Dielectric α-relaxation and ionic conductivity in propylene glycol and its oligomers measured at elevated pressure

Riccardo Casalini[a]

Naval Research Laboratory, Chemistry Division, Code 6120, Washington, DC 20375-5342
and Chemistry Department, George Mason University, Fairfax, Virginia 22030

C. Michael Roland[b]

Naval Research Laboratory, Chemistry Division, Code 6120, Washington, DC 20375-5342

Structural dynamics and volume were measured as a function of both temperature and pressure for a propylene glycol and its oligomers (PPG), and the results compared with previous data on higher molecular weight polypropylene glycols. PPG is of special interest because the terminal groups form hydrogen bonds; thus, by studying different molecular weights, the manner in which hydrogen bonding influences the dynamics in the supercooled regime can be systematically investigated. The fragility (T_g-normalized temperature dependence) of the dimer and trimer of PPG increases with pressure, similar to results for other H-bonded liquids, but different from van der Waals glass formers. This behavior is believed to be due to the effect of pressure in decreasing the extent of hydrogen bonding. From the combined temperature and volume dependences of the relaxation times, the relative degree to which thermal energy and volume govern the dynamics was quantified. With decreasing molecular weight, the relative contribution of thermal energy to the dynamics was found to strongly increase, reflecting the role of hydrogen bonding. By comparing the ionic conductivity and the dielectric relaxation times, a decoupling between rotational and translational motions was observed. Interestingly, this decoupling was independent of both pressure and molecular weight, indicating that hydrogen bonds have a negligible effect on the phenomenon. © *2003 American Institute of Physics.* [DOI: 10.1063/1.1624401]

INTRODUCTION

Propylene glycol (PG) and polypropylene glycols (PPG) of various molecular weights have been studied using dielectric spectroscopy by various groups,[1–12] including measurements at elevated pressure.[13–18] The use of pressure evokes particular interest, because it allows the separation of the different relaxation modes in PPG.[17,18] For PPG, the shape of the α-relaxation function is invariant to pressure,[13,18] while the T_g-normalized temperature dependence (fragility) increases with pressure.[16] Similar behavior was observed for glycerol[19,20] (a hydrogen bonded liquid), whereas the fragility of the intramolecularly H-bonded salol is a decreasing function of pressure.[21]

Generally, cooling towards T_g causes a decoupling of relaxation and transport processes in glass-forming liquids and polymers.[22] The ionic conductivity, σ, arising from the diffusion of ionic contaminants, exhibits the same temperature dependence as the α-process at high temperatures, but as T_g is approached from above, translational motions are enhanced relative to reorientations. Decoupling of the viscosity and τ is also expected near T_g, although Suzuki *et al.*[15] were able to approximately predict the viscosity and its variation with pressure from measurements of τ and the bulk modulus, suggesting only weak decoupling in PPG.

Another interesting feature of PPG is its capacity for hydrogen bonding, arising from the terminal hydroxyl groups. For H-bonding glass formers, the contribution of thermal energy to the temperature dependence of the relaxation is strongly enhanced, relative to the effect of volume changes.[23,24] This is due in part to the effect a reduction in volume has on the ease of H-bond formation.[25–27] Fluorescent lifetime measurements on PPG demonstrate directly that pressure reduces the concentration of H bonds in PPG.[28] Since the number of hydrogen bonds in these materials also depends on molecular weight, quantifying the molecular weight dependence of the degree to which temperature and volume govern the temperature dependence of τ is of great interest.

Herein we describe high pressure measurements of the specific volume, ionic conductivity and dielectric α-relaxation in PG, and oligomers having two and three repeat units. From these results, together with published literature on a higher molecular weight PPG,[18] we show how systematic changes in the degree of hydrogen bonding influences the dynamics in the supercooled regime.

EXPERIMENT

Propylene glycol, dipropylene glycol, and tripropylene glycol were obtained from Aldrich Chemical Company. These materials have the chemical formula $H-(C_3H_6O)_N-OH$ with $N=1$, 2, and 3, respectively. To re-

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[a]Electronic mail: casalini@ccs.nrl.navy.mil
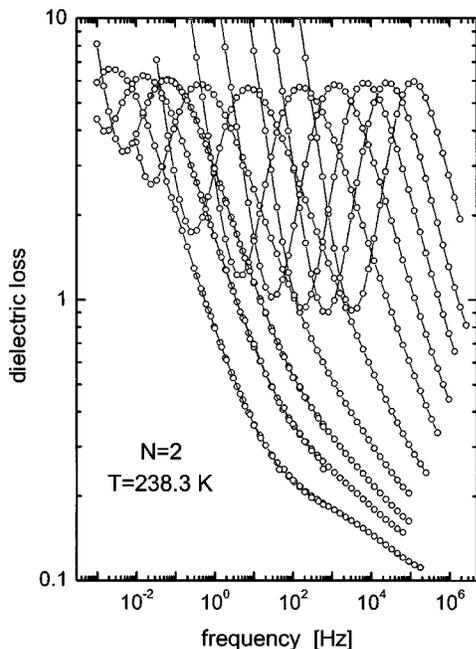[b]Electronic mail: roland@nrl.navy.mil

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FIG. 1. Dielectric loss spectra for PG dimer at 238.3 K and (from right to left) $P=0.1$, 75.2, 140.9, 225.6, 319.7, 427.3, 512.2, 561.1, 593.5, and 634.4 MPa. The dc conductivity can be observed on the low frequency side of the α-dispersion.

FIG. 2. Pressure dependence of the α-relaxation times (upper panel) and conductivity (lower panel) for PPG dimer ($\blacksquare$) at 216.8, 225.6, and 238.4 K, and trimer ($\blacktriangle$) at 223.5, 235.4, and 245.3 K. Also shown are τ for the monomer ($\blacktriangledown$) at 216.7 K. The solid lines are fits to Eq. (1).

move absorbed moisture, immediately prior to all measurements, samples were maintained for 1 h at 125 C in a nitrogen atmosphere.

Dielectric spectra were obtained using a parallel plate geometry with an IMASS time domain dielectric analyzer (10^{-4}–10^4 Hz) and a Novocontrol Alpha Analyzer (10^{-2}–10^6 Hz). For measurements at elevated pressure, the sample was contained in a Manganin cell (Harwood Engineering), with pressure applied using an Enerpac hydraulic pump in combination with a pressure intensifier (Harwood Engineering). Pressures were measured with a Sensotec tensometric transducer (resolution= 150 kPa). Temperature control was at least ±0.1 K.

Pressure–volume–temperature (PVT) measurements were carried out using a Gnomix instrument, a detailed description of which can be found elsewhere.[29] Isobaric volume changes were measured during cooling at 0.5 deg/min for pressures over the range from 10 to 200 MPa.

RESULTS

Representative spectra at $T=238.3$ K and various pressures are shown in Fig. 1. There is a prominent peak due to the α-relaxation, with the direct current (dc) conductivity falling toward lower frequencies. In the spectra for the highest pressures, an extra contribution is evident in the high frequency flank of the α-peak, due to the Johari–Goldstein secondary process.[17] The relaxation times and conductivities extracted from the spectra measured at elevated pressure are shown in Fig. 2. The sensitivity to pressure systematically increases with molecular size. This effect can be quantified using the activation volume, defined as $\Delta V_\tau = RT(\partial \ln \tau/\partial P)|_P$ and $\Delta V_\sigma = -RT(\partial \ln \sigma/\partial P)|_P$ for the re-
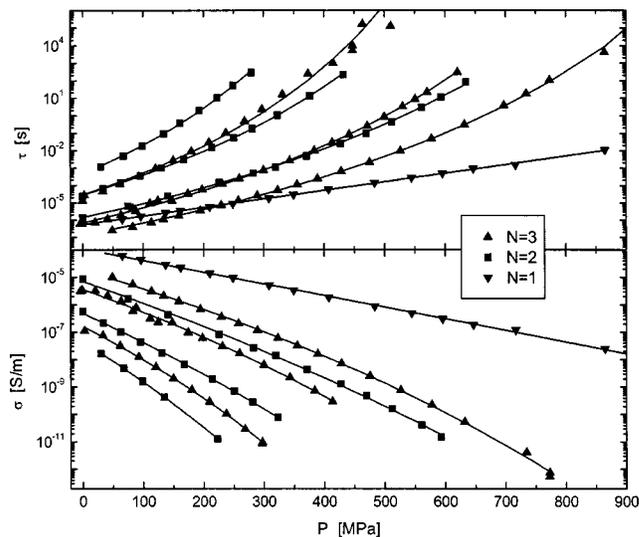
laxation times and ionic conductivities, respectively. Since the curves in Fig. 2 are nonlinear, ΔV is calculated for the limit of zero pressure. There is the customary decrease in activation volume with increasing temperature. We make comparisons among the three samples at respective temperatures for which their relaxation times are equal, with the results listed in Table I. The activation volume increases with increasing molecular size, similar to results found for other glass formers in which structure was systematically varied and comparisons were made for fixed values of τ.[30,31] For the dimer and trimer, we also calculated the activation volume for $\tau=10$ s (i.e., in proximity to the glass transition), and in both cases, ΔV is about equal to the molar volume, as seen for other materials.[32,33]

To describe the full pressure dependence of the relaxation times, various expressions have been proposed. Their utility is mainly for data interpolation. The results in Fig. 2 were fit to the empirical equation[34]

$$\tau(P) = \tau_0 \exp\left(\frac{DP}{P_0-P}\right) \tag{1}$$

in which P_0 and τ_0 are pressure independent, while D is independent of both pressure and temperature. An analogous expression can be applied to the conductivity data.

TABLE I. Results for PG and PPG ($P=0.1$ MPa).

N	ΔV^a (ml/mol)	$T_\alpha{}^b$	dT_α/dP	K^c (GPa)	$-\alpha_\tau/\alpha_P{}^c$
1	9.4	184.8	37	4.42	8.3
2	17.9	210.4	80	3.29	6.0
3	19.5	205.9	109	2.82	4.9
69	⋯	209.6	192	2.73	2.0

[a]At respective temperatures for which $\tau \sim 10^{-6}$ s.
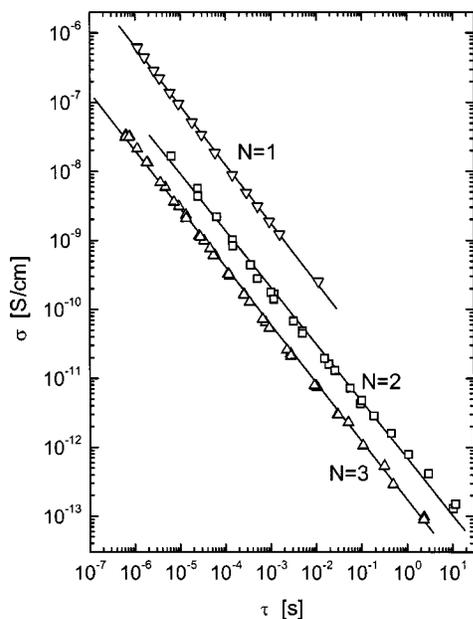[b]Temperature at which $\tau=0.01$ s at $P=0.1$ MPa.
[c]At T_α.

FIG. 3. Conductivity vs α-relaxation time for propylene glycol ($\triangledown$) at $T = 216.7$ K and $65 < P$ (MPa) < 865, PPG dimer ($\square$) at $T = 216.8$, 225.6, and 238.4 K and $0.1 < P$ (MPa) < 594, and PPG trimer ($\triangle$) at $T = 223.5$, 235.4, and 245.3 K and $0.1 < P$ (MPa) < 632. The power-law fits to the data (solid lines) give $k = 0.84 \pm 0.02$.

FIG. 4. Pressure dependence of the temperature at which the α-relaxation time equals 0.01 s for PPG having the indicated degree of polymerization. The inset shows the pressure dependence of the fragility calculated from Eq. (4) for the dimer ($\blacksquare$) and trimer ($\blacktriangle$), along with the ambient pressure value for PG ($\blacktriangledown$).

Similar to the slowing down of the relaxation times with pressure, there is a decrease in the ionic conductivity (Fig. 2). However, it is known that supercooling enhances translational motions relative to reorientations.[22] This gives rise to a decoupling, characterized by an empirical power law[35]

$$\sigma \tau^k = \text{constant} \tag{2}$$

in which $k \leq 1$. Results are plotted in Fig. 3 for the three samples. Note that measurements obtained for different combinations of temperature and pressure are indistinguishable; that is, the data superimpose. The decoupling constant, $k = 0.84 \pm 0.02$, is also equal, within the experimental error, for the three PPG.

From the data in Fig. 2 we can define a characteristic temperature, T_α, as the (pressure-dependent) temperature at which the relaxation time equals an arbitrary value. For dielectric spectroscopy, relatively short times are used to avoid extrapolation, and given the limited range of the measurements for PG, herein we take $\tau(T_\alpha) = 0.01$ s. T_α is about 13° larger than T_g, with the latter defined as $\tau(T_g) = 100$ s. The results, shown in Fig. 4, are fitted to the equation[16,36]

$$T_\alpha = a \left(1 + \frac{b}{c} P \right)^{1/b}. \tag{3}$$

For the dimer, $a = 210$, $b = 2.88$, and $c = 2630$, while for the trimer, $a = 206$, $b = 5.22$, and $c = 1890$. Only two data were obtained for the monomer, and thus Eq. (3) was not applied. T_α is slightly higher for $N = 2$ than for $N = 3$, consistent with previous literature.[8] We ascribe this anomaly to the competing effects of chain length and hydrogen bonding, the dimer having more H bonds per unit volume. Note that for methyl-terminated PPG oligomers,[9] which lack H bonding, T_g is much lower than for the materials herein, but equal to the
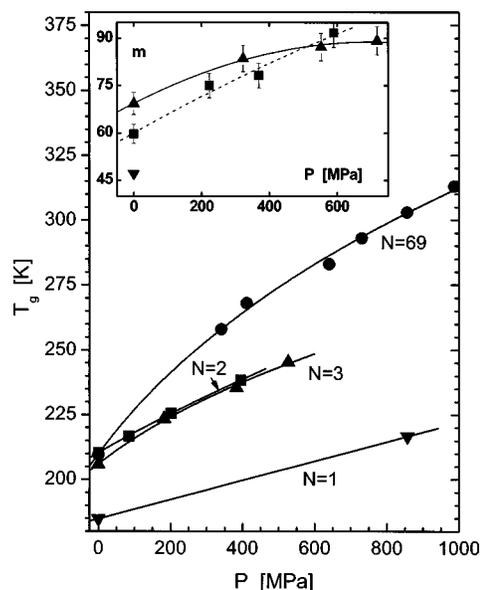
glass transition temperature of hydroxyl-terminated PPG of very high molecular weight, for which H-bonding effects are negligible.

Included in Fig. 4 are results for a higher molecular weight PPG, obtained by reanalyzing published data.[18] There is a systematic increase in the pressure coefficient of the glass transition temperature with molecular weight (Table I). This parallels the variation of the activation volume with M_w, both effects reflecting a decreased degree of hydrogen bonding.

In the inset to Fig. 4 are the fragilities, m, calculated for $\tau = 10$ s, at different pressures for the dimer and trimer, and at atmospheric pressure for PG. The values of m at high pressure were obtained from the relation[20]

$$m = \frac{\Delta V}{R \ln(10) \left. \dfrac{dT}{dP} \right|_\tau}, \tag{4}$$

where R is the gas constant. Previous measurements at atmospheric pressure showed that with increasing molecular weight of the PPG, m decreases.[8] However, the fragility increases with pressure, ameliorating the effect of N on m.

The increase of m with increasing pressure for glycerol was ascribed to a decrease of hydrogen bonding,[19] although experimental data concerning the effect of pressure on hydrogen bonding are somewhat contradictory.[25–27,37] For PPG, there is no ambiguity about the decrease of H bonding with increasing N. Moreover, when comparisons are made at equal τ, higher pressure corresponds to higher temperature, which will also contribute to the loss of hydrogen bonds.

PVT measurements were carried out on the three samples, with the results displayed in Figs. 5–7. These data were fit to the Tait equation[38]
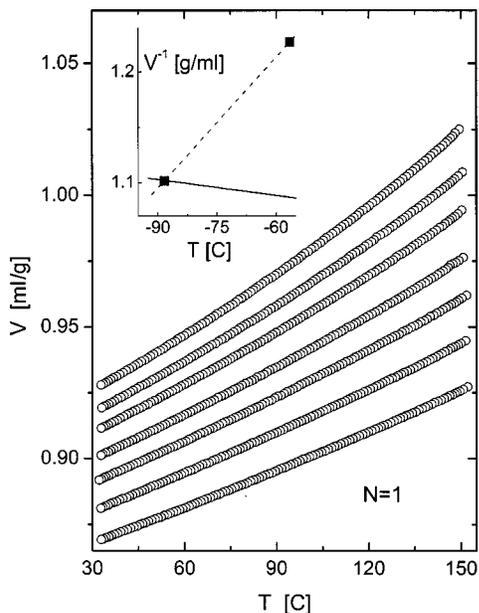
FIG. 5. The specific volume measured at pressures equal to (from top to bottom) 10, 30, 50, 80, 110, 150, and 200 MPa for PG. The inset shows the variation of the density measured isochronally at $\tau = 0.01$ s (■) and isobarically at $P = 0.1$ MPa (solid line), from which the ratios in Fig. 5 were calculated.
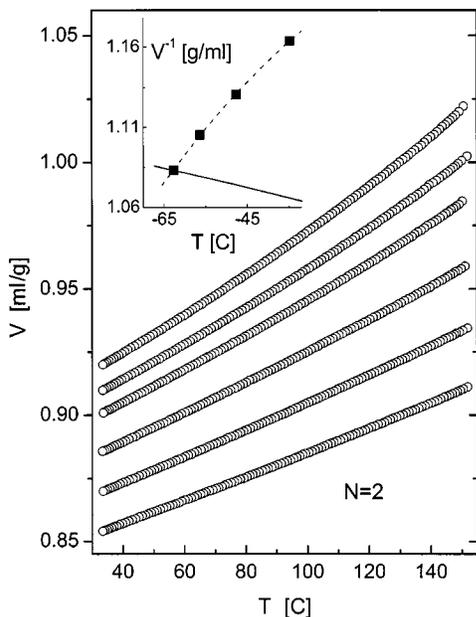

FIG. 7. The specific volume measured at pressures equal to (from top to bottom) 10, 30, 50, 90, 140, and 200 MPa for PPG trimer. The inset shows the variation of the density measured isochronally at $\tau = 0.01$ s (■) and isobarically at $P = 0.1$ MPa (solid line), from which the ratios in Fig. 5 were calculated.

$$V(T,P) = V(T,0)\{1 - 0.0894 \ln[1 + P/B(T)]\}, \qquad (5)$$

where the specific volume at zero pressure is

$$V(T)|_{P=0} = \nu_0 + \nu_1 T + \nu_2 T^2 \qquad (6)$$
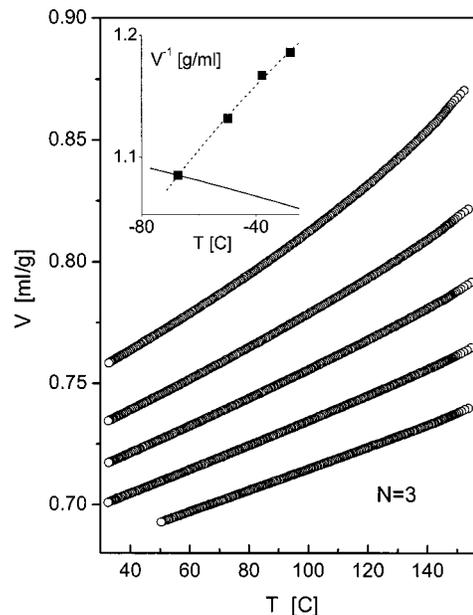
and

$$B(T) = b_0 \exp(-b_1 T). \qquad (7)$$

FIG. 6. The specific volume measured at pressures equal to (from top to bottom) 10, 30, 50, 90, 140, and 200 MPa for PPG dimer. The inset shows the variation of the density measured isochronally at $\tau = 0.01$ s (■) and isobarically at $P = 0.1$ MPa (solid line), from which the ratios in Fig. 5 were calculated.

The obtained parameters are listed in Table II.

Using the fitted equation of state, the data in Fig. 2 can be expressed as a function of the volume. Representative results for the PPG dimer are shown in Fig. 8. The isobar and each isotherm yield different curves, since volume does not uniquely define the relaxation time. The greater steepness of the $\tau(V)$ curve for fixed pressure, as opposed to fixed temperature, reflects the larger contribution of thermal energy to the dynamics. We can quantify the effect that volume and thermal energy have on the relaxation time from the ratio of the thermal expansion coefficient at constant pressure, $\alpha_P = V^{-1} (\partial V/\partial T)_P$, to that at constant relaxation time, $\alpha_\tau = V^{-1} (\partial V/\partial T)_\tau$.[39] The expansion coefficients are determined from the PVT results in combination with the data in Fig. 2. These data are shown in the insets to Figs. 5–7. The calculation is for $P = 0.1$ MPa and, to avoid extrapolation in the analysis of the data for PG, for $\tau = 0.01$ s. (Note that calculating $-\alpha_\tau/\alpha_P$ for $\tau = 1$ s gives values of the ratio that are roughly 10% smaller.) As seen in Fig. 9, $-\alpha_\tau/\alpha_P$ varies inversely with molecular weight of the PPG. This means that thermal energy exerts a progressively weaker effect on the temperature dependence of the relaxation times with increasing N, due to a diminishing extent of H bonding. The largest value, $-\alpha_\tau/\alpha_P = 8.3$ for $N=1$, is intermediate to the ratios

TABLE II. Equation of state results.

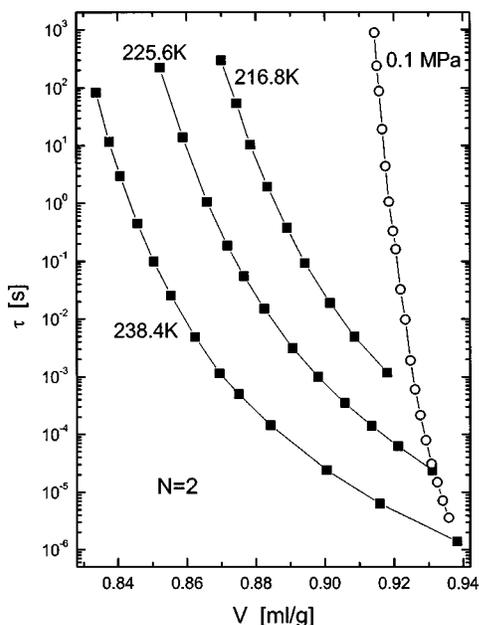| N	ν_0 (ml/g)	ν_1 (ml/g C)	ν_2 (ml/g C^2)	b_0 (MPa)	b_1 (C^{-1})
1	0.910	6.00×10^{-4}	1.455×10^{-6}	221	5.93×10^{-3}
2	0.901	6.79×10^{-4}	1.339×10^{-6}	184	6.08×10^{-3}
3	0.742	6.70×10^{-4}	0	114	6.760×10^{-3}

FIG. 8. The variation of the dielectric α-relaxation times of the PPG dimer with specific volume, for measurements as a function of temperature at ambient pressure (○) and as a function of pressure at the indicated temperatures (■).

reported for the polyalcohols glycerol[39] and sorbitol,[40] two other strongly hydrogen-bonded liquids.

CONCLUDING REMARKS

The decrease in hydrogen bonding with molecular weight gives rise to systematic variations in properties (Table I). While ameliorating the increase in T_g with chain length, a decreased degree of H-bonding amplifies the pressure coefficient of T_g. This is in accord with the finding that associ-
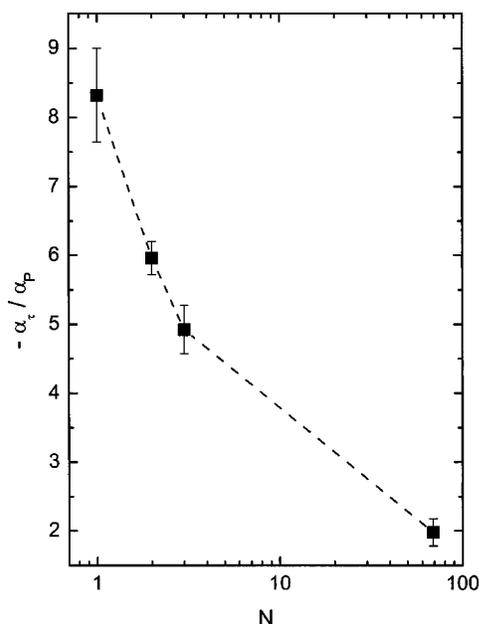

FIG. 9. Ratio of the isochronic ($\tau = 10^{-2}$ s) and isobaric ($P = 0.1$ MPa) thermal expansion coefficients (■) as a function of the degree of polymerization of the PPG.

ated liquids exhibit smaller dT_g/dP than are found for van der Waals glass formers.[41] Likewise, the influence of temperature, relative to volume, on $\tau(T)$ increases with the degree of hydrogen bonding. This trend, which appears to be quite general, reflects the opposite effect that changes in volume and changes in temperature exert on the propensity of liquids for H-bond formation.[24,31]

A further consequence of H-bonding sensitivity to pressure is that as the degree of polymerization of the PPG increases, the activation volume increases, since the higher molecular weight PPG molecules are less H bonded. Larger ΔV implies that molecular motions are more delocalized, so that we might expect concomitantly less resistance to changes in volume *per se*; that is, a smaller bulk modulus, K. Included in Table I are values of K for T_α and $P = 0.1$ MPa calculated from the PVT data. There is indeed a systematic decrease in K with increasing activation volume. The generality of such a relationship requires further exploration.

The slowing down of the dynamics upon approach to T_g in PPG is accompanied by a decoupling of the α-relaxation time and the ionic conductivity. For a given M_w, the results for different temperatures and pressures superimpose. Moreover, the magnitude of the exponent relating τ and σ, $k = 0.84$, is invariant to molecular weight. These two results imply that the decoupling phenomenon is unaffected by hydrogen bonding.

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