51. C. Glandt, H. K. Toh, J. K. Gillham, and R. F. Boyer, *Amer. Chem. Soc., Polym. Prepr.*, **16**(2), 126 (1975); *J. Appl. Polym. Sci.*, **20**, 1277 (1976).

52. S. J. Stadnicki, J. K. Gillham, and Y. Hazony, *J. Appl. Polym. Sci.*, in press (1976); *Amer. Chem. Soc., Polym. Prepr.*, **15**(1), 549, 556, 562 (1974).

53. K. Ueberreiter and J. Naghizadeh, *Kolloid-Z. Z. Polym.*, **250**, 927 (1972).

54. J. K. Gillham, R. F. Boyer, and Y. Hazony, unpublished results. We are grateful to Professor K. Ueberreiter, Fritz Haber-Institut der Max-Planck Gesellschaft, Berlin, for providing the fraction of poly(methyl methacrylate).

55. M. Furuta, *Jap. J. Appl. Phys.*, **12**, 1143 (1973).

56. K. Ueberreiter and S. Purucker, *Kolloid-Z.*, **144**, 120 (1955).

57. R. S. Colborne, *J. Macromol. Sci., Phys.*, **B-1**, 517 (1967).

58. W. A. Geiszler, J. A. Koutsky, and A. T. DiBenedetto, *J. Appl. Poly. Sci.,* **14,** 89 (1970).

59. L. A. Utracki, *J. Macro. Sci., Phys.,* **B-10,** 477 (1974).

60. K. S. Hyun, *Polym. Eng. Sci.,* **14,** 666 (1974).

61. G. W. Bender and G. L. Gaines, *Macromolecules,* **3,** 128 (1970).

62. G. Rehage and H. Breuer, Untersuchungen über die glasige Erstarrung von Hochpolymeren unter hohen Drucken, Doctoral Dissertation published by Westdeutscher Verlag, Cologne, 1967.

63. K. Ueberreiter and G. Kanig, *Z. Naturforsch.,* **6A,** 551 (1951).