

Relationship between the primary and secondary dielectric relaxation processes in propylene glycol and its oligomers

C. León,^{a)} K. L. Ngai, and C. M. Roland

Naval Research Laboratory, Washington, DC 20375-5320

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Dielectric relaxation measurements were performed on propylene glycol (PG) and oligomers having different number of repeat units ($N=2, 3$, and 69). The primary α -relaxation had the Kohlrausch–Williams–Watts (KWW) form, with a stretch exponent $(1-n)$ which decreased with increasing N . The temperature dependence of the α -relaxation time, as reflected in the fragility index, increased with N . A broad, rather symmetric secondary β -relaxation was observed at higher frequencies in the dielectric loss spectrum for all samples with $N>1$. This is the first observation of the β -relaxation peak in dipropylene glycol ($N=2$) and tripropylene glycol ($N=3$). The separation between the α - and β -relaxations increased with increasing N . This trend indicates that the separation is minimal in PG, which makes it difficult to resolve the β -relaxation from the more intense α -relaxation. This, together with the fact that the strength of the β -relaxation decreases with the molecular weight of PPG, as found by Johari and coworkers, explains the absence of an observable β -peak or shoulder in isothermal or isochronal dielectric measurement on PG. It is proposed that the deviation of the dielectric loss peak for PG from either the KWW or the Cole–Davidson functions at higher frequencies is due to a β -relaxation masked by the α -process. The same conclusion was reached by Johari and co-workers, based on evidence from their “difference isochrone method.” Finally, we show that the data from oligomers of propylene glycol support the recently proposed correlation of $\tau_\beta(T_g)$ with $(1-n)$ and the rough agreement between $\tau_\beta(T_g)$ and the primitive relaxation time of the coupling model at temperatures above T_g . [S0021-9606(99)51423-2]

I. INTRODUCTION

An important feature in the dynamics of glass-forming liquids is the nonexponential time dependence of the primary relaxation process (α -relaxation), which can be described by a correlation function having the Kohlrausch–Williams–Watts¹ (KWW) (stretched exponential) form

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

We eschew the more usual “ β ” notation for the stretch exponent in order to avoid confusion with the designation of the secondary relaxation process. The use of $1-n$ follows from the analysis detailed below. For dielectric relaxation, the complex dielectric response function $\epsilon^*(\omega)$ obtained from a Fourier transform of the time derivative of the KWW function usually does not fit experimental data at frequencies high relative to the maximum in the loss peak. This limitation of the KWW function was also found in mechanical stress relaxation. Other empirical functions, such as the Havriliak–Nagami function,² are often used to fit dielectric data. In fact, the Havriliak–Nagami function² usually give a better fit than the KWW function. Nevertheless, for our purpose, we use Eq. (1) because it has one less parameter and has a connection to the theory we shall later invoke.

A striking characteristic of the α -process is the dramatic increase of its relaxation time, τ_α , as the liquid is cooled

toward the glassy state. A glass transition temperature, T_g , can be defined as the temperature at which τ_α reaches an arbitrary value of 10^2 – 10^4 s, that is, a time sufficiently long that the primary process below this temperature is effectively frozen on the time scale of experimental observation. The non-Arrhenius temperature dependence of τ_α near T_g usually follows the Vogel–Fulcher–Tamman (VFT) equation³

$$\tau_\alpha(T) = \tau_{\alpha\infty} \exp\left(\frac{A}{T-T_0}\right) \quad (2)$$

in which $\tau_{\alpha\infty}$, A , and T_0 are material constants.

Another near-universal property of glass-forming liquids is the presence of a secondary process, or β -relaxation, at shorter times.^{4–7} This secondary relaxation is associated with a broad, and often much weaker, peak in the dielectric loss spectrum in comparison to the primary dispersion. However, for some glass formers, no clearly resolvable β -relaxation is evident.^{5–10} This may be due to a very weak β -relaxation strength, the limited experimental frequency range, or the proximity of the α - and β -relaxations.⁵ Under these circumstances, a “difference isochrone” method was employed to reveal the β -process in glasses in which it appears to be absent in either isothermal or isochronal dielectric spectra.^{11,12} These results^{11,12} confirm the belief that the oc-

^{a)}Permanent address: F. CC. Físicas, Ciudad Universitaria, 28040 Madrid, Spain.

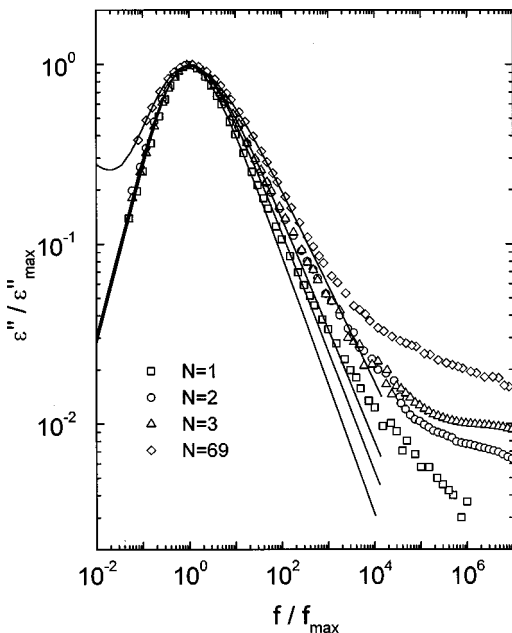


FIG. 1. Dielectric loss spectra at $T \approx T_g$ for propylene glycol (\square), dipropylene glycol (\bullet), tripropylene glycol (\triangle), and poly(propylene glycol) of 4000 molecular weight (\blacklozenge). Both axes have been normalized to bring the maxima into coincidence. Note that the width of the α peak increases with increasing the number of repeat units. Solid lines are fits to equation Eq. (1), with the respective values of the stretch exponent listed in Table I.

currence of a β -process in glasses is universal. The mean relaxation time of the secondary relaxation has an activated temperature dependence,

$$\tau_{\beta}(T) = \tau_{\beta\infty} \exp\left(\frac{E_{\beta}}{T}\right), \quad (3)$$

with E_{β} equal to a few tenths of an eV. The fact that the activation energy has the magnitude of real energy barriers, and that $\tau_{\beta\infty}$ is on the order of molecular vibrational times ($10^{-16} < \tau_{\beta\infty} < 10^{-13}$ s) suggest that the β -relaxation is comprised of simple molecular motions. However, its exact origin remains unknown.

There is increasing interest in the role played by the β -relaxation in the dynamics of the glass transition, including the possible existence of some relation between the α - and β -relaxations.¹³ Recently, it was found on empirical grounds^{14,15} that near T_g , a correlation exists between the value of the secondary relaxation time and the KWW exponent for the α -relaxation. Experimental data suggest that the separation of the α - and β -relaxations at T_g is not random; rather, $\log[\tau_{\beta}(T_g)/\tau_{\alpha}(T_g)]$ has a roughly linear dependence on the magnitude of the KWW exponent $(1-n)$ at $T = T_g$.^{14,15} This relationship was rationalized^{14,15} in terms of the coupling model.^{16,17} Interestingly, those glass formers not exhibiting a β -relaxation peak have α -relaxations characterized by large values of $(1-n)$,^{14,15} and almost invariably a small fragility index m (Ref. 18) defined as the derivative, $d \log \tau_{\alpha} / d(T_g/T)$, evaluated at $T = T_g$. For glass formers having large $(1-n)$, the absolute value of $\log[\tau_{\beta}(T_g)/\tau_{\alpha}(T_g)]$ is small; consequently, $\tau_{\beta}(T_g)$ is close to $\tau_{\alpha}(T_g)$. This prox-

imity precludes resolution of a β -relaxation peak from the more dominant α -relaxation, as was originally suggested by Johari and Pathmanathan.¹¹

Previous dielectric^{11,19,20} and photon correlation spectroscopy²¹ measurements on the glass-former propylene glycol have shown its "strong" character, along with an absence of a secondary relaxation peak. On the other hand, similar studies on the polymeric form, poly(propylene glycol),²⁰⁻²³ found the latter to be more fragile, have a smaller KWW exponent, and to exhibit a resolved β peak well separated from the α peak. From such results, we expect that lowering the molecular weight of poly(propylene glycol) towards the monomer should decrease the fragility, increase the KWW exponent, and cause the β -relaxation peak to shift closer to the α -relaxation. Such an investigation could also shed light on the relation between primary and secondary relaxation processes in glass formers.

In this work, we present dielectric spectroscopy results on the relaxation dynamics above and below T_g for poly(propylene glycol) having different number of repeat units $N = 1, 2, 3$, and 69. The dimer and trimer are of particular interest, in light of previous studies of the α -relaxation reporting that for $N=7$, the relaxation behavior already attains that shown by higher molecular weights.^{20,21} A number of investigations have demonstrated that chain length can exert a significant effect on the local dynamics.²⁴⁻²⁶

II. EXPERIMENT

Propylene glycol, dipropylene glycol, tripropylene glycol, and poly(propylene glycol) having an average molecular weight of 4000 were obtained from Aldrich Chemical Company. These materials have the chemical formula $H-(C_3H_6O)_N-OH$ with $N=1, 2, 3$, and ≈ 69 , respectively. Immediately prior to measurements, samples were maintained for one hour at 125 °C in a nitrogen atmosphere.

Dielectric spectroscopy was performed over the frequency range from 10^{-4} to 10^6 Hz, by the combined use of an IMASS Time Domain Spectrometer (10^{-4} – 10^4 Hz) and an HP4284 A LCR meter (20 – 10^6 Hz). The sample cell consisted of parallel plates, 41 mm in diameter, whose separation was varied between 0.25 and 1 mm to bring the admittance within the instrumental range.

Differential scanning calorimetry was carried out using a Perkin-Elmer DSC7, with liquid nitrogen cooling. Data were collected during cooling of samples (10–15 mg) at 10 deg/min.

III. RESULTS AND DISCUSSION

The complex permittivity, $\epsilon^*(\omega) = \epsilon'(\omega) - i\epsilon''(\omega)$, was obtained at several temperatures above and below T_g . Figure 1 shows representative dielectric loss spectra for all samples at a temperature near the glass transition temperature. Herein, we define T_g to be the temperature at which $\tau_{\alpha}(T) = 100$ s (see Table I). The data in Fig. 1 have been superposed in order to allow comparison of the peak shapes. The solid lines in the figure represent fits to the KWW function [Eq. (1)]. For $N=69$, a power law dependence has been included to the fitting, to account for the intensity observed at

TABLE I. Glass transition temperature [defined as $\tau_\alpha(T_g)=10^2$ s], KWW exponent at T_g , and the fragility index m . $N=1$ refers to propylene glycol, $N=2$ dipropylene glycol, $N=3$ tripropylene glycol, and $N=69$ poly(propylene glycol) of MW=4000.

	T_g (K)	$(1-n)$ at T_g	m
$N=1$	168	0.72	53
$N=2$	195	0.67	64
$N=3$	193	0.63	71
$N=69$	198	0.55	83

lower frequencies.²² The widths of the peaks increase with increasing molecular weight, as seen from the values listed in Table I for $(1-n)$ obtained at T_g .

The coupling model¹⁴⁻¹⁷ provides an interpretation for the inverse relationship observed in Table I between $(1-n)$ and the molecular weight of the PPG. According to this model, intermolecular interactions only become important beyond a temperature-insensitive crossover time $t_c \approx 2$ ps. For $t < t_c$, the molecular units relax independently of each other, giving rise to an exponential correlation function, $\phi(t) = \exp(-t/\tau_0)$, where τ_0 is the primitive (noncooperative) α -relaxation time. At times longer than t_c , intermolecular interactions (i.e., cooperativity) slow down the relaxation, whereupon the averaged correlation function assumes the KWW stretched exponential form. The α -relaxation times τ_α and τ_0 are related by¹⁴⁻¹⁷

$$\tau_\alpha = (t_c^{-n} \tau_0)^{1/(1-n)}. \quad (4)$$

The coupling parameter n , reflecting the degree of intermolecular cooperativity, varies from 0 to 1. A larger value of n implies more cooperativity, and thus a more pronounced slowing down of the relaxation process; that is, the effective relaxation time τ_α becomes much longer than τ_0 . Thus the data in Table I reveal an increase in intermolecular cooperativity with increasing number of repeat units in the oligomers.

Dielectric permittivity, ϵ' , and loss ϵ'' data of the dimer at several temperatures are shown in Figs. 2(a) and 2(b), respectively. For the temperatures over which the α -relaxation peak fell within the experimental frequency range, at least approximate conformance of the α -relaxation to the time-temperature superposition principle was observed. This is illustrated in the inset of Fig. 2(b). The other samples behaved similarly, except for $N=1$. For propylene glycol, increasing temperature gave rise to a small increase in $(1-n)$, from 0.72 to 0.78 over the measured range.

For the dimer, trimer, and polymer at temperatures below T_g , a secondary process is evident in the dielectric loss spectra. In Fig. 3, this β -relaxation is shown at several temperatures for the trimer, which is representative of the other two. While the relaxation strength of the α -relaxation decreases with increasing temperature, the strength of the β -relaxation increases with temperature. As is common for secondary relaxations,²⁷ the peaks in Fig. 3 are much broader and weaker than the primary dispersion. These loss peaks appear to be almost symmetric, although our data are only for a limited frequency range. β -relaxations are often described in the frequency domain using the empirical Cole-

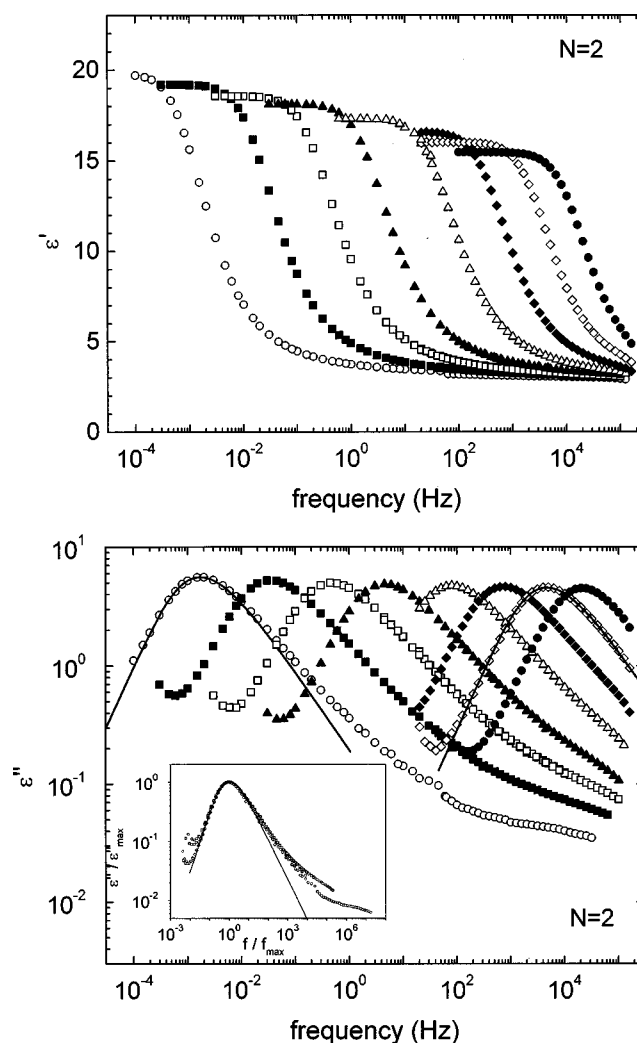


FIG. 2. (a) Dielectric permittivity spectra for dipropylene glycol above T_g : (\circ) 195 K, (\blacksquare) 199 K, (\square) 203.5 K, (\blacktriangle) 207.8 K, (\triangle) 213.5 K, (\blacklozenge) 219 K, (\diamond) 221 K, (\bullet) 231 K. (b) Dielectric loss spectra for dipropylene glycol above T_g : (\circ) 195 K, (\blacksquare) 199 K, (\square) 203.5 K, (\blacktriangle) 207.8 K, (\triangle) 213.5 K, (\blacklozenge) 219 K, (\diamond) 221 K, (\bullet) 231 K. The shape of the α -dispersion is virtually independent of temperature over the experimental range. Solid lines are illustrative fits to Eq. (1), with $(1-n)=0.67$ at 195 K and $(1-n)=0.68$ at 225 K.

Cole function,²⁸ $\Delta \epsilon_\beta^*(\omega) = \Delta \epsilon_\beta / [1 + (i\omega\tau_{CC})^{\alpha_{CC}}]$, which gives symmetric peaks for the imaginary part $\epsilon''(\omega)$. The solid lines in Fig. 3 are fits to this expression. The fit parameter τ_{CC} can be identified with the mean relaxation time τ_β , equal to $1/(2\pi f_{p\beta})$, where $f_{p\beta}$ is the frequency of the maximum in ϵ'' .

The temperature dependencies of the α - and β -relaxation times are displayed in Fig. 4. The solid lines through the data points are fits to the VFT expression for τ_α and the Arrhenius equation for τ_β , with the fitting parameters collected in Tables II and III, respectively. Of course, the VFT parameters represent nothing more than the best fit over our limited experimental range; extrapolation to higher temperatures might differ from measurements actually carried out at higher frequency.

To compare non-Arrhenius temperature dependencies for the α -relaxation, we follow the suggestion of Laughlin

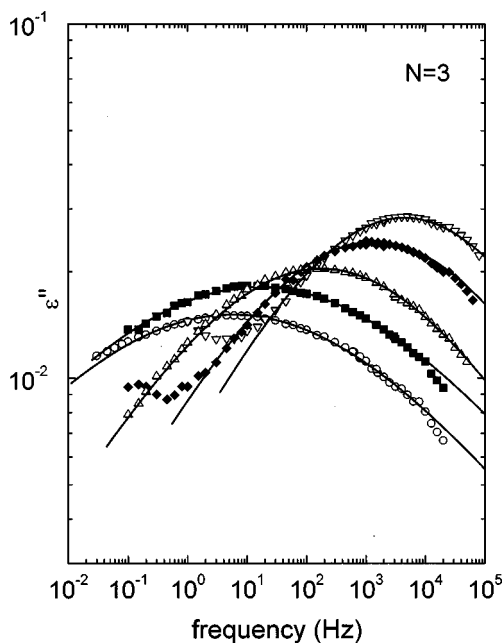


FIG. 3. Shape of the dielectric loss peak associated to the secondary relaxation process in tripropylene glycol below T_g : (○) 137 K, (■) 142 K, (△) 153 K, (◇) 167 K, and (▽) 178 K. The broad, symmetric peaks are fit to the Cole-Cole relaxation function (solid lines).

and Uhlmann²⁹ and Angell,³⁰ by plotting the logarithm of the relaxation times τ_α versus the quantity T_g/T (Fig. 5). The slope of these curves at $T_g/T=1$ is referred to as the fragility¹⁸ or cooperativity^{31,32} index m , defined earlier. The values of m determined herein for the different samples are listed in Table I. It is an empirical fact that the T_g -scaled temperature dependence correlates with the value of the KWW exponent at T_g .^{18,32-34} Systems with larger m are

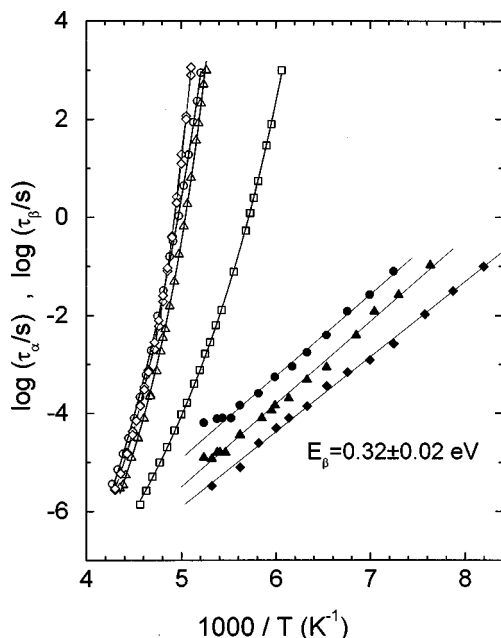


FIG. 4. Temperature dependence of the respective relaxation times for the primary (hollow symbols) and secondary (solid symbols) processes: (□) $N=1$; (○, ●) $N=2$; (△, ▲) $N=3$; (◇, ◆) $N=69$. Solid lines are fits to Eq. (1) for the α -relaxation times and to Eq. (2) for the β -relaxation times.

TABLE II. Parameters from fitting the α -relaxation times to Eq. (2) (see Fig. 4), along with the temperature range of each fit.

	$\log \tau_{\alpha\infty}(s)$	A (K)	T_0 (K)	Range (K)
$N=1$	-12.95	1630.4	120.4	165-219
$N=2$	-15.27	2021.2	143.9	192-234
$N=3$	-13.29	1312.1	155.4	190-230
$N=69$	-11.64	878.4	170.1	196-233

almost invariably associated with smaller stretch exponents $(1-n)$, although there are exceptions (e.g., propylene carbonate¹⁸). This correlation is also evident herein for PPG with increasing N , m increases and $(1-n)$ decreases (see Fig. 5). According to the coupling model, the increase in the fragility (cooperativity) index, as well as the decrease in $(1-n)$, are consequences of enhanced intermolecular cooperativity.³¹⁻³⁴ The primitive relaxation times, $\tau_0(T)$, were calculated as a function of temperature for $N=1, 2, 3$, and 69 using Eq. (4) and the experimental values of $\tau_\alpha(T)$, $(1-n(T))$ and $t_c=2 \times 10^{-12}$ s.⁶ The inset of Fig. 5 shows that the dependence of the scaled primitive relaxation times, $\tau_0(T)/\tau_0(T_g)$, on the scaled reciprocal temperature, T_g/T , is almost the same for $N=1, 2, 3$, and 69.

The secondary relaxations in Fig. 4 have Arrhenius temperature dependencies, with a molecular weight-independent $E_\beta \approx 0.3$ eV. Although the values deduced for $\tau_{\beta\infty}$ are sensitive to small uncertainties in the activation energies, they are of the order of 10^{-13} – 10^{-14} s. These results offer support to the notion that secondary relaxations involve independent, non-cooperative motions.^{6,27,35,36} In this respect, the β -relaxation bears resemblance to the primitive α -relaxation of the coupling model. However, the two processes cannot be identical, since only the latter is slowed down by intermolecular interactions to become the cooperative α -relaxation observed at longer times. Nevertheless, as we shall show later, the fact that $\tau_\beta(T)$ and $\tau_0(T)$ are comparable in magnitude suggests that the primary and secondary processes bear some similarity to each other, at least at temperatures above the glass transition temperature. It has recently been established from experimental data on many glass formers that there is a relationship between the β -relaxation time at T_g and the KWW exponent $(1-n)$ of the α -relaxation.^{14,15} According to this empirical relation, the separation between the α and β peaks at T_g tends to zero as the KWW exponent for the α -relaxation approaches unity.³⁷

The present results on PPG samples differing only in molecular weight offers an interesting test for this correlation. Following Refs. 14 and 15, in Fig. 6 we have plotted the β -relaxation times as a function of the KWW exponent

TABLE III. Parameters obtained from the fits of the β -relaxation times to an Arrhenius law [Eq. (3)] over the indicated range of temperatures. The results are plotted in Fig. 4.

	$\log \tau_{\beta\infty}(s)$	E_β (eV)	Range (K)
$N=2$	-12.70	0.31	138-191
$N=3$	-14.09	0.34	131-191
$N=69$	-13.57	0.30	122-188

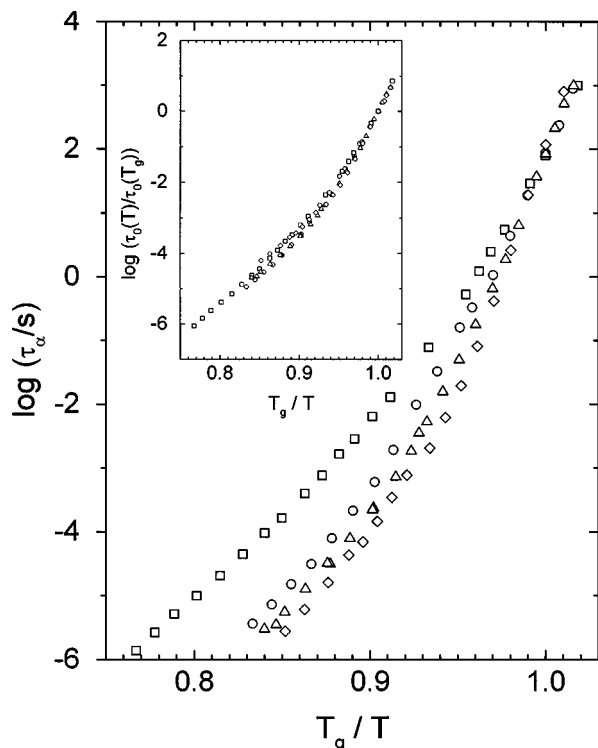


FIG. 5. The α -relaxation times from Fig. 4, with the abscissa scaled by the temperature at which $\tau_\alpha=10^2$ s (symbols are as defined in Fig. 4). The fragility index m (see Table I) increases with the number of repeat units. The inset shows that the scaled noncooperative relaxation times, calculated from Eq. (4), have T_g -scaled temperature dependences that are almost independent of N .

for $N=2, 3$, and 69 (open circles). We have also included experimental data from Refs. 14 and 15 (solid squares), which reveal the proposed trend. The τ_β plotted in Fig. 6 are for temperatures at which the corresponding τ_α equals (by extrapolation) 10^4 s. It can be observed that for larger values of $(1-n)$, the β -relaxation time becomes longer, and consequently closer to the α -relaxation time. The thick line is τ_0 calculated as a function of $(1-n)$ from Eq. (4) with $\tau_\alpha=10^4$ s and $t_c=2 \times 10^{-12}$ s. To demonstrate that this correlation is not dependent on the definition of the glass temperature T_g , the inset in the figure shows the same data but with T_g now taken to be the temperature at which $\tau_\alpha=10^{-2}$ s. Figure 6 and the inset illustrate that at the same temperature above T_g , the relaxation time τ_β is close to the primitive α -relaxation time τ_0 deduced from the coupling model.

Note that in Fig. 6 there is no data for large values of $(1-n)$. The single point for $(1-n)$ greater than 0.7 corresponds to the β -relaxation resolved in cyclo-octanol in the ordered state.³⁸ The anticorrelation between the value of $(1-n)$ and the separation of the α - and β -relaxation times accounts for the absence of a β peak in the dielectric loss spectra of glass formers having large values of $(1-n)$ such as propylene glycol. The proximity of the dispersions makes it difficult to resolve the β -relaxation from the more intense α -relaxation. Together with the fact that the strength of the β -relaxation increases with the molecular weight of PPG, as found by Johari and co-workers,^{11,12} this explains the absence of an observable β peak or shoulder in isothermal or

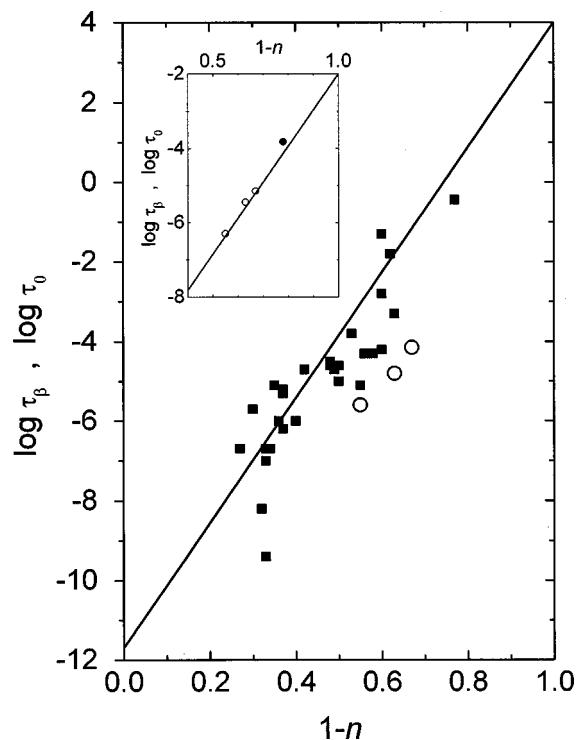


FIG. 6. Values calculated for τ_β (open circles) at temperatures corresponding to $\tau_\alpha=10^4$ s, for di-, tri-, and poly(propylene glycol), revealing an increasing τ_β for larger $(1-n)$. The solid squares represent similar β -relaxation times of a large number of glass formers taken from Ref. 14. The line is τ_0 calculated from the coupling model [Eq. (4)] for the same temperature. The inset shows for the same data at a different reference temperature at which $\tau_\alpha=0.01$ s. The solid circle is the value for $N=1$ at 184 K deduced from fitting its spectrum to a superposition of two processes (see Fig. 7).

isochronal dielectric measurement on PG. It was proposed³⁹ that the deviation of the dielectric loss peak for PG from either the KWW or the Cole–Davidson fits at higher frequencies in the form of an excess “wing” is due to a β -relaxation masked by the α -process. The same conclusion was reached by Johari and co-workers earlier based on weakening of the strength of the β -process with decreasing molecular weight and evidence of the existence of β -process in PG from analysis of data using their “difference isochrone method.”^{11,12} Figure 7 displays the dielectric loss spectra for propylene glycol at two temperatures, near and above the glass transition. Although a distinct secondary peak cannot be resolved, the data at higher frequencies depart from KWW behavior. It is tempting to conclude that this reflects the presence of a β -relaxation under the more prominent α -relaxation. The solid lines in Fig. 7 are fits to a superposition of a KWW and a Cole–Cole function, to account for the α - and the β -processes, respectively. The values obtained for τ_β are close to those calculated for τ_0 (see Fig. 6), and consistent with a trend with increasing N . This fitting procedure has been successfully employed previously for other strong glass-forming liquids, such as glycerol⁴⁰ and cyclo-octanol.³⁸ Moreover, in the case of cyclo-octanol, Brand *et al.*³⁸ were able to resolve a distinct peak for the ordered state, providing additional evidence for the presence of a β -relaxation.

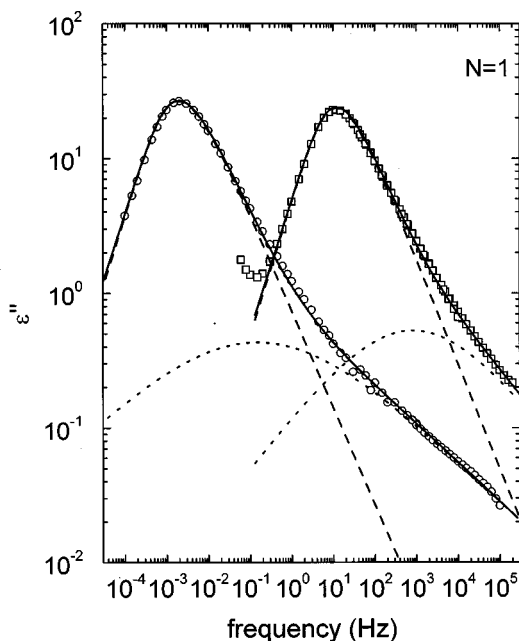


FIG. 7. Dielectric loss for propylene glycol at 168 K (\circ) and 184 K (\square). Solid lines represent fits to two processes: a KWW function (dashed lines) describing the α -relaxation peak, and a Cole–Cole function (dotted lines) to account for the β -process and the high frequency wing. The peak frequency of the β -process at 184 K yields τ_β (see inset of Fig. 6).

IV. CONCLUSIONS

The results presented herein on the α - and the β -processes in propylene glycol and three oligomers having repeat units $N=2, 3$, and 69 demonstrate several experimental facts. The first is a strong correlation between the separation of the α - and the β -relaxation times, $\log[\tau_\beta(T_g)/\tau_\alpha(T_g)]$, and the stretch exponent, $(1-n)$, of the α -relaxation. This finding is consistent with the correlation previously observed in a large number of glass formers with diverse chemical structures. The trend seen in PPG with $N=2, 3$, and 69 implies the absence of a resolved β -relaxation peak in the dielectric loss spectra of glass-forming liquids such as PG ($N=1$) is due to the proximity of the two processes. Consequently, the β peak is masked by the α -process. This scenario was originally suggested by Johari and co-worker, based on their difference isochrone method of analysis of dielectric data of PG and other glass formers.^{11,12} The ultimate origin of this trend is the difference in the degree of intermolecular cooperativity, as reflected in the magnitude of n in the KWW exponent $(1-n)$ of the α -relaxation function [Eq. (1)].^{14,15}

The second fact drawn from the results herein is that above T_g the measured β -relaxation times are the same order of magnitude as the primitive relaxation times. This suggests a relationship between, but not necessarily equality of, the β -relaxation time and the noncooperative or “primitive” α -relaxation time of the coupling model. This near coincidence of the two times supports the notion that the β -process involves independent or non-cooperative motions occurring, for example, in “loosely packed” sites, as suggested by Johari and co-workers and others.^{11,35,36}

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