Normalization of the Temperature Dependence of Segmental Relaxation Times

C. M. Roland* and K. L. Ngai

Naval Research Laboratory, Washington, D.C. 20375-5000

ABSTRACT: The validity of T_G-scaled Arrhenius plots of segmental relaxation times for glass-forming liquids is assessed by comparing the results on polymers differing only in molecular weight. The differences result in identical segmental relaxation dispersions which occur, however, at different times and temperatures. It is verified herein that the T_G-normalization scheme is a self-consistent means to classify and distinguish segmental relaxation behavior of polymers. Contrarily, changes in glass transition temperature effected by hydrostatic pressure alter the segmental dynamics in a manner such that the fragility of the polymer is altered.

Introduction

The time and temperature dependencies of the rheological response of polymers are central issues in the study of the viscoelasticity of polymers. Over the range of most experimental measurements, temperature dependencies are non-Arrhenius; consequently, some normalization scheme must be invoked to allow comparisons among different fluids of the effect of temperature on the measured relaxation times. Recently, a correlation was demonstrated between the shape of the relaxation function of several amorphous polymers and the magnitude of the time–temperature shift factors.[1] Specifically, a broader segmental dispersion was associated with a stronger temperature dependence of the segmental relaxation time. This conclusion was reached by comparing the shift factors as a function of inverse temperature normalized by T_G, the glass transition temperature. Although the glass transition temperature is an obvious normalizing parameter, this specific basis for comparing different materials is not obviously the correct one.

Angell[2,3] has proposed a classification based on the density of available configurations (corresponding to minima on a potential energy "hypersurface") for an N-particle fluid. If the liquid gains access to a high density of these energetically preferred configurational states when temperature is raised through T_G, the glass to liquid transition will be accompanied by a large entropy increase; consequently, the heat capacity and relaxation time change markedly with temperature near T_G. Such a liquid is classified as "fragile", an allusion to the loss of short- or intermediate-range order accompanying the transition from the glassy state. "Strong" liquids, characterized by fewer potential energy minima in configuration space, suffer little loss of local "structure" and thus exhibit smaller increments in heat capacity at T_G. This thermally induced structure degradation refers only to the loss of local order; it is unrelated to chemical stability.

Consideration of the heat capacity change at T_G provides a means for comparing the temperature dependencies of different glass-forming liquids.[2,3] In the Adam and Gibbs theory of relaxation[4] the liquid is comprised of cooperatively rearranging regions (CRR's), defined as the smallest volume element that can relax to a new configuration independently of neighboring regions. The energy barrier hindering transition of the CRR to a new configuration is proportional to the size of the CRR, with the average

transition rate for the CRR's given by

$$W(T) = A \exp(-C/TS_c) \tag{1}$$

where A is a constant. The parameter C is proportional to the product of $\Delta\mu$, the energy barrier per molecule, and s_c, the configurational entropy of the smallest CRR

$$C = \Delta\mu S_c / k \tag{2}$$

where k is the Boltzmann constant. The configurational entropy of the macroscopic sample, S_c, can be expressed in terms of the difference in heat capacity between the liquid and glassy states[2,3]

$$S_c = \int_{T_K}^{T} \frac{\Delta C_p}{T'} dT' \tag{3}$$

where T_K, identifiable with the Kauzmann temperature,[3,5-8] is the temperature at which $S_c = 0$. Assuming a hyperbolic dependence of heat capacity on temperature, it can be shown that[2,3]

$$S_c = \alpha \frac{T - T_K}{T_K T} \tag{4}$$

where α is a constant. Substituting into eq 1 gives

$$W = A \exp(DT_K/T - T_K) \tag{5}$$

with

$$D = C/\alpha \tag{6}$$

Equation 5 corresponds to the empirical VFTH equation[9] with the average transition rate of the CRR's identified with the inverse relaxation time. Non-Arrhenius temperature dependency data from glass-forming liquids near T_G can be represented well using this relation. If both the energy barrier per molecule and the configurational entropy of the smallest CRR are constant, then D is constant, at least to the extent the heat capacity can be adequately described by a hyperbolic relation. It follows from eq 5 that two liquids having the same D and A (but possibly different T_K's) will have identical "fragility plots", that is, plots of log ($W(T)$) versus T_G/T, where T_G can be operationally defined to be the temperature at which the transition rate attains a constant (arbitrary) value. Such plots have been used to depict relaxation times and viscosities of small-molecule glasses in order to illustrate the contrasting behavior of strong versus fragile liquids.[2,3] An extension of the Adam and Gibbs model to include

dynamic correlations between the CCR's provides a rationale for the observed correlations between time and temperature dependencies in small-molecule liquids.[10]

More recently this approach has been applied to amorphous polymers,[1,11] although the appellations strong and fragile may be misleading therein, since there is no modification of structure at the glass transition. For polymers the term "cooperativity plot" is more accurate. From comparisons of segmental relaxation times for various polymers made on the basis of T_G-scaled Arrhenius plots, correlations have been adduced.[1,11] These have been used to draw inferences concerning fundamental relationships between chain structure, intermolecular interactions, and segmental dynamics. Fragility plots have also been extended to miscible polymer blends to demonstrate the effect of local compositional variations on segmental relaxation.[12-14]

Fragility plots embody the assumptions of constancy of s_c and $\Delta\mu$, the correctness of which cannot be directly demonstrated. The need to take account of differences in T_G among liquids is apparent, and a simple T/T_G construct is plausible. However, it is not obvious that comparisons of different and decidedly non-Arrhenius temperature dependencies of different liquids are made meaningful so simply.

To assess this approach to the study of chain dynamics, it would be useful to demonstrate its validity with liquids identical in chemical structure but differing in their dynamics. This is conspicuously impossible for small-molecule liquids; however, the chain-length dependence of a polymer's glass transition temperature provides such an opportunity. Chemically identical materials differing only in molecular weight will necessarily have the same energy barrier to conformational transitions, and both s_c and ΔC_p will be essentially equal. While the differences in T_G confer differences in temperature dependencies, since the degrees of intermolecular cooperativity of their segmental relaxation are equivalent, the relaxation times should superimpose when expressed in terms of the reduced variable T/T_G. We emphasize that T_G-normalized Arrhenius plots may provide a meaningful basis for comparing segmental relaxation of different polymers, aside from the particular model (e.g., the theory of Adam and Gibbs) from which the approach originated. Accordingly, herein we employ the VFTH expression only to interpolate experimental measurements of segmental relaxation. The adequacy of the fragility plot approach is considered apart from the specific assumptions that enable one to derive the T/T_G normalization scheme.

The glass transition temperature of a given material is strongly dependent on pressure, reflecting the molecular crowding induced by pressure. Isothermal relaxation times and their temperature dependence are therefore functions of pressure. The changes in segmental dynamics engendered by pressure, however, are expected to alter $\Delta\mu$ and ΔC_p, thus undermining the basis of the fragility plot approach. Speaking loosely, the "strength" of a liquid should increase upon densification. It is interesting to explore the consequences of pressure variations on the fragility characteristics of glass-forming liquids.

The present study was intended to assess the utility of fragility plots in accounting for changes in segmental dynamics of amorphous polymers induced by changes in T_G. The latter were effected by variations in molecular weight and pressure.

Results

Polystyrene. Compliance measurements at temperatures encompassing the glass to liquid transition have
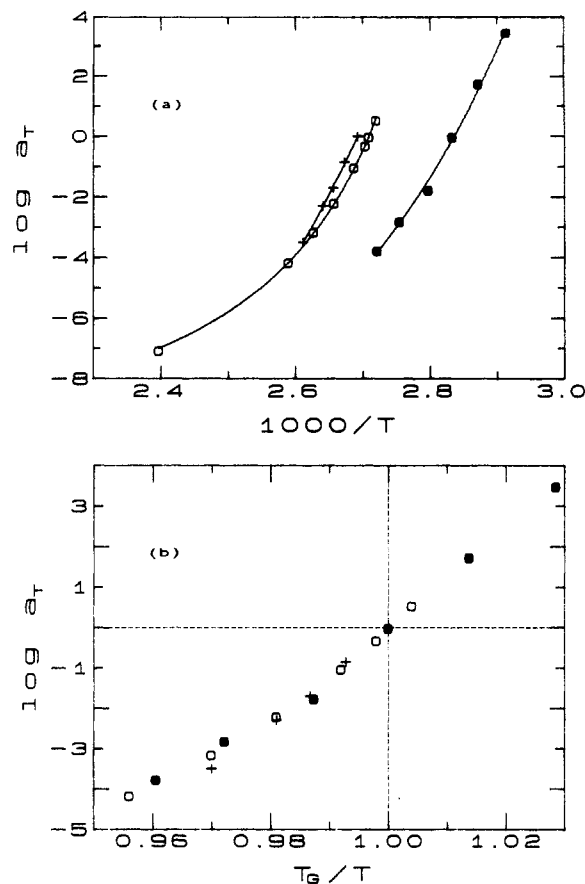

Figure 1. (a) Shift factors determined from compliance measurements on polystyrenes of molecular weights equal to 3.4 × 10^3 (●), 1.6 × 10^4 (○), and 1.2 × 10^5 (+).[15] (b) Segmental relaxation times that become coincident when the temperatures are scaled by the respective T_G's (Table I) of each polymer.

Table I

polymer	MW	T_G
polystyrene	3.4 × 10^3	353[a]
polystyrene	1.6 × 10^4	369[a]
polystyrene	1.2 × 10^5	372[a]
poly(propylene oxide)	1.0 × 10^3	202[b]
poly(propylene oxide)	9.5 × 10^5	205[b]
poly(phenylmethylsiloxane)	2.5 × 10^3	235[b]
poly(phenylmethylsiloxane)	8.3 × 10^5	245[b]

[a] Temperature at which compliance increases by a factor of 10 from the glassy level in 100 s. [b] Temperature at which the segmental relaxation time equals 1 s.

been reported for polystyrenes of various molecular weight.[15] The obtained shift factors (the ratio of the relaxation time, τ, measured at a given temperature to the relaxation time at an arbitrary reference temperature) are displayed in Figure 1 for the three polystyrenes listed in Table I. It is evident that the differences in molecular weights give rise to substantial differences in temperature dependencies for the segmental relaxation. The VFTH parameters, determined by fitting eq 5 with W taken to be τ^{-1}, vary with molecular weight due to the variation of T_G with molecular weight. However, no molecular weight dependence was found for the shape of the segmental relaxation dispersion (reflecting the degree of intermolecular cooperativity[16,17]). Thus, these data provide an opportunity to evaluate the fragility approach to scaling the results from polystyrenes of different T_G.

From the original compliance data,[15] a glass transition temperature is defined for each molecular weight as the temperature at which the compliance increases 10-fold from the glassy compliance over a 100-s time span. Using
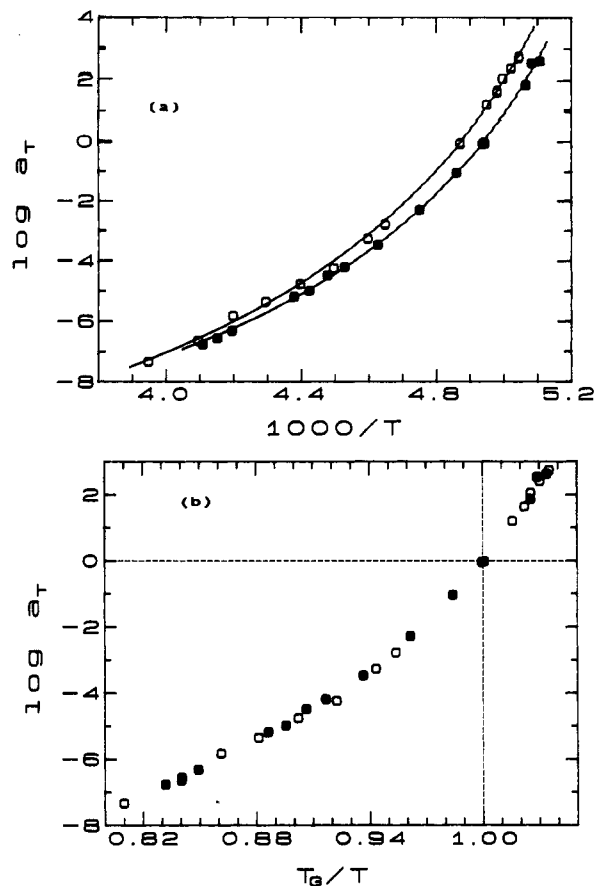
Figure 2. (a) Shift factors for segmental relaxation obtained from dielectric spectroscopy for 1.0×10^3 (●)[18] and 9.5×10^5 (O)[19] molecular weight PPO. (b) Data replotted with temperature normalized by the respective T_G of each polymer (Table I).
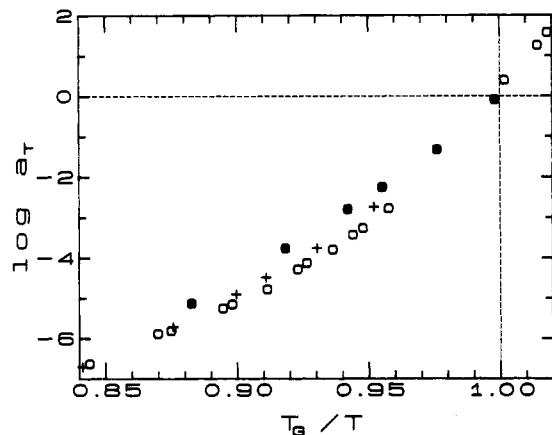

Figure 3. Shift factors determined for amorphous PPO (MW $= 9.5 \times 10^5$) at 1 (O), 1000 (+), and 2000 (●) atmospheres of pressure.[19] The T_G was taken to be the temperature at which the relaxation time equaled 1 s at that pressure.

the T_G's so determined, the shift factors of Figure 1a are replotted in Figure 1b, with the temperatures normalized by the respective T_G's of each polystyrene. It is seen that this scaling unifies the behavior, indicating that at least for mechanical measurements on these polymers the disparate characteristics of the molecular weight dependent T_G and molecular weight independent fragility can be distinguished.

Poly(propylene oxide). Dielectric spectroscopy has been carried out on both low[18] and high[19] molecular weight poly(propylene oxide) (PPO) in the vicinity of its glass transition. The frequency, f_p, of the maximum in the dielectric loss defines a peak relaxation time, $\tau_p = (2\pi f_p)^{-1}$. The variation with temperature of τ_p is found to be well
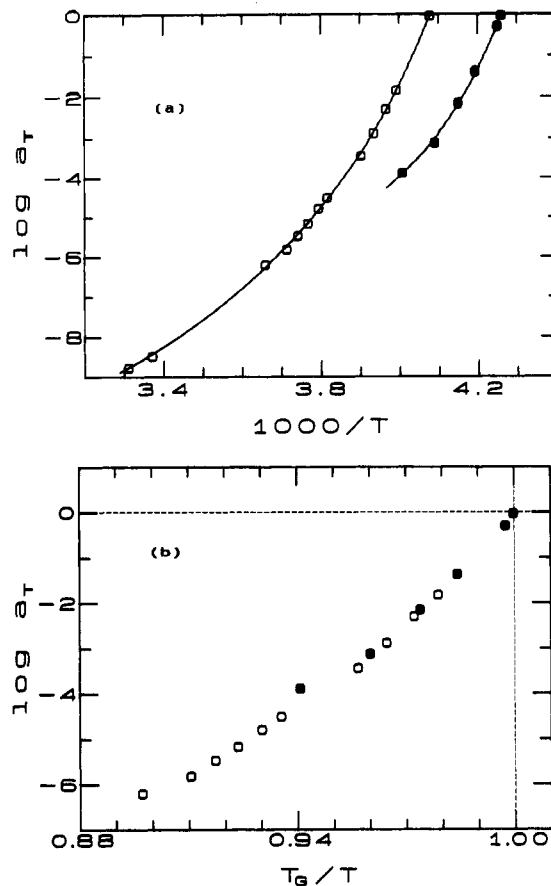

Figure 4. (a) Shift factors determined for PPMS of molecular weight equal to 2.5×10^3 (●) and 8.3×10^5 (O).[20] (b) Data replotted with the abscissa values normalized by the respective T_G of each polymer (Table I).

described by the VTHF equation. The temperature at which $\tau_p = 1$ s is determined and identified as T_G. A 1-s time scale is employed since the dielectric data are available only over a limited range of frequencies. T_G is arbitrary as far as dynamics are concerned, so that any convenient operational definition suffices. Using the T_G so determined, shift factors are calculated as shown in Figure 2a. Since the glass transition temperatures are different for the two molecular weights, nonparallel curves are obtained. Similarly as for PS above, we normalize the temperatures by the respective T_G of each species and replot the data (Figure 2b). The plots for the two molecular weights are coincident, supporting the normalization scheme.

The T_G of a polymer can be altered by the application of hydrostatic pressure. Dielectric loss measurements have in fact been reported for the higher molecular weight PPO at high pressure.[19] From this data we determine the pressure dependence of T_G and thereby construct fragility curves (Figure 3). However, it is seen that the changes in temperature dependence brought about by changing pressure cannot be accounted for simply by scaling the temperatures by the T_G^{-1}. The change in T_G with pressure can be attributed to changes in the intramolecularly correlated conformational transition rates, similar to the effect of changing molecular weight. However, whereas the increase in T_G with increasing molecular weight has no effect on the normalized temperature dependence, the T_G increase brought about by higher pressure is accompanied by a reduction in the fragility of the liquid.

Poly(phenylmethylsiloxane). Dielectric and photon correlation spectroscopy results have been obtained on poly(phenylmethylsiloxane) (PPMS) of molecular weight $= 8.3 \times 10^5$,[20,21] and both techniques yielded equivalent
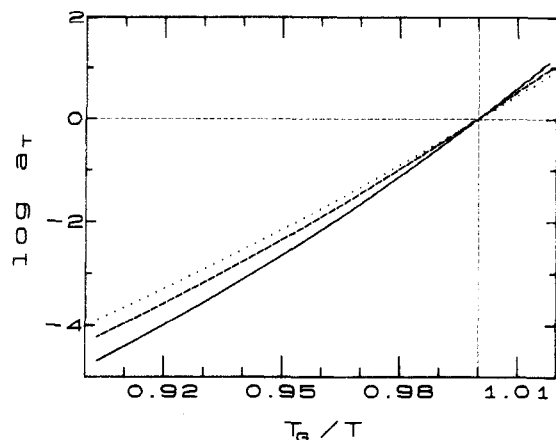
Figure 5. Shift factors determined for low molecular weights PPMS at 1 (—), 450 (- - -), and 900 (· · ·) bar hydrostatic pressure.[20] T_G was taken to be the temperature at which the relaxation time equaled 1 s, with temperature and pressure dependencies for the latter obtained from eq 7.

temperature dependencies for segmental relaxation. In Figure 4a the shift factors for the dielectric loss maximum are displayed for this PPMS, along with shift factors determined for a low molecular weight (=2.5 × 10³) PPMS.[20] When a glass transition temperature is defined as the temperature at which the relaxation time equals 1 s, the data are replotted in the T_G-normalized Arrhenius form (Figure 4b). Superpositioning of the data is again observed.

The pressure dependence of the relaxation time was determined for the low molecular weight PPMS to be[20]

$$\tau = 7.94 \times 10^{-19} \exp\{(1659 + 0.813P)/(T - 207)\} \quad (7)$$

where P is in units of bar. Using eq 7, the pressure dependence of the τ vs T/T_G relation was calculated, where T_G is again the temperature at which the relaxation time equals 1 s. The results (shown in Figure 5) are in agreement with the data in Figure 3 for PPO; that is, the fragility curves diverge at different pressures, with increasing pressure reducing the temperature sensitivity when the latter is normalized by T_G.

Summary

The log τ vs T_G/T form has been tested herein and verified to be a rational means to classify and distinguish the segmental relaxation characteristics of polymers. The original derivation of this normalization relied on several assumptions as discussed above; however, the corrobo-

ration of the fragility plot approach (Figures 1b, 2b, and 4b) is not taken as confirmation of any connection between temperature dependencies and the heat capacity difference of the liquid and glassy states. In fact, for polymers no such relationship is expected. Correlations have been demonstrated previously between the degree of intermolecular cooperativity of a polymeric liquid and the temperature dependence of segmental relaxation.[1,11] The present assessment of the T_G-normalized scaling procedure is made possible because of the equivalence of this cooperativity (and thus the shape of segmental relaxation dispersions) for polymers differing only in molecular weight.

References and Notes

(1) Plazek, D. J.; Ngai, K. L. *Macromolecules* **1991**, *24*, 1222.
(2) Angell, C. A. In *Relaxations in Complex Systems*; Ngai, K. L., Wright, G. B., Eds.; Government Printing Office: Washington, DC, 1985; p 3; *Proceedings of the Materials Research Society Symposium on the Physical Aging of Glasses*; Boston, 1990.
(3) Angell, C. A. *J. Non-Cryst. Solids* **1991**, *131-133*, 13.
(4) Adam, G.; Gibbs, J. H. *J. Chem. Phys.* **1965**, *43*, 139.
(5) Birge, N.; Nagel, S. *Phys. Rev. Lett.* **1985**, *54*, 2674.
(6) Dixon, P.; Nagel, S. *Phys. Rev. Lett.* **1988**, *61*, 341.
(7) Richet, P. *Geochim. Cosmochim. Acta* **1984**, *48*, 417.
(8) Tweer, H.; Laberge, N.; Macedo, P. B. *J. Am. Ceram. Soc.* **1971**, *54*, 122.
(9) Ferry, J. D. *Viscoelastic Properties of Polymers*; Wiley: New York, 1980.
(10) Ngai, K. L.; Rendell, R. W.; Plazek, J. *J. Chem. Phys.* **1991**, *94*, 3018.
(11) Roland, C. M.; Ngai, K. L. *Macromolecules* **1991**, *24*, 5315.
(12) Roland, C. M.; Ngai, K. L. *Macromolecules* **1991**, *24*, 2261.
(13) Roland, C. M.; Ngai, K. L.; O'Reilly, J. M.; Sedita, J. S. *Macromolecules* **1992**, *25*, 3906.
(14) Roland, C. M.; Ngai, K. L. *J. Rheol.*, in press.
(15) Plazek, D. J.; O'Rourke, V. M. *J. Polym. Sci., Polym. Phys. Ed.* **1971**, *9*, 209.
(16) Ngai, K. L.; Rendell, R. W.; Rajagopal, A. K.; Teitler, S. *Ann. N.Y. Acad. Sci.* **1986**, *484*, 150.
(17) Ngai, K. L.; Rendell, R. W. *J. Non-Cryst. Solids* **1991**, *131-133*, 942.
(18) Schönhals, A.; Schlosser, E. Presented at the 27th Europhysics Conference on Macromolecular Physics, Heraklion, Crete, Greece, 1991. *Colloid Polym. Sci.*, in press.
(19) Williams, G. *Trans. Faraday Soc.* **1965**, *61*, 1564.
(20) Fytas, G.; Dorfmuller, Th.; Chu, B. *J. Polym. Sci., Polym. Phys. Ed.* **1984**, *22*, 1471.
(21) Boese, D.; Momper, B.; Meier, G.; Kremer, F.; Hagenah, J.-U.; Fischer, E. W. *Macromolecules* **1989**, *22*, 4416.