Effect of volume changes on segmental relaxation in siloxane polymers

M. Paluch,¹ R. Casalini,² A. Patkowski,³ T. Pakula,⁴ and C. M. Roland⁵
¹Institute of Physics, Silesian University, Uniwersytecka 4, 40-007 Katowice, Poland
²Chemistry Department, George Mason University, Fairfax, Virginia 22030, USA
³Institute of Physics, A. Mickiewicz University, Umultowska 85, 61-614 Poznan, Poland
⁴Max Planck Institute for Polymer Research, D-55021 Mainz, Germany
⁵Chemistry Division, Naval Research Laboratory, Code 6120, Washington, D.C. 20375-5342, USA

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From dielectric relaxation and equation-of-state measurements on polymethylphenylsiloxane and polymethyl-
ylolsiloxane, 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
dynamic 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 Tg [6,7].

These effects can be quantified from two ratios: The ratio of the activation energy at constant volume, E\text{V}(T,V) = R(∂ ln π/∂T)\text{V}, to the activation energy at constant pressure, E\text{P}(T,P) = R(∂ ln π/∂T)\text{P}, would vary from near zero (volume-governed relaxation) to unity (thermal energy dominates) [8]. For van der Waals molecular liquids, E\text{V}/E\text{P} ~ 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\text{V}/E\text{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-
ylolsiloxane (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\text{V}/E\text{P}. As detailed herein, near Tg, 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.

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 Tg [6,7].

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EXPERIMENT

The PMTS (obtained from G. Meier of the Institute of Solid State Research, Jülich, Germany) had a weight average molecular weight, Mw, 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 Mw = 23 360 and a polydispersity of 1.16. Dielectric measurements were carried out over the frequency range from 10⁻² to 10⁶ 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 (≥ Tg) 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]
For PMPS, the linear least-squares best fits are $a_0 = 0.8835 \text{ mL g}^{-1}$, $a_1 = 5.1 \times 10^{-4} \text{ mL g}^{-1} \text{ C}^{-1}$, $a_2 = 1.06 \times 10^{-7} \text{ mL g}^{-1} \text{ C}^{-2}$, $b_0 = 220.1 \text{ MPa}$, and $b_1 = 4.01$. 

\[
V(T,P) = (a_0 + a_1 T + a_2 T^2) \times \left[1 - 0.0894 \ln\left(1 + \frac{P}{b_0 \exp(-b_1 T)}\right)\right].
\]
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.

\[ \log_{10} \tau = (E V - E P) / (2.303 R T) \]

for the PMTS, \( a_0 = 0.7928 \text{ mL g}^{-1} \), \( a_1 = 5.0 \times 10^{-4} \text{ mL g}^{-1} \text{ C}^{-1} \), \( a_2 = 6.49 \times 10^{-7} \text{ mL g}^{-1} \text{ C}^{-2} \), \( b_0 = 179.7 \text{ MPa} \), and \( b_1 = 4.73 \times 10^{-3} \text{ C}^{-1} \). 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 \( P = 0.1 \text{ MPa} \), 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 odds with a free volume interpretation of the glass transition.

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 \( T_g (\tau = 1 \text{ s}) \), this ratio is \( 0.52 \pm 0.06 \) for PMPS. This indicates that the temperature dependence of \( \tau \) 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 \( \tau \) is from the ratio of the thermal expansion coefficients measured isochronally, \( \alpha_T = -\rho^{-1} (\partial \rho / \partial T)_p \), and at constant pressure, \( \alpha_P = -\rho^{-1} (\partial \rho / \partial T)_P \) [9]. The ratio \( \alpha_T / \alpha_P \), 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 \( \tau = 1 \text{ s} \). Numbers in square brackets denote powers of 10. |
|-----------------|-----------------|-----------------|-----------------|-----------------|
| \( T_g (K) \)   | \( E_V / E_P \)  | \( \alpha_T \)  | \( \alpha_P \)  | \( -\alpha_T / \alpha_P \) |
| (\( P = 0.1 \text{ MPa} \)) |                  |                 |                 |                 |
| 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     |
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 $|\alpha_v|/\alpha_P$) 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.

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