Molecular Weight Dependence of Fragility in Polystyrene

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ABSTRACT: Segmental relaxation was measured for a series of polysytrenes (PS) of varying molecular weight. The normalized Arrhenius plots of segmental relaxation times (fragility curves) become less steep for shorter chain lengths. Since the shape of the relaxation function is invariant to molecular weight, such behavior is a deviation from the usual correlation between time and temperature dependencies. Although the dependence of relaxation times on T_g-normalized temperature is weaker (less fragile), lower molecular weight PS has a larger heat capacity change at T_g. This result is at odds with an interpretation of temperature dependencies in terms of the degrees of freedom available to the glass upon transition to the viscous liquid.

Introduction

The segmental relaxation times of polymers exhibit non-Arrhenius temperature dependencies, precluding direct comparisons of polymers having different glass transition temperatures. The "fragility" classification scheme—Arrhenius plots employing a dimensionless temperature scale—has become a common method of circumventing this problem. The steepness of semi-logarithmic plots of relaxation time versus T_{ref}/T (where T_{ref} can be T_g but more often is defined as the temperature at which the relaxation time assumes some arbitrary value) provides a measure of relative temperature sensitivities.[1-3] This fragility property has been related to the chemical structure of polymers.[4-8] Smooth, compact, symmetrical chains exhibit "strong" relaxation behavior, while fragile polymers are those with more rigid backbones or sterically hindering pendant groups.[8] The T_g-normalized temperature dependence is also correlated with the nonexponentiality of the relaxation function,[9,10] with diffusion properties of supercooled liquids,[11,12] and to nonlinear behavior in the glassy state.[13-15] Recently, Angell pointed out a possible connection between the fragility of polymers and the microscopic relaxation time characterizing vibrational motions.[16]

A validation of T_g-scaled Arrhenius plots can be obtained from comparison of results from polymers differing only in molecular weight. Although both T_g and the segmental relaxation times depend on molecular weight, at least at low M_W, the shape of the relaxation function is generally independent of molecular weight. The latter implies that the fragility curves should be equivalent, as shown to be the case for a few polymers.[17,18]

Drawing on the Adam–Gibbs model,[19] an interpretation for the fragility scheme has been proposed by Angell.[2,3,11] The terms "fragile" and "strong" refer to the rapidity with which the properties associated with the glassy state are modified (degraded) as the temperature is increased through the glass transition region. More fragile liquids exhibit relaxation times that change more with temperature. According to Angell,[2,3,11] this strength or fragility reflects the topology of the potential energy hypersurface governing diffusions, reorientations, and for the case of polymers, segmental reconfigurations.

Fragile liquids are associated with potential surfaces having a high density of minima, and hence such liquids exhibit high configurational heat capacity changes at T_g, $\Delta C_p(T_g)$. When such a glass is warmed through the transition, a wide variety of structural arrangements become available. Strong liquid behavior, on the other hand, arises from potential energy surfaces with few minima, and thus small differences between the respective heat capacities of the glassy and liquid states. Many small molecule glass-forming liquids conform well to this model.[2,3,11] An exception is found for alcohols, which have large $\Delta C_p(T_g)$ but intermediate fragilities. Angell has pointed out that hydrogen bonding may inhibit molecular rearrangements, by increasing the barrier heights separating the various minima, and thus contribute to less fragile behavior.[2,3,11]

Polystyrene provides a challenging test of theory, since both T_g and ΔC_p are expected to become strong functions of molecular weight at sufficiently low M_W. Of course, for very low degrees of polymerization, the chemical structure of the chain end moiety per se may influence the relaxation dynamics. Such end group effects, however, are most prominent in hydrogen bonding and associating liquids.[20,21] Herein we describe a study of fragility and its relationship to heat capacity changes at T_g in PS of varying molecular weight.

Experimental Section

The polystyrenes (Table 1) were obtained from various sources and used as received. Dynamical mechanical spectra were obtained with a Bohlin VOR rheometer with a parallel plate geometry (sample radii and gaps were ca. 6 and 1.3 mm, respectively). The dynamic shear modulus was measured from 1 Hz down to as low as 10^{-5} Hz, at strains in the range from 0.01 to 4%.

Differential scanning calorimetry (Perkin-Elmer DSC-7) was carried out over temperatures encompassing the glass transition. Sample weights varied between 2 and 16 mg. For high molecular polystyrenes an Intracooler provided cooling to -40 C, with indium and lead used for temperature and enthalpy calibrations. For lower molecular weight PS, cooling was accomplished with liquid nitrogen, calibrated with cyclohexane. In all cases, samples were heated to 50 deg above T_g, followed by data acquisition during subsequent cooling at 10 deg/min to ca. $T_g - 50$. The specific heat increment at T_g, $\Delta C_p(T_g)$, was determined from the difference between the extrapolated values of the glassy and liquid states. The glass
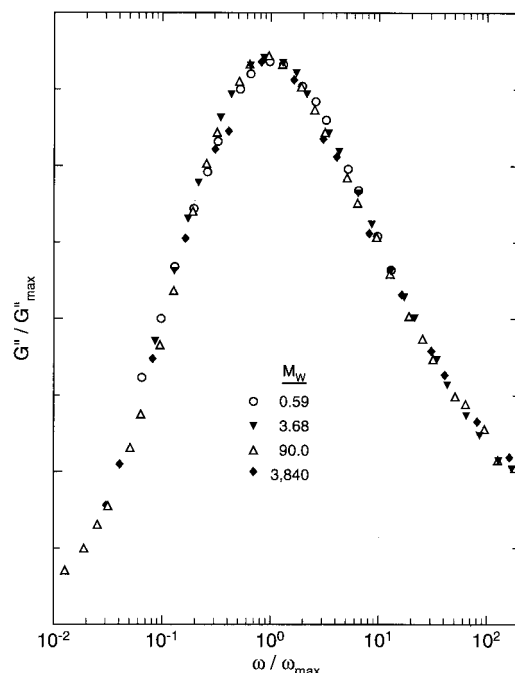
Figure 1. Segmental relaxation dispersion in the loss modulus of PS of the indicated weight average molecular weights ($\times 10^3$). The curves have been superimposed to demonstrate the absence of any systematic variation in shape of the relaxation function with chain length.

Table 1. Polystyrenes

DP	$10^{-3}M_W$	M_W/M_N	source
5.7	0.590	1.07	Scientific Polymer Products
7.3	0.760	1.12	Scientific Polymer Products
11	1.11	1.12	Scientific Polymer Products
23	2.36	1.08	Scientific Polymer Products
35	3.68	1.09	Scientific Polymer Products
87	9.00		Johnson Matthey
130	13.7		Scientific Polymer Products
240	23.8		Aldrich
480	50.0	1.06	Pressure Chemical Co.
870	90.0		Johnson Matthey
2240	233	1.06	Pressure Chemical Co.
8930	929	1.04	Scientific Polymer Products
36900	3840	1.04	Tosoh Corporation

transition temperature was taken as the midpoint (half-height) of the exothermic shift.

Results

The dispersion in the loss modulus associated with segmental relaxation was measured over a series of temperatures for polystyrenes of different molecular weights. Representative spectra, shown in Figure 1, illustrate that the shape of the segmental relaxation function is not sensitive to molecular weight. This agrees with previous dielectric spectroscopy results on poly(dimethylsiloxane) (PDMS).[18] A relaxation time can be defined as $\tau \equiv 1/2\pi f_{peak}$, where f_{peak} is the frequency of the loss modulus maximum. This τ corresponds to the most probable relaxation time, a quantity not dependent on fitting the dispersion to an arbitrary function.

These segmental relaxation times are plotted in Figure 2, along with the fitted Vogel–Fulcher equation[22] (which is equivalent to the WLF equation[23])

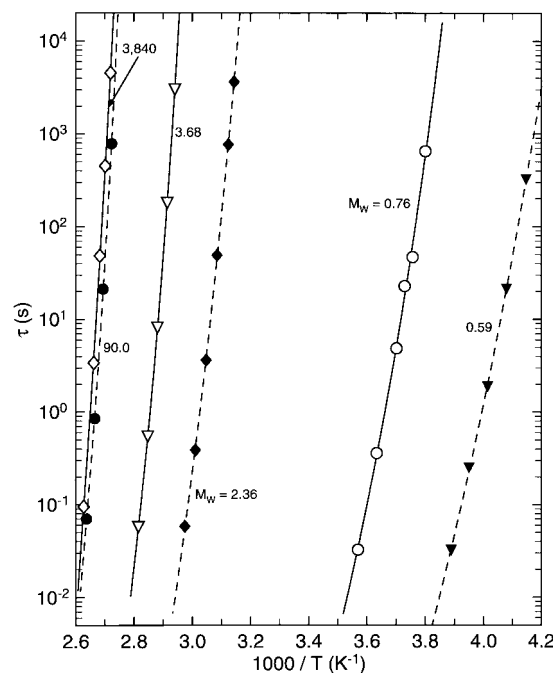$$\tau = \tau_0 \exp\left(\frac{B}{T - T_0}\right) \qquad (1)$$

Figure 2. Segmental relaxation times, defined from the peak in the loss modulus, for PS (designations as in Figure 1). The curves through the experimental data represent fits to eq 1, with the fitting parameters listed in Table 2.

Table 2. Vogel–Fulcher Parameters for Polystyrenes[a]

$10^{-3} M_W$	$\log \tau_0$ (s)	B	T_0 (K)	$T_{ref}{}^b$ (K)	$\mathrm{d} \log(\tau)/\mathrm{d}(T_g/T)$ (at $T = T_g$)
0.59	-17.54	2982	176.5	242.8	72
0.76	-13.89	1914	213.2	265.6	80
2.36	-16.72	2699	260.4	323.0	97
3.68	-13.72	1570	300.5	343.9	125
90.0	-21.27	3288	308.0	369.4	140
3840	-18.66	2493	319.3	371.2	146

[a] These fits, which are not necessarily unique, are used to interpolate the data for determination of T_{ref}. [b] Temperature at which the segmental relaxation time equals 100 s.

The values for the Vogel–Fulcher parameters, obtained using a nonlinear least-squares fitting procedure, are listed in Table 2. The preexponential in eq 1 is sometimes identified with vibrational lifetimes,[14,16] and thus its value may be fixed, e.g., $\tau_0 = 10^{-14}$ s. However, herein the Vogel–Fulcher equation is only used to provide a smooth line through the data points. Figure 2 reveals the strong dependence of τ on molecular weight, when PS is below some high molecular weight limit (ca. 10^2 kg/mole). This, of course, just reflects the molecular weight dependence of the glass transition temperature.

We now replot the data of Figure 2 using a dimensionless temperature scale. Since the purpose of this fragility plot is to correlate time scales for relaxation, temperature data are normalized by a quantity more appropriate for dynamics than the glass transition temperature. Common practice is to use the temperature at which $\tau = 100$ s.[2,24] We obtain this T_{ref} by interpolating the data in Figure 2 using eq 1. The resulting fragility plots are shown in Figure 3.

The surprising feature in Figure 3 is the systematic decrease in fragility (i.e., smaller value of $\mathrm{d} \log(\tau)/\mathrm{d}(T_g/T)$ at T_g) with decreasing molecular weight. Some limited results for a few polymers[17] as well as extensive dielectric measurements on PDMS,[18] had shown the
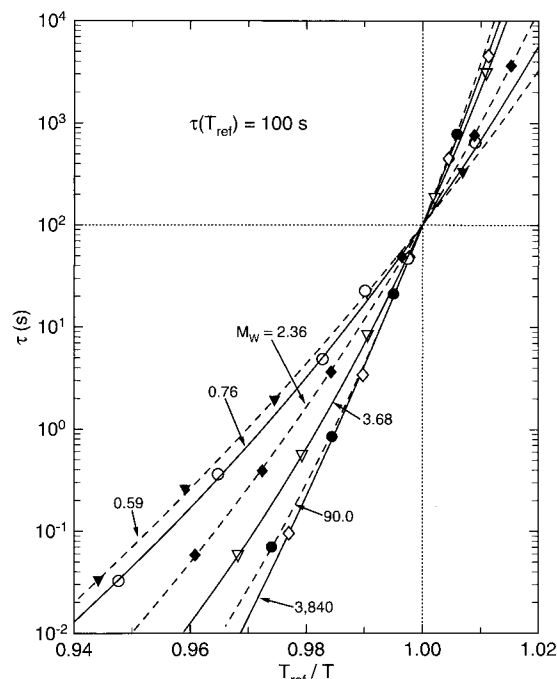
Figure 3. Data of Figure 2 after normalizing by the temperature, T_{ref}, at which the segmental relaxation time, measured mechanically, equals 100 s. There is a systematic increase in fragility with increasing molecular weight. The slope of the curves at $T = T_{ref}$ is given in Table 2.

Figure 4. DSC scans (vertically shifted for clarity) for PS of the indicated weight average molecular weight ($\times 10^3$).

normalized temperature dependence of segmental relaxation times to be independent of chain length. The variation of the fragility herein occurs despite the similar shape of the dispersions for PS of different molecular weights (Figure 1). Thus, PS is a rare exception to the well-known correlation between temperature dependency and the breadth of the segmental relaxation function (i.e., greater fragility associated with a broader dispersion).[9,10,25]

This correlation is predicted by the coupling model of relaxation.[5,6,26] While the data in Figure 3 are at odds with the coupling model, Angell's interpretation of fragility leads to a different prediction, which can also be tested. The idea that fragile liquids are those whose glassy state reorganizes to a wide variety of different structural arrangements when heated through T_g implies that more fragile glass formers will have larger values of $\Delta C_p(T_g)$.[2,3,11] Since the fragility of PS is an increasing function of molecular weight, the expectation is that $\Delta C_p(T_g)$ for PS should increase with molecular weight as well.

DSC curves, obtained on cooling at 10 deg/min, are shown in Figure 4 for PS of different molecular weights. The glass transition temperature was taken to be the midpoint; i.e., the temperature corresponding to half the exothermic shift. Plotted in Figure 5, these T_g's conform to the Kanig–Ueberreiter equation [27]

$$\frac{1}{T_g(M_N)} = \frac{1}{T_g(\infty)} + \frac{K}{M_N} \tag{2}$$

with $K = 0.78$ and the asymptotic value $T_g = 374$ K. This expression is equivalent to the Fox–Flory equation[28] at high molecular weights but gives a better fit for PS of $M_N < 1k$.[29] Also shown in Figure 5 is T_{ref}, the temperature at which $\tau = 100$ s; these are close to the calorimetric glass transition temperature.

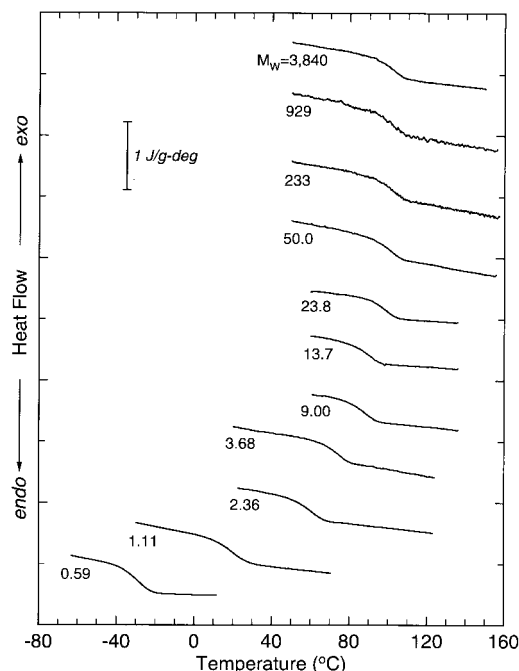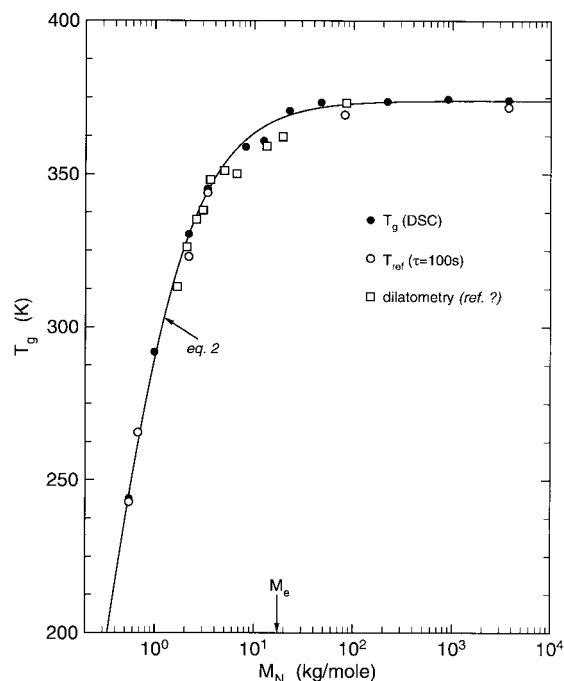**Figure 5.** Glass transition temperatures, measured calorimetrically during cooling at 10 deg/min, versus number average molecular weight. The solid line represents the fit to eq 2. The T_g data of Fox and Flory[29] for PS are shown for comparison ($\square$), along with the temperatures at which the segmental relaxation time equals 100 s ($\bigcirc$). The entanglement molecular weight of PS[22] is indicated.

The magnitude of the heat capacity change at T_g, obtained from the data in Figure 4, is shown as a function of M_W in Figure 6. Below about 30k, $\Delta C_p(T_g)$ is inversely related to molecular weight. Such behavior is also known for PDMS, polycarbonate, and poly(α-methylstyrene).[30] Note that the molecular weight at which ΔC_p(Tg) becomes invariant to M_W is comparable to the value associated with a constant T_g (Figure 5).
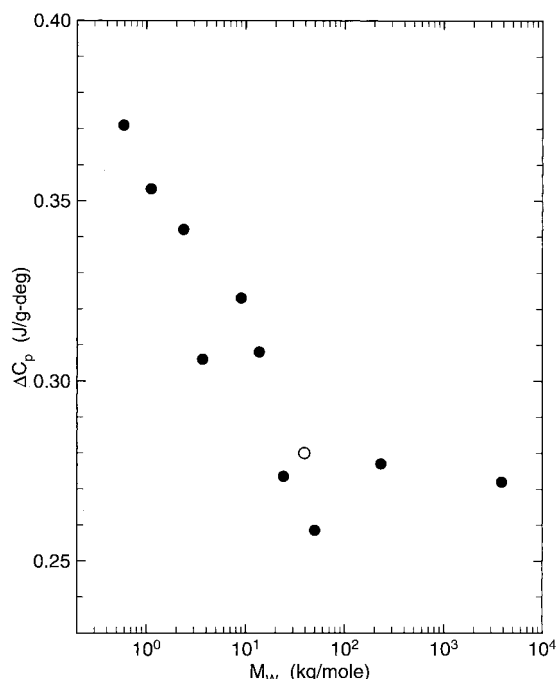
Figure 6. Molecular weight dependence of the heat capacity change at T_g measured by DSC. The hollow symbol was taken from ref 35.

This is also close to the entanglement molecular weight of PS.[22]

Recently, Sahnoune and Piché [31] reported ultrasonic measurements on PS of various molecular weights. Glass transition temperatures were defined from the inflection point of modulus versus temperature curves (the former deduced from the longitudinal sound velocity). Such a definition of T_g yields relaxation times at T_g that are molecular weight dependent, decreasing by 10 orders of magnitude in going from the lowest to highest molecular weights studied.[31] Since relaxation times become less sensitive to temperature at higher temperatures, this approach led Sahnoune and Piché to conclude that the fragility of PS is a *decreasing* function of molecular weight. The apparent discrepancy with the results in Figure 3, however, is entirely an artifact of the manner in which T_g was determined. More usual (and for dynamics more appropriate) is to normalize temperatures using the temperature at which the relaxation time assumes an arbitrary value (e.g., 100 s). From the Vogel–Fulcher parameters extracted from the ultrasonic data,[31] fragilities can be assessed from the relation[14]

$$\frac{d \log(\tau)}{d(T_g/T)}\Big|_{T=T_g} = \frac{B/T_g}{(\ln 10)(1 - T_0/T_g)^2} \quad (3)$$

The fragilities calculated in this manner increase with increasing molecular weight, a result in accord with the data of Figure 3.

Conclusions

Dynamic mechanical and calorimetry measurements on PS of varying molecular weight yield two unexpected findings. Below a degree of polymerization of roughly 1000, the fragility of PS decreases with decreasing molecular weight. Since the breadth of the segmental relaxation function remains invariant to chain length over this same range, PS departs from the usual correlation between time and temperature dependencies.

The heat capacity change at T_g varies inversely with chain length for lower molecular weight PS. For other polymers, in particular PDMS, $\Delta C_p(T_g)$ behaves in a qualitatively similar manner. However, dielectric relaxation spectroscopy for PDMS revealed its fragility to be independent of chain length;[18] hence, PDMS deviates from Angell's prediction of larger $\Delta C_p(T_g)$ effecting more fragile behavior. PS, on the other hand, is diametrically opposite to this prediction—lower molecular weight PS has a *larger* heat capacity change at T_g but is *less* fragile.

Angell[32] has suggested that the higher T_g of higher molecular weight polymers is associated with higher vibrational contributions to the configurational heat capacity, and thus the possibility exists of deviations from a simple relationship between ΔC_p and fragility. More general is the question of why the fragility of PS is molecular-weight dependent, yet for PDMS fragility is constant down to degrees of polymerization as low as 8. This difference may be related to the substantial difference in flexibility of the two species. The ether linkage in the PDMS backbone confers nearly free rotation with consequently low T_g. Any configurational freedom conferred by chains ends has a small effect, and thus T_g is independent of molecular weight down to very low M_w. The bulky side groups of PS enhance intermolecular cooperativity, resulting in a relatively high T_g, and one that is more molecular-weight dependent. The T_g of high T_g polymers is generally more sensitive to molecular weight.[33,34]

Similar considerations may prevail regarding the temperature dependence of segmental relaxation times. Primarily because of weak intermolecular cooperativity,[6] PDMS has minimal fragility. At T_g, d $\log(\tau)$/d$(T_g/T) \approx 90$, which is much less that the slope of the fragility curve for high molecular weight PS (Table 2). Evidently, intermolecular constraints are sufficiently weak in PDMS to obscure any further alleviation resulting from a high concentration of chain ends in low molecular weight samples.

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