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Chemical Structure and Local Segmental Dynamics in 1,2-Polybutadiene

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ABSTRACT: The segmental dynamics in 1,2-polybutadiene was studied over a broad range of temperature and pressure using dielectric spectroscopy. The glass transition temperature was found to be strongly dependent on pressure ($dT_g/dP = 240$ K/GPa). Moreover, while no appreciable change in the shape of the relaxation function with pressure was observed for spectra compared at a fixed value of the relaxation time, the fragility (T_g -normalized temperature dependence) increased with pressure. From the ratio of the isochronal to isobaric expansivities, and consistently from the ratio of the isochoric and isobaric activation energies, temperature was found to exert a stronger influence on the dynamics than does the volume. This is similar to results for other polymers as well as small molecule glass-formers (when the latter lack hydrogen bonds). Finally, a comparison was made of the properties of 1,2-PBD with those of other vinyl polymers having different pendent groups. The different segmental dynamics reflect the manner in which local relaxation is governed by intermolecular cooperativity. Consistent with this interpretation, 1,2-PBD exhibits an activation volume more than 9 times the molar volume of its repeat unit; this is significantly larger than the values for the other vinyl polymers.

Introduction

Local segmental relaxation in polymers is usually observed near the glass transition temperature and involves both intra- and intermolecularly correlated backbone motions. Focusing on the latter, there have been various efforts to relate the segmental relaxation properties to chemical structure.^{1–5} We have previously demonstrated a correlation of both the breadth of the relaxation function and the temperature dependence of the segmental relaxation times, τ , with the propensity of the molecular structure to engender steric interactions with neighboring segments.^{6–8} Intermolecular cooperativity is weaker in polymers with smoother, less polar, more compact, symmetric or flexible backbones and/or having less sterically hindering pendant groups. Less effective intermolecular constraints on local motion give rise to a narrower relaxation function and more nearly Arrhenius temperature dependence of the relaxation times. Given the correlation of chemical structure with both the shape of the relaxation function and the temperature dependence of τ , a mutual correlation of these latter two properties is expected and well-established.^{6–13}

Although this approach to interpreting the dynamics near the glass transition emphasizes density and steric constraints, other workers in the field embrace a somewhat different viewpoint. Experiments quantifying the relative degree to which temperature and density govern local motions in various glass-formers, both molecular and polymeric, have been interpreted to indicate that temperature is the dominant control variable, with volume exerting an almost negligible influence.^{14,15} Such conclusions are hard to reconcile with an interpretation of segmental relaxation based on

intermolecular cooperativity, as engendered by steric constraints from local chemical structure. More recent experiments have shown, however, that the effect of density on local relaxation times can be significant and in some cases exceeds that due to thermal energy.^{16,17}

To probe this issue further, we have carried out dielectric spectroscopy measurements on 1,2-polybutadiene (1,2-PBD), with both temperature and pressure used as experimental variables. This allows the segmental relaxation times to be expressed as a function of volume for both isobaric and isothermal pathways. From such information, the relative contribution of temperature and density can be assessed. Polybutadiene having high vinyl content is of particular interest because intermolecular constraints therein are among the strongest of any glass-former.^{6,13} We compare our findings for 1,2-PBD to literature results on polymers having a similar chemical structure.

Experimental Section

The 1,2-polybutadiene (1,2-PBD) was Nisso B3000 from the Nippon Soda Co. It had a vinyl content of 88% and a molecular weight of 3000 Da (about 56 monomer units). For pressure–volume–temperature (PVT) measurements, we used a Gnomix apparatus. The method is based on the confining fluid technique, with the sample surrounded by mercury. A detailed description of the apparatus can be found elsewhere.¹⁸ Isobaric volume measurements were carried out during cooling at a rate of 0.1 deg/min at hydrostatic pressures from 10 to 200 MPa.

Dielectric measurements used a Novo-Control GmbH Alpha dielectric spectrometer, with the sample contained in a parallel plate cell. Temperature was controlled using either a nitrogen-gas cryostat or a thermostatic bath, with temperature stability better than 0.1 K. For measurements under pressure, the sample (wrapped in Teflon) was compressed via silicone fluid, using a piston in contact with a hydraulic press. The pressure was measured by a Nova Swiss tensometric pressure meter (resolution = 0.1 MPa). A detailed description of the high-pressure dielectric equipment can be found elsewhere.¹⁹

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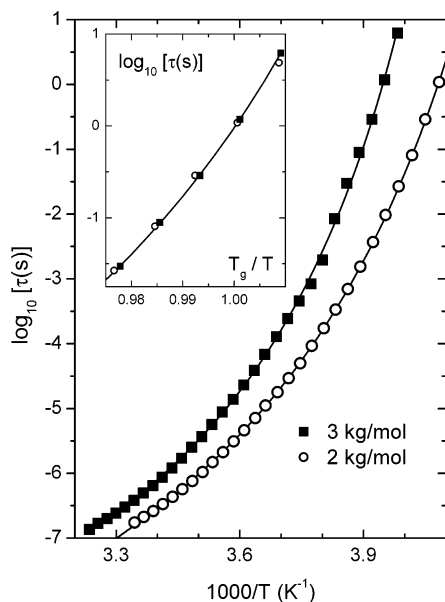


Figure 1. Dielectric relaxation times measured at atmospheric pressure (■) along with results for a lower molecular weight PBD taken from ref 23 (○). The lines through the data are the best fits to eq 1 yielding for PBD2000: $\log(\tau_\infty [\text{s}]) = -11.2 \pm 0.04$, $T_0 = 209.1 \pm 0.3 \text{ K}$, and $B = 939 \pm 12 \text{ K}$; and for PBD3000: $\log(\tau_\infty [\text{s}]) = -10.7 \pm 0.1$, $T_0 = 222.3 \pm 0.7 \text{ K}$, and $B = 769 \pm 24 \text{ K}$. The inset shows the same data as a function of the reciprocal temperature normalized by the respective temperatures for which $\tau = 1 \text{ s}$. The errors are less than the symbol size in this and all other figures, unless noted otherwise.

Results

Dielectric spectra were measured at atmospheric pressure over a range of temperatures. The relaxation times, taken as the inverse circular frequency of the maximum in the dielectric loss, $\tau = 1/(2\pi f_{\text{max}})$, are shown in Figure 1, along with the fit to the Vogel–Fulcher–Tammann–Hesse (VFTH) equation²⁰

$$\tau = \tau_\infty \exp\left(\frac{B}{T - T_0}\right) \quad (1)$$

in which τ_∞ , B , and T_0 are constants. For the 1,2-PBD investigated herein, the best fit yields $\tau_\infty = (2.0 \pm 0.5) \times 10^{-11} \text{ s}$, $T_0 = 222.3 \pm 0.7 \text{ K}$, and $B = 769 \pm 24 \text{ K}$. Using eq 1 to interpolate, we obtain the temperature at which $\tau = 1 \text{ s}$, $T_g = 253.4 \text{ K}$. (The particular characteristic time used to define T_g is arbitrary; $\tau(T_g) = 1 \text{ s}$ avoids extrapolation.) Replotting the data as a function of T_g/T in the inset to Figure 1, the slope at T_g yields the fragility, $m = d \log(\tau)/d(T_g/T)$. Fragility is a useful metric of the temperature sensitivity of the relaxation times,^{21,22} expressed in terms of the VFTH parameters as

$$m = \log(e) \frac{B/T_g}{(1 - T_0/T_g)^2} \quad (2)$$

As shown in Figure 1, the fragility of the 1,2-PBD measured herein is equal to that of a lower molecular weight ($M_w = 2 \text{ kg/mol}$) sample of the same polymer.²³ The value, $m = 88$, is less than the fragility of a polybutadiene having a higher vinyl content (96%), for which $m = 99$ at $\tau = 1 \text{ s}$.²⁴ The fragility of polybutadiene is known to increase with increasing vinyl content.^{6,25}

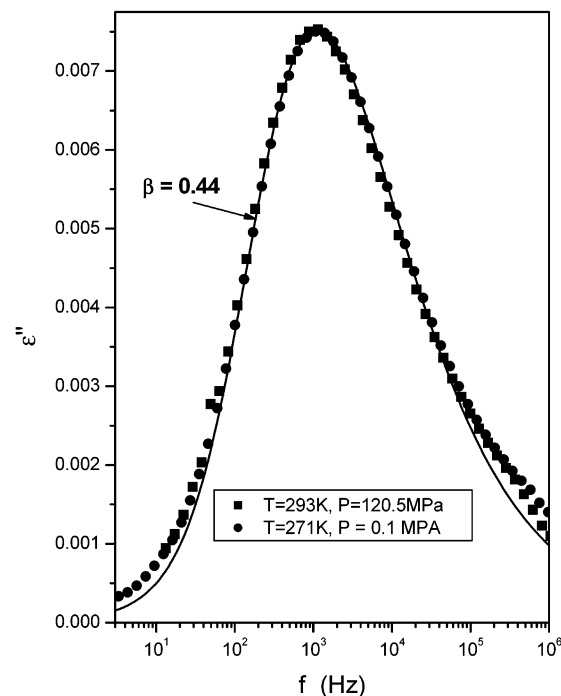


Figure 2. Dispersion in the dielectric loss of PBD measured at atmospheric (●) and at elevated (■) pressure. Compared at equal value of the relaxation time, there is no change with pressure in the shape of the relaxation function. The solid curve is the transform of the Kohlrausch function (eq 3) having the indicated value of the stretch exponent. The ordinate values for ambient pressure were multiplied by 0.37 to superpose vertically.

However, as indicated by Figure 1, it is not dependent on molecular weight. This is usually the case for flexible chain polymers,^{7,26–28} polystyrene being an exception.^{29,30}

Dielectric spectra were also obtained at elevated pressures, with representative spectra shown in Figure 2. There is no change in the shape of the segmental relaxation dispersion with pressure when compared at a fixed value of the relaxation time. The central portion of the peak can be described using the transform of the Kohlrausch function³¹

$$\epsilon''(\omega) = \Delta\epsilon \int_0^\infty dt \left[\frac{-d}{dt} \exp(-t/\tau_K)^\beta \right] \sin(\omega t) \quad (3)$$

with a temperature-independent $\beta = 0.44$. τ_K is the time for the relaxation to decay to e^{-1} of its initial value. The Kohlrausch relaxation time is 0.76 times the τ defined from the maximum in the dielectric loss. The τ , measured at elevated pressure, are displayed in Figure 3. Over moderate ranges of pressure, $\log \tau$ is proportional to P , with an activation volume, $\Delta V^\ddagger = 2.303RT[(\partial \log \tau)/(\partial P)]_T$. Over the range of pressures in Figure 3, the data are clearly nonlinear; however, for $P < 40 \text{ MPa}$, we can calculate an apparent activation volume, $100 < \Delta V^\ddagger (\text{mL/mol}) < 167$, decreasing with increasing temperature.

To describe the full pressure dependence, we employ a pressure variant of the VFTH equation^{27,32}

$$\tau = \tau_0 \exp\left(\frac{DP}{P_0 - P}\right) \quad (4)$$

where D , P_0 , and τ_0 are constants, the latter obtained from the measurements at atmospheric pressure. The

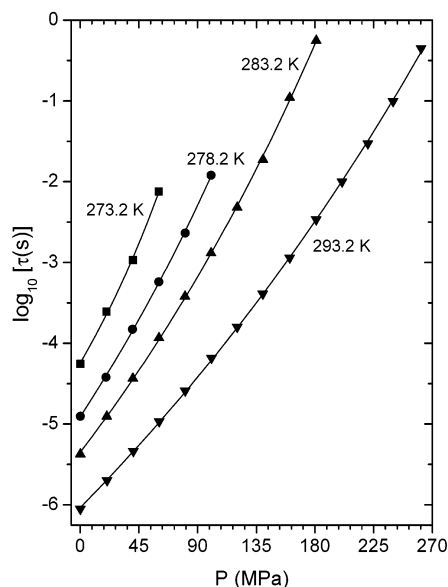


Figure 3. Dielectric relaxation times measured as a function of pressure at the indicated temperatures. The solid lines are the fits to eq 4.

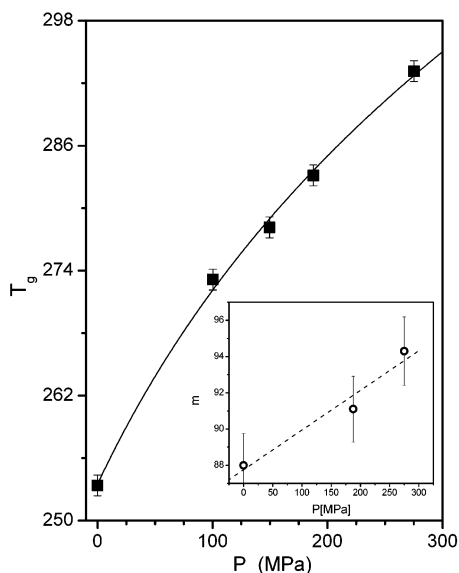


Figure 4. Temperature at which $\tau = 1$ s for various pressures. The line through the data is the fit to eq 5, yielding in the limit of low pressure 0.24 ± 0.02 K/MPa for the pressure coefficient of the glass transition temperature. At ambient pressure, $T_g = 253.4$ K. In the inset, the fragility, m , as calculated at $\tau = 1$ s for different pressures using eq 6; the dashed line is a linear fit to the data.

fits to eq 4 are included in Figure 3. Using these fits to extrapolate the two lower temperature measurements, we can calculate T_g at each pressure. These results are shown in Figure 4, with the pressure variation described using

$$T_g = k_1 \left(1 + \frac{k_2}{k_3} P \right)^{1/k_2} \quad (5)$$

For 1,2-PBD, $k_1 = 253.5 \pm 0.2$ K, $k_2 = 7.3 \pm 0.9$, and $k_3 = 1075 \pm 150$ MPa. Originally conceived as an empirical relation,³³ eq 5 can be derived from a model for the pressure dependence of τ .²⁸ In the limit of zero pressure, the pressure coefficient of T_g ($= k_1/k_3$) is 0.24 ± 0.02 K/MPa. From this we obtain the activation

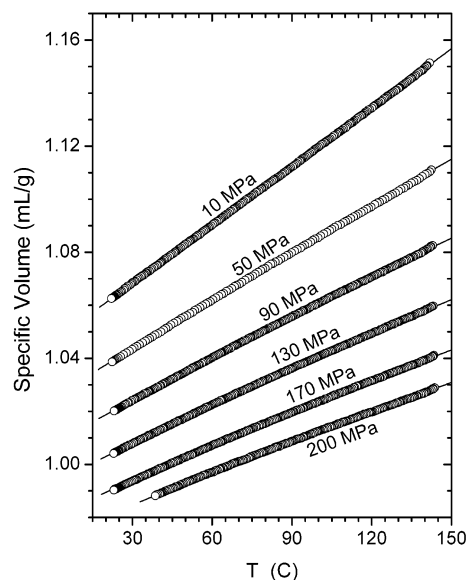


Figure 5. Pressure–volume–temperature data for the PBD. The lines through the measurements are the best fits to eq 7.

volume at T_g using

$$\Delta V^\# = 2.303 R m \frac{dT_g}{dP} \quad (6)$$

The result is $\Delta V^\# = 480$ mL/mol at 253.4 K and $P = 0.1$ MPa; of course, this is larger than the activation energies deduced for higher temperatures. Using eq 6, we can in turn calculate m (for $\tau = 1$ s) as a function of pressure, with the results shown in the inset to Figure 4. The fragility is observed to increase slightly with pressure ($dm/dP \sim 2 \times 10^{-2}$ MPa⁻¹). For polymers, previously it has been reported that m remains constant or slightly decreases with pressure,³⁴ while an increase of fragility with P had been found only for some molecular glass-formers.³⁵

To quantify the relative contribution of temperature and volume to the relaxation times, it is necessary to express the data in Figures 1 and 3 as a function of volume. Toward this end, we measured the volume of the 1,2-PBD from room temperature to ca. 428 K at a series of pressures up to 200 MPa; the results are shown in Figure 5. While various equations of state have been proposed for PVT data on polymer melts,^{18,36} the empirical Tait equation is the most common

$$V(T, P) = \left(a_0 + a_1 T + a_2 T^2 \right) \left(1 - 0.0894 \ln \left(1 + \frac{P}{b_0 \exp(-b_1 T)} \right) \right) \quad (7)$$

In this equation, the units of temperature are (by convention) centigrade. We simultaneously fit eq 6 to all the PVT data, obtaining $a_0 = 1.060$ mL/g, $a_1 = 7.5 \times 10^{-4}$ mL/(g °C), $a_2 = 2.0 \times 10^{-7}$ mL/(g °C²), $b_0 = 148$ MPa, and $b_1 = 4.79 \times 10^{-3}$ °C⁻¹. As seen in Figure 5, the fits describe the specific volume data well.

Using these parametrized PVT data, the respective temperature and pressure abscissas in Figures 1 and 3 can be converted to specific volume, with the results shown in Figure 6. The relative slope of the isobaric (ambient pressure) curve is substantially greater than the slopes for the isotherms; that is, for a given volume change, τ is more affected by changes in temperature

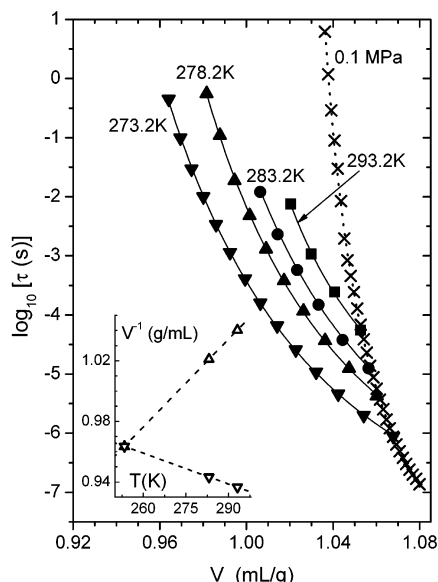


Figure 6. Relaxation times from Figures 1 (isobar) and 3 (isotherms) expressed as a function of the specific volume. The inset shows the temperature coefficient of the density for constant $P = 0.1$ MPa (∇) and for constant $\tau = 1$ s (Δ). The respective slopes yield $\alpha_P = 7.03 \times 10^{-4} \text{ K}^{-1}$ and $\alpha_\tau = -2.00 \times 10^{-3} \text{ K}^{-1}$.

than by changes in pressure. This must be, since temperature alters the thermal energy as well as the volume. The relative contributions of the two quantities can be determined by evaluating the thermal expansion coefficient at constant pressure, $\alpha_P = -\rho^{-1}(\partial\rho/\partial T)_P$, and the thermal expansivity at constant relaxation time, $\alpha_\tau = -\rho^{-1}(\partial\rho/\partial T)_\tau$. The ratio $|\alpha_\tau|/\alpha_P$ will be close to unity if the role of volume is equal to that of temperature but much larger than one if temperature dominates the relaxation times.¹⁵

In the inset to Figure 6, the specific volume is displayed vs temperature for $P = 0.1$ MPa (obtained from the fit of eq 6 to the PVT data) and as calculated for the pressures at which $\tau = 1$ s. Using $\rho = 0.963 \text{ g/mL}$ (the density at T_g and ambient pressure), from the slopes we obtain $\alpha_\tau = -2.00 \times 10^{-3} \text{ K}^{-1}$ and $\alpha_P = 7.03 \times 10^{-4} \text{ K}^{-1}$, whereby $|\alpha_\tau|/\alpha_P = 2.8$. This implies that temperature exerts a stronger influence than volume. However, the effect of the latter is not negligible. The change in relaxation time induced by temperature (wherein both thermal energy and volume are altered) would require at constant thermal energy a 2.8-fold larger change in density.

The ratio of the activation energy at constant volume, E_V , to that at constant pressure, E_P , is another measure of the relative contributions from temperature and volume to the relaxation times.^{14,37} If temperature dominates, $E_V \sim E_P$, while $E_V/E_P \sim 0.5$ if volume and temperature exert an equivalent influence on τ . The ratio is related to the temperature–pressure coefficient for a constant value of the relaxation time³⁸

$$E_V/E_P = 1 - \gamma(\partial T/\partial P)_\tau \quad (8)$$

where γ is the thermal-pressure coefficient (temperature dependence of the pressure at constant volume), calculated from the PVT data. For $V = 1.0381 \text{ mL/g}$ (the specific volume of the 1,2-PBD at T_g and ambient pressure), $\gamma = 1.27 \text{ MPa/K}$. Taking $dT/dP|_\tau \equiv dT_g/dP = 0.24 \text{ K/MPa}$, we obtain $E_V/E_P = 0.70 \pm 0.03$. This result,

indicating a stronger role for temperature than volume, is consistent with the ratio of the thermal expansivities.

Discussion

It is known^{6,13} that 1,2-polybutadiene has one of the broadest segmental relaxation functions and largest fragilities of any glass-former, molecular or polymeric. We have previously ascribed these properties to the steric constraints, and consequent strong intermolecular cooperativity, engendered by the inflexible pendant vinyl moiety.⁶ In Table 1, our results for 1,2-PBD are listed, along with data for three other vinyl polymers, polyethylene (PE),⁸ poly(vinyl acetate) (PVAc),²⁸ and poly(vinyl methyl ether) (PVME).³⁹ These polymers differ in the nature of the pendant groups, the main-chain atoms being the same. PE is the least fragile polymer ($m = 62$), consistent with weak intermolecular cooperativity of its smooth, symmetric backbone. (No meaningful stretch exponent is available for PE, since its relaxation is inhomogeneously broadened by crystallinity.^{8,40}) The intermediate materials in Table 1 with regard to cooperativity are PVAc and PVME; in fact, their relaxation properties are quite close. Both have a pendant ether linkage, which confers rotational flexibility, mitigating intermolecular constraints. It is surprising, however, and perhaps an indictment of drawing overly general conclusions from simple arguments, that PVAc is not more cooperative, given its bulky pendant group. The strong intermolecular cooperativity of 1,2-PBD is the result of steric constraints from the relatively inflexible vinyl carbon, which projects $>3 \text{ \AA}$ from the chain backbone.

We can extend this comparison to experimental results on these materials at elevated pressure (data are not available for PE). These results, presented in Table 1, were calculated for $T_g(\tau = 1 \text{ s})$. Of interest is the activation volume, normalized by the repeat unit molar volume, V_m . The activation volume represents the difference between the volume occupied by a molecule initially and in its transition state. ΔV^\ddagger is a function of temperature, so making the comparison in the vicinity of T_g , PVAc and PVME are quite similar, $\Delta V^\ddagger/V_m \sim 4.2$. This is consistent with the similar shape of their relaxation functions and their comparable fragilities, implying similar intermolecular cooperativity. However, for 1,2-PBD, wherein local segmental relaxation is more constrained by neighboring segments, the activation volume is more than 9 times the molar volume.

Results for $|\alpha_\tau|/\alpha_P$ and E_V/E_P are also collected in Table 1. Strong intermolecular cooperativity does not necessarily imply that volume dominates the segmental relaxation of 1,2-PBD. On the contrary, as seen in Table 1, there is a greater contribution from temperature, relative to that from volume, for 1,2-PBD than for the other two vinyl polymers. A strict distinction between relaxation governed by temperature and by volume is misleading, in that potential energy barriers are directly influenced by local steric constraints. In fact, we find for most polymers, the roles of temperature and volume are quite similar, with temperature exerting a somewhat larger influence. This is illustrated in Figure 7, showing the two ratios, for various polymers. Although we limit Figure 7 to results close to the glass transition, earlier work by Williams et al.³⁷ found $0.55 \leq E_V/E_P \leq 0.75$ from measurements at higher temperatures.

Also shown in the figure are data for several small-molecule glass-formers,^{16,28,30,39,41,42} which exhibit a

Table 1. Segmental Relaxation Properties ($\tau(T_g) = 1$ s)

	pendant group	T_g [K]	β	m	dT_g/dP [K/MPa]	$\Delta V^\#(T_g)$ [L/mol]	$\Delta V^\# / V_m$	$ \alpha_t /\alpha_P$	E_v/E_P	ref
PE	H	197		62						8
PVAc	—O—COCH ₃	318	0.48	71	0.25	0.34	4.1	1.8	0.67	28
PVME	—O—CH ₃	251	0.47	69	0.18	0.24	4.3	2.1	0.69	39
1,2-PBD	—CH=CH ₂	253	0.44	88	0.24	0.48	9.2	2.8	0.70	herein

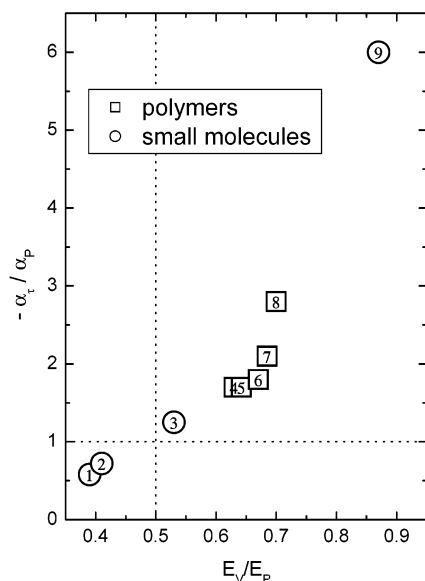


Figure 7. Comparison of two measures of the relative contribution of thermal energy and volume to the relaxation times of various glass-formers: 1, 1,1'-bis(*p*-methoxyphenyl)-cyclohexane;⁴¹ 2, 1,1'-di(4-methoxy-5-methylphenyl)cyclohexane;⁴¹ 3, phenylphthalin-dimethyl ether;¹⁶ 4, poly[(phenyl glycidyl ether)-*co*-formaldehyde];¹⁶ 5, polystyrene;³⁰ 6, poly(vinyl acetate);²⁸ 7, poly(vinyl methyl ether);³⁹ 8, 1,2-PBD; 9, sorbitol.⁴²

broad range of behavior. For the only hydrogen-bonded liquid in Figure 7, sorbitol, temperature dominates the relaxation. Similar results were reported for glycerol, $|\alpha_t|/\alpha_P > 10$.¹⁵ For extensively H-bonded liquids, the effect of volume is almost negligible due to competing effects. However, for the other glass-formers in Figure 7, all of which are nonassociated liquids, the relaxation times depend on both volume and thermal energy, with volume in some cases even exerting a more significant role than thermal energy.

Conclusions

Dielectric relaxation measurements over an extended range of temperature and pressure have been carried out on a high vinyl polybutadiene. The fragility ($m = 88$) was calculated at $\tau = 1$ s from data at ambient pressure. It is independent of molecular weight and varies only weakly with pressure. In contrast, no appreciable change in the shape of the relaxation function with pressure was observed for spectra compared at a fixed value of the relaxation time.

Using PVT data together with the dielectric relaxation times, the relative contribution of volume and temperature to the relaxation dynamics was determined. The ratio of the thermal expansion coefficient for constant relaxation time to that at constant pressure ($|\alpha_t|/\alpha_P$), as well as the ratio of isochoric and isobaric activation energies (E_v/E_P), indicates that temperature plays a more important role than volume, although the effect of the latter is not negligible. Figure 7, showing

values of these two ratios for 1,2-PBD and other polymers and molecular glass-formers, demonstrates that (i) the two quantities give comparable information and (ii) temperature and volume have approximately equal roles for polymers and nonassociated small molecules.

Finally, the segmental relaxation properties for various vinyl polymers are shown to be consistent with an interpretation in terms of the strength of the intermolecular cooperativity and the degree to which the latter is governed by chemical structure. The inflexible pendant vinyl carbons of 1,2-PBD enhance this intermolecular coupling, giving rise to the fragile behavior and an activation volume that is larger, relative to the molar volume, than for the structurally similar PVME and PVAc.

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