Temperature and pressure dependence of the α-relaxation in polymethylphenylsiloxane

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The α-relaxation process in polymethylphenylsiloxane was studied over a broad temperature and pressure range by dielectric spectroscopy. In the vicinity of the glass temperature, the shape of the dielectric loss peak is independent of both temperature and pressure. The steepness index (fragility), describing the temperature dependence of the relaxation times, is also independent of pressure (and of molecular weight as well). Thus, the correlation between fragility and nonexponentiality of the relaxation function is maintained under conditions of high compression. The combined temperature and pressure dependences of the relaxation time conformed to the Avramov equation. This model offers a means to relate the relaxation behavior to thermodynamic properties of the material. © *2002 American Institute of Physics.* [DOI: 10.1063/1.1478767]

INTRODUCTION

The local dynamics underlying relaxation of a system are identical to its equilibrium molecular motions, and thus a connection exists between relaxation properties and thermodynamic properties. Establishing this connection is essential to understanding, in a fundamental way, the molecular basis for the physical properties of materials. Experimental efforts along these lines usually focus on the effect of temperature, attempting to determine their link to thermodynamic data.[1–3] Correlations of temperature dependences with the shape of the relaxation function[4–7] and with chemical structure[5,7–9] are of related import. An experimental variable potentially having equal utility is pressure, and the effect of pressure on relaxation properties near the glass temperature has received increasing attention.[10–17] The interrelationship between pressure- and temperature-dependences, and how these are governed by chemical structure, are outstanding issues in the field.

In this paper we report dielectric data for polymethylphenylsiloxane (PMPS). Measurements of the α-relaxation were carried out over a range of temperatures and pressures. The temperature dependence of the relaxation time (fragility) was compared to that of PMPS having different molecular weights. We also examine the effect of pressure on fragility. To do this, we use a recently proposed model for the combined pressure- and temperature-dependences.

EXPERIMENT

The PMPS, obtained from Dr. T. Wagner of the Max Planck Institute for Polymer Research, Mainz, Germany, had a molecular weight of 23 360 daltons, with a polydispersity of 1.16.

For ambient pressure measurements, we used a Novo-Control GmbH dielectric spectrometer, equipped with a Solatron SI1260 frequency response analyzer and broadband dielectric converter. We measured the dielectric permittivity, $\epsilon^*(\omega) = \epsilon'(\omega) - i\epsilon''(\omega)$, in the frequency range $10^{-2} - 10^6$ Hz. The sample was contained in a parallel plate cell (diameter 10 mm, gap 0.1 mm). Temperature was controlled using a nitrogen-gas cryostat, with temperature stability better than 0.1 K.

For the high-pressure studies we used the high-pressure equipment described in Ref. 18. The capacitor, filled with test material, was placed in the high-pressure chamber. Pressure was exerted on the chamber via silicone fluid, using a chamber with a piston in contact with a hydraulic press. The sample capacitor was sealed and mounted inside a Teflon ring to separate the sample from the silicon oil. Pressure was measured by a Nova Swiss tensometric pressure meter (resolution=0.1 MPa). The temperature was controlled within 0.1 K by means of a liquid flow provided by thermostatic bath.

RESULTS AND DISCUSSION

Isobar measurements

Displayed in Fig. 1 are representative measurements of the dispersion in the dielectric loss due to the α-relaxation. The shape of the peak is essentially independent of temperature, aside from the broadening on the low-frequency side at higher temperatures due to encroachment of the DC conductivity. Included in the figure is the fit of the data to the transform of the Kohlrausch–William–Watts (KWW) function[19]

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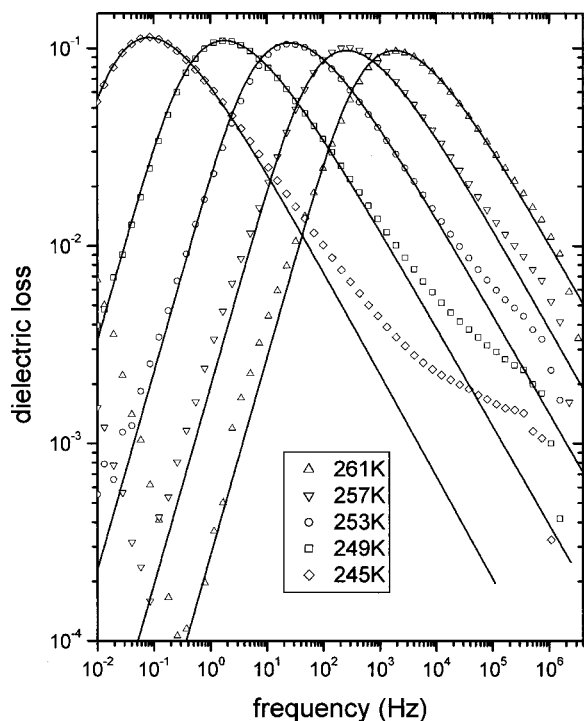
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FIG. 1. Representative dielectric loss curves for PMPS measured at the indicated temperatures. The solid lines are the fits to Eq. (5), with $\beta=0.51 \pm 0.01$. The deviations toward low and high frequencies reflect conductivity and an excess wing respectively.

$$\phi(t) \sim \exp - (t/\tau_{\mathrm{KWW}})^{\beta}, \qquad (1)$$

where τ_{KWW} is a relaxation time and the shape factor $\beta=0.51\pm0.01$. Note the deviation from Eq. (1) at higher frequencies; this is the well-known "excess wing" seen in the spectra of type A glass-formers.[20–22]

In Fig. 2 we show the isobaric ($P=1$ bar) relaxation times, τ, defined as the inverse of the frequency of the maxima in the dielectric loss (note that for $\beta=0.51$, $\tau = 1.35 \times \tau_{\mathrm{KWW}}$). Over the range of most experimental measurements, the temperature dependence of the α-relaxation times in molecular glass-formers and polymers can be described using the Vogel–Fulcher equation[23]

$$\tau(T) = \tau_0 \exp\left(\frac{D_T T_0}{T - T_0}\right), \qquad (2)$$

in which τ_0 is of the order of a lattice vibration, and the strength parameter, D_T, and the Vogel temperature, T_0, are constant with temperature. The latter can sometimes be identified with the Kauzman temperature.[24] The fit of the data to Eq. (2) yields $\tau_0 = 8.12 \times 10^{-17}$ s, $D_T = 8.48$, and $T_0 = 200.0$ K.

Also included in Fig. 2 are dielectric measurements on PMPS of slightly higher molecular weight ($M_w = 28\,500$ g/mol),[25] and photon correlation data for a low $M_w (=5000$ g/mol) PMPS.[26] As can be seen, the molecular weight dependences of τ and T_g alter the curvature.

Comparisons of the effect of temperature on relaxation for different glass-formers usually rely on normalizing temperature by the glass temperature. The temperature dependence is then assessed from the steepness of the consequent
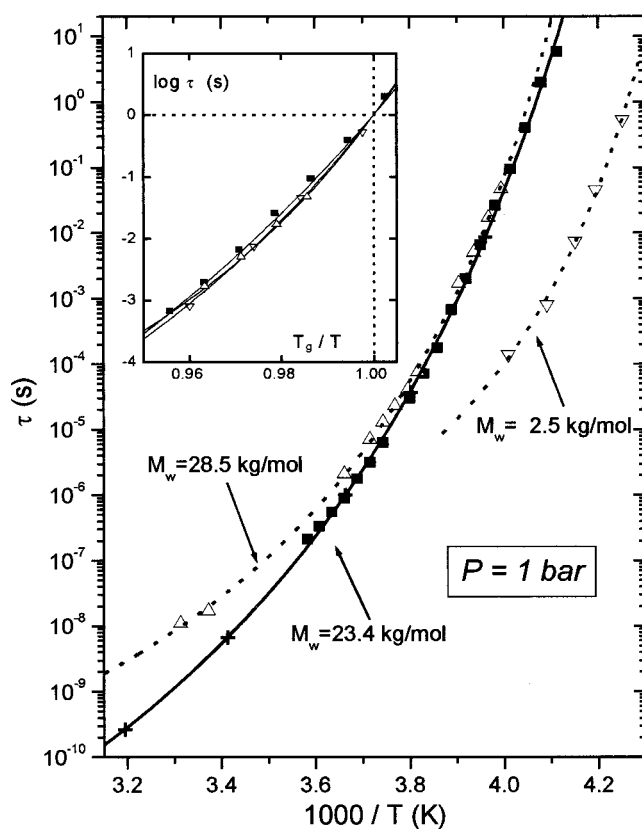

FIG. 2. The α-relaxation times measured at 1 bar for the PMPS herein (■), and for a higher ($M_w = 28.5$ kg/mol, △) (Ref. 25) and a lower ($M_w = 2.5$ kg/mol, ▽) (Ref. 26) molecular weight PMPS. The crosses (×) indicate the values of τ_P used in fitting Eq. (4) to the isothermal data (Fig. 3). The T_g-normalized data are shown in the insert, yielding $m_T = 86$ for T_g taken to be the temperature at which $\tau = 1$ (which avoids extrapolation of the data).

scaled Arrhenius plot evaluated at T_g.[27,28] A fragility (or steepness index) can be defined as $m_T \equiv d \log(\tau)/d(T_g/T)\big|_{T=T_g}$. In terms of the Vogel–Fulcher parameters, $m_T = D_T T_0 (\ln 10 T_g)^{-1}(1 - T_0/T_g)^{-2}$.

Fragility curves for the three PMPS are shown in the inset to Fig. 1. The data coincide exactly when plotted in the T_g-normalized Arrhenius form, with T_g taken to be the temperature at which $\tau = 1$ s. (This definition of a dynamic glass temperature, while arbitrary, avoids extrapolation beyond our measurement range.) An invariance of fragility to molecular weight appears to be the rule for low T_g polymers,[6,29] but not necessarily the case for all polymers.[30] The value obtained, $m = 86$, conforms closely to the reported correlation with the stretch exponent in Eq. (1); viz., $m_T = 250(\pm 30) - 320\beta$.[4] The steepness index, of course, is temperature dependent, since the data in Fig. 2 are non-Arrhenius. Using $\tau(T_g) = 100$ s would yield a larger value for m_T.[31]

Based on an energy landscape interpretation of fragility, attempts have been made to correlate m_T with thermodynamic quantities, such as the heat capacity or configurational entropy.[1] The idea is that thermal excitation induces a breakdown of configurational structure, the rapidity of which defines the temperature sensitivity of τ. At least for polymers, experimental data are at odds with the predictions of such models.[32] Since the heat capacity of a polymeric liquid varies
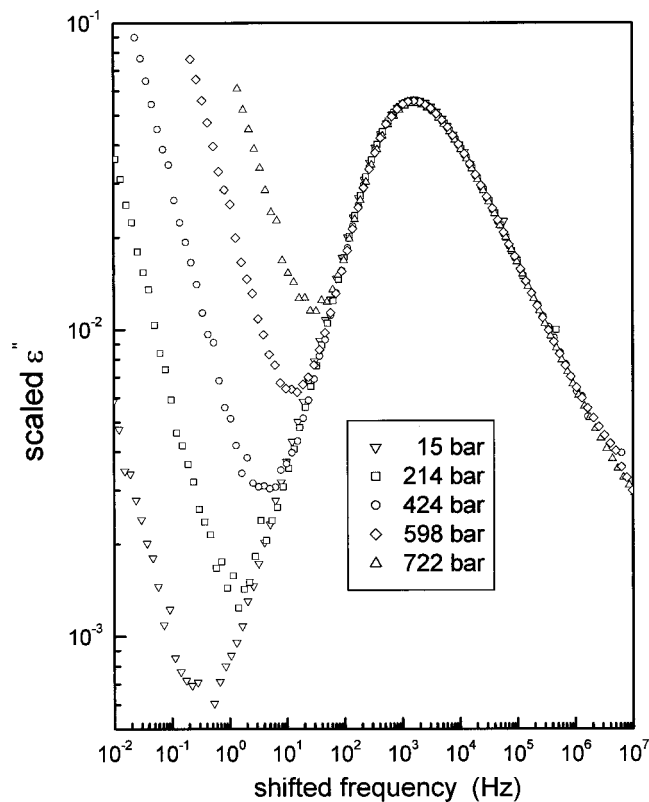
FIG. 3. Representative dielectric loss curves for PMPS measured at the indicated pressures. The data have been shifted to superimpose on the curve for $P = 42.4$ MPa.

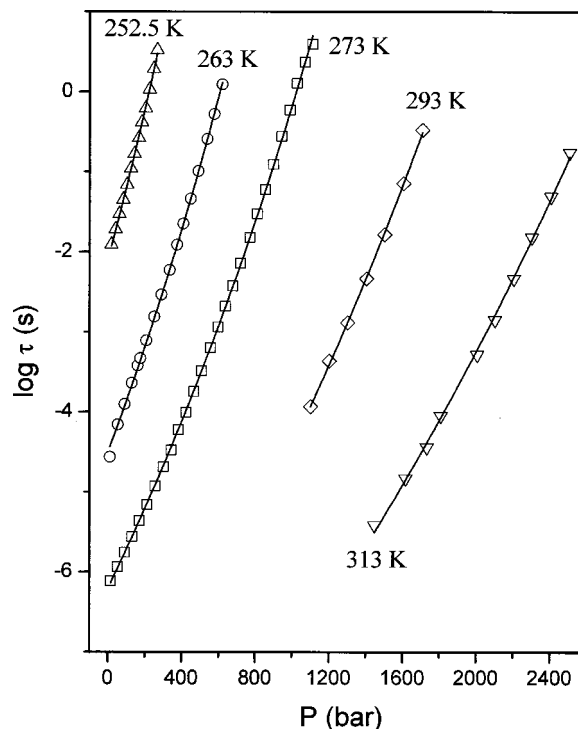FIG. 4. The α-relaxation times of PMPS at the indicated temperatures. The solid lines are the fits to Eq. (4), constrained such that $D_P (= 34.5)$ is constant with temperature. The τ_P are taken from the fit of the ambient pressure data to Eq. (1) (see Fig. 2).

inversely with molecular weight (for molecular weights below the high polymer limit),[3] the expectation from an energy landscape model is that fragility should vary inversely with molecular weight.[30] This prediction is at odds with the results in Fig. 2.

Isotherm measurements

Shown in Fig. 3 are representative measurements of the α-dispersion measured at various pressures. The curves have been shifted to superimpose, whereby it is seen that the shape of the peak is independent of pressure. This implies that pressure will not affect the fragility of PMPS, given the correlation between the breadth of the α-relaxation function and the T_g-normalized temperature dependence.[4–7]

In Fig. 4 we display the isothermal relaxation times as a function of pressure. The segmental relaxation times for PMPS are extraordinarily sensitive to pressure, in comparison to small molecule glass formers.[33] When pressure is used as an experimental variable, an obvious approach to describe the relationship is adoption of an analogous form of the Vogel–Fulcher equation;[34] i.e.,

$$\tau(P) = \tilde{\tau}_0 \exp\left(\frac{\tilde{D}_P \tilde{P}_0}{\tilde{P}_0 - P} \right). \tag{3}$$

However, for small molecule glass-formers, Eq. (3) has been shown to yield different values for the exponential prefactor

then those obtained from isobaric measurements; moreover, $\tilde{\tau}_0$ can assume unphysically small values.[10,33] An alternative relation is[33,34]

$$\tau(P) = \tau_P \exp\left(\frac{D_P P}{P_0 - P} \right), \tag{4}$$

in which τ_P can be obtained from isobaric data at ambient pressure, and D_P is assumed to be independent of both pressure and temperature. Isothermal and isobaric data are related by the Vogel parameters P_0 and T_0, at which the relaxation time diverges. In fitting our isotherm results, we use for τ_P the value of $\tau(T)$ calculated from the ambient pressure data using Eq. (2) (these are indicated in Fig. 2). The strength parameter is assumed to be independent of temperature; that is, we use a common value of $D_P = 34.5$ for all temperatures. The fits of Eq. (4) to the pressure data are shown in Fig. 4.

Since Eq. (2) can be derived from the Adam–Gibbs model for the α-relaxation,[35] the strength parameter, D_T, is sometimes taken to be a reflection of the temperature dependence of τ. Although D_P herein does not vary with temperature, nevertheless, the isothermal fragility, defined as $m_P = d \log(\tau_\alpha)/d(P/P_g)|_{T=T_g}$ changes inversely with temperature (Fig. 5). For analysis of isotherm data, the concept of fragility may need to be reexamined.

The best-fit values of T_0 are shown in Fig. 6, along with the datum obtained from the isobaric measurements. The latter departs from the linear relationship between T_0 and P_0 observed at higher pressures. In Fig. 6 we also plot the values of temperature and pressure for which $\tau = 1$ s (our opera-
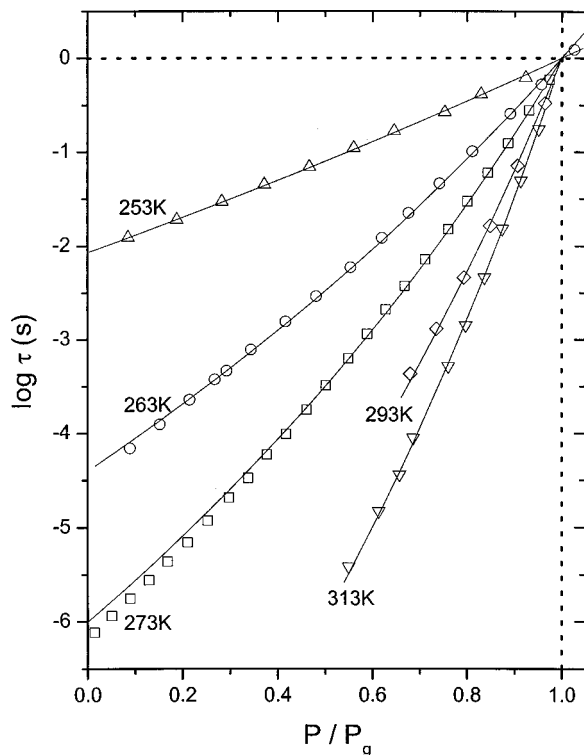
FIG. 5. P_g-normalized pressure dependence of the relaxation time. The isothermal steepness index, m_P, is a decreasing function of temperature.

FIG. 6. Vogel pressure (▲) determined from fitting Eq. (3) to the isothermal data, along with the corresponding Vogel temperature (▼) determined from fitting the isobaric data to Eq. (1). Also displayed is the glass temperature (○), which has a stronger pressure dependence than does T_0.

tional definition of T_g). T_g is approximately proportional to P, yielding 0.28 K/MPa for the pressure coefficient of T_g at low P. For small molecule glass-formers, this quantity may be correlated with the fragility.[33] PMPS is moderately fragile ($m = 86$), in comparison to other polymers;[4] however, at present, dT_g/dP data obtained from dynamic measurements are too scarce to assess this correlation for polymers.

Since the Vogel temperature can be identified with the Kauzman temperature (an "ideal" glass temperature[24]), the expectation is that T_g and T_0 will have similar pressure dependences. In fact, their behaviors are quite different (Fig. 6). While for all isotherm results ($P_0 > 180$ MPa), the Vogel temperature is also proportional to pressure, the slope is much less, $dT_0/dP \approx 0.12$, than the T_g dependence on pressure. We also note that the single datum in Fig. 6 obtained under isobaric conditions has a value of T_0 much lower than the extrapolation of pressure data. This may reflect a departure from the linear $T_0 - P_0$ relationship at low pressures. Very limited data for small molecule glass-formers suggest that $T - P_0$ and $T_0 - P$ results fall on a single curve.[36] Clearly, isothermal data for PMPS at lower temperatures would be useful.

Avramov analysis

Since the shape of the relaxation function does not change with pressure, we anticipate that pressure will not affect the fragility. However, a determination of m_T at various pressures requires extrapolation of the data in Fig. 4 beyond the measured range of frequencies. This extrapolation, in turn, requires fitting the combined pressure and temperature dependencies of τ.
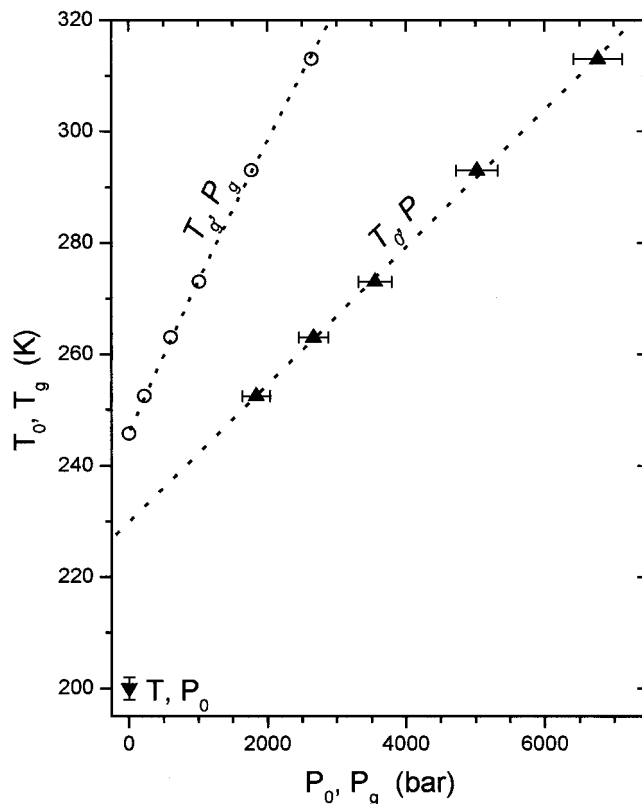
Various approaches have been proposed to treat the mutual dependences on temperature and pressure. Fytas and co-workers generalized the Vogel–Fulcher equation to include the effects of both temperature and pressure simultaneously.[37] However, their expression predicts a linear dependence of T_g on pressure, which is at odds with experimental data,[38] including Fig. 6. Casalini *et al.*[39,40] used the Adam–Gibbs model to derive an expression having the form of the Vogel–Fulcher equation, but with T_0 now dependent on both temperature and pressure. Since the temperature- and pressure-dependences are not factorable, this approach formally predicts that fragility must be pressure dependent. The defect diffusion model of Bendler and Shlesinger[41] has recently been extended to include the effect of pressure.[42]

Herein we make use of an entropy-based model for the combined effects of T and P on relaxation, which has been developed by Avramov.[43,44] Offering an explicit connection to thermodynamic quantities, the model assumes that the cooperative motions underlying the α-relaxation are thermally activated. From a consideration of the manner in which structural disorder gives rise to a distribution of these local energy barriers, the following expression is obtained:

$$\tau = \tau_\infty \exp\left[\epsilon \left(\frac{T_R}{T} \right)^a \left(1 + \frac{P}{\Pi} \right)^b \right], \tag{5}$$

where ϵ (≈ 30) is a dimensionless quantity (equal to a local activation energy prevailing at the glass temperature), and τ_∞, T_R, a, Π, and b are temperature- and pressure-
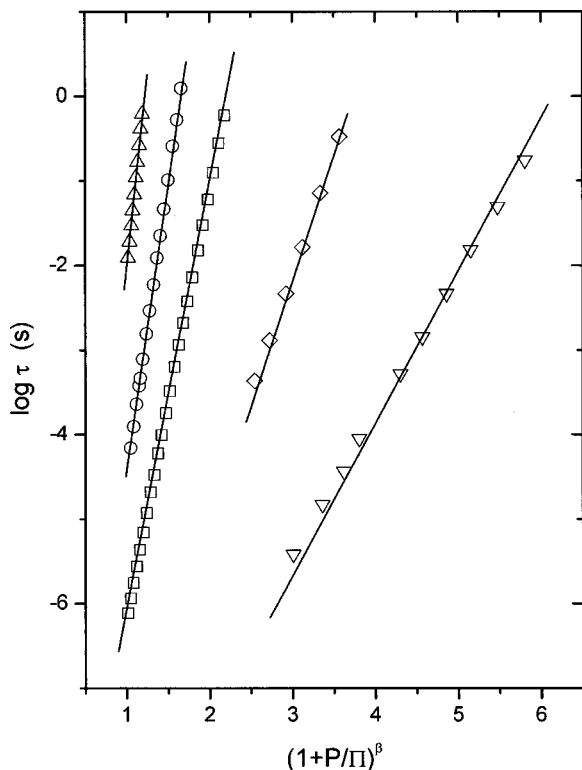
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FIG. 7. The α-relaxation times of PMPS at the indicated temperatures. The solid lines are calculated from Eq. (5), using log $\tau_\infty = -11.086$, $a = 7.52$, $T_R = 240.6$ K, $b = 4.32$, and $\Pi = 498.9$ MPa.

independent material constants. Since temperature- and pressure-effects are factorable, conformance of data to Eq. (5) implies that fragility is not a function of pressure. In terms of the Avramov parameters, the steepness index is given by $m = \alpha(\log \tau(T_g) - \log \tau_\infty)$.

The isobaric and isothermal data were fit to Eq. (5), with the obtained parameters given in the caption to Fig. 7. Since these calculated curves are not easily distinguished from the Vogel–Fulcher fits in Figs. 2 and 4, we plot the logarithm of the isothermal relaxation times as a function of $[1 + (P/\Pi)]^b$. This yields a straight line, which according to Eq. (5) should have a slope, equal to $\epsilon/2.303(T_R/T)^a$, determined by the temperature dependence, and an intercept equal to log τ_∞. The lines through the data points were calculated accordingly. The agreement is satisfactory.

The value of the Avramov model, aside from any ability to describe experimental data, is that the exponents in Eq. (5) can be directly related to known physical quantities. According to the model[43]

$$a = \frac{2\Delta C_p}{RZ} \qquad (6)$$

and

$$b = \frac{2\kappa_0 V_m}{ZR}. \qquad (7)$$

In these expressions, ΔC_p is the (assumed constant) heat capacity, R the gas constant, κ_0 the thermal expansion coefficient of the volume, and V_m the molar volume. The parameter Z represents the number of available pathways for local

motion of a molecule (or polymer segment), reflecting the short-range order of the liquid state. Z cannot be independently determined by experiment; however, it should be roughly proportional to the coordination number of the liquid lattice.[44] Avramov has suggested $Z = 10$ for most small molecule glass-formers.[45]

The heat capacity of PMPS shows a weak temperature dependence.[46] Nevertheless, the reported specific heat of 1.5 J/g-K[47] gives $\Delta C_p = 200$ J/mol-K. From this and the obtained $a = 7.52$, Eq. (6) yields $Z = 6.4 \pm 1.3$. From the isotherm results, we obtained $b = 4.32$. The thermal expansion coefficient of PMPS in the limit of zero pressure is 4.7×10^{-4} K^{-1},[14] and the molar volume calculated from the mass density is 0.116 1/mol. Using these values in Eq. (7), we obtain $Z = 7.3 \pm 1$.

Although the isobar and isotherm results are not identical, the results are close, given the uncertainties in the quantities in Eqs. (6) and (7). For example, while we have identified V_m with a polymerization unit (monomer), it is not clear that this is the appropriate length scale for the relaxing unit. The assumption of a constant ΔC_p is another approximation. Notwithstanding these considerations, both the isobar and isotherm data indicate fewer pathways for segment "hopping" in PMPS than has been found for small molecules, for which typically $Z \approx 10$.[45] This is a natural consequence of the constraints imposed by the connectivity of the chain units in a polymer. Whether Z (or perhaps the ratio $C_{p/Z}$[43]) can be related in a general way to fragility and the chemical structure of polymers remains to be investigated.

SUMMARY

Dielectric spectroscopy was employed to study segmental relaxation of polymethylphenylsiloxane over a wide pressure and temperature range. It was found that the shape of the α-relaxation function is invariant to both variables, for temperatures approaching the glass transition; thus, frequency-temperature-pressure superpositioning is valid. Since pressure had no effect on the steepness index (fragility), the correlation between fragility and the breadth of the relaxation function (nonexponentiality) is preserved under high compression.

The measured isotherms were well described by a pressure counterpart of the temperature Vogel–Fulcher law, using a strength parameter that is independent of temperature. Satisfactory fits of the combined temperature and pressure dependences of the α-relaxation times were achieved using the Avramov model. The two exponents of the Avramov equation can be related, and using known thermodynamic quantities for PMPS, yield ~7 for Z, a parameter describing the short-range dynamical order.

ACKNOWLEDGMENTS

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