

Anomalous Narrowing of the Structural Relaxation Dispersion of Tris(dimethylsiloxy)phenylsilane at Elevated Pressures

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Broadband dielectric relaxation measurements of tris(dimethylsiloxy)phenylsilane were made at ambient pressure and at elevated pressures. The data show an anomalous behavior not previously seen in any other glass-formers; namely, the structural α -relaxation loss peak narrows with increasing pressure and temperature at constant peak frequency. Interpreted by the coupling model, the effect is due to reduction of intermolecular coupling at elevated pressures. This interpretation has support from the observed decrease of the separation between the α -relaxation and the Johari–Goldstein secondary relaxation, as well as the smaller steepness or “fragility” index m of the data obtained at 1.7 GPa than at ambient pressure.

1. Introduction

It has been established as a general experimental fact in many glass-formers that for a given material at a fixed value of the structural α -relaxation, τ_α , the dispersion is constant, independent of the combinations of temperature and pressure that maintain τ_α constant.¹ This general property implies that the dispersion of the α -relaxation is defined by τ_α , or at least τ_α and the dispersions have to be coupled predictions of any viable theoretical interpretation. If the dispersion of the structural relaxation is derived independently of τ_α , it is unlikely to be a unique function of τ_α . This observation from the general property has important consequences for studies of the glass transition, an unsolved problem in condensed matter physics. Since this property is so general, any exception to the rule deserves attention and explanation. So far, there are only a few exceptions to this general property and all come from hydrogen-bonded glass-formers where the α -relaxation dispersion *broadens* at elevated pressure and temperature at constant τ_α . This deviation occurs because high pressure and temperature disrupt the hydrogen-bonded network as in glycerol² or remove the hydrogen-bonded clusters as in *m*-fluoranol,³ resulting in enhanced intermolecular coupling between the molecules, increased stretching of the correlation function of the α -relaxation or a broader frequency dispersion. This explanation has independent support from the concomitant *increase* of separation between the α -relaxation and the Johari–Goldstein secondary relaxation,^{4,5} which is an independent indication of the enhanced intermolecular coupling and the extent of the many-molecule relaxation dynamics in the context of the coupling model.^{6–12} In this paper, we report broadband dielectric relaxation data of a siloxyl-based glass-former, tris(dimethylsiloxy)phenylsilane (TDMSPS), which is another rare exception to the general rule.¹ Its α -relaxation dispersion *narrows* at elevated pressures and temperatures at constant τ_α , in contrast to broadening exhibited by some of the hydrogen-bonded glass-formers. This observed

opposite effect brings out new physics and yet another challenge for theories and models of glass transition to explain. Naturally, the coupling model explanation of the narrowing R-dispersion in TDMSPS has to be reduced intermolecular coupling at elevated pressures and temperatures, for consistency with the previously proposed explanation of the opposite effect observed in some of the hydrogen-bonded glass-formers. Furthermore, for complete consistency, the separation between the α -relaxation and the Johari–Goldstein secondary relaxation of TDMSPS should show a concomitant *decrease*, instead of an increase observed in some hydrogen-bonded glass-formers. This opposite trend is indeed found in the experimental data of TDMSPS at elevated pressures and temperatures. These novel experimental findings together with the consistency of the explanation provided by the coupling model are the physical insights provided by this study into the relaxation dynamics of glass-formers.

2. Experimental Section

The TDMSPS sample was purchased from Aldrich and used as received. Dielectric measurements were carried out in a frequency range from 10^{-2} to 10^8 Hz using a Novocontrol Alpha dielectric spectrometer together with Agilent 4291B impedance analyzer. The sample was placed in a parallel plate cell (diameter, 20 mm; gap, 0.1 mm). Temperature control was performed using a dry-nitrogen stream-based system, thermostated with a precision better than 0.1 K. The high-pressure technique used herein is very similar to that of Johari and Whalley.¹³ Pressure system was constructed by UNIPRESS with a homemade special flat parallel capacitor. The pressure was exerted on the sample by a steel piston. The sample tested was in contact only with stainless steel and Teflon.¹⁴ The temperature was controlled to within 0.1 K by liquid flow provided by a thermostatic bath.

3. Results and Discussion

Isothermal dielectric relaxation spectra were measured at ambient pressure of 0.1 MPa and at elevated pressures. Shown

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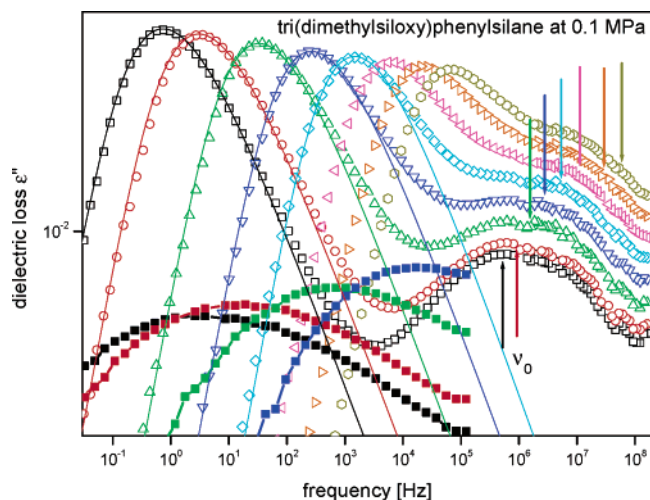


Figure 1. Dielectric loss spectra of TDMSPS at ambient pressure and eight selected different temperatures above the vitrification temperature T_g , 141, 139, 137, 135, 133, 131, 129, and 128 K (starting from right to left), showing both the primary and the secondary relaxations. Lines are representative fits of the data by the one-sided Fourier transform of the KWW functions. The vertical arrows indicate the locations of the calculated ν_0 . Only the secondary relaxation is seen at the four selected lower temperatures below T_g , 104.6, 94.6, 84.6, and 81.3 K (from right to left).

in Figure 1 are representative loss spectra taken at 0.1 MPa and eight selected different temperatures above the vitrification temperature T_g , 141, 139, 137, 135, 133, 131, 129, and 128 K (starting from right to left). The lines are fits to the α -loss peaks seen at these eight temperatures above T_g by the one-sided Fourier transforms of the Kohlrausch–Williams–Watts (KWW) function,

$$\phi(t) = \exp[-(t/\tau_\alpha)^{1-n}]. \quad (1)$$

The stretch exponent, $1 - n$, increases slightly with increasing temperature, and its values are 0.54 for 141 and 139 K, 0.53 for 137 and 135 K, 0.51 for 133 K, and 0.50 for 129 and 128 K. The relaxation times τ_α obtained from the fits are shown in Figure 2 in an Arrhenius plot against reciprocal temperature. A secondary β -relaxation is already resolved at temperatures above T_g , and it becomes the only feature within the experimental spectral range at the four selected lower temperatures, 104.6, 94.6, 84.6, and 81.3 K (from right to left) below T_g . The temperature dependence of its relaxation time, τ_β , is shown in Figure 2. Dielectric measurements at the constant temperature of 292 K and different applied pressures show that the secondary relaxation is shifted to lower frequencies (data not shown). In other words, τ_β is pressure-dependent and hence the secondary relaxation of TDMSPS satisfies one of the criteria of belonging to the class of Johari–Goldstein (JG) relaxation.⁵ Another criterion for JG relaxation is the good correspondence between the secondary β -relaxation time τ_β and the primitive relaxation time τ_0 of the coupling model (CM)^{15–18} calculated at any temperature T and pressure P from the parameters τ_α and $(1 - n)$ of the α -relaxation in the KWW function by the CM equation,

$$\tau_0(T, P) = t_c^n [\tau_\alpha(T, P)]^{1-n}, \quad (2)$$

where $t_c \approx 2$ ps for molecular glass-formers. This criterion, i.e.,

$$\tau_\beta(T, P) \approx \tau_0(T, P), \quad (3)$$

is also fulfilled by τ_β . This can be seen in Figure 1 for each

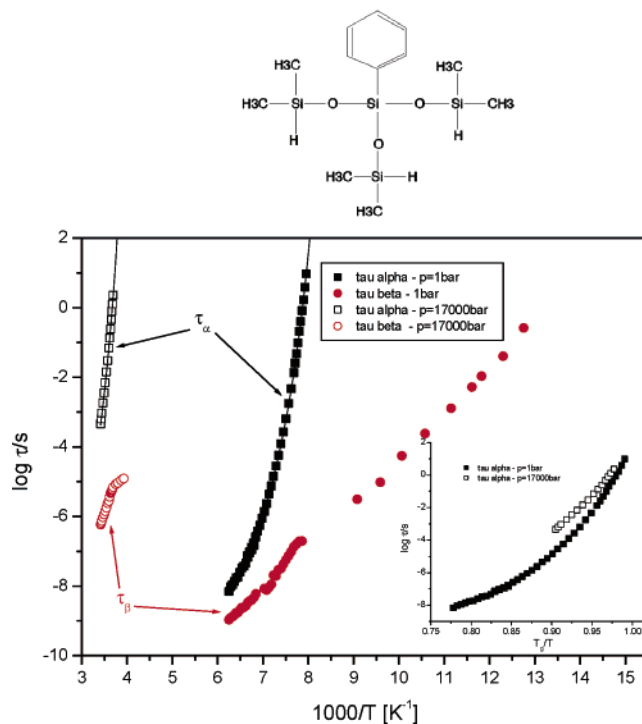


Figure 2. Relaxation map showing the primary and the secondary times at ambient pressure and applied pressure of 1.7 GPa. Solid curves represent the VFT fits.

temperature by the good correspondence between the observed β -relaxation peak frequency, ν_β , and the calculated primitive relaxation frequency, $\nu_0 \equiv 1/(2\pi\tau_0)$, indicated by a vertical arrow pointing at the spectrum for which ν_0 or τ_0 is calculated.

Isothermal dielectric relaxation spectra also were measured at elevated pressures. In Figure 3 we show the data obtained under the applied pressure of 1.7 GPa for eight selected temperatures of 292.4, 288.1, 284.0, 279.9, 276.3, 273.7, 272.7, and 266.6 K (from right to left). Shown also are representative fits of the data by the one-sided Fourier transform of the KWW function. In fitting the data, the emphasis is in obtaining the best agreement of the fit with the data at frequencies in the vicinity of the α -loss peak and below the frequency of the α -loss peak. Deviations of the fit from the data at higher frequencies come from the contribution of the β -relaxation, which is more significant at 1.7 GPa because the β -loss peak is closer to the α -loss peak than at 0.1 MPa (Figure 1). The stretch exponent, $1 - n$, increases slightly with increasing temperature, and its values are 0.57 for 292.4 K, 288.1, 284.0, and 279.9 K, 0.56 for 276.3 K, 0.55 for 273.7 and 272.7, and 0.55 for 272.7 K. The α -loss peak of 266.6 K is outside the experimental frequency range, and hence the stretched exponent is not available. The α -loss peak at the elevated pressure of 1.7 GPa is categorically narrower than at ambient pressure, as can be inferred from the larger stretch exponent of the former compared with the latter. To the best of our knowledge, this property, namely, narrowing of the α -loss peak with applied pressure, has not been observed before. The relaxation times τ_α obtained from the fits are shown in Figure 2 in an Arrhenius plot against reciprocal temperature. In the inset in Figure 2, the T_g -scaled temperature dependences of τ_α at ambient pressure and at 1.7 GPa are compared, where in each case T_g is defined as the temperature at which $\tau_\alpha = 100$ s. The steepness or fragility index m is smaller at 1.7 GPa than at ambient pressure ($m(0.1\text{MPa}) = 113$, $m(1.7\text{GPa}) = 81$). This change of m and the corresponding change of the stretch exponent, $1 - n$, are

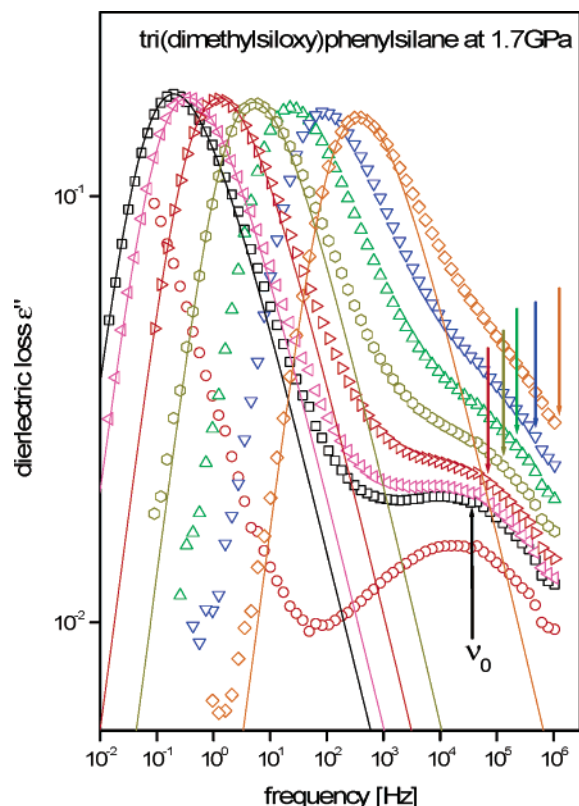


Figure 3. Dielectric loss spectra of TDMSPS at 1.7 GPa and eight selected temperatures of 292.4, 288.1, 284.0, 279.9, 276.3, 273.7, 272.7, and 266.6 K (from right to left). Lines are representative fits of the data by the one-sided Fourier transform of the KWW functions. The vertical arrows indicate the locations of the calculated ν_0 .

consistent with established correlation between m and n .¹⁹ The secondary β -relaxation found at ambient pressure remains to be seen at 1.7 GPa. Its relaxation times, τ_β , determined from the spectra for a number of temperatures straddling the vitrification temperature are shown in Figure 2.

Again having the stretch exponents and τ_α determined from the fits, the primitive relaxation time τ_0 and the frequency, $\nu_0 \equiv 1/(2\pi\tau_0)$, are calculated by eq 2. The locations of the calculated ν_0 are indicated by the vertical arrows pointing at the corresponding spectra for which the ν_0 are calculated. There is good agreement between the calculated ν_0 and the frequency of the secondary relaxation $\nu_\beta \equiv 1/(2\pi\tau_\beta)$.

From eqs 2 and 3 and $t_c \approx 2 \times 10^{-12}$ s; the separation between the α -relaxation frequency $\nu_\alpha \equiv 1/(2\pi\tau_\alpha)$ from ν_β or ν_0 (all in hertz) on the logarithmic scale is given by

$$\log \nu_\beta - \log \nu_\alpha \approx n(10.9 - \log \nu_\alpha). \quad (4)$$

This relation indicates that, for the same ν_α , the separation is smaller if n is smaller or the stretch exponent $(1 - n)$ is larger. From the fact that the stretch exponent $(1 - n)$ increases on applying a pressure of 1.7 GPa, it follows that, for the same ν_α , the separation $(\log \nu_\beta - \log \nu_\alpha)$ becomes smaller. This expected change of $(\log \nu_\beta - \log \nu_\alpha)$ is illustrated in Figure 4, where spectra taken at 1.7 GPa (open symbols) and at ambient pressure (closed symbols) with approximately the same ν_α are compared. As mentioned before, the narrowing of the α -dispersion under applied pressure at any fixed ν_α is unique to TDMSPS. For most glass-formers, the α -dispersion is invariant to changes of pressure and temperature as long as ν_α is the same, and the separation $(\log \nu_\beta - \log \nu_\alpha)$ also remains constant whenever the data of the Johari–Goldstein β -relaxation at elevated

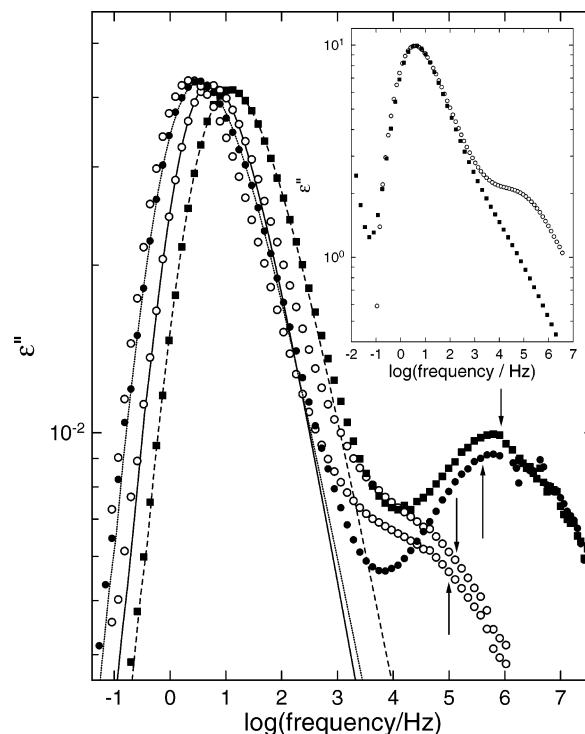


Figure 4. Narrowing of the α -loss peak with applied pressure of 1.7 GPa accompanied by smaller separation distance between the α - and the β -relaxations, $(\log \nu_\beta - \log \nu_\alpha)$, in TDMSPS. This unique behavior of TDMSPS is contrasted by the changes in opposite directions of hydrogen-bonded glass-formers, where the α -loss peak broadens and the separation distance increases with applied pressure as shown in the inset for xylitol.

pressures are available. The glass-formers having hydrogen bonds including *m*-floroaniline³ and the polyols such as glycerol and xylitol²⁰ are the known exceptions in which the α -dispersion broadens under applied pressure at any fixed ν_α (see the inset in Figure 4). The loss spectra of xylitol obtained at $T = 293$ K, $P = 1$ GPa (open circles) are broader than those at $T = 258$ K, $P = 0.1$ MPa (closed squares). The fit by the KWW function to the 1 GPa data requires a larger $n = 0.51$ than $n = 0.46$ for the 0.1 MPa data. Thus, the changes of the α -dispersion of xylitol and TDMSPS with applied pressure are in opposite directions. Remarkably the corresponding changes of the separation $(\log \nu_\beta - \log \nu_\alpha)$ are also in opposite directions, adhering to the rule set forth by eq 4.

To emphasize this difference, we subtract the β -process from the two loss spectra of TDMSPS, and the results are given in the Figure 5. Narrowing of the α -relaxation peak at high pressure is again demonstrated. The dashed line is the same KWW fit to the same experimental data in Figure 1 at 0.1 MPa. The full line is the same KWW fit to the same data in Figure 3 at 1.7 GPa. Although the fits to the data are not as good as in Figures 1 and 3 at lower frequencies due to the subtraction, they continue to serve as adequate fits to the data and as indicators of the narrowing of the α -dispersion at high pressure.

What makes TDMSPS so unique is likely due to the bulky but flexible Si-based part of the molecule joined to the otherwise rigid phenyl ring. High pressure can alter the relation of the phenyl rings to each other through shielding by the compressed Si-based parts of the molecules. According to the coupling model, the intermolecular coupling is thereby reduced and the frequency dispersion of the α -relaxation is narrowed as observed. Support of this explanation comes from the concomitant decrease of the separation between the α -relaxation and the Johari–Goldstein (JG) secondary relaxation and from the

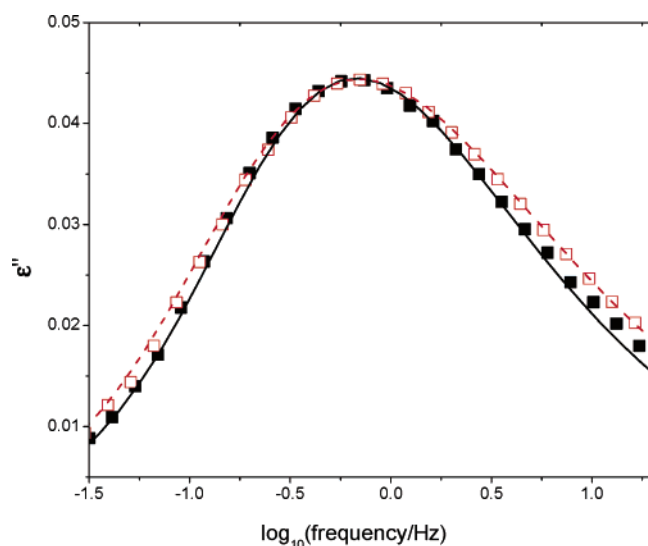


Figure 5. Dielectric loss spectra of TDMSPS at 0.1 MPa, $T = 128$ K (open squares), and 1.7 GPa, $T = 274.7$ K (solid squares), after subtraction of the β -process. The dashed line is the KWW fit to the same experimental data in Figure 1 at 0.1 MPa. The full line is the KWW fit to the data measured at 1.7 GPa.

decrease in the fragility index m . It is worthwhile to stress the following points. On elevating pressure and temperature while maintaining the α -relaxation time constant, irrespective of whether the α -relaxation dispersion is invariant as in most glass-formers, broadened as in some hydrogen-bonded glass-formers, or narrowed as in the present and unique case of TDMSPS; the experimental JG relaxation time τ_{JG} is always in accord with the calculated primitive relaxation time τ_0 of the coupling model. The experimental findings of this study and the consistency with the coupling model predictions give new physical insights into the relaxation dynamics of glass-formers.

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