

Temperature dependence of local segmental motion in polystyrene and its variation with molecular weight

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Dielectric measurements are reported for the α -relaxation in polystyrene (PS) of varying molecular weights. Although the segmental relaxation dispersion was essentially invariant to M_w , the T_g -normalized temperature dependence (fragility) increases systematically with molecular weight. The latter result corroborates dynamic mechanical and light scattering studies, but is at odds with the reported $(T - T_g)$ superpositioning of the shift factors for the recoverable creep compliance of PS. The failure of the dielectric relaxations time to superimpose when expressed as a function of $T - T_g$ is consistent with the analysis of equation of state data for PS. We find that volume is not the dominant control variable, and in fact, temperature exerts a stronger influence on the relaxation times. © 2003 American Institute of Physics. [DOI: 10.1063/1.1581850]

INTRODUCTION

The effect temperature has on the viscoelastic behavior of polymers is an issue of obvious significance, both for practical applications and in understanding the origin of their physical properties. The time-temperature superposition principle, which enables creation of master curves encompassing many decades of frequency, is based on the assumption that the underlying molecular motions all have the same temperature dependence. The observation of a breakdown of time-temperature superpositioning evokes great interest, since it can reveal new insights into the chain dynamics. In the field of rheology, the effect long-chain branching has on the temperature dependence of the viscosity is a much studied problem, that is yet to be satisfactorily resolved.¹⁻⁵ At higher frequencies, the temperature dependence of a polymer changes, as the response becomes governed more by local segmental motion than by the chain modes operative at longer times.⁶⁻⁸ This phenomenon was discovered over 35 years ago,⁹ and remains one of the intriguing problems of polymer science. Our focus herein is the effect temperature has on local segmental relaxation, in particular how this varies with molecular weight.

A problem in studying the effect of temperature is to select an appropriate basis for comparing polymers with different glass transition temperatures. With the exception of measurements at very low¹⁰ or very high temperatures,¹¹ local segmental relaxation times are non-Arrhenius, so that a direct comparison of activation energies cannot be made. The “fragility” classification scheme has gained wide acceptance as a means to quantify relative temperature sensitivities,¹²⁻¹⁵ with the fragility index defined as $m = d \log(\tau) / d(T_g/T) |_{T=T_g}$. For the study of dynamics, T_g is taken to be the temperature at which the relaxation time assumes some arbitrary long value, e.g., $\tau = 100$ s. This fragility can be related to the chemical structure of polymers¹⁶⁻¹⁹

Smooth, compact, symmetrical chains have smaller values of m , while large m is associated with polymers having more rigid backbones or sterically-hindering pendant groups. Fragility is also correlated with the breadth (nonexponentiality) of the relaxation function,^{20,21} with diffusion properties of super-cooled liquids,^{22,23} and even with nonlinear behavior in the glassy state.²⁴⁻²⁶ The terminology “fragile” and “strong” for large and small values of m derives from an energy landscape interpretation of the dynamics near T_g .^{14,15} Fragile glass-formers are presumed to exhibit a rapid change in liquid structure (local packing and positioning) with changing temperature, and hence a marked change in $\tau(T_g/T)$. An alternative viewpoint, for which this terminology is less apt, is that fragility is just one reflection of the effect intermolecular cooperativity has on the dynamics in the supercooled regime.^{18,27}

Notwithstanding its utility in correlating various relaxational properties of glass-formers, the theoretical justification for fragility is problematic, being based on assumptions about the temperature dependence of the configurational entropy and the energy barriers to local reorientations.^{14,15} An alternative classification, less in vogue of late, is to plot relaxation times as a function of the temperature difference, $T - T_g$. This method has its origin in free volume models of polymer dynamics.^{28,29} The change in unoccupied volume accompanying thermal expansion of a polymer above T_g is assumed to govern the viscoelastic properties; thus, comparisons at equal $T - T_g$ is a first-order correction for differences in glass transition temperature.

Obviously, inferences drawn from a $\log \tau$ versus T_g/T representation differ from those based on plotting $\log \tau$ as a function $T - T_g$. Superposition of relaxation data for different T_g materials by one method necessarily implies the data diverge by the other method. Thus, it is important to assess these two approaches to interpreting temperature depen-

dences, in particular their theoretical basis. The contribution of free volume to structural relaxation is minimized by some workers,^{30–33} although recent measurements of dielectric relaxation using high pressure indicate the role of volume cannot be discounted.^{34–36}

The present work is concerned with the effect of chain length on the temperature dependence of local segmental relaxation; that is, the α -process in the dielectric spectrum of polymers. While the temperature response of the chain modes of linear polymers is invariant to molecular weight,²⁸ the behavior of the local segmental dynamics is more complicated. It appears that the fragilities of some materials, such as polyphenylmethylsiloxane³⁷ and polydimethylsiloxane,³⁸ do not change with molecular weight, whereas for polypropyleneglycol,³⁹ fragility increases with chain length. The situation for polystyrene (PS) is confused. An early study⁴⁰ of the mechanical creep of PS found that time-temperature shift factors for the recoverable compliance of PS of different molecular weights could be described by the same function of $T - T_g$. However, the fragility of PS determined by dynamic mechanical spectroscopy was found to *increase* with molecular weight, up to molecular weights at which T_g becomes invariant (roughly $M_w < 40$ kg/mol).⁴¹ Subsequent results from photon correlation spectroscopy⁴² and calorimetry,⁴³ although not corresponding to the identical frequency range, likewise indicated that the T_g -normalized temperature dependence of PS varies with M_w . Conversely, from ultrasonic measurements on PS of varying molecular weights,⁴⁴ it was concluded that the fragility *decreased* with increasing molecular weight. This latter study, however, defined T_g from the inflection point of modulus versus temperature curves, yielding relaxation times at T_g which are molecular weight dependent, rather than a fixed $\tau = 100$ s.

The successful superpositioning of creep data using $T - T_g$ scaling implies that free volume concepts may have some validity. This is important to present day interpretations of the glass transition. One possibly important difference between the aforementioned studies is that different experimental quantities were utilized. The modulus includes any contribution from the viscosity, whereas viscous deformation is absent from the recoverable compliance, by virtue of how the experiment is carried out.⁴⁵ Since the viscosity contribution to the dynamic modulus will be molecular weight dependent, at least in principle this could skew the apparent temperature dependences of the local segmental relaxation times.

In this work we present dielectric measurements on PS of varying molecular weights, analyzing specifically the temperature dependence of the dielectric α -relaxation times. Dielectric spectroscopy is advantageous, since there is no contribution from viscous flow. And since the dielectric strength of PS is very low, the analysis is essentially the same whether relaxation times or retardation times are utilized. This is not the case for mechanical measurements, wherein the modulus and compliance can yield different results.⁴⁶ We also analyze equation of state data on PS to assess the extent to which volume exerts a role on the local segmental relaxation times.

TABLE I. Polystyrene samples.

M_w (kg/mol)	M_w/M_n	T_g^a (K)	T_0 (K)
0.590 ^b	1.07	253.9	189.7
0.760 ^b	1.12	280.7	233.3
2.36 ^b	1.08	333.1	271.8
3.68 ^b	1.09	346.1	296.7
6.40 ^b	1.05	360.2	322.7
90.0 ^c	1.06	373.2	341.3
3840 ^d	1.04	373.4	344.3

^aTemperature at which $\tau = 100$ s.

^bScientific Polymer Products.

^cJohnson Matthey.

^dTosoh Corporation.

EXPERIMENT

Samples are listed in Table I, along with the name of the manufacturer. Dielectric spectra were obtained with an IMASS time domain dielectric analyzer (10^{-4} to 10^4 Hz) and a Novocontrol Alpha Analyzer (10^{-2} to 10^6 Hz). The sample was contained between parallel plates, placed into an oven in a nitrogen atmosphere. The temperature control for all experiments was at least ± 0.1 K. Sample preparation varied depending of the T_g . Low molecular weight PS could be directly inserted between the electrodes (kept at a fixed distance by the use of a Teflon ring spacer), while for the sample having a high T_g , films were prepared in a press, applying a moderate pressure and heating the sample to a temperature slightly higher than T_g .

RESULTS AND DISCUSSION

Dielectric spectroscopy data

In Fig. 1 are shown the dielectric loss, ϵ'' , spectra for two PS samples having the extremes in molecular weight, $M_w = 590$ and 3.84×10^6 g/mol, respectively. The T_g of the latter is 128 deg higher, and by measuring it at a temperature 114.5 deg higher, the relaxation times become equal to within a factor of 2. Making a small adjustment in the frequency, we can superimpose the two loss curves; that is, the shape of the dielectric relaxation function is invariant to molecular weight. This is also the case for the mechanical loss modulus.⁸ Included in Fig. 1 is the fitted Kohlrausch–Williams–Watts function. The best-fit value of the stretch exponent is 0.44, in accord with previous results.⁴⁷

From the angular frequency of the maximum in the dielectric loss, we can define a relaxation time $\tau = 1/\omega_{\max}$ (roughly equal to the most probable relaxation time). These are plotted in Fig. 2 versus the inverse temperature for all seven samples. Below $M_w = 90$ kg/mol, the data shift towards lower temperatures, reflecting the molecular weight dependence of T_g . The temperature dependences are described by the Vogel–Fulcher equation²⁸

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

where τ_0 , B and T_0 are constants. The latter, referred to as the Vogel temperature, are listed in Table I.

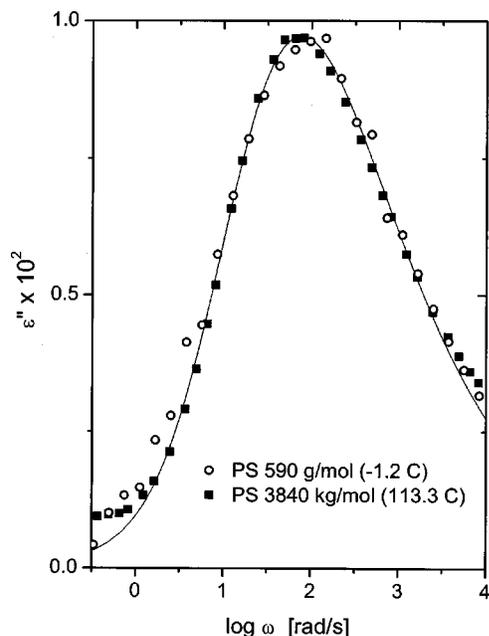


FIG. 1. α -dispersion in the dielectric loss of polystyrenes having the indicated molecular weights, at respective temperatures for which the segmental relaxation times are almost equal. The frequencies for the higher M_w sample have been multiplied by 1.3 to superpose the data. The solid line represents the transform of the Kohlrausch-William-Watts function, having a value of the stretch exponent equal to 0.44.

The temperatures, T_g , at which the relaxation time equals 100 s, are also listed in Table I and plotted as a function of molecular weight in Fig. 3. As seen in the figure, we can superpose the Vogel temperatures onto the T_g data, by plotting $T_0 + 38$. T_g results from dynamic mechanical measurements,⁴¹ as well as a single datum measured by photon correlation spectroscopy,⁴² are also shown in the figure; these T_g are consistent with the dielectric results. Also included in Fig. 3 is a curve representing the fictive temperatures measured by differential scanning calorimetry for PS of various molecular weights.⁴³ There is good agreement be-

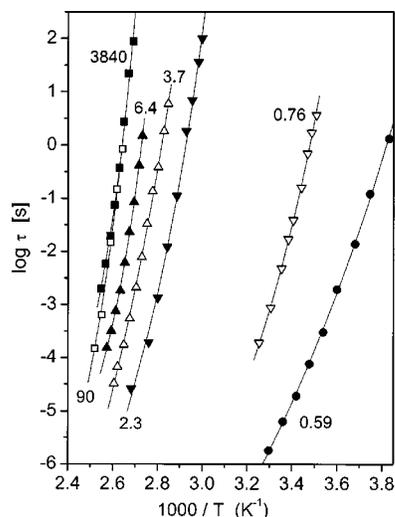


FIG. 2. α -relaxation times PS having the indicated molecular weight in kg/mol. The lines represent fits to the Vogel-Fulcher equation, with the Vogel temperatures listed in Table I.

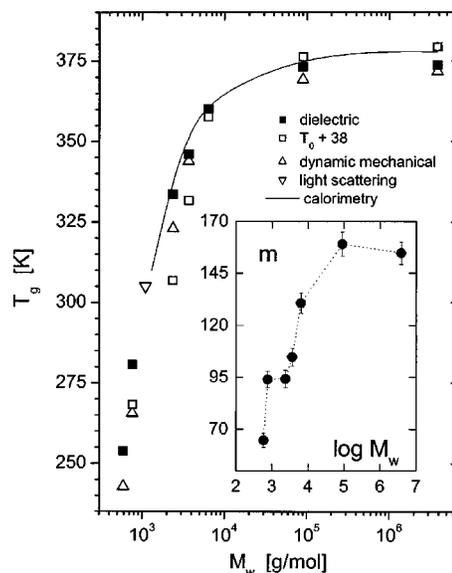


FIG. 3. Temperature at which the relaxation time for local segmental motion equals 100 s for PS of varying molecular weight, as measured by dielectric, dynamic mechanical (Ref. 41), and depolarized photon correlation spectroscopies (Ref. 42). In all cases, τ is defined from the maximum of the dielectric loss. The solid lines represent the calorimetric fictive temperatures determined at a heating rate of 10 deg/min, following cooling at 100 deg/min (Ref. 43). The fragility index calculated from the dielectric relaxation measurements is shown in the inset.

tween the fictive temperature determined using a heating rate of 10 deg/min, following cooling at 100 deg/min, and the temperatures for which $\tau = 100$ s.

From the slope of the Arrhenius curves in Fig. 2, the fragility index is calculated for each PS; these results are plotted in the inset to Fig. 3. There is a systematic increase with molecular weight, in qualitative agreement with results from other experimental techniques.⁴¹⁻⁴³

In Fig. 4, the dielectric relaxation times are plotted ver-

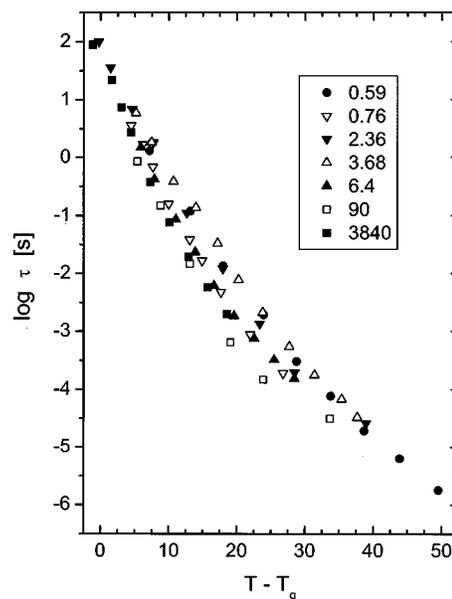


FIG. 4. Dielectric relaxation times from Fig. 2 plotted vs the difference between the measurement temperature and the temperature at which $\tau = 100$ s. The symbols are the same as in Fig. 2.

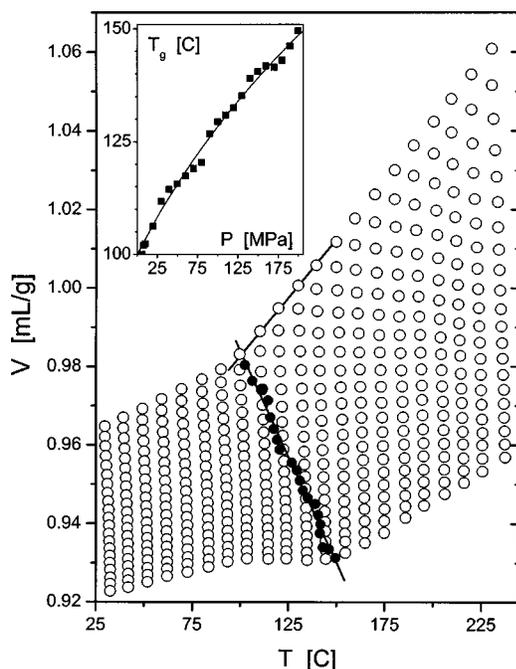


FIG. 5. PVT data from Ref. 48. From top to bottom, the pressure ranges from 0 MPa to 200 MPa, in 10 MPa increments. At atmospheric pressure, $\alpha_p = 6.08 \times 10^{-4} \text{ C}^{-1}$. The glass transition temperatures shown in the inset are obtained from the deviation of the liquid expansivity. These are denoted by the filled circles in the V of T plot, from which we calculate $\alpha_\tau = 1.04 \times 10^{-3} \text{ C}^{-1}$.

sus the quantity $T - T_g$. This only roughly superposes the data. Although there is significant scatter, the deviations are systematic with molecular weight. Superpositioning of these curves would require adjusting the abscissa values by as much as 3 degrees. Near T_g , this corresponds to about a fivefold change in the relaxation times, which is well beyond the experimental error.

Relative influence of thermal energy and volume on τ

Pressure-volume-temperature (PVT) measurements have been reported for a PS with a molecular weight of 34.5 kg/mol.⁴⁸ At this M_w , T_g is about 3 deg below the limiting value for the high polymer. The PVT data are displayed in Fig. 5.

The deviation at low temperature in the thermal expansion coefficient of the liquid defines a pressure-dependent transition temperature. These volumetric T_g 's are shown in the inset to Fig. 5. The pressure dependence of T_g can be parameterized using the Andersson equation,⁴⁹

$$T_g = a \left(1 + \frac{b}{c} P \right)^{1/b}, \quad (2)$$

which can be derived from the Avramov structural relaxation model.⁵⁰ In Eq. (2), a , b , and c are constants. Fitting this expression to the data in the Fig. 5 inset yields $a = 373 \text{ K}$, $b = 6.79$, and $c = 1,044 \text{ MPa}$. Thus, in the limit of zero pressure, $dT_g/dP = 0.36 \pm 0.05 \text{ K/MPa}$, a very large value. It is intermediate between the pressure coefficients of T_g reported in the literature, for PS of different molecular weights.^{51,52}

The relative degree to which volume and thermal energy govern the relaxation times can be assessed from the ratio of the apparent activation energy at constant volume, $E_V(T, V) = R (\partial \ln \tau / \partial T^{-1})|_V$ to that at constant pressure, $E_P(T, P) = R (\partial \ln \tau / \partial T^{-1})|_P$.^{31,53} This ratio varies between 0 and 1, smaller values reflecting volume-dominated relaxation, and a value near unit indicating that temperature is the dominant control variable. Although E_P can be obtained from data at ambient pressure such as in Fig. 2, determination of E_V requires dielectric measurements at elevated pressure. These are difficult for the weakly polar PS, and also require very high temperatures (since dT_g/dP is large). However, the ratio can be calculated from the relation⁵⁴

$$E_V/E_P = 1 - \left(\frac{\partial P}{\partial T} \right)_V \left(\frac{\partial T}{\partial P} \right)_\tau. \quad (3)$$

From the PVT data, we calculate $\partial P / \partial T|_V = 0.9942 \text{ MPa/K}$. We have previously shown that the T_g deduced from PVT data is equal to the temperature at which the relaxation time assumes a constant value.^{55,56} Thus, $\partial T / \partial P|_\tau = dT_g/dP$, whereby Eq. (3) yields $E_V/E_P = 0.64 \pm 0.05$. This is greater than one-half, indicating that while volume exerts an effect, the relaxation times are governed to a somewhat greater extent by temperature.

The relative contribution of volume and temperature can be also assessed from the ratio of the expansivity calculated for a fixed value of the relaxation time, $\alpha_\tau (= -V^{-1}(\partial V / \partial T)_\tau)$, to the isobaric expansivity, $\alpha_p (= -V^{-1}(\partial V / \partial T)_p)$.³³ The ratio $|\alpha_\tau|/\alpha_p$ will be much larger than unity if volume exerts a negligible effect on the relaxation times; that is, if temperature is the dominant control variable. The expansivity at atmospheric pressure is obtained directly from the data, $\alpha_p = -6.08 \times 10^{-4} \text{ K}^{-1}$. In the inset to Fig. 5, the glass transition temperatures are denoted by filled circles in the V versus T plot, with the $V(T_g)$ corresponding to the volumes at a fixed value of τ . From this we obtain $\alpha_\tau = 1.04 \times 10^{-3} \text{ K}^{-1}$, and thus the ratio of the isochronal and isobaric expansivities is equal to 1.7. The magnitude of $|\alpha_\tau|/\alpha_p$ reinforces the analysis of the activation energies. Thermal energy exerts a larger effect on the relaxation times than does volume, although both quantities contribute. This conclusion is also consistent with the findings of Huang *et al.*,⁵⁷ that the fragility of polystyrene is sensitive to volume, and that the isochoric fragility is less than the isobaric fragility, both indications that volume effects are not negligible in PS.

SUMMARY

Dielectric spectroscopy results for PS of various chain lengths corroborate previous results from other techniques, showing that the fragility of PS increases with M_w . In this respect, PS is similar to polypropylene glycol, but distinct from polymers such as the siloxanes. Attempting to superimpose the relaxation times by plotting them as a function of $(T - T_g)$ gives poor superposition of the data. This result differs from creep mechanical measurements,⁴⁰ although the data herein cover a significantly broader range of molecular weights. Consistent with the failure of $T - T_g$ superposition-

ing, an analysis of equation of state data reveals that thermal energy exerts a stronger influence on the relaxation times than does volume. However, volume does exerts some effect on τ , contrary to the idea that temperature alone is the dominant control variable for structural relaxation.

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