Effect of volume changes on segmental relaxation in siloxane polymers

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From dielectric relaxation and equation-of-state measurements on polymethylphenylsiloxane and polymethyltolylsiloxane, the relative contributions of volume and thermal energy to the temperature dependence of the segmental relaxation times are quantified. In both polymers, volume exerts a substantial effect, being almost as significant as thermal energy. A possible consequence of this prominent role of volume in governing the segmental dynamics is the finding that the relaxation times, measured for a series of temperature at various (fixed) pressures, can be expressed as a single function of the volume normalized by the volume at the glass transition temperature. A similar result is found for the (isothermal) relaxation times measured at various pressures.

INTRODUCTION

Glassy materials pervade virtually all aspects of life, being found in everything from common plastics and skidding automobile tires to preserved food and cosmic ice. Although the vitrification process is centrally important to many technologies, a quantitative understanding of the dynamics near the glass transition remains to be realized. As observed using various spectroscopies, the time scale of molecular motion undergoes a spectacular slowing down upon approach to the glassy state, with a characteristic time τ which increases from nanoseconds to immeasurably long durations. This increase in τ with decreasing temperature is induced by two effects: (i) densification, which causes congestion and jamming of molecular segments and (ii) the loss of thermal energy, leading to entrapment within the potential energy barriers. Theories of the glass transition usually focus on only one aspect (e.g., free volume models [1–3] or energy landscape models [4,5]); however, recent experimental work has made clear that density and thermal energy both exert an influence on τ near T_g [6,7].

These effects can be quantified from two ratios: The ratio of the activation energy at constant volume, $E_V(T,V) = R(\partial \ln \tau/\partial T^{-1})_V$, to the activation energy at constant pressure, $E_P(T,P) = R(\partial \ln \tau/\partial T^{-1})_P$, would vary from near zero (volume-governed relaxation) to unity (thermal energy dominates) [8]. For van der Waals molecular liquids, $E_V/E_P \sim 0.5$, since the respective contributions from volume and thermal energy are nearly equal [6,7]. This ratio approaches one for associated liquids, reflecting the changing degree of specific interactions with changing P and T [9,10]. For polymers, E_V/E_P has been found to usually be larger than 0.6, indicating that the influence of temperature has been found to be more important [11,12]. It is ironic that volume should be of lesser importance in the very class of materials for which free volume models have been historically so popular.

In this paper we describe results for two siloxane polymers, polymethylphenylsiloxane (PMPS) and polymethyl-

tolylsiloxane (PMTS). We have previously reported the differing effect of pressure on the relaxation properties of these two polymers [13,14]. At ambient pressure, the segmental relaxation functions and fragilities for the two materials are the same. However, while PMTS has a larger activation volume, both its glass transition temperature and fragility change more with pressure than found for PMPS. In combination with equation-of-state measurements, the dielectric relaxation times, measured as a function of both temperature and pressure, can be used to determine the E_V/E_P. As detailed herein, near T_g, volume can becomes *more* important than thermal energy. This is a departure from the usual behavior reported for other polymers. A scaling of the volume dependence of the relaxation times is demonstrated.

EXPERIMENT

The PMTS (obtained from G. Meier of the Institute of Solid State Research, Jülich, Germany) had a weight average molecular weight, M_w, equal to 35 300 daltons with a polydispersity of 1.10. The PMPS (from T. Wagner of the Max Planck Institute for Polymer Research, Mainz, Germany) had $M_w = 23\,360$ and a polydispersity of 1.16. Dielectric measurements were carried out over the frequency range from 10^{-2} to 10^6 Hz, at ambient and elevated pressures (≤ 260 MPa). A description of the equipment can be found elsewhere [13,14]. Equation-of-state data were obtained using a Gnomix instrument [15], with all measurements taken in the equilibrium ($> T_g$) state, using a cooling rate of 0.5 K/min. Specific volumes were calculated from the measured volume change using the density determined for ambient pressure and room temperature.

RESULTS

The pressure-volume-temperature (PVT) results for PMPS and PMTS are displayed in Figs. 1 and 2, respectively. These were fit to the Tait equation of state [15]
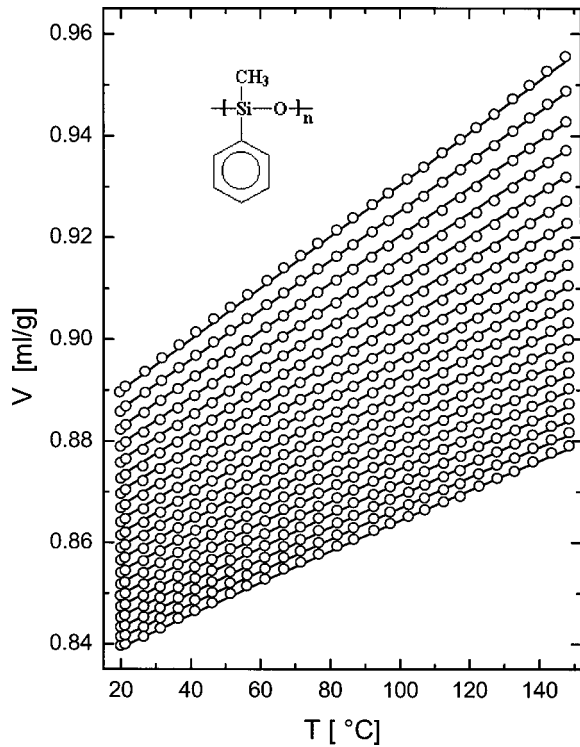
FIG. 1. (a) Equation-of-state data for polymethylphenylsiloxane. The pressure ranges from 10 to 200 MPa (from top to bottom) with 10-MPa increments.
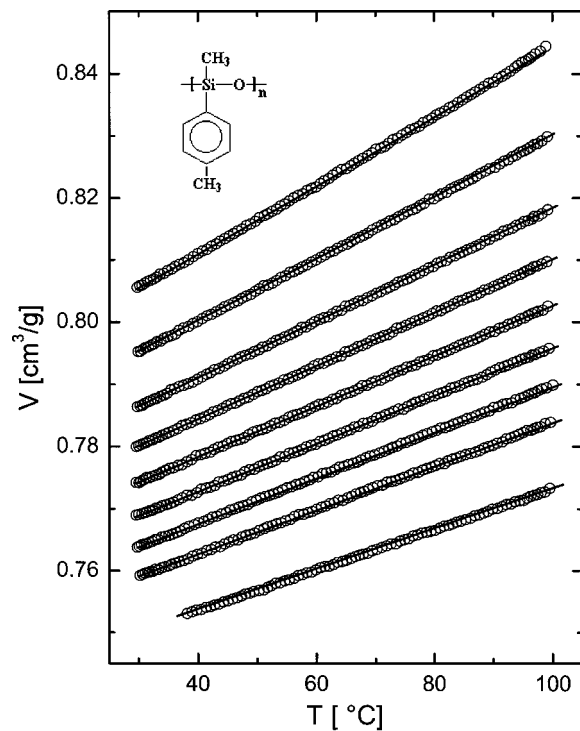

FIG. 2. Equation-of-state data for polymethyltolylsiloxane. The pressure (from top to bottom) is 10, 35, 60, 80, 100, 120, 140, 160, and 200 MPa.
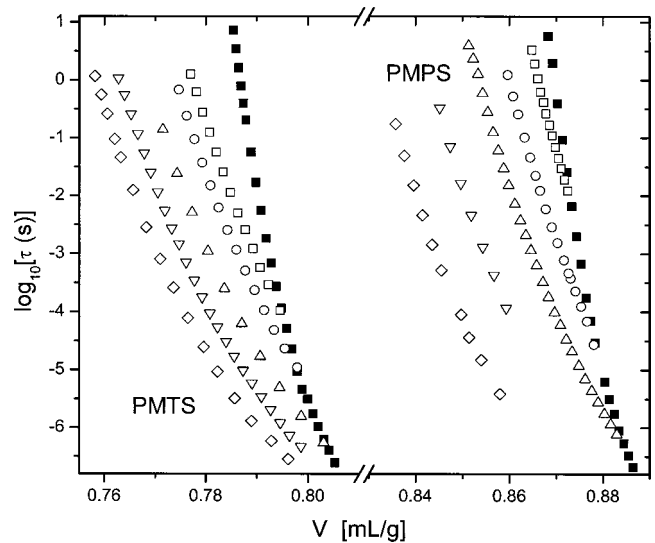

FIG. 3. Segmental relaxation times vs specific volume. The solid symbols are isobars measured at $P = 0.1$ MPa, and the hollow symbols represent isotherms for PMPS at 253 K ($\square$), 263 K ($\bigcirc$), 273 K ($\triangle$), 293 K ($\triangledown$), and 313 K ($\diamond$), and for PMTS at 276.6 K ($\square$), 283 K ($\bigcirc$), 293 K ($\triangle$), 303 K ($\triangledown$), and 313 K ($\diamond$).

$$V(T,P) = (a_0 + a_1 T + a_2 T^2)$$

$$\times \left\{ 1 - 0.0894 \ln \left[1 + \frac{P}{b_0 \exp(-b_1 T)} \right] \right\}. \quad (1)$$

For PMPS, the linear least-squares best fits are $a_0 = 0.8835$ mL g^{-1}, $a_1 = 5.1 \times 10^{-4}$ mL g^{-1} C^{-1}, $a_2 = 1.06 \times 10^{-7}$ mL g^{-1} C^{-2}, $b_0 = 220.1$ MPa, and $b_1 = 4.01$
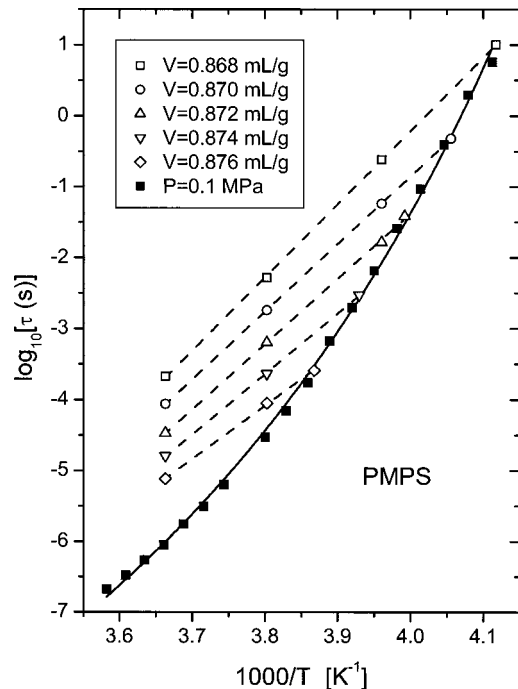

FIG. 4. Isochoric relaxation times (hollow symbols) at the indicated specific volumes, along with the relaxation times for ambient pressure (solid symbols) for PMPS. The dashed lines are VFTH fits.
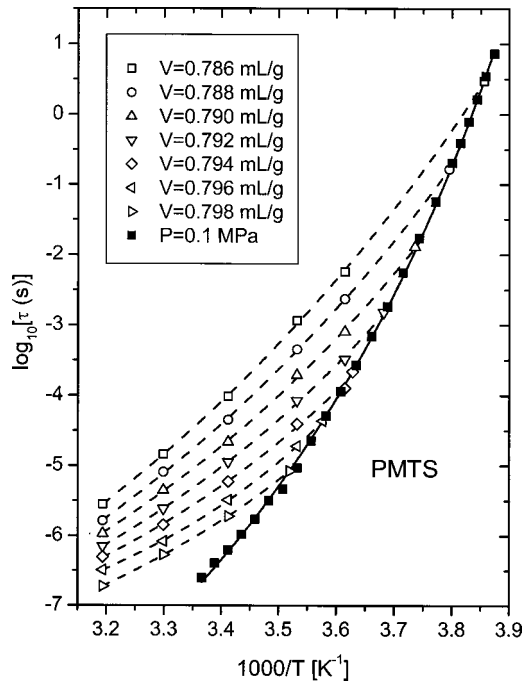
FIG. 5. Isochoric relaxation times (hollow symbols) at the indicated specific volumes, along with the relaxation times for ambient pressure (solid symbols) for PMTS. The dashed lines are VFTH fits.
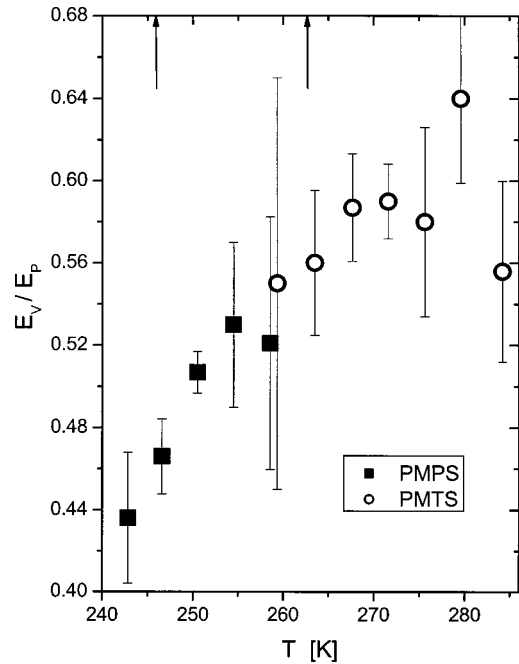

FIG. 6. Ratio of the apparent activation energies for isochoric and isobaric conditions, obtained from the intersection of the respective curves in Figs. 3 and 4. The arrows at the top denote the temperatures at which the respective relaxation times equal 1 s.

$\times 10^{-3}$ C^{-1}, while for the PMTS, $a_0 = 0.7928$ mL g^{-1}, $a_1 = 5.0 \times 10^{-4}$ mL g^{-1} C^{-1}, $a_2 = 6.49 \times 10^{-7}$ mL g^{-1} C^{-2}, $b_0 = 179.7$ MPa, and $b_1 = 4.73 \times 10^{-3}$ C^{-1}. Using this parametrization of the PVT data, we convert the measured temperature and pressure dependences of the relaxation times to the volume dependences displayed in Fig. 3.

Each isotherm in Fig. 3, as well as the isobar for $P = 0.1$ MPa, yields a different curve. The fact that the relaxation times are not a single function of the volume is not at odds with a free volume interpretation of the glass transition, since the free volume varies less with pressure than does the total volume [1]. In principle, one can deduce the free volume, for example, using lattice models [16]. We eschew this approach herein, and instead extract isochoric, $\tau(T)|_V$, and isobaric, $\tau(T)|_P$, from the results in Fig. 3. These are plotted for the two siloxanes in Figs. 4 and 5, along with the fits to the Vogel-Fulcher-Tamann-Hesse (VFTH) equation [1]. The slopes at the intersection of the isochoric and isobaric curves yield the respective activation energies. These are apparent values only, given the non-Arrhenius behavior, particularly at constant pressure.

In Fig. 6, we display the ratio of these activation energies, E_V/E_P, as a function of temperature. The two data sets are almost continuous, with the values for PMTS falling at

higher temperature reflecting its higher T_g. There is a small increase in E_V/E_P with temperature $\sim 1\%$ per K. At T_g ($\tau = 1$ s), this ratio is 0.52 ± 0.06 for PMPS. This indicates that the temperature dependence of τ for PMPS is due almost as much to the volume change accompanying a change in temperature as to the change in thermal energy. This ratio is the smallest observed to date for any polymer. For the PMTS, $E_V/E_P = 0.55 \pm 0.05$, indicating that volume and thermal energy both exert a substantial influence on the temperature dependence of the relaxation times. The ratio for PMTS appears to increase with increasing temperature, although the scatter in the data precludes definitive assessment of the effect of temperature on E_V/E_P. The large influence of volume on the dynamics for PMTS and PMPS, in comparison to other polymers, may be related to the large degree of flexibility of the siloxane backbone. However, there is no simple relationship between E_V/E_P and chemical structure [17].

A second measure of the relative contribution of thermal energy and volume to the temperature dependence of τ is from the ratio of the thermal expansion coefficients measured isochronally, $\alpha_\tau = -\rho^{-1}(\partial\rho/\partial T)_\tau$, and at constant pressure, $\alpha_P = -\rho^{-1}(\partial\rho/\partial T)_P$ [9]. The ratio $|\alpha_\tau|/\alpha_P$, which quantifies how much the volume would have to be adjusted to maintain a constant relaxation time, in response to a

TABLE I. Results for siloxane polymers at $\tau = 1$ s. Numbers in square brackets denote powers of 10.

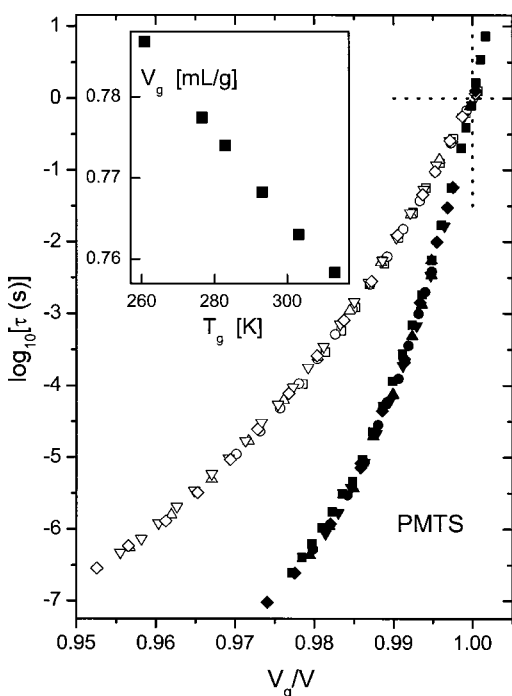|	T_g (K) (P = 0.1 MPa)	E_V/E_P	α_τ (C^{-1})	α_P (C^{-1})	$-\alpha_\tau/\alpha_P$
PMPS	245.7	0.52 ± 0.06	-6.933 [4]	5.803 [4]	1.19 ± 0.01
PMTS	260.8	0.55 ± 0.05	-7.572 [4]	6.251 [4]	1.21 ± 0.02

FIG. 7. Relaxation times for PMTS measured as a function of pressure at constant $T = 276.6$ K ($\square$), 283 K ($\bigcirc$), 293 K ($\triangle$), 303 K ($\triangledown$) and 313 K ($\diamond$), and as a function of temperature at constant $P = 0.1$ MPa ($\blacksquare$), 50 MPa ($\bullet$), 100 MPa ($\blacktriangle$), 200 MPa ($\blacktriangledown$), and 250 MPa ($\blacklozenge$). The inset shows the variation of V_g with temperature, for $0.1 \leqslant P$ (MPa) $\leqslant 171$.

change in temperature, is simply related to the ratio of activation energies [17].

We evaluate the expansivities from the dielectric and PVT data, obtaining for $\tau = 1$ s the results listed in Table I. The ratio $|\alpha_\tau|/\alpha_P = 1.2$ is equivalent for the two siloxanes within the experimental error. A value near unity implies that volume and thermal energy have a comparable influence on $\tau(T)$, corroborating the analysis of the activation energies.

Since volume plays an important role in the supercooled dynamics of these materials, it is of interest to determine if volume can be utilized in some fashion to normalize the data. For PMTS, we calculate the volume at the glass transition, V_g that is, the volume for various combinations of T and P at which $\tau = 1$ s. These are shown as an inset to Fig. 7. As is well known, V_g is not a constant, but decreases with increasing pressure [1].

In analogy to fragility plots [18], in Fig. 7 the relaxation times of PMTS are displayed as a function of the reciprocal volume normalized by V_g. The isobars all superimpose, as do the isotherms; however, the constant pressure and constant temperature pathways yield different curves. This is a remarkable result—the relaxation times, all obtained in equilibrium, show a V_g/V dependence that is path-dependent. The greater steepness of the isobaric curves is evidently due to the convoluted contributions of the volume and thermal energy. If volume were dominant, the two sets of curves would superimpose, while larger separation indicates a stronger effect of temperature.

SUMMARY

Dielectric measurements of the segmental relaxation mode in PMPS and PMTS, obtained as a function of temperature and pressure, were analyzed, in combination with equation-of-state data. The main findings are as follows.

(i) For both polysiloxanes, the respective contributions from volume and thermal energy are comparable.

(ii) The values of E_V/E_P (as well as $|\alpha_\tau|/\alpha_P$) for PMPS and PMTS are lower than has been reported for other polymers. This is ascribed to the enhanced flexibility of the siloxane backbone.

(iii) Segmental relaxation times obtained isobarically or isothermally can be superposed to yield a single function of volume, when the latter is normalized by the volume at the (pressure-dependent) glass transition temperature.

ACKNOWLEDGMENTS

[1] J. D. Ferry, *Viscoelastic Properties of Polymers*, 3rd ed. (Wiley, New York, 1980).

[2] M. H. Cohen and G. S. Grest, Phys. Rev. B **20**, 1077 (1979); G. S. Grest and M. H. Cohen, Adv. Chem. Phys. **48**, 455 (1981).

[3] J. T. Bendler, J. Fontanella, and M. Schlesinger, Phys. Rev. Lett. **87**, 195503 (2001).

[4] M. Goldstein, J. Chem. Phys. **51**, 3728 (1969).

[5] C. A. Angell, Science **267**, 1924 (1995).

[6] M. Paluch, R. Casalini, and C. M. Roland, Phys. Rev. B **66**, 092202 (2002).

[7] C. M. Roland, M. Paluch, T. Pakula, and R. Casalini, Philos. Mag. B (to be published).

[8] G. Williams, in *Dielectric Spectroscopy of Polymeric Materials*, edited by J. P. Runt and J. J. Fitzgerald (ACS, Washington, D.C., 1997), Chap. 1.

[9] M. L. Ferrer, C. Lawrence, B. G. Demirjian, D. Kivelson, C. Alba-Simionesco, and G. Tarjus, J. Chem. Phys. **109**, 8010 (1998).

[10] C. M. Roland, T. Psurek, S. Pawlus, and M. Paluch (to be published).

[11] G. Williams, Trans. Faraday Soc. **60**, 1548 (1964); **60**, 1556 (1964); **61**, 1564 (1965).

[12] C. M. Roland and R. Casalini, Macromolecules **36**, 1361 (2003).

[13] M. Paluch, C. M. Roland, and S. Pawlus, J. Chem. Phys. **116**, 10 932 (2002).

[14] M. Paluch, S. Pawlus, and C. M. Roland, Macromolecules **35**, 7338 (2002).

[15] P. Zoller and D. J. Walsh, *Standard Pressure-Volume-*

Temperature Data for Polymers (Technomic, Lancaster, PA, 1995).

[16] M. Paluch, R. Casalini, and C. M. Roland, Phys. Rev. E **67**, 021508 (2003).

[17] R. Casalini and C. M. Roland, J. Chem. Phys. **119**, 4052 (2003).

[18] R. Bohmer, K. L. Ngai, C. A. Angell, and D. J. Plazek, J. Chem. Phys. **99**, 4201 (1993).