Volume and Temperature Dependences of the Global and Segmental Dynamics in Polymers: Functional Forms and Implications for the Glass Transition

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ABSTRACT: Previously, from dielectric relaxation measurements obtained for various temperatures T and pressures P on polypropylene glycol, 1,4-polyisoprene, and poly(oxybutylene) [Roland, C. M.; Casalini, R.; Paluch, M. *J. Polym. Sci. Polym. Phys. Ed.* **2004**, *42*, 4313. R. Casalini and C. M. Roland, *Macromolecules*, **2005**, *38*, 1779], both the primary α-relaxation time τ_α and the normal mode relaxation time τ_n were shown to yield master curves when plotted versus the quantity $T^{-1}V^{-\gamma}$. Moreover, the value of γ is the same for the two processes (here V is the specific volume and γ is a material-specific constant). Such a result appears to be consistent with an assumption underlying models for polymer viscoelasticity that the friction coefficient governing motions over large length scales can be identified with the local segmental friction coefficient. However, notwithstanding the superpositioning obtained using the same value of γ, τ_α and τ_n differ in their dependences on either the product variable $T^{-1}V^{-\gamma}$, V at constant T, or T at constant P. In each case, the difference is more pronounced at longer τ_α. Such behavior is inconsistent with the Rouse and tube models. However, these differences in the respective dependences of τ_α and τ_n can be accounted for quantitatively by the coupling model. The framework of the solution of the problem supports the proposal that the temperature and volume dependences of molecular mobility, which trigger the glass transition, do not originate from the primary α relaxation. Instead, they have their origin in the primitive relaxation of the coupling model.

1. Introduction

It has been discovered[1–4] that in many small molecules and polymeric glass-formers, the logarithm of the primary (or α) relaxation time, $\log(\tau_\alpha)$, obtained by dielectric measurements for various temperatures T and pressures P, yields a master curve when plotted versus the quantity $T^{-1}V^{-\gamma}$. Here V is the specific volume and γ is a material-specific constant, found to vary over a broad range $0.14 \leq \gamma \leq 8.5$ for the glass-formers investigated to date. By combining the dielectric results for any of these glass-formers with the corresponding equation of state (*PVT* data), the volume-dependence of the relaxation times can be obtained. Until recently, this type of analysis for polymers has been carried out only for the segmental relaxation (i.e., the primary α) process.[5–8] Recently, the analysis was extended to the polymer chain dynamics (i.e., the dielectric normal mode) for type-A polymers, polypropylene glycol[9] (PPG), 1,4-polyisoprene[9] (PI), and polyoxybutylene (POB).[10] The normal mode relaxation times (strictly speaking, the longest normal mode relaxation times, τ_n) superpose to a single master curve when plotted against $T^{-1}V^{-\gamma}$, using the same value of γ as for the segmental relaxation times, τ_α. The result that τ_α and τ_n are functions of the same product variable is written explicitly as

$$\log(\tau_\alpha) = f_\alpha(T^{-1}V^{-\gamma}) \tag{1}$$

and

$$\log(\tau_n) = f_n(T^{-1}V^{-\gamma}) \tag{2}$$

The equivalence of the scaling parameter for the two processes suggests that the factors underlying the dynamics must be related. At first sight, this equivalence even seems to suggest that the normal mode and the segmental modes might have exactly the same temperature and volume dependences, consistent with the assumption of thermorheological simplicity underlying some models of polymer dynamics.[11] However, this inference cannot be correct because data for many polymers have revealed unambiguously that the segmental and chain modes have different temperature[11–22] and volume (or pressure) dependences.[23,24] Thus, the chain modes are not governed by the friction coefficient associated with local segmental motion. The fact that the segmental and chain modes have different temperature dependences has been known for many years. First demonstrated by creep compliance data by Plazek and co-workers on several polymers, including polystyrene, atactic polypropylene, and poly(methylphenylsiloxane), it has subsequently been confirmed by others using various techniques.[13,16,19,25] It was also shown to be the case specifically for PPG,[15,25] PI,[16] and POB,[26] the polymers of interest herein. The immediate effect

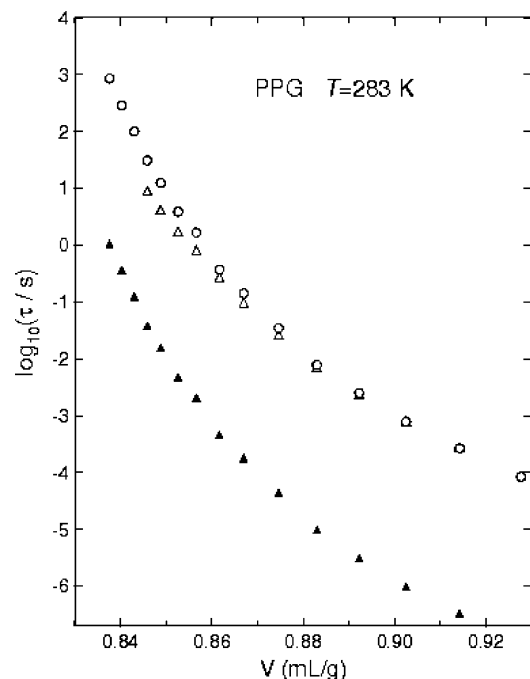* Author to whom correspondence should be addressed. E-mail: roland@nrl.navy.mil.

Figure 1. Segmental (▲) and normal mode (△) relaxation times for PPG as a function of the specific volume. The measurements[22] were carried out at the indicated temperature at varying pressures. Open circles represent segmental relaxation times shifted vertically to reveal their stronger volume dependence in comparison to the normal mode.

Figure 2. Segmental (●) and normal mode (▲) relaxation times for PI as a function of the specific volume. The measurements[23] were carried out at the indicated temperature and at varying pressures. Open circles represent segmental relaxation times shifted vertically to show their stronger volume dependence in comparison to the normal mode.

is a breakdown of thermorheological simplicity, i.e., failure of time–temperature superposition of viscoelastic data.[12,17,18,24,25] Less well-known is the fact that the segmental and chain modes have different pressure (or volume) dependences. Again, by combining the dielectric data for the two modes with equation of state (*PVT*) data,[9] the volume-dependence of their relaxation times τ_n and τ_α were obtained. Shown in Figures 1 and 2 are the results for PPG and PI with molecular weight M = 4.0 and 11.1 kg/mol, respectively.[22,23] The measurements were carried out at the indicated temperatures at varying pressures. The stronger specific volume dependence of τ_α than τ_n is brought out clearly by comparing $\log(\tau_n)$ with $\log(\tau_\alpha)$ after applying a vertical shift to the latter to make the curves coincide at shorter times. From the trends seen in Figures 1 and 2, the difference in volume dependences is expected to be greater at longer τ_α and τ_n, were such data available. This trend is similar to that actually seen in comparing the temperature dependences of τ_α and τ_n.[14,17]

It is paradoxical that τ_n and τ_α are functions of the same quantity, $T^{-1}V^{-\gamma}$, yet have different $T^{-1}V^{-\gamma}$-, T- and V-dependences. The purpose of this paper is to resolve this conundrum by applying the coupling model (CM).[27–32] This solution of the problem has the implication that the origin of the temperature and volume dependences of molecular mobility lies in the primitive relaxation time τ_0 of the CM. The dependences are magnified in τ_α by the many-molecule dynamics, which generate the α-relaxation from the primitive relaxation. In the final part of this paper, we describe additional evidence, linking the Johari–Goldstein (JG) relaxation to the primitive relaxation of the CM.

2. The Coupling Model Solution

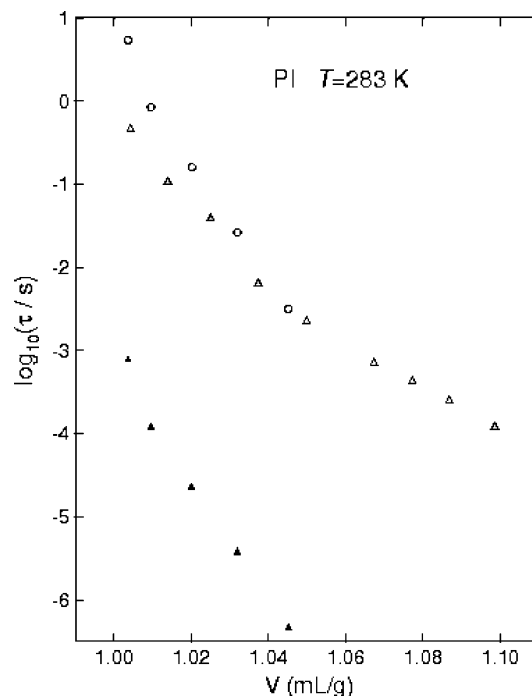A quantitative explanation by the CM of the stronger temperature and pressure dependences of τ_α than τ_n has

been detailed elsewhere.[30,31] The CM is a general approach to treat relaxation of interacting many-body systems. The microscopic details of relaxation in a coupled many-body system are complicated; nevertheless, these many-body dynamics must originate from relaxation or attempts to relax by individual units. Therefore, in deriving the CM, consideration starts with the independent or primitive relaxation rate, τ_0^{-1}, of individual units (e.g., molecules or polymer chain segments). The dynamic constraints of a coupled many-body system prevent the attempts of all relaxing units to be simultaneously successful, resulting in the coincident existence of both fast and slowly relaxing molecules, i.e., heterogeneous dynamics. However, when averaged, the effect is equivalent to the slowing down of τ_0^{-1} by another multiplicative factor. This factor must be time dependent because dynamics is not stationary but evolves with time. The time-dependent rate $W(t)$ has the product form, $\tau_0^{-1}f(t)$, where $f(t) < 1$. In particular,

$$W(t) = \tau_0^{-1}(\omega_c t)^{-n} \qquad (3)$$

with $0 \leq n < 1$, so that the solution of the averaged correlation function ϕ from the rate equation, $d\phi/dt = -W(t)\phi$, yields the empirical Kohlrausch stretched exponential function,

$$\phi(t) = \exp[-(t/\tau)^{1-n}] \qquad (4)$$

Here n is the coupling parameter of the CM and β_K ($= 1 - n$) is the fractional Kohlrausch exponent. The stronger the coupling of the relaxing units in the many-body system, the larger is the length-scale of the dynamic heterogeneity, and thus the more retarded is the primitive rate; these all correspond to a larger coupling parameter. The time-dependent rate $\tau_0^{-1}(\omega_c t)^{-n}$

also leads immediately to an important relation between τ and τ_0 of the CM

$$\tau = (t_c^{-n}\tau_0)^{1/(1-n)} \tag{5}$$

where t_c is identified by $t_c = (1-n)^{-(1/n)}/\omega_c$. Many-body dynamics cannot start instantly, and t_c marks the crossover of the correlation function from $\exp(-t/\tau_0)$ to the Kohlrausch function. This transition transpires over a range of t for which the derivatives are continuous. The magnitude of t_c depends on the coupling strength of the many-body system but is insensitive to temperature.[28] Solutions of simple coupled systems[27] support the premise of the CM.

A major application of the CM is describing the properties of the primary α-relaxation of glass-formers. From neutron scattering experiments and molecular dynamics simulations of polymeric and small molecule liquids at short times,[28] the Kohlrausch function

$$\phi_\alpha(t) = \exp[-(t/\tau_\alpha)^{1-n_\alpha}] \tag{6}$$

is found not to hold for times shorter than approximately 2×10^{-12} s and is replaced by the linear exponential time dependence of the primitive relaxation. Note that the transport properties, including viscosity and conductivity, assume the Arrhenius temperature dependence of the primitive relaxation when the relaxation time becomes less than 2 ps.[33,34] These properties indicate that t_c is approximately equal to 2 ps for small molecule and polymeric glass-formers. Because we shall consider relaxation of coupled normal modes of polymer chains, described by their own primitive relaxation time, coupling parameter, and crossover time, the suffixes α and n are added to all quantities related to the α-relaxation and normal mode, respectively. The relation between the α-relaxation time τ_α and its primitive relaxation time $\tau_{\alpha 0}$ (eq 5) is now written as

$$\tau_\alpha = [(t_{\alpha c})^{-n_\alpha}\tau_{\alpha 0}]^{1/(1-n_\alpha)} \tag{7}$$

Only the slowing down of the α-relaxation by the many-body dynamics is accounted for by eq 7, but it implies that if τ_α is a function of the product variable $T^{-1}V^{-\gamma}$ (as found experimentally (eq 1)[1–4,8–10]), then $\tau_{\alpha 0}$ must also be a function of the same variable $T^{-1}V^{-\gamma}$. This turns out to be an important point, even though the CM does not predict the dependence of either τ_α or $\tau_{\alpha 0}$ on $T^{-1}V^{-\gamma}$. With time being a natural variable, the fact that $\tau_{\alpha 0}$ precedes τ_α implies that the dependence of molecular mobility on $T^{-1}V^{-\gamma}$ originates from $\tau_{\alpha 0}$. That is, the dependence of τ_α on $T^{-1}V^{-\gamma}$ is not original but derived from that of $\tau_{\alpha 0}$ (via eq 7) by raising it to the superlinear power $1/(1-n_\alpha)$. Changes in volume and temperature are related to changes in pressure and entropy because of the thermodynamic relation, $(\partial S/\partial P)_T = -(\partial V/\partial T)_P$. Hence, the same conclusion applies to the dependences of $\tau_{\alpha 0}$ and τ_α on pressure and entropy. Following the usual practice of polymer viscoelasticity,[11,24,32] we define a monomeric friction coefficient $\zeta_\alpha(T, V)$ that contains the dependences of $\tau_\alpha(T, V)$ on T and V, and a primitive monomeric friction coefficient $\zeta_0(T, V)$ for $\tau_{\alpha 0}(T, V)$. From eq 7, the relation between the two friction coefficients is

$$\zeta_\alpha(T, V) = [\zeta_0(T, V)]^{1/(1-n_\alpha)} \tag{8}$$

The coupling parameter n_α has been determined for PPG ($M_w = 4000$ g/mol, as herein)[35] and for a high molecular weight PI[36] by fitting the frequency-dependent dielectric loss data by the one-sided Fourier transform of the Kohlrausch−Williams−Watts function. The results for τ_α in the range 10^{-5}–10^2 s are

$$n_\alpha = 0.45 \tag{9a}$$

for PPG and

$$n_\alpha = 0.47 \tag{9b}$$

for PI.

The normal modes of polymer chains are intermolecularly coupled if the molecular weight is comparable or exceeds the critical molecular weight for entanglements. For the PI sample of Figure 2, $M_w = 11.1$ kg/mol, which is almost a factor of 2 larger than the entanglement molecular weight.[9] The PPG sample has a molecular weight equal to 4.0 kg/mol, with coupling between the chains caused by transient linkages of chain ends via hydrogen bonding.[15] Although the interactions between chains are different (entanglement interaction in PI versus hydrogen bonding interaction in PPG), the many-chain dynamics can be taken into account by the CM. Description by the CM[15,21,30,31] starts with the primitive normal mode relaxation rate $(\tau_{n0})^{-1}$, a coupling parameter n_n of the normal modes, and a crossover time t_{nc} that is about 1 ns for entanglement couplings.[28] The slowed chain relaxation time τ_n is given by

$$\tau_n = [(t_{nc})^{-n_n}\tau_{n0}]^{1/(1-n_n)} \tag{10}$$

$(\tau_{n0})^{-1}$ is identified with the relaxation rate of the longest wavelength mode of the Rouse model, $(\tau_R)^{-1}$, because the Rouse modes stem from relaxation dynamics of a free chain without any chain−chain coupling. It follows that τ_{n0} has the well-known $M^{2.0}$-dependence of the Rouse model. For this reason, in the framework of the CM, the friction coefficient of the Rouse modes is the same as the primitive monomeric friction coefficient $\zeta_0(T, V)$ for $\tau_{\alpha 0}(T, V)$.[30] Thus, in the CM, the Rouse modes, the entangled chain modes, and the local segmental mode each have different friction factors. This feature delineates the CM from all other models of polymer viscoelasticity[11,12] in which a *single* friction factor, namely $\zeta_\alpha(T, V)$ of $\tau_\alpha(T, V)$, governs these three modes of motion.

Although all primitive relaxation modes in the CM have the same friction coefficient, i.e.,

$$\tau_\alpha 0(T, V), \tau_{n0}(T, V), \tau_R(T, V) \propto \zeta_0(T, V) \tag{11}$$

this is not true for modes having a nonzero coupling parameter. From eqs 7 and 11, it follows that

$$\tau_\alpha(T, V) \propto [\zeta_0(T, V)]^{1/(1-n_\alpha)} \tag{12}$$

and from eqs 10 and 11

$$\tau_n(T, V) \propto [\zeta_0(T, V)]^{1/(1-n_n)} \tag{13}$$

In general, τ_α and τ_n have different friction coefficients because their respective coupling parameters, n_α and n_n, are different. The molecular weight dependence of τ_n has the $M^{2/(1-n_n)}$-dependence, a result that follows

from eq 10 and the M^2-dependence of τ_R for the Rouse modes. PPG for M up to 4000 g/mol is not entangled, as evidenced by published viscoelastic data,[37] but the observed molecular weight dependence of τ_n is $M^{2.95}$, significantly stronger than the $M^{2.0}$-dependence expected if the normal mode is governed by Rouse dynamics. This enhanced molecular weight dependence comes from many-chain dynamics involving transient linkages of the chain ends via hydrogen bonding. The CM is a general framework for many-chain dynamics, and eq 13 remains valid for PPG. Hence, by comparing the predicted $M^{2/(1-n_n)}$-dependence of τ_n from eq 13 and the observed $M^{2.95}$-dependence, the coupling parameter of the normal modes of PPG is given by[15]

$$n_n = 0.32 \qquad (14)$$

The PI sample[23] with number-averaged molecular weight of 10 600 is barely entangled, and hence its τ_n lies between the $M^{2.0}$-dependence of Rouse chains and the $M^{3.7}$-dependence of fully entangled PI chains, as observed by dielectric measurements.[38,39] Therefore, for this PI, the normal mode coupling parameter n_n falls between 0 for Rouse chains and $n_n = 0.46$ for fully entangled chains (i.e., $M \gg M_c$), the latter obtained from the experimental $M^{3.7}$-dependence using the theoretical $M^{2/(1-n_n)}$-dependence.[31]

By comparing eq 9a with eq 14 for PPG and eq 9b with the estimate of n_n given above for PI, it is clear that the value of n_α is larger than n_n for both polymers. Then, eqs 12 and 13 lead to the conclusion that τ_α has stronger temperature and volume dependences than τ_n. This result, τ_α having a stronger temperature dependence than τ_n, explains quantitatively the experimental data, not only of PPG[16] and PI[17,24] but also of other polymers, both entangled and unentangled.[13,17,18,19] By the same line of reasoning and using eqs 12 and 13, the stronger volume dependence of τ_α is predicted to exceed that of τ_n, in accord with the experimental findings[9,23] shown in Figures 1 and 2.

From eq 12 and the experimental result that τ_α is a function of the product variable, $T^{-1}V^{-\gamma}$, it follows that $\zeta_0(T, V)$ also is a function of $T^{-1}V^{-\gamma}$ over the range of τ_α for which n_α is a constant. And by eq 13, τ_n is also a function of $T^{-1}V^{-\gamma}$, having the same exponent γ as in eq 12. The dependences of τ_α and τ_n on the product variable $T^{-1}V^{-\gamma}$ are written explicitly as

$$\tau_\alpha(T^{-1}V^{-\gamma}) = f_\alpha([\zeta_0(T^{-1}V^{-\gamma})]^{1/(1-n_\alpha)}) \qquad (15)$$

and

$$\tau_n(T^{-1}V^{-\gamma}) = f_n([\zeta_0(T^{-1}V^{-\gamma})]^{1/(1-n_n)}) \qquad (16)$$

It is clear from these two equations that τ_α and τ_n are functions of the same product variable $T^{-1}V^{-\gamma}$, although the functions are not the same, because in general, $n_\alpha > n_n$. Both $\log(\tau_\alpha)$ and $\log(\tau_n)$ data for various T and P yield a master curve when plotted versus the product variable $T^{-1}V^{-\gamma}$ for the same γ. Thus, the apparent conundrum is resolved when the segmental and chain dynamics are described within the framework of the CM.

Like τ_α and τ_n, their corresponding friction coefficients, ζ_α and ζ_n, are functions of the product variable $T^{-1}V^{-\gamma}$ with the same value of γ. According to eqs 15
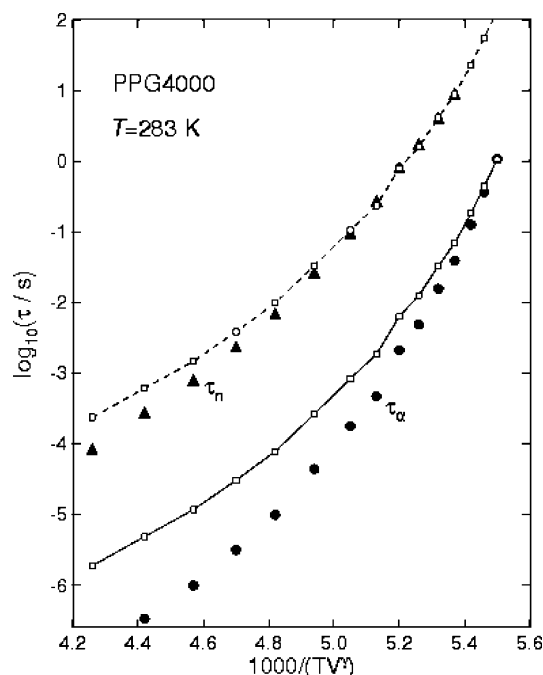

Figure 3. Relaxation times of PPG at $T = 283$ K from Figure 1 as a function of $Y \equiv T^{-1}V^{-\gamma}$, with $\gamma = 2.5$: segmental relaxation times ($\bullet$) and normal mode relaxation times ($\blacktriangle$). The shift factors a_{nY} for the normal mode calculated from the segmental relaxation data using $n_\alpha = 0.45$ (eq 9a) and $n_n = 0.32$ (eq 14) are also shown ($\square$ connected by solid line). A vertical upward shift is then applied to the calculated a_{nY} ($\square$ connected by dashed line) to compare with the temperature dependence of the $\log(\tau_n(Y))$ data.

and 16, $\zeta_\alpha(T^{-1}V^{-\gamma})$ and $\zeta_n(T^{-1}V^{-\gamma})$ are different functions of $Y \equiv T^{-1}V^{-\gamma}$, but they are related by

$$(1 - n_n) \log[\zeta_n(T^{-1}V^\gamma)] = (1 - n_\alpha) \log[\zeta_\alpha(T^{-1}V^\gamma)] =$$
$$\log[\zeta_0(T^{-1}V^\gamma)] \quad (17)$$

With n_α and n_n known, this relation is tested against the $\log \tau_\alpha(T^{-1}V^{-\gamma})$ and $\log \tau_n(T^{-1}V^{-\gamma})$ data of PPG in Figures 3 and 4. The tests of PPG are carried out for two representative temperatures and shown separately for the sake of clarity. From the data of $\tau_\alpha(T^{-1}V^{-\gamma})$, we first determine the shift factor $a_{\alpha Y} \equiv \tau_\alpha(Y)/\tau_\alpha(Y_{ref})$, where $Y \equiv T^{-1}V^{-\gamma}$ and Y_{ref} is a reference value. It follows from eq 17 that the shift factor $a_{nY} \equiv \tau_n(Y)/\tau_n(Y_{ref})$ of the normal mode can be calculated by the equation

$$\log(a_{nY}) = \frac{(1 - n_\alpha)}{(1 - n_n)}\log(a_\alpha Y) \qquad (18)$$

The calculated results of a_{nY} with $n_\alpha = 0.45$ for PPG (eq 9a), assuming n_α is constant for the entire range of the τ_α data shown, are presented by the open squares connected by the solid lines in Figures 3 and 4. A vertical shift is then applied to the calculated a_{nY} and the results (open squares connected by the dashed line) are compared with the $\log(\tau_n(Y))$ data (closed triangles). There is good agreement in the region where $\tau_\alpha(Y)$ is longer than 10^{-4} s. However, the predicted values of $\tau_n(Y)$ tend to be longer than the data for $\tau_\alpha(Y) < 10^{-4}$ s. The assumption that n_α has a constant value usually breaks down at shorter $\tau_\alpha(Y)$, which is an empirical result found by broadband dielectric relaxation spectroscopy of glass-formers.[40,41] Therefore, in this region, the departure of the calculated temperature dependence of
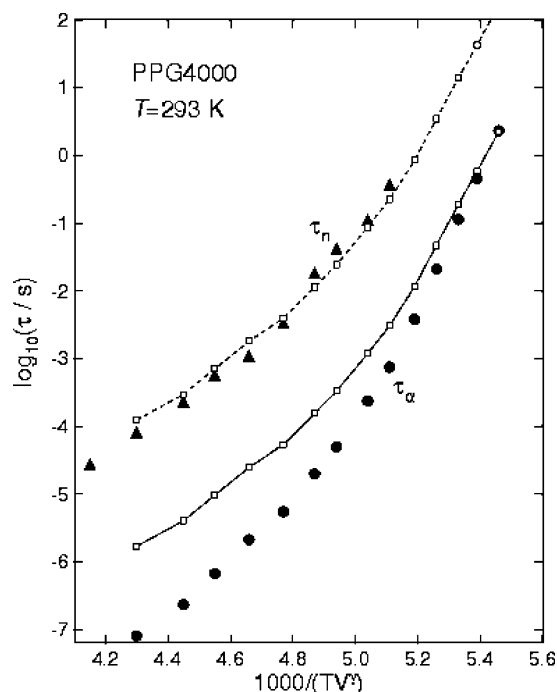
Figure 4. Relaxation times of PPG at $T = 293$ K as a function of $Y \equiv T^{-1}V^{-\gamma}$, with $\gamma = 2.5$: segmental relaxation time ($\bullet$) and normal mode relaxation times ($\blacktriangle$), The shift factors a_{nY} for the normal mode calculated from the segmental relaxation data using $n_\alpha = 0.45$ (eq 9a) and $n_n = 0.32$ (eq 14) are presented ($\square$ connected by solid line). A vertical upward shift is then applied to the calculated a_{nY} ($\square$ connected by dashed line) to compare with the temperature dependence of the $\log(\tau_n(Y))$ data.

Figure 5. Segmental ($\bullet$) and normal mode ($\blacktriangle$) relaxation times for PI as a function of $Y \equiv T^{-1}V^{-\gamma}$, with $\gamma = 3.0$. The measurements[24] were carried out under ambient pressure at varying temperatures. The shift factors a_{nY} calculated with $n_\alpha = 0.47$ (eq 9b) and $n_n = 0.41$ are presented ($\square$ connected by solid line). A vertical upward shift is then applied to the calculated a_{nY} ($\square$ connected by dashed line) to compare with the temperature dependence of the $\log(\tau_n(Y))$ data.

of $\log(\tau_n(Y))$ from the data is possibly due to a decrease of n_α, not taken into account in Figures 3 and 4.

The situation for the PI data is different. As discussed before, n_n of the PI sample cannot be directly determined. It is certainly smaller than 0.47 (eq 9b) because the sample is barely entangled. This fact alone, that $n_n < n_\alpha$, accounts for the stronger volume dependence (Figure 2) or greater $Y \equiv T^{-1}V^{-\gamma}$ dependence (Figure 5) of the segmental relaxation in comparison to those of the normal mode. We can determine n_n by carrying out the same calculation via eq 18 as done for PPG in Figures 3 and 4. Now, n_n is treated as a floating parameter, and its value is determined by the best fit to the weaker Y-dependence of the normal mode from the stronger Y-dependence of the segmental mode. This fit in Figure 5 yields $n_n = 0.41$. From this value and $\tau_n \propto M^{2/(1-n_n)}$, we deduce that the molecular weight dependence of τ_n is $M^{3.4}$, which is consistent with the observed transition from the $M^{2.0}$ to the $M^{3.7}$-dependence[39,40] at the molecular weight 10 600 of the PI sample.

In a very recent work,[10] the relaxation times of the normal mode and the local segmental mode for a POB sample with $M_n = 4800$ g/mol and $M_w/M_n = 1.10$ were again found to be functions of the product variable $Y \equiv T^{-1}V^{-\gamma}$ with $\gamma = 2.65$, but they are *not* governed by the same local friction coefficient, as revealed by the differences in their dependences on T or V as τ_α becomes large. In an ambient pressure dielectric study of POB,[27] the loss peaks for the normal mode for samples with $M_n = 4500$ and 1810 g/mol were resolved and their respective frequencies located at approximately 300 Hz and 4 kHz. These two data, when used to determine n_n from the molecular weight dependence $\tau_n \propto M^{2/(1-n_n)}$, gives $n_n \approx 0.30$. (Note that for POB samples with $M_n =$
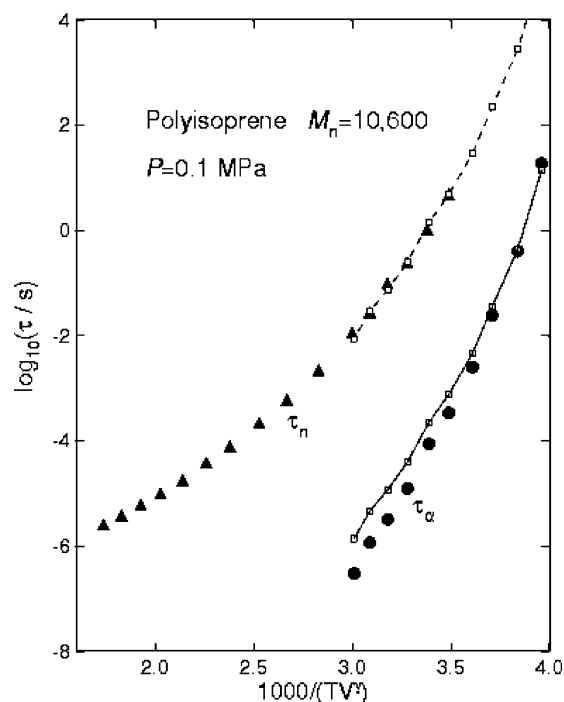
970 and 460 g/mol, the normal modes were not resolved[27] and thus cannot be used to determine n_n.) This estimate of $n_n \approx 0.30$ is consistent with the fit of the dielectric loss spectrum of the 4800 g/mol sample at 246.6 K and 210.4 MPa,[10] shown in Figure 6 by the sum of one-sided Fourier transforms of two KWW functions with $n_n = 0.30$ for the normal mode and $n_\alpha = 0.41$ for the local segmental mode. The deviations from the fit at low frequencies is due to ionic conduction and at high frequencies from contributions of a secondary relaxation. In fitting the data, we have considered only the longest normal mode and ignored the much smaller contribution to the dielectric loss from the higher-order normal modes.[43] The 4800 g/mol sample has a polydispersity $M_w/M_n = 1.10$, which contributes to the breadth of the loss peak. Thus, the value of n_n deduced from the dielectric spectrum can be smaller than the value of 0.30 deduced from the molecular weight dependence.

The shift factors, a_{nY}, calculated from this value of n_α (assumed to be constant for the entire range of the data) are displayed as the open squares connected by a solid line in Figure 7. By applying a vertical shift to these data points (open squares connected by the dashed line), a comparison is made to the $\log(\tau_n(Y))$ data (closed triangles). There is good agreement in the region where $\tau_\alpha(Y)$ is longer than 10^{-4} s. The discrepancy with the predicted values of $\tau_n(Y)$ for $\tau_\alpha(Y) < 10^{-4}$ s is possibly due to n_α not having a constant value as assumed. We have mentioned in connection with the fit to the dielectric spectrum that n_n may be less than 0.30 because of polydispersity. A smaller n_n is still consistent with the observed weaker $T^{-1}V^{-\gamma}$-dependence of the normal mode compared with that of the local segmental relaxation. The fit of the calculated values of τ_n to the
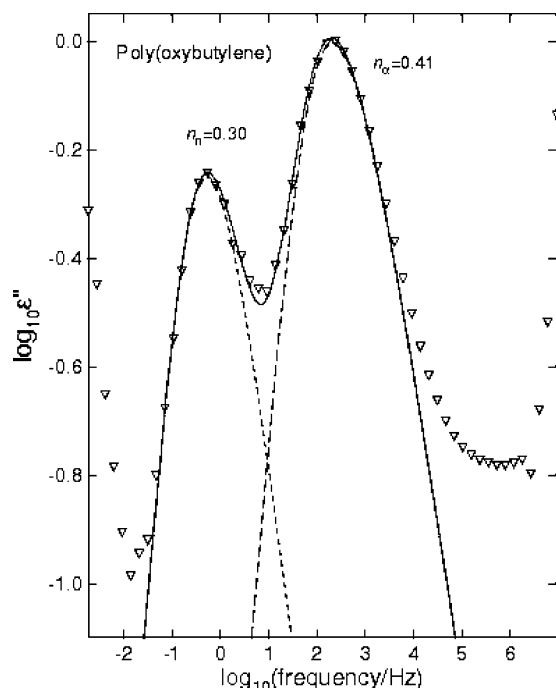
Figure 6. Representative dielectric loss data for POB at $T = 246.6$ K and $P = 201.4$ MPa showing the fits to the normal mode (short dashed line) and the segmental peak (long dashed line) of the one-sided Fourier transform of the KWW function with $n_n = 0.30$ and $n_\alpha = 0.41$. The sum of the losses is shown by the solid line.
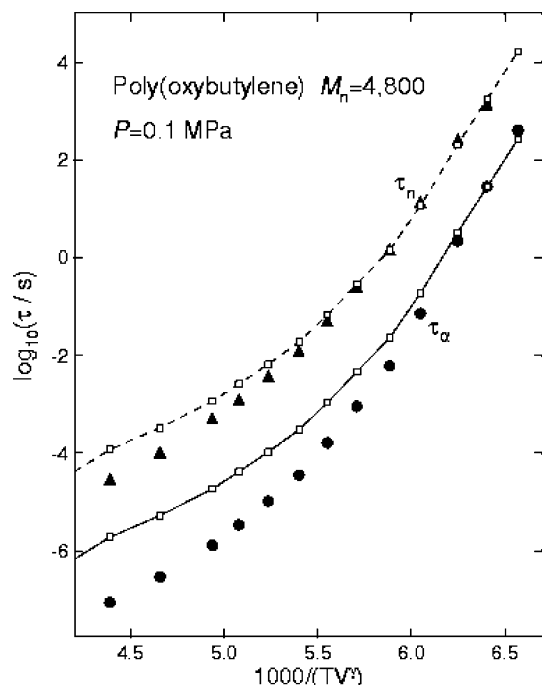

Figure 7. Relaxation times of POB at ambient pressure as a function of $Y \equiv T^{-1}V^{-\gamma}$, with $\gamma = 2.65$: segmental relaxation time (●) and normal mode relaxation times (▲), Shift factors a_{nY} for the normal mode were calculated from the segmental relaxation data using $n_\alpha = 0.41$ and $n_n = 0.30$ (□ connected by the solid line). A vertical upward shift is then applied to the calculated a_{nY} (□ connected by the dashed line) to compare with the temperature dependence of the $\log(\tau_n(Y))$ data.

data is still reasonably good for n_n as low as 0.26. Parenthetically, we note that the POB sample corresponds to 67 repeat units per chain, equal to that of the PPG, and because the coupling of the normal modes in

both cases arises from hydrogen bonding at chain ends, it is unsurprising that the value of n_n of POB is close to that of PPG (eq 14). The slightly smaller n_α for POB compared with PPG is possibly due to the flexible ethyl side chains in POB, which may mitigate intermolecular constraints and hence reduce the segmental relaxation coupling parameter.

3. Implications for the Mechanism of Glass Transition

The main purpose of the present work is to explain the experimental finding that although τ_α and τ_n are functions of the same product variable $Y \equiv T^{-1}V^{-\gamma}$ with the same γ, the functions per se are not the same. The proffered explanation accounts quantitatively for the difference between the two functions. The key eqs 7, 11, 12, and 17 used above involve the primitive relaxation time $\tau_{\alpha 0}$ and its friction coefficient ζ_0. From the experimental result that τ_α, and thus its friction coefficient ζ_α, are functions of $T^{-1}V^{-\gamma}$, these equations lead to the ancillary result that $\tau_{\alpha 0}$ and its friction coefficient ζ_0 are also functions of $T^{-1}V^{-\gamma}$. Because the primitive relaxation transpires earlier than the α-relaxation, the dependences of molecular mobility on volume and temperature cannot originate from the α-relaxation but from the primitive relaxation, as exemplified by the $T^{-1}V^{-\gamma}$ -dependences of its relaxation time $\tau_{\alpha 0}(T^{-1}V^{-\gamma})$ and friction coefficient $\zeta_0(T^{-1}V^{-\gamma})$. This conclusion has an important implication for the mechanism of the glass transition. Conventional theories of the glass transition, including free volume models and configurational entropy models, consider only the α-relaxation, and the latter is where the dependences of molecular mobility on temperature, pressure, volume, and entropy are assumed to originate. The CM fosters a different viewpoint; the dependence of τ_α on $T^{-1}V^{-\gamma}$ is derived from that of $\tau_{\alpha 0}$ according to the relation,

$$\tau_\alpha(T^{-1}V^{-\gamma}) = [(t_{\alpha c})^{-n_\alpha}\tau_{\alpha 0}(T^{-1}V^{-\gamma})]^{1/(1-n_\alpha)} \quad (19)$$

which is eq 7 with the dependence on $T^{-1}V^{-\gamma}$ written out explicitly. Note that $t_{\alpha c}$ equals about 2 ps for molecular and polymeric glass-formers.[28,33] The operation of raising $\tau_{\alpha 0}(T^{-1}V^{-\gamma})$ to the power $(1 - n_\alpha)^{-1}$ and obtaining the dependence of τ_α on $T^{-1}V^{-\gamma}$ arises from the many-body relaxation dynamics and consequent slowing down of the average relaxation rate. Because the power $(1 - n_\alpha)^{-1}$ is superlinear, the resulting $T^{-1}V^{-\gamma}$ -dependence of τ_α is stronger than that of $\tau_{\alpha 0}$. Nevertheless, the dependence of τ_α on $T^{-1}V^{-\gamma}$ is not fundamental, but only a consequence of $\tau_{\alpha 0}(T^{-1}V^{-\gamma})$. There is another experimental result supporting $\tau_{\alpha 0}$ as the origin of the dependence of molecular mobility on $T^{-1}V^{-\gamma}$. This is discussed in the following section.

4. Evidence of the Primitive Relaxation

Because the analysis herein is based on consideration of the primitive relaxation time $\tau_{\alpha 0}$, it is worthwhile to show direct evidence of it from experiments, particularly for polyisoprene, PPG, and POB. Secondary relaxations are commonly found in polymers, although some involve intramolecular degrees of freedom and thus bear no relation to the α-relaxation. An example of these trivial secondary relaxations would be the isolated motion of a pendant group on a polymer chain. However, there is a special kind of secondary relaxation that involves all atoms in the molecule or the entire repeat unit for

polymers such as 1,4-polybutadiene[45] and polyisoprene[36] (not including the very fast rotation of the methyl group). In the research community of nonpolymeric glass-formers, these secondary relaxations are sometimes called Johari–Goldstein relaxations. JG secondary relaxations are potentially the originator of the α-relaxation, in the manner of the primitive relaxation of the CM. The CM primitive relaxation time $\tau_{\alpha 0}$ calculated from the parameters of the α-relaxation via eq 7 turns out to be approximately the same as the most probable relaxation time of the JG secondary relaxation, τ_β, in many glass-formers,[43–49] including polyisoprene.[36]

Another experimental evidence for a close connection between the two processes is the size of their jump angles. Multidimensional NMR[50,51] experiments have shown that the dynamically heterogeneous molecular reorientations of the α-relaxation (i.e., the primitive relaxation in the coupling model) occur by relatively small jump angles, which have an exponential time dependence. Furthermore, from one- and two-dimensional 2H NMR studies,[52] the secondary relaxation in toluene-d5 and polybutadiene-d6 is seen to also involve angular jumps of similar magnitude for temperatures above T_g. This similarity in size of the jump angles supports a connection between these two relaxation processes.

Because the α-relaxation time τ_α is in general pressure dependent and non-Arrhenius in the equilibrium liquid state, it follows from eq 7 that the primitive relaxation time $\tau_{\alpha 0}$ is also pressure dependent and non-Arrhenius. Dielectric measurements at elevated pressure of JG secondary relaxations have found that, at constant temperature in the equilibrium liquid state, τ_β is indeed pressure (and hence volume) dependent. Examples include dipropyleneglycol dibenzoate,[47] benzoin-isobutyl ether,[53] dimer and trimers of propylene glycol[54] (i.e., lower molecule versions of PPG), sorbitol, and xylitol.[55] The dependences of $\tau_{\alpha 0}$ and τ_β on temperature and pressure are approximately the same, i.e.,

$$\tau_\beta(T, P) \approx \tau_\alpha 0(T, P) \tag{20}$$

These various experimental facts indicate that the primitive relaxation of the CM can indeed be identified with the JG relaxation.

5. Conclusions

The coupling model accounts for the stronger volume, V, and temperature, T, dependences of the segmental α-relaxation time τ_α in comparison to those of the normal mode relaxation time τ_n in PPG, PI, and POB. It further shows how both relaxation times can be a function of the product variable $T^{-1}V^{-\gamma}$, notwithstanding that the dependence of τ_α on this variable is also stronger than that of τ_n. For PPG and POB, we can quantitatively account for the difference between the two $T^{-1}V^{-\gamma}$-dependences without adjustable parameters.

Related to this explanation is the additional result that the dependence of τ_α on $T^{-1}V^{-\gamma}$ is not original but derives from that of the primitive relaxation of the coupling model $\tau_{\alpha 0}(T^{-1}V^{-\gamma})$. In other words, the temperature, pressure, volume, and entropy dependences of molecular mobility originate from the primitive relaxation and become magnified for the α-relaxation because of many-body dynamics. There is support for

this result from the observed volume and temperature dependences of the secondary relaxation time in the equilibrium liquid state, which is the same as $\tau_{\alpha 0}$ both conceptually and experimentally. Because the secondary relaxation or the primitive relaxation transpire long before the α-relaxation, this indicates that the temperature, volume, and entropy dependences of molecular mobility originate from that of the secondary relaxation time or the primitive relaxation time. The origin of the dependence of τ_β or $\tau_{\alpha 0}$ on the variable TV^γ is an open question.

References and Notes

(1) Casalini, R.; Roland, C. M. *Phys. Rev. E* **2004**, *69*, 062501.
(2) Roland, C. M.; Capaccioli, S.; Lucchesi, M.; Casalini, R. *J. Chem. Phys.* **2004**, *120*, 10640.
(3) Roland, C. M.; Casalini, R. *J. Chem. Phys.* **2004**, *121*, 11503.
(4) Casalini, R.; Roland, C. M. *Colloid Polym. Sci.* **2004**, *283*, 107.
(5) Williams, G. In *Dielectric Spectroscopy of Polymeric Materials*; Runt, J. P., Fitzgerald, J. J., Eds.; American Chemical Society: Washington DC, **1997**.
(6) Dreyfus C.; Le Grand A.; Gapinski, J.; Steffen, W.; Patkowski A. *cond-mat*/0410299.
(7) Paluch, M.; Casalini, R.; Roland, C. M. *Phys. Rev. B* **2002**, *66*, 092202.
(8) Roland, C. M.; Paluch, M.; Pakula, T.; Casalini, R. *Philos. Mag. B* **2004**, *84,* 1573.
(9) Roland, C. M.; Casalini, R.; Paluch, M. *J. Polym. Sci., Polym. Phys. Ed.* **2004**, *42*, 4313.
(10) Casalini R.; Roland, C. M. *Macromolecules,* **2005**, *38*, 1779.
(11) Ferry, J. D. *Viscoelastic Properties of Polymers*; Wiley: New York, 1980.
(12) Plazek, D. J. *J. Phys. Chem.* **1965**, *69*, 3480.
(13) Santangelo, P. G.; Ngai, K. L.; Roland, C. M. *Macromolecules* **1996**, *29*, 3651.
(14) Plazek, D. J.; Chay, I.-C.; Ngai, K. L.; Roland, C. M. *Macromolecules* **1995**, *28*, 6432.
(15) Ngai, K. L.; Schonhals, A.; Schlosser, E. *Macromolecules* **1992**, *25*, 4915.
(16) Schönhals, A. *Macromolecules* **1993**, *26*, 1309.
(17) Ngai, K. L.; Plazek, D. J. *Rubber Chem. Technol.* **1995**, *68*, 376.
(18) Plazek, D. J. *J. Rheol.* **1996**, *40*, 987.
(19) Roland, C. M.; Ngai, K. L.; Santangelo, P. G.; Qiu, X. H.; Ediger, M. D.; Plazek, D. J. *Macromolecules* **2001**, *34*, 6159.
(20) Santangelo, P. G.; Roland, C. M. *Macromolecules* **1998**, *31*, 3715.
(21) Roland, C. M.; Ngai, K. L.; Plazek, D. J. *Macromolecules* **2004**, *37*, 7051.
(22) Roland, C. M.; Psurek, T.; Pawlus, S.; Paluch, M. *J. Polym. Sci., Part B: Polym. Phys.* **2003**, *41*, 3047.
(23) Floudas, G.; Reisinger, T. *J. Chem. Phys.* **1999**, *111*, 5201.
(24) Ngai, K. L. In *Physical Properties of Polymers*, 3rd ed.; Cambridge University Press: Cambridge, 2004.
(25) Cochrane, J.; Harrison, G.; Lamb, J.; Phillips, D. W. *Polymer* **1980**, *21*, 837.
(26) Kyritsis, A.; Pissis, P.; Mai, S.-M.; Booth, C. *Macromolecules* **2000**, *33*, 4581.
(27) Ngai, K. L.; Tsang, K. Y. *Phys. Rev. E* **1999**, *60*, 4511.
(28) Ngai, K. L.; Rendell, R. W. In *Supercooled Liquids, Advances and Novel Applications;* Fourkas, J. T., Kivelson, D., Mohanty, U., Nelson, K., Eds.; ACS Symposium Series; American Chemical Society: Washington DC, 1997; p 45.
(29) Ngai, K. L. *IEEE Trans. Dielectr. Electr. Insul.* **2001**, *8*, 329.
(30) Ngai, K. L.; Plazek, D. J.; Rendell, R. W. *Rheol. Acta* **1997**, *36*, 307.
(31) Ngai, K. L.; Plazek, D. J. *J. Polym. Sci. Part B: Polym. Phys. Ed.* **1986***, 24*, 619.
(32) Ngai, K. L.; Floudas, G.; Rizos, A. K.; Plazek, D. J. Amorphous Polymers, *Encyclopedia of Polymer Properties;* Wiley: New York, 2002.
(33) Ngai, K. L.; Habasaki, J.; León, C.; Rivera, A. *Z. Phys. Chem.* **2004**, *218*, 1.
(34) Ngai, K. L.; Greaves, G. N.; Moynihan, C. T. *Phys. Rev. Lett.* **1998***, 80*, 1018.

(35) León, C.; Ngai, K. L.; Roland, C. M. *J. Chem. Phys.* **1999**, *110*, 11585.

(36) Roland, C. M.; Schroeder, M. J.; Fontanella, J. J.; Ngai, K. L. *Macromolecules* **2004**, *37,* 2630.

(37) Cochrane, J.; Harrison, G.; Lamb, J.; Phillips, D. W. *Polymer* **1980**, *21*, 837.

(38) Adachi, K.; Kotaka, T. *Macromolecules* **1985**, *18*, 466.

(39) Boese, D.; Kremer, F. *Macromolecules* **1990**, *23*, 829.

(40) Stickel, F.; Fischer, E. W.; Richert, R. *J. Chem. Phys.* **1996**, *104*, 2043. Stickel, F. Ph.D. Thesis, Mainz University, Shaker, Aachen, Germany, 1995.

(41) Casalini, R.; Ngai, K. L.; Roland, C. M. *Phys. Rev. B* **2003**, *68*, 014201.

(42) Stockmayer, W. H. *Pure Appl. Chem. Phys.* **1967**, *15*, 247.

(43) Ngai, K. L.; Paluch, M. *J. Chem. Phys.* **2004**, *120*, 857.

(44) Ngai, K. L. *J. Chem. Phys.* **1998,** *109*, 6982.

(45) Ngai, K. L. *J. Phys.: Condens. Matter* **2003** *15*, S1107.

(46) Ngai, K. L.; Lunkenheimer, P.; León, C.; Schneider, U.; Brand, R.; Loidl, A. *J. Chem. Phys.* **2001**, *115*, 1405.

(47) Prevosto, D.; Capaccioli, S.; Lucchesi, M.; Rolla, P. A.; Ngai, K. L. *J. Chem. Phys*. **2004**, *120*, 4808.

(48) Ngai, K. L.; Capaccioli, S. *Phys. Rev. E* **2004**, *69*, 031501.

(49) Ngai, K. L. *AIP Conf. Proc*. **2004,** *708*, 515.

(50) Böhmer, R.; Diezemann, G.; Hinze, G.; Rössler, E. *Prog. Nucl. Magn. Reson. Spectrosc.* **2001,** *39*, 191.

(51) Sillescu, H.; Böhmer, R.; Diezemann, G.; Hinze, G. *J. Non-Cryst. Solids* **2002**, *307−310*, 16.

(52) Vogel, M.; Tschirwitz, C.; Schneider, G.; Koplin, C.; Medick, P.; Rössler, E. *J. Non-Cryst. Solids* **2002,** *307−310,* 326.

(53) Capaccioli, S.; Prevosto, D.; Lucchesi, M.; Rolla, P.; Casalini, R.; Ngai, K. L. *J. Non-Cryst. Solids*, **2005**. In press.

(54) Casalini, R.; Roland, C. M. *Phys. Rev. B* **2004**, *69*, 094202.

(55) Paluch, M.; Roland, C. M.; Pawlus, S.; Zioło, J.; Ngai, K. L. *Phys. Rev. Lett.* **2003**, *91*, 115701.