Macromolecules **1996,** *29,* 5747−5750

Notes

Segmental Relaxation in Poly(dimethylsiloxane)

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

Naval Research Laboratory, Washington, D.C. 20375-5320

Received January 12, 1996

Introduction

Comparing the temperature dependences of the viscoelastic mechanisms in polymers is useful, both to assess theoretical models and for applications. Recently, much attention has been given to the relationship between the shape of a relaxation function (e.g., the spectral breadth of a dispersion) and its temperature dependence (i.e., the magnitude of change in relaxation times with temperature). In particular, many investigations have revealed a correlation between the time and temperature dependences of the glass transition relaxation in polymers and in small-molecule glass formers.[1−10] Such a correlation is predicted by the coupling model of relaxation. In this model, at times longer than a time t_c, the relaxation function is given by

$$\phi(t) = a \exp -\left(\frac{t}{\tau}\right)^{\beta} \tag{1}$$

where τ is the observed relaxation time and the coupling parameter ($=1 - \beta$) is a measure of the strength of the intermolecular constraints on molecular motions. The quantity t_c defines a characteristic time for the onset of the slowing down of the relaxation due to this intermolecular cooperativity. For polymers, t_c is typically of the order 10^{-12} s.[11−13] Prior to this characteristic time, intermolecular torques and unbalanced forces have not built up to a degree sufficient to impede the relaxation. The short-time, intermolecularly noncooperative relaxation is governed by local friction and, at least for polymers, the rate of conformational transitions of the polymer backbone. The latter, of course, may be subject to intramolecular constraints, even for $t < t_c$.[14−16]

The most important result of the coupling model is obtained by setting the two relaxation functions (noncooperative relaxation for $t < t_c$ and intermolecularly cooperative relaxation when $t > t_c$) equal to one another at t_c. With the former taken to be simple Debye relaxation[13,16]

$$\tau = [t_c^{\beta-1}\tau_0]^{1/\beta} \tag{2}$$

The relaxation time in the absence of intermolecular coupling, τ_0, can rarely be determined directly; however, its magnitude can be deduced from eq 2, with β and τ determined by fitting the observed relaxation to eq 1.

From eq 2 it is seen that any temperature dependence of τ_0 will be amplified by the $1/\beta$ power. This means that the temperature dependence of segmental relaxation observed for a neat polymer will parallel the magnitude of its coupling parameter. The main assumption underlying eq 2—that t_c is invariant to temperature—has been borne out by experiment.[10−13] Thus, the coupling model predicts the often observed correlation between time and temperature dependences.

The foregoing discussion begs the question of how the dependence of a relaxation mechanism on temperature might be assessed. In the case of Arrhenius behavior, one can simply compare activation energies. Unfortunately, with the exception of secondary relaxation phenomena and sometimes the terminal relaxation of polymers at high temperature, semilogarithmic plots of relaxation times (or their shift factors) versus reciprocal temperature are rarely linear; thus, no temperature-invariant activation energy is available. For terminal relaxations, free-volume-based arguments are sometimes used to justify making comparisons of relaxation times at constant temperature minus T_g. This approach assumes that free volume governs molecular motions. Problematic for terminal relaxations, this assumption is clearly untenable for segmental relaxation. Evaluating the effect of temperature on the latter requires some other approach.

The Adam and Gibbs theory of relaxation[17] provides a basis for a scheme to classify temperature dependences of segmental (for polymers) and reorientational (for small-molecule glass formers) times. Non-Arrhenius temperature dependency data from glass-forming liquids near T_g can be represented well using semilogarithmic plots of the relaxation time versus T_g/T. These T_g-normalized Arrhenius plots were termed “fragility curves” by Angell,[4−6] who developed a classification scheme for network and small-molecule liquids. Relaxation behavior is considered as strong or fragile, depending on the rapidity with which the liquid’s “structure”, or actually the properties associated with the glassy state, is modified or degraded as the temperature is increased through the glass transition region.[4−6,10] These alterations give rise to the large reduction in relaxation times over this temperature range. More fragile liquids have a larger apparent activation energy near T_g, and hence their relaxation times exhibit in the vicinity of T_g a more marked dependence on temperature. The relaxation behavior of strong liquids, on the other hand, exhibits less sensitivity to temperature.

According to Angel,[4−6] the strength and fragility of liquids reflect 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 have a high density of minima, and hence such liquids are expected to exhibit high configurational heat capacity changes, ΔC_p.[6] Surfaces with few minima and high energy barriers between minima, corresponding to low ΔC_p, would then give rise to strong liquids. Whether the nature of this putative energy surface is actually the cause of the temperature dependence of the behavior of glass formers near T_g remains to be seen. When applied to segmental relaxation in polymers, the terminology “strong” and “fragility” is certainly inappropriate, since for macromolecules there is no degradation of structure with temperature variation. For this

S0024-9297(96)00045-9

reason, we use the term “cooperativity plots”,[1] as implied by the coupling model approach, in which stronger temperature sensitivity reflects more intermolecularly cooperative dynamics.

We have previously pointed out[18] that the validity of the cooperativity plot method of assessing temperature dependencies can be assessed by comparing two liquids having the same chemical structure but differing in their relaxation times. The obvious way to realize this is to compare relaxation data on polymers differing only in molecular weight. Below some high-polymer limit, the glass transition temperature becomes a function of chain length, whereby isothermal segmental relaxation times will be strongly dependent on molecular weight. The fact that the shape of the relaxation function should be independent of molecular weight (since intermolecular cooperativity is governed by chemical structure[1,2,19,20]) leads to the prediction of an invariance of the cooperativity curves for different molecular weight samples. This has been verified from mechanical data on polystyrene and poly(phenylmethylsiloxane),[18] dielectric relaxation data for poly(propylene oxide),[18] and both mechanical and dielectric data on poly(vinylethylene).[21] Unfortunately, for all these cases, data for only two or three molecular weight samples were available.

Recently, dielectric relaxation measurements were reported[22] for 13 different poly(dimethylsiloxanes), ranging in degree of polymerization from 8 to 139 (310 $\leq$ MW $\leq$ 10 370). The chains were trimethyl terminated, so that the end groups are nonpolar and do not contribute to the measured dielectric response. Such data afford an opportunity to stringently test the T_g-normalization approach. The glass transition temperatures of these PDMS samples varied from 129 to 150K, producing an enormous variation in relaxation times at any given temperature. However, since the functional form of the relaxation process describing the local segmental motion was independent of molecular weight,[22] the T_g-scaled Arrhenius plots for the various siloxanes should be equivalent if the correlation between the time and temperature dependences continues to hold. We can also take advantage of the availability[23] of heat capacity data at T_g for PDMS of molecular weights varying in the range of those studied dielectrically to assess the implied correlation[6] between fragility and the heat capacity change at T_g.

In addition to the data on PDMS, dielectric results are available for poly(methylphenylsiloxane).[24] The backbone of PMPS chains is identical in chemical structure to PDMS, leading to the expectation that the noncooperative relaxation times, τ_0, for PDMS and PMPS will have similar temperature dependences. However, the replacement of a pendant methyl group with the bulkier phenyl ring should enhance the intermolecular cooperativity of PMPS segmental dynamics. This will be reflected in both a larger coupling parameter and a steeper cooperativity curve.

Results

Poly(dimethylsiloxane). In Figure 1 are reproduced representative segmental relaxation times as reported for the various molecular weight PDMS.[22] The lines correspond to the WLF equation[25] fits to the dielectric data. Reflecting their lower T_g, the lower MW chains have much shorter relaxation times at any given temperature. Since the concentration of chain ends, and hence their effect, is reduced as molecular weight increases, the data merge for the higher molecular weight PDMS.

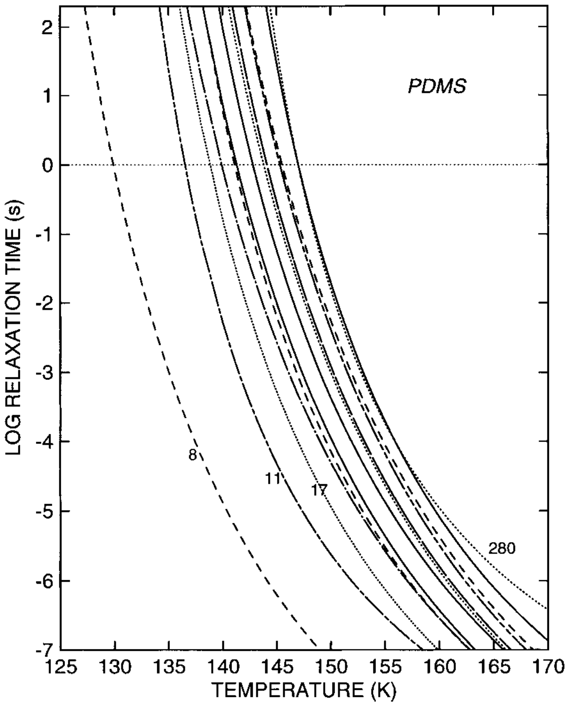

Figure 1. Segmental relaxation times for PDMS varying in molecular weight from 310 to 10 370. The numbers in the figure are the degree of polymerization for representative samples. The glass transition temperatures ranged from 129 to 150 K.

Consistent with previous work,[26,27] we define a glass transition temperature as the temperature at which the relaxation time equals 1 s. The temperature values of Figure 1 are divided by the respective glass transition temperatures of each sample, and T_g-scaled Arrhenius plots are constructed. As seen in Figure 2, this causes the relaxation times, which differed by as much as 9 orders of magnitude in Figure 1, to collapse into a single curve. As expected from eq 2, materials whose segmental relaxation functions have the same shape (i.e., same β) have the same T_g-normalized temperature dependence. This verifies the cooperativity plot as a self-consistent method for classifying the segmental relaxation behavior of polymers.

One of the prime uses of the cooperativity plot has been to infer the magnitude of the intermolecular cooperativity when β cannot be determined directly. This situation occurs whenever the segmental relaxation function is broadened inhomogeneously; examples include miscible blends,[26−29] semicrystalline polymers,[30] and networks.[21] Analyses of cooperativity plots have yielded many insights concerning the effect of chemical structure on intermolecular cooperativity in polymers and small-molecule liquids.[1,2,19,20]

For the siloxanes studied herein, there are no interfering contributions to the measured dielectric relaxation functions, and thus the shape parameters for segmental relaxation are obtained via fitting to eq 1. The dielectric data of PDMS reported in ref 22 were fit to the Havriliak−Negami equation.[31] We obtain the stretch exponents, β, from the Havriliak−Negami fit parameters α and γ by the empirical relationship[32]

$$\alpha\gamma = \beta^{1.23} \tag{3}$$

The values of β for the 13 linear PDMS samples are almost the same, deviating only slightly from a mean value of 0.485. The invariance of the relaxation function

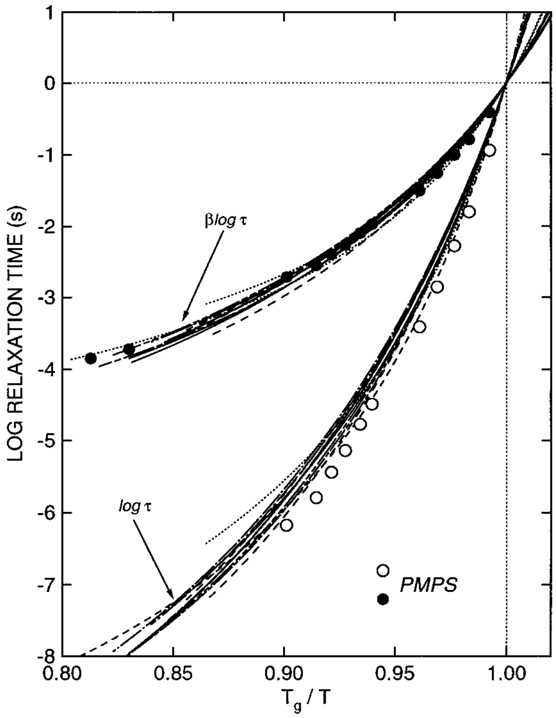

Figure 2. T_g-normalized Arrhenius plots (lower curves) for the PDMS data in Figure 1. The T_g scaling brings the curves into near coincidence. The outlying curves correspond to the lowest (dotted line) and highest (dashed line) molecular weight samples. Relaxation times for PMPS (open circles), whose segmental relaxation function is slightly broader (larger n in eq 1), change more with change in T_g-scaled temperature. When the relaxation times are raised to the power of β, the data for PDMS (upper curves) and PMPS (solid circles) come together, as expected from eq 2.

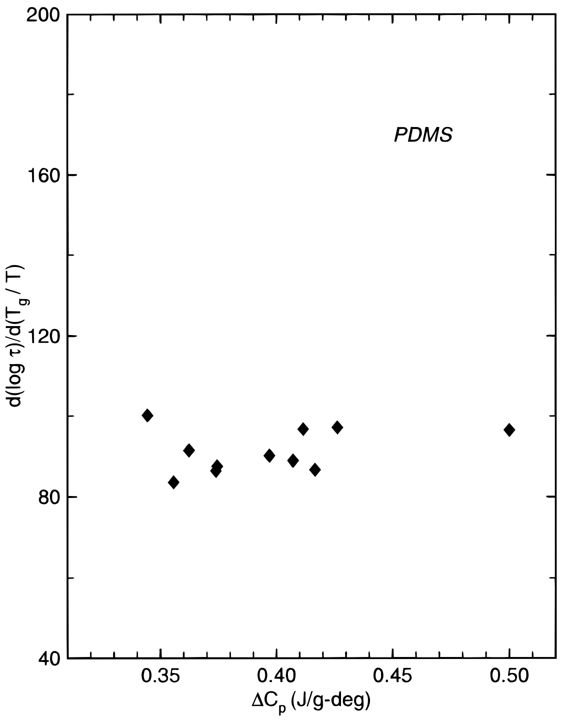

Figure 3. Slope of the T_g-normalized Arrhenius curves of Figure 2 (evaluated at T_g) versus the heat capacity change at T_g (as obtained from ref 23). The ordinate scale corresponds to the range of values (fragilities) reported in the literatue for different polymers.[9,10] The molecular weight of the PDMS is increasing from right to left. Note the absence of any correlation between these two properties.

for local segmental motion to molecular weight, over a range from oligomers to high polymers, indicates that the origin of the deviation of the relaxation function from the Debye exponential form cannot easily be attributed to any distribution of environments or free volumes.[33] Since intermolecular interactions remain the same with molecular weight, the result in Figure 2 is consistent with theory that is based on intermolecular interactions.

The heat capacity change at T_g has been measured for PDMS over a range of molecular weights encompassing those in Figures 1 and 2.[23] At sufficiently high molecular weight, the heat capacity change becomes a constant. However, when the number of repeat units per chain is less than about 100, the heat capacity jump at T_g increases inversely with chain length.[23] In Figure 3 the values for ΔC_p of PDMS are plotted against the slope of the T_g-normalized Arrhenius curves (evaluated at T_g). Each point in Figure 3 represents a particular molecular weight. The ordinate scale spans the range of slopes found for various polymers.[8,9] While there is some scatter in the values for the PDMS, no correlation between the heat capacity change at T_g and the fragility is in evidence. According to Angel,[4−6] greater T_g-normalized temperature sensitivity should arise in liquids having more minima in their potential energy hypersurface. Since the latter would contribute to a higher ΔC_p, the absence of such a correlation in Figure 3 is inconsistent with this interpretation.

Poly(methylphenylsiloxane). PMPS has the same backbone as PDMS, but with a bulkier pendant group. The enhancement of intermolecular cooperativity, via steric interactions, leads to a broader segmental relaxation function for PMPS (for which $\beta = 0.44^{24}$). From the correlation of time and temperature dependences, we expect that PMPS will exhibit relaxation times that change more with temperature than do those for PDMS. Indeed, it is seen in Figure 2 that the data for PMPS have a steeper slope than for PDMS. The difference in steepness of the curves for the two polymers is not large, but the difference between their coupling parameters is not large either. The PMPS data do lie beyond the range of the scatter in the PDMS data.

Equation 2 makes a quantitative prediction for the difference in T_g-normalized temperature dependences, which will be valid if the noncooperative relaxation times for the two species have a similar temperature dependence. This should be true for PMPS and PDMS, since they have the same chemical backbone and since τ_0 reflects backbone conformation transitions.[16] To test the prediction of eq 2, we multiple the log τ values by the value of the stretch exponent, using the respective β for PDMS and for PMPS. This scaling brings the curves for the two siloxanes into coincidence (Figure 2). Hence, the time−temperature correlation is borne out quantitatively. Although the differences in T_g-normalized temperature dependence are not large, the magnitude of their difference is consistent with the difference in the respective breadths of the relaxation functions.

Summary

The results herein confirm the log τ vs T_g/T plot as a valid method of comparing segmental relaxation behavior of polymers and other glass-forming liquids. Differences in relaxation times and temperature dependences for PDMS of varying molecular weight are removed when the temperature is normalized by the glass transition temperature. Together with the results for PMPS, this corroborates the previously established correlation between the shape of the segmental relaxation function and the temperature dependence of the segmental relaxation times. However, an interpretation of the cooperativity curves in terms of the topology of the potential energy hypersurfaces is at odds with the constancy of the T_g-normalized temperature dependence for PDMS of varying ΔC_p.

Acknowledgment. This work was supported by the Office of Naval Research, in part under Contract No. N0001495WX20203.

References and Notes

(1) Roland, C. M.; Ngai, K. L. *Macromolecules* **1991**, *24*, 5315; **1992**, *25*, 1844.
(2) Ngai, K. L.; Roland, C. M. *Macromolecules* **1993**, *26*, 6824.
(3) Roland, C. M.; Nagi, K. L. *Macromolecules* **1992**, *25*, 5765.
(4) Angell, C. A. In *Relaxations in Complex Systems*; Ngai, K. L., Wright, G. B., Eds.; Government Printing Office: Washington, DC, 1985; p 3.
(5) Angell, C. A. *J. Non-Cryst. Solids* **1991**, *131–133*, 13.
(6) Angell, C. A. *Science* **1995**, *267*, 1924.
(7) Torell, L. M.; Grimsditch, M. *Springer Proc. Phys.* **1989**, *37*, 196.
(8) Ngai, K. L. *J. Non-Cryst. Solids* **1987**, *95–96*, 969.
(9) Plazek, D. J.; Ngai, K. L. *Macromolecules* **1991**, *24*, 1222.
(10) Bohmer, R.; Ngai, K. L.; Angell, C. A.; Plazek, D. J. *J. Chem. Phys.* **1993**, *99*, 4201.
(11) Colmenero, J.; Arbe, A.; Alegria, A. *Phys. Rev. Lett.* **1993**, *71*, 2603.
(12) Roland, C. M.; Ngai, K. L.; Lewis, L. J. *J. Chem. Phys.* **1995**, *103*, 4632.
(13) Roland, C. M.; Ngai, K. L. *J. Chem. Phys.* **1995**, *103*, 1152.
(14) Hall, C. K.; Helfand, E. *J. Chem. Phys.* **1982**, *77*, 3275.
(15) Bahar, I.; Erman, B.; Monnerie, L. *Macromolecules* **1991**, *24*, 3618.
(16) Ngai, K. L.; Rendell, R. W. *J. Non-Cryst. Solids* **1991**, *131–133*, 942.
(17) Adam, G.; Gibbs, J. H. *J. Chem. Phys.* **1965**, *43*, 139.
(18) Roland, C. M.; Ngai, K. L. *Macromolecules* **1992**, *25*, 5765.
(19) Roland, C. M. *Macromolecules* **1992**, *25*, 7031.
(20) Ngai, K. L.; Roland, C. M. *Macromolecules* **1993**, *26*, 6824.
(21) Roland, C. M. *Macromolecules* **1994**, *27*, 4242.
(22) Kirst, K. U.; Kremer, F.; Pakula, T.; Hollingshurst, J. *Colloid Polym. Sci.* **1994**, *272*, 1420.
(23) Bershstein, V. A.; Egorov, V. M. *Differential Scanning Calorimetry of Polymers*; Horwood: New York, 1994; Chapter 2.
(24) Boese, D.; Momper, B.; Meier, G.; Kremer, F.; Hagenah, J.-U.; Fischer, E. W. *Macromolecules* **1989**, *22*, 4416.
(25) Ferry, J. D. *Viscoelastic Properties of Polymers*; Wiley: New York, 1980.
(26) Roland, C. M.; Ngai, K. L. *Macromolecules* **1992**, *25*, 363.
(27) Roland, C. M.; Ngai, K. L.; O'Reilly, J. M.; Sedita, J. S. *Macromolecules* **1992**, *25*, 3906.
(28) Roland, C. M.; Ngai, K. L. *J. Rheol.* **1992**, *36*, 1691.
(29) Roland, C. M.; Ngai, K. L. *Macromolecules* **1991**, *24*, 2261.
(30) Roland, C. M.; Ngai, K. L. *Macromolecules* **1993**, *26*, 2688.
(31) Havriliak, S.; Negami, S. *J. Polym. Sci., Part C* **1966**, *14*, 99.
(32) Alvarez, F.; Alegria, A.; Colmenero, J. *Phys. Rev.* **1991**, *B44*, 5196.
(33) Bueche, F. *Physical Properties of Polymers*; Interscience: New York, 1962.

MA960045D