Macromolecules **2002,** *35,* 7338−7342

Pressure and Temperature Dependence of the α-Relaxation in Poly(methyltolylsiloxane)

M. Paluch,[†,‡] S. Pawlus,[‡] and C. M. Roland*,[†]

Naval Research Laboratory, Chemistry Division, Code 6120, Washington, D.C. 20375-5342, and Institute of Physics, Silesian University, Uniwersytecka 4, 40-007 Katowice, Poland

Received April 12, 2002

ABSTRACT: The α-relaxation, involving local segmental motion, of poly(methyltolylsiloxane) (PMTS) was measured using dielectric spectroscopy, over a temperature range in excess of 100 deg at pressures up to 250 MPa. The data conformed to time−temperature−pressure superpositioning, although the T_g-normalized temperature dependence of the relaxation times exhibited a weak dependence on pressure. The combined temperature and pressure dependences could be accurately described using a generalized Vogel−Fulcher expression, with the Vogel temperature having the same pressure dependence as the glass temperature. In comparing the relaxation properties of PMTS to the structurally similar poly(methylphenylsiloxane) (PMPS), we found that while their ambient pressure behaviors were equivalent, the relaxation times, T_g-scaled temperature dependence, and T_g itself for PMTS were all more sensitive to pressure. These differences are consistent with a larger activation volume for PMTS, which is indeed comprised of proportionally larger chain units than is PMPS.

Introduction

Hydrostatic pressure is increasingly employed as an experimental variable, for example in the study of blends[1−5] and polymer dynamics.[6−9] Being a fundamental thermodynamic quantity, pressure is of obvious importance to the study of structural relaxation and the local dynamics in polymers and small molecule glass-formers. The characterization of pressure dependences can help quantify the respective contributions from density (or free volume), thermal energy and configurational entropy to the relaxation properties.[10−12] The application of pressure also can offer direct advantages, such as facilitating the resolution of overlapping resonances.[13,14] Our interest in the use of pressure is toward establishing the connection between the chemical structure of polymers and various characteristics of their local relaxation.[15,16]

This paper reports dielectric measurements of the combined effects of pressure and temperature on the α-relaxation in poly(methyl-*p*-tolylsiloxane) (PMTS). The aim is to develop structure/property relationships, with a focus on local segmental relaxation in polymers. Previous work along these lines, but limited to ambient pressure data, established a connection between structural relaxation properties and the degree to which the chemical structure engenders intermolecular constraints on the local motion.[15−20] Polymers with polar, bulky, asymmetric, or rigid chain backbones and/or having sterically hindering pendant groups undergo segmental relaxation that is more constrained by interactions with neighboring chain segments. Such highly cooperative dynamics is manifested in greater nonexponentiality of the relaxation function and more departure of the relaxation times from an Arrhenius temperature dependence.

This correlation interprets the behavior in terms of steric effects and backbone structure, without explicit consideration of free volume and its role in overcoming potential barriers. The use of pressure allows assessment of the relative importance of free volume and thermal energy to the local dynamics.[21−24] Formally, the pressure dependence of the relaxation times can be expressed as an activation volume, which is the pressure dependence counterpart to the activation energy used to quantify temperature dependences. Herein we describe for PMTS the effect of both pressure and temperature on the shape of the relaxation function and the magnitude of the segmental relaxation times. The results are compared to recently reported data[25] for the structurally similar poly(methylphenylsiloxane).

Experimental Section

The poly(methyl-*p*-tolylsiloxane) was provided by G. Meier. It had a weight-average molecular weight of 35 300 Da with a polydispersity equal to 1.10. For ambient pressure measurements, we used a Novo-Control GmbH dielectric spectrometer, equipped with an Novocontrol Alpha dielectric analyzer, having a frequency range of 10^{-2}−10^{7} Hz. The sample was contained in a parallel plate cell (diameter = 20 mm, gap = 0.1 mm). Temperature was controlled using a nitrogen gas cryostat, with the stability better than 0.1 K. For measurements at elevated pressure, the sample capacitor was sealed and mounted inside a Teflon ring to isolate it from the silicone oil used to transfer the pressure. The capacitor was placed in a chamber, with pressure applied via a hydraulic press. This pressure was measured by a Nova Swiss tensometric pressure meter (resolution = 0.1 MPa). The temperature was controlled (±0.1 K) by liquid flow from a thermostatic bath.

Results

Figure 1 shows representative dispersions in the dielectric loss, $\epsilon''(\omega)$, where ω is angular frequency, measured for different conditions of temperature and pressure. These particular combinations of T and P

[†] Naval Research Laboratory.
[‡] Silesian University.

10.1021/ma020587x CCC: $22.00

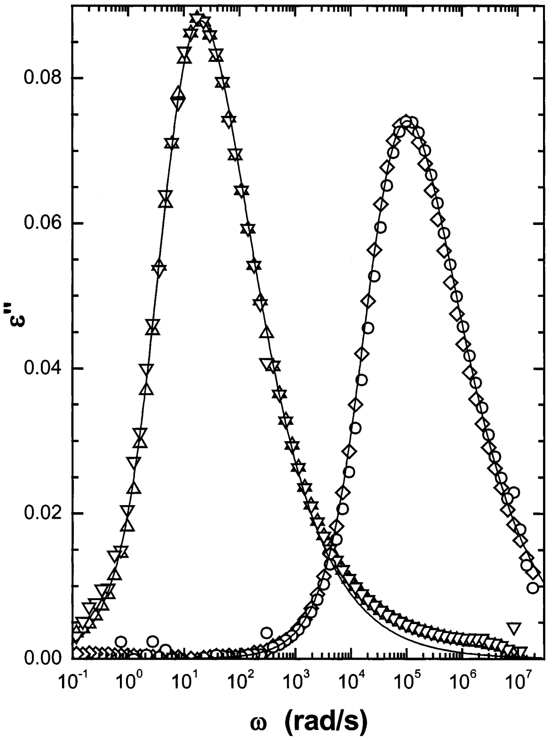

Figure 1. α-Dispersion in the dielectric loss for PMTS measured at ambient pressure (△, 265.2 K; ◇, 283.2 K) and elevated pressure (▽, 118 MPa, 303.2 K; ○, 81 MPa, 313.2 K). The solid lines represent the fits to the transform of eq 1, with $\beta = 0.51 \pm 0.01$. The ordinate values for the 118 and 81 MPa peaks have been multiplied by a factor of 2.10 and 2.19, respectively, to superimpose on the ambient pressure measurements. All frequencies are as measured; that is, the relaxation times are the same for the respective combinations of *T*, *P*, so that no horizontal shifting was necessary.

cause the peaks to superimpose. The spectra could be described using the LaPlace transform of the Kohlrausch function,[26] with the dielectric loss given by

$$\epsilon''(\omega) = \Delta\epsilon \int_0^{\infty} \mathrm{d}t \left[\frac{-\mathrm{d}}{\mathrm{d}t} \exp(-t/\tau_{\mathrm{K}})^{\beta}\right] \sin(\omega t) \qquad (1)$$

in which $\Delta\epsilon$ is the dielectric strength, τ_{K} the Kohlrausch relaxation time, and β the stretch exponent. A value of the latter equal to 0.51 ± 0.01 gave a good fit to the data over the entire experimental range; that is, for our measurements, the shape of the loss spectrum was invariant to both temperature and pressure.

The α-relaxation times, τ_{α}, defined as the inverse of the frequency of the maximum in the dielectric loss ($=\omega_{\max}^{-1}$), are plotted in Figures 2 and 3. (Note that since structural relaxation peaks are skewed toward higher frequencies, the most probable relaxation time is longer than the Kohlrausch relaxation time; for $\beta = 0.51$, $\tau_{\alpha} = 1.35\tau_{\mathrm{K}}$.) The data in Figure 2 are the isobaric measurements, while Figure 3 shows the isotherms. (Of course, this refers only to the experimental procedure; each measurement per se was done at constant *T* and *P*.) The temperature dependence of the α-relaxation times in Figure 2 can be described using the Williams–Landel–Ferry equation,[27] or equivalently the Vogel–Fulcher equation[28]

$$\tau_{\alpha}(T) = \tau_{\infty} \exp\left(\frac{D_T T_0}{T - T_0}\right) \qquad (2)$$

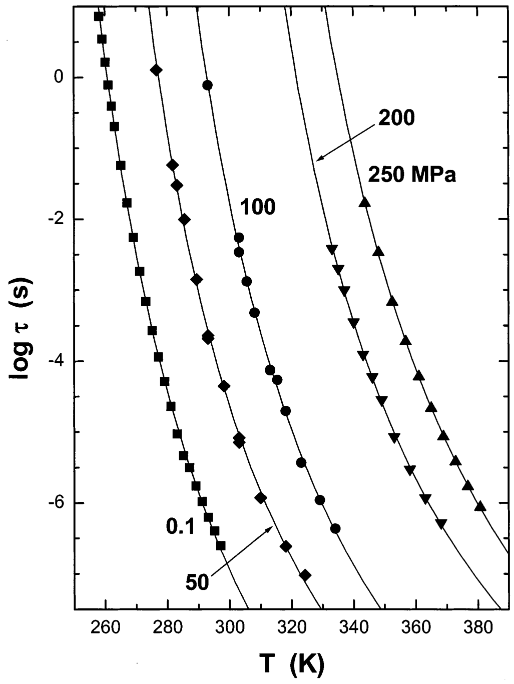

Figure 2. α-Relaxation times for PMTS measured as a function of temperature at the indicated pressures (in MPa).

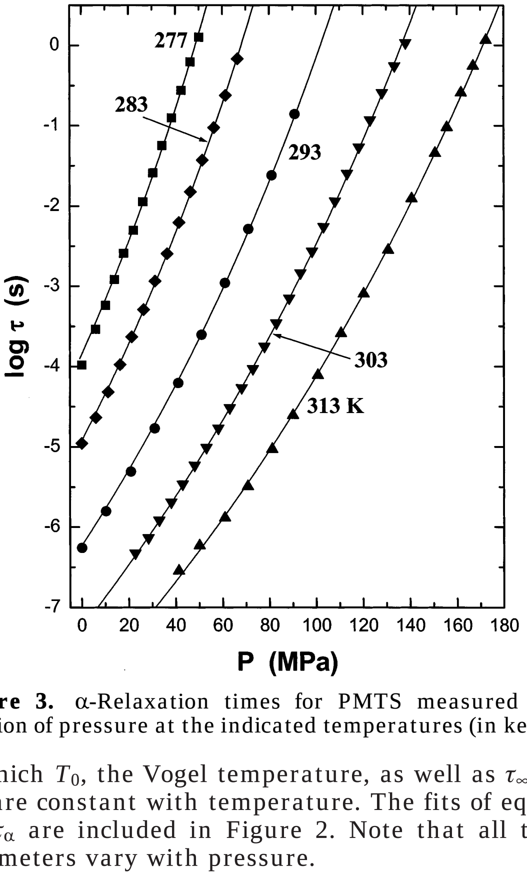

Figure 3. α-Relaxation times for PMTS measured as a function of pressure at the indicated temperatures (in kelvin).

in which T_0, the Vogel temperature, as well as τ_{∞} and D_T, are constant with temperature. The fits of eq 2 to the τ_{α} are included in Figure 2. Note that all three parameters vary with pressure.

Recognizing that temperature and pressure act inversely, a pressure counterpart to the Vogel–Fulcher equation can be obtained by substituting P^{-1} for T in eq 2, yielding[29,30]

$$\tau_{\alpha}(P) = \tau_0 \exp\left(\frac{D_P P}{P_0 - P}\right) \qquad (3)$$

in which D_P and P_0 are adjustable parameters. The

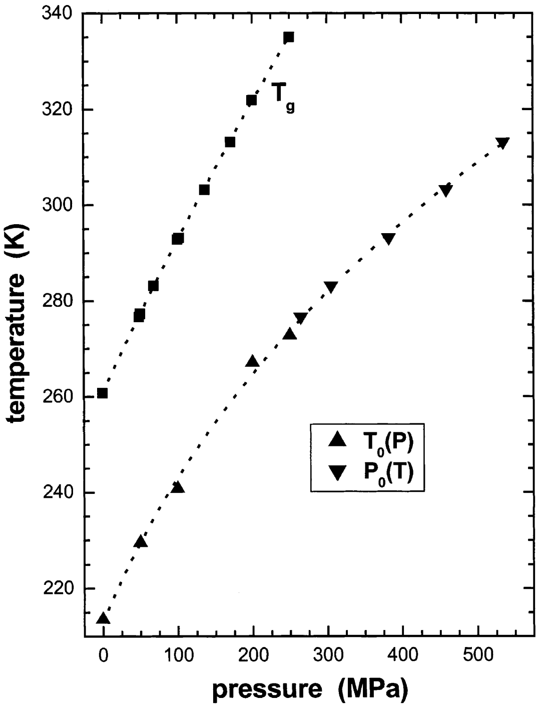

Figure 4. Pressure dependence of the Vogel temperature (▲, eq 2), along with the temperature dependence of the corresponding pressure parameter (▼, eq 3). Also shown are the temperatures at which $\tau_\alpha = 1$ s (■). The curves through the data represent the respective fits to eq 4.

Table 1. Fitting Parameters for Eq 4 (Figure 4)

	a	*b*	*c*
T_0, P_0	213.0 ± 1	4.1 ± 0.3	571 ± 43
T_g, P_g	260.9 ± 0.2	1.9 ± 0.1	776 ± 12

prefactor τ_0 is obtained from the ambient pressure, isobaric data. This expression has been shown to satisfactorily described $\tau_\alpha(P)$ data for a variety of supercooled liquids.[25,31-36] We fit the data in Figure 3 to eq 3 by assuming that D_P is independent of temperature. Thus, using a common value of $D_P = 41.8$ for all temperatures, we obtain the fits shown in Figure 3.

In Figure 4 we plot the values of T_0 from the fits to the data in Figure 2, together with the best-fit values of P_0 for each T (Figure 3). This is a rare case where isothermal $T_0(P)$ and isobaric $P_0(T)$ results are obtained over a range sufficient to demonstrate that the two data sets fall on a single curve. The T_0−P_0 relationship is nonlinear, with a slope at zero pressure equal to 0.37 ± 0.03 K/MPa.

Also shown in Figure 4 are the conditions of temperature and pressure for which $\tau_\alpha = 1$ s. (The value is arbitrary; using 1 s avoids extrapolation of the data.) At ambient pressure, this "dynamic" glass temperature equals 260.8 K, which is quite close to the calorimetric T_g of 259.5 K. The data in Figure 4 conform to the empirical equation[7]

$$T_g = a\left(1 + \frac{b}{c}P\right)^{1/b} \tag{4}$$

Note that eq 4 describes not only the pressure dependence of T_g but also the T_0 and P_0 data obtained by fitting the isobars and isotherms to eqs 2 and 3, respectively. The obtained parameters are listed in Table 1. In the limit of zero pressure, $dT_g/dP|_{P\to 0} = 0.34 \pm 0.01$ K/MPa; thus, the respective pressure coefficients of T_0 and T_g are equal to within the experimental error.

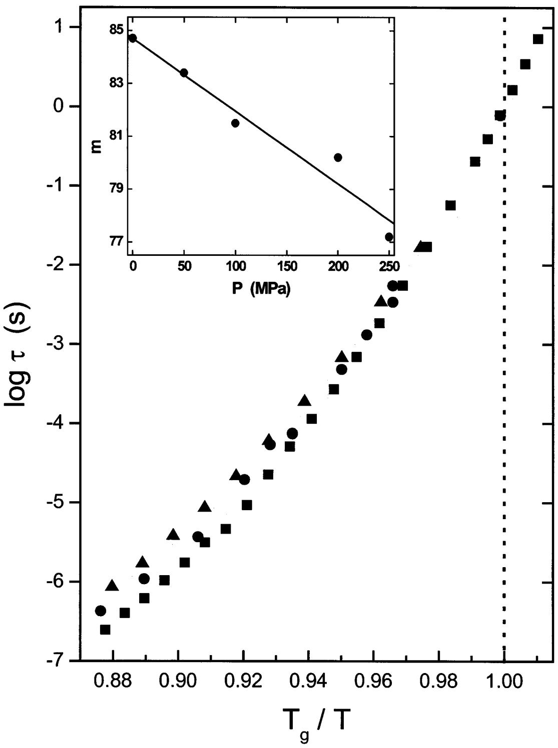

Figure 5. T_g-normalized temperature dependence of the α-relaxation times for PMTS at ambient pressure (■), 100 MPa (●), and 250 MPa (▲). The inset shows the steepness index (eq 5) for all measured pressures.

It is common practice to assess the effect of temperature on the relaxation time by normalizing temperature by the glass temperature. Figure 5 shows such T_g-scaled Arrhenius plots (using $\tau_\alpha(T_g) = 1$ s) for the relaxation times measured at three pressures (0.1, 100, and 250 MPa). There is a small, but significant, decrease in the steepness of the curves with increasing pressure. We can quantify this by calculating the steepness index (or "fragility") at T_g,[37,38]

$$m_T \equiv \frac{d \log(\tau)}{d(T_g/T)}\Big|_{T=T_g} = D_T \log(e)\,\frac{T_0/T_g}{(1 - T_0/T_g)^2} \tag{5}$$

This relationship between m_T and D_T underlies use of the terms "fragility" and "strength" parameters in reference to these quantities. In the inset to Figure 5, we plot the steepness index as a function of pressure. This yields $dm_T/dP = -0.027 \pm 0.004$ MPa^{-1}, with a value at atmospheric pressure equal to 85 ± 4. Of course, a different m_T would be obtained for a different choice of T_g. The more usual $\tau_\alpha(T_g) = 100$ s would yield larger values of the steepness index but require extrapolation beyond the measured data.

Discussion and Summary

Structural relaxation was measured for PMTS over a very broad range of temperature and pressure. As seen in Figure 4, this enables determination of $T_0(P)$ and $P_0(T)$, without the usual gap between isobaric and isothermal experiments. These results reveal the nonlinear relationship between the two quantities, and demonstrate the congruence of eqs 3 and 4, used to parametrize the respective relaxation times. For the pressure

Table 2. Relaxation Properties of Poly(methylphenylsiloxane) and Poly(methyltolylsiloxane)

	$T_g(\tau_\alpha$=1 s)^a (K)	β^b	$m_T{}^a$	dm_T/dp (MPa^{-1})	D_P	dT_0/dP^a (K/MPa)	dT_g/dP^a (K/MPa)	ΔV^c (mL/mol)
PMPS	245.7	0.51	86	0	34.5		0.28 ± 0.01	361 ± 5
PMTS	260.8	0.51 ± 0.01	85 ± 4	−0.027 ± 0.004	41.8	0.37 ± 0.03	0.34 ± 0.01	394 ± 10

[a] $P = 0.1$ MPa. [b] $P = 0.1$ MPa and temperature at which $\tau_\alpha = 5$ ms. [c] See Figure 6.

dependences of both T_0 and T_g, we obtain ca. 0.35 K/MPa. This equivalence supports identification of the former as an "ideal" glass temperature.[39]

At atmospheric pressure, the steepness of T_g-scaled Arrhenius plots evaluated at T_g is known to correlate with the breadth of the relaxation peak.[37,38] In fact, this correlation has been quantified as[38]

$$m_T = 250(\pm 30) - 320\beta \tag{6}$$

For PMTS, we determine $\beta = 0.51 \pm 0.01$ (Figure 1) and $m_T = 85$ (Figure 5), in good accord with the proposed correlation. Since the shape of the dielectric loss peak shows no variation with pressure (Figure 1), we expect minimal change in the T_g-scaled temperature dependence with pressure. Experimentally, as seen in Figure 5, there is a small variation, dm_T/d$P = -0.03$ MPa^{-1}. From eq 6, this corresponds to a change of the stretch exponent of less than 0.03, which is barely more than the error in its determination.

We can compare the properties determined herein for PMTS with results for the very similar poly(methylphenylsiloxane).[25] The absence of the pendant methyl on the phenyl moiety lowers T_g by 15 deg. Nevertheless, at ambient pressure, both the shape of the α-relaxation functions and the fragility for the two polymers are identical. However, as seen in Table 2, the application of high pressure brings out differences between their respective dynamics. The relaxation times, T_g-scaled temperature dependence, and T_g itself of PMTS are all more sensitive to pressure than are the corresponding quantities for PMPS. Such results make clear the utility of pressure as an experimental variable, in developing structure−property relationships.

While we have used a generalized Vogel−Fulcher approach (eqs 2 and 3) to analyze our experimental results, other models have been proposed to treat the effect of temperature and pressure on structural relaxation. However, these alternative equations of state either require more adjustable parameters,[40] which cannot be independently assessed for PMTS, or provide a less accurate fit of our measured τ_α.[41−43] The concept of an activation volume, reflecting the volume required for the relaxation process to take place, has been invoked to interpret pressure dependences of the dynamics.[12,44,45] This approach implies a proportionality between τ_α and P as well as a linear dependence of both T_g and T_0 on pressure. These predictions contradict the results seen in Figures 3 and 4.

Nevertheless, it can be instructive to compare the behavior of PMPS and PMTS in terms of an activation volume. From its definition[12]

$$\Delta V = \frac{RT}{\log(e)P} \log (\tau_\alpha/\tau_0) \tag{7}$$

and eq 5, we obtain

$$\Delta V = m_T \frac{\log(e)}{R} \frac{dT_g}{dP} \tag{8}$$

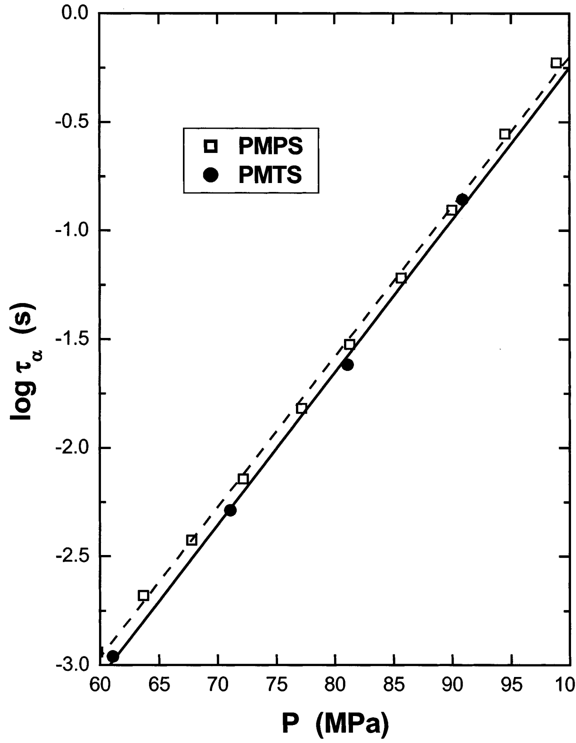

Figure 6. Structural relaxation times for PMTS ($T = 293$ K) and PMPS ($T = 273$ K). From the slope of the curves we obtain the activation volumes listed in Table 2.

As shown in Table 2, the steepness indices for PMPS and PMTS are the same, while the pressure coefficient of T_g is larger for PMTS. This implies that the activation volume for PMTS is larger than ΔV for PMPS.

We illustrate this in Figure 6, showing data for PMTS and PMPS at temperatures for which their respective τ_α and its pressure dependence are almost equal. Limiting the pressures to a range over which log τ_α is proportional to P, the activation volume is obtained from the slope, $\Delta V = 2.303RT(\partial \log \tau_\alpha/\partial P)_T$, with the results given in Table 2. The activation volume increases 10% in going from PMPS to PMTS, implying a chain segment of the latter sweeps out a proportionally greater volume during local relaxation. This is consistent with the relative size of the chain units, the molecular weights differing by roughly 10% as well. Similarly for small molecule glass-formers, a direct proportionality between ΔV and the molar volume has been reported.[46,47] This apparent correlation of the dynamics to the size of the local units is intriguing,[45] although clearly more results on other polymers are necessary.

Acknowledgment. M. Paluch acknowledges financial support by the State Committee for Scientific Research (KBN; Poland) under Project No. 5PO3B 022 20. The work at NRL was supported by the Office of Naval Research. We thank G. Meier of the Max-Planck-Institut für Polymerforschung in Mainz for kindly providing the polymer.

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