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Excess wing in the dielectric loss spectra of propylene glycol oligomers at elevated pressure

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Dielectric loss spectra at both ambient and elevated pressure are presented for propylene glycol (PG), dipropylene glycol, and tripropylene glycol. While in previous literature the excess wing (EW) was observed only for PG, we show herein that under high pressure an EW (coexistent with a secondary β relaxation) is present for all these materials. Furthermore, at higher pressures the EW evolves into a well-separated peak. The pressure sensitivity of the EW is very different from that of the β relaxation, being close to that of the structural relaxation, whereas the β peak is virtually insensitive to pressure. These differences imply a very different degree of intermolecularity of the underlying motions. A similarly small sensitivity to pressure has been observed for the β relaxation in sorbitol. We have measured the spectrum of sorbitol at high pressure, and likewise it indicates the presence of a submerged EW. Finally, the behavior observed for the EW in the glycols is shown to be consistent with predictions of the coupling model, relating the most probably relaxation time for the secondary process to a noncooperative relaxation time. This suggests that the EW may be the precursor to the α relaxation and therefore of fundamental importance to understanding the vitrification process in supercooled liquids and polymers.

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INTRODUCTION

Glasses of every sort are found throughout modern life; nevertheless, the rich phenomenology of the glass transition remains to be completely understood. Certainly the diverse aspects are hard to reconcile within a single theoretical framework. An important aspect is to better classify the processes transpiring near the glass transition temperature T_g. Prominent among these are the secondary relaxations observed by dielectric,[1] mechanical,[2] and photon correlation[3] techniques. While the main focus of studies of the glass transition has been the strong (greater than Arrhenius) increase of viscosity and structural relaxation time τ_α on approaching T_g from above, there are other, faster processes, having a distinctive Arrhenius behavior below T_g. Some of these can be attributed to intramolecular motions, for example involving pendant moieties in polymers;[2] however, as first shown by Johari and Goldstein,[1,4] secondary β relaxations are also present in rigid molecules which lack internal degrees of freedom. Such processes must have an intermolecular origin. The situation is confused by the not uncommon practice of referring to all β relaxations as Johari-Goldstein (JG) processes, whether or not they involve intramolecular degrees of freedom.[5,6] This may reflect the idea that such β relaxations are characteristic of liquids in or near the glassy state, and that, in principle, every molecular motion may be affected by neighboring molecules. A good illustration of the problem can be found in experimental results on bis(methoxyphenyl)cyclohexane (BMPC),[7–11] which has many of the features expected of a JG process, yet has been identified by NMR as involving intramolecular motion.[7] A discussion on this subject can be found in a recent review,[12] which suggested that "true" JG processes can be identified by the sensitivity of their β-relaxation times to pressure.

Another "class" of secondary relaxations comprises those manifested as an extra contribution on the high-frequency flank of the structural relaxation peak. Referred to as an excess wing (EW), this secondary process is coupled to the structural relaxation, and on the basis of successful scaling of the α peak and EW for several materials, the EW is regarded by some as part of the α relaxation.[13] Contrary to this interpretation, it has been found that materials having very similar α relaxations may not have the same EW,[14] and that the α peak and EW can be separated by physical aging[15,16] or with high pressure.[17] Such results indicate that the EW may be a submerged peak.[18]

Selected liquids under high pressure show a very different behavior for the EW and the secondary peak.[10] At a fixed temperature, while the relaxation times of the secondary peak for di-isobutyl phthalate and BMPC are almost insensitive to a volume change (and therefore easily separable from the α relaxation), the EW for cresolphthalein dimethylether and phenolphthalein dimethylether have volume sensitivities close enough to those of the respective α relaxations that the EW cannot be resolved as a separate peak. Similar results have been found for the EW in salol, BMMPC, and polychlorinated biphenyls.[19] Since an intermolecular process is expected to be more sensitive to pressure than an intramolecular process, it is useful to clarify this aspect of the behavior of secondary relaxations. Potentially, pressure can be used to distinguish between these two types of dynamics.

When the secondary relaxation is a JG process, an interesting correlation is found between the τ_β of the secondary relaxation and the primitive relaxation τ_0 of the coupling model (CM).[20,21] The CM predicts that

$$\tau_{\mathrm{KWW}}=[t_c^{\beta_{\mathrm{KWW}}-1}\tau_0]^{1/\beta_{\mathrm{KWW}}}, \tag{1}$$

in which t_c is a temperature-insensitive crossover time (equal to about 2 ps) and τ_{KWW} is the correlation time for the α

relaxation having the Kohlrausch-Williams-Watts (KWW) form[22]

$$\phi(t) = \exp[-(t/\tau_{\mathrm{KWW}})^{\beta_{\mathrm{KWW}}}], \tag{2}$$

where β_{KWW} is a fractional exponent. τ_0 gives a characteristic time for onset of cooperative dynamics, and in many materials it has been found that $\tau_\beta \approx \tau_0$.[21,23,24] The connection between τ_β and τ_0 for not only some intermolecular secondary relaxations (i.e., JG processes), but also the EW with τ_β then representing a characteristic time,[18] suggests that the two processes (EW and JG) are the same. The idea is that the JG is the precursor of the α relaxation, implying that the JG (and EW) have a fundamental role in the structural relaxation, and therefore in the glass transition. In the coupling model, τ_0 is the relaxation time for the escape of molecules from their liquid-structure cages.[24]

Propylene glycol (PG) and polypropylene glycols (PPGs) of different molecular weights have been studied using dielectric spectroscopy by various groups,[6,25–36] including measurements at elevated pressure.[37–43] Recently, we reported results for the trimer of propylene glycol (tri-PPG) at high pressure. This liquid has a well-known secondary peak, which had previously been regarded as a JG process.[6,34] However, under high pressure, we discovered the existence of an EW simultaneous with this secondary peak. Upon further increases in pressure, the EW evolves into a distinct relaxation peak.[42] In this paper, we present dielectric relaxation data on tri-PPG under high pressure, together with data on propylene glycol, dipropylene glycol (di-PPG), and sorbitol. The different behavior of the EW and the secondary peak is discussed.

It is useful to clarify the nomenclature used herein, since the literature can be confusing. We adopt the designation "JG" for secondary relaxations which involve the entire molecule, while the term β relaxation is used to refer to the lowest-frequency process (excluding the EW) which is higher in frequency than the primary α relaxation. Herein, "EW" refers to the secondary process closest to the α relaxation, whereby the β relaxation is no longer the lowest-frequency secondary process.

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. Samples were dried by using molecular sieves and, immediately prior to all measurements, were maintained for one hour at 125 °C in a nitrogen atmosphere. The *d*-sorbitol, obtained from Aldrich and used as received, was the same sample used in Ref. 44.

Dielectric spectra were obtained with a parallel plate geometry using an IMASS time domain dielectric analyzer (10^{-4}–10^{3} 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 a hydraulic pump (Enerpac) 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.

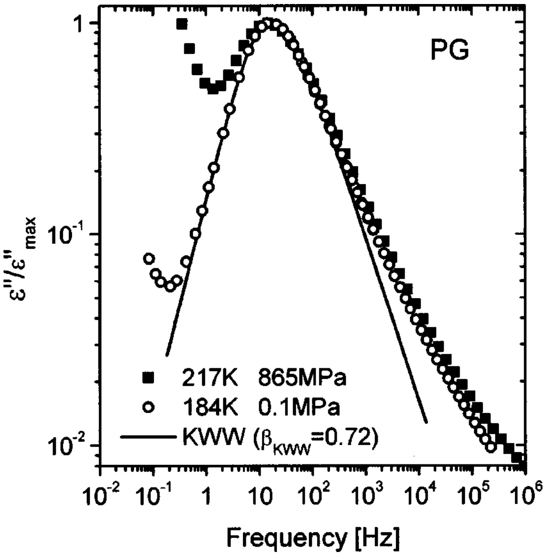

FIG. 1. Comparison of dielectric loss spectra for PG at atmospheric and high pressure. The solid line is the fit of the transform of Eq. (2) to the spectra at atmospheric pressure, with $\beta_{\mathrm{KWW}} = 0.72$. The data at atmospheric pressure where shifted on the abscissa by a factor of 1.4 toward higher frequency to superimpose the peak maxima.

RESULTS

Pressure effect on propylene glycol

An interesting property of PPGs is the ability of their terminal groups to form hydrogen bonds, whereby the number of H bonds is inversely proportional to the molecular weight. The pressure dependence of the structural relaxation in PG and PPG oligomers has been the subject of a recent publication.[45] More H bonds emphasize the effect of thermal energy on the structural dynamics and are also reflected in a smaller sensitivity of the structural relaxation time to pressure. This pressure sensitivity can be quantified by the pressure coefficient of T_g, which for PG is $dT_g/dP = 33$ K/GPa,[45] comparable to that of other hydrogen bonded glass formers, like glycerol ($dT_g/dP = 35$ K/GPa),[17] sorbitol ($dT_g/dP = 40$ K/GPa),[44] and xylitol ($dT_g/dP = 34$ K/GPa).[44] The comparison with glycerol is especially interesting, since like PG it has an EW. Under high pressure[46] (~910 MPa) the structural relaxation function of glycerol is broader than at atmospheric pressure,[47] which suggests[17] an increase of the separation of α relaxation and EW [viz. Eq. (1)].

PG spectra at atmospheric pressure (184 K) and at high pressure (217 K and 865 MPa) are shown in Fig. 1. It is evident that pressure broadens the peak, similar to results for salol[19,48] although not as dramatic as the broadening observed for glycerol.[17] We have previously pointed out that such changes in the α peak and EW under high pressure are found only for H-bonded materials, with such broadening

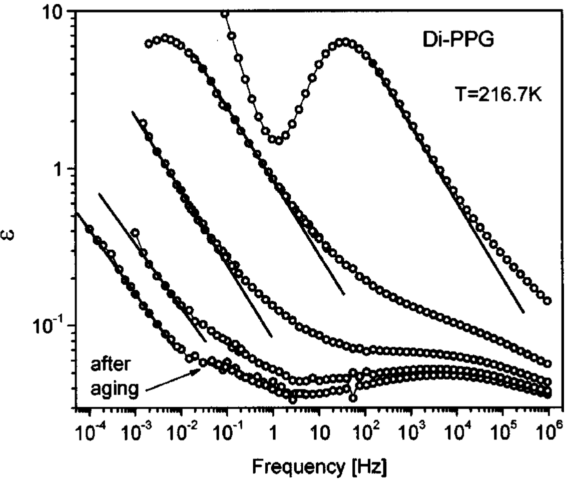

FIG. 2. Dielectric loss for PPG dimer (○) at the indicated temperature and pressures (from right to left) of 67.6, 248.7, 335.7, 520, and 510 MPa. The last was measured after 12 h aging. The lines indicate the slopes of the high-frequency flank of the α process.

absent for simple van der Waals liquids.[19] This difference in behavior for associated and nonassociated glass formers is ascribed to the modification of the degree of H bonding caused by changes in temperature or pressure.[19]

Pressure effect on dipropylene glycol

The pressure sensitivity of di-PPG was found to be $dT_g/dP = 80$ K/GPa, which is intermediate between those of PG and tri-PPG ($dT_g/dP = 109$ K/GPa).[45] This reflects the relative degrees of H bonding.

Representative dielectric loss spectra for di-PPG at $T = 216.7$ K and various pressures are shown in Fig. 2. At low pressure, only the dc conductivity and the α-relaxation peak are observed. At higher pressures, a virtually pressure-independent secondary peak and an excess wing emerge. As shown in the spectra at higher pressure, with physical aging the EW becomes more prominent, while the secondary peak is unaffected. Comparing spectra at atmospheric and high pressure having the same relaxation time τ_α (Fig. 3), there is broadening of the primary peak, with an increased separation from the secondary relaxation, and the EW showing up as a deviation from the KWW function. To better quantify the pressure dependence of the relaxation time for each process, we analyzed the spectra using a Cole-Cole[49] relaxation function to describe both the EW and the β peak, and a Havriliak-Negami[50] function for the α relaxation.[51] For the spectra at higher pressures, where only the high-frequency side of the α relaxation is present, a power law was used to describe the α relaxation. At lower pressures, the masking of the EW by the other two relaxations precludes its deconvolution, and only the secondary peak was considered. The fit parameters of the secondary peak below T_g were used as starting parameters for the fits at lower pressure. All these fits were carried out simultaneously on both the ε' and ε'' spectra. The relaxation times of the three processes, calculated from the frequency of the maximum ($\tau = 1/2\pi f_{\max}$), are reported in Fig. 4.

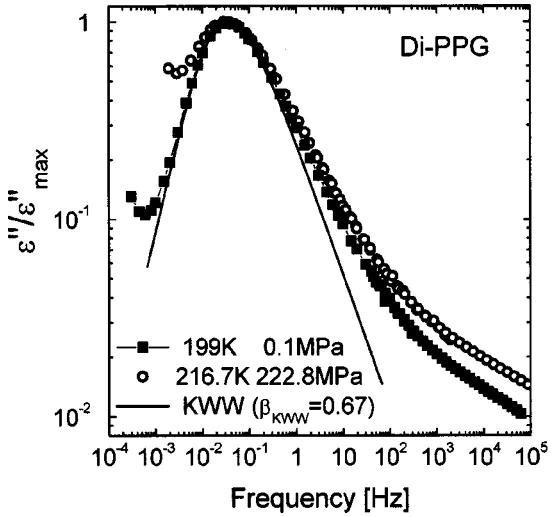

FIG. 3. Comparison of dielectric loss spectra for di-PPG at atmospheric and high pressure. The solid line represents the transform of Eq. (2), with $\beta_{\mathrm{KWW}} = 0.67$. The data at atmospheric pressure where shifted on the abscissa by a factor of 1.9 toward higher frequency to superimpose the maxima.

These results show that the sensitivity to pressure is comparable for the EW and α relaxation, while that of the β peak is much less. The activation volume

$$\Delta V^{\#} = RT \left.\frac{\partial \ln \tau}{\partial P}\right|_P , \qquad (3)$$

where R is the gas constant, for the three processes is listed in Table I. $\Delta V^{\#}_{\mathrm{EW}}$ is about half of $\Delta V^{\#}_{\alpha}$, while $\Delta V^{\#}_{\beta}$ is almost two orders of magnitude smaller.

Pressure effect on tripropylene glycol

As mentioned above, we recently showed that, under elevated pressure, the dielectric loss spectrum of tri-PPG exhibits simultaneously an EW and a secondary peak, the latter

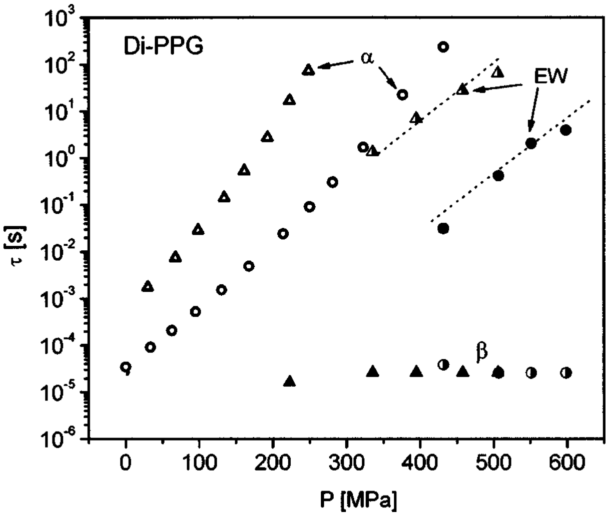

FIG. 4. Relaxation times obtained from fitting the di-PPG spectra at $T = 216.7$ (triangles) and 225.6 K (circles).

TABLE I. Activation volumes for the α relaxation, β relaxation, and EW and their ratios for di-PPG and tri-PPG.

Sample	T (K)	$\Delta V_{\alpha}^{\#}$	$\Delta V_{\mathrm{EW}}^{\#}$	$\Delta V_{\beta}^{\#}$	$\Delta V_{\mathrm{EW}}^{\#}/\Delta V_{\alpha}^{\#}$	$\Delta V_{\beta}^{\#}/\Delta V_{\alpha}^{\#}$
di-PPG	216.7	99 ± 3	50 ± 10	3 ± 1	0.50 ± 0.11	0.03 ± 0.01
di-PPG	225.6	85 ± 2	56 ± 10	3 ± 1	0.66 ± 0.13	0.03 ± 0.01
tri-PPG	218.4	96 ± 4	49 ± 5	1.3 ± 0.7	0.51 ± 0.07	0.01 ± 0.005
tri-PPG	245.2	85 ± 2	45 ± 8	1 ± 0.4	0.53 ± 0.11	0.01 ± 0.004

commonly regarded as a JG process.[42] This is similar to the results herein for di-PPG; however, at sufficiently high pressures and low temperature (>0.5 GPa, $T=225.6$ K), the EW in the trimer becomes a distinct peak. In Fig. 5 the dielectric loss peak for tri-PPG is compared at atmospheric (193 K) and high pressure (220.5 K, 373.4 MPa). After scaling the high-pressure spectra to superimpose the α relaxations, the β peak can be seen to be further separated from the α relaxation, and, more interestingly, the EW has become more prominent. Also included in Fig. 5 is the KKW function with $\beta_{\mathrm{KWW}}=0.63$, which accurately describes the α relaxation at atmospheric pressure.[34]

The spectra of tri-PPG at two different temperatures were analyzed, using the same procedure as for the di-PPG. The obtained relaxation times are displayed for all three relaxations in Fig. 6, which demonstrates the stronger pressure dependence of the α and EW relaxation in comparison to the secondary peak. The corresponding activation volumes are given in Table I, and again $\Delta V^{\#}$ for the EW is about half that for the α relaxation, while $\Delta V_{\beta}^{\#}$ is two orders of magnitude smaller.

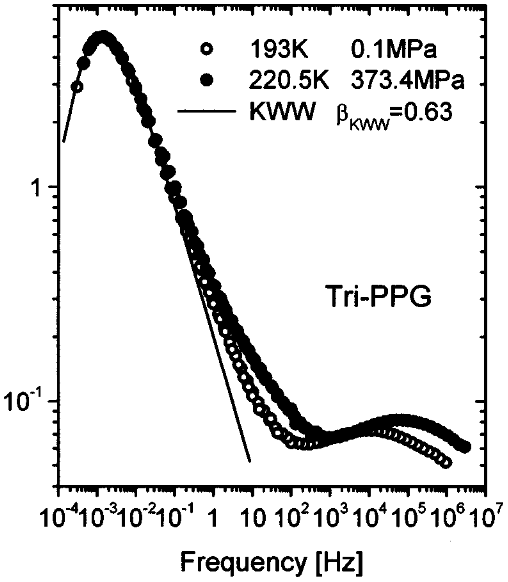

FIG. 5. Comparison of dielectric loss spectra for tri-PPG at atmospheric and high pressure. The solid line is the transform of Eq. (2), with $\beta_{\mathrm{KWW}}=0.63$. The data at high pressure were shifted on the abscissa by a factor of 2.2 toward higher frequency, with ε'' divided by 0.78, to superimpose the maxima.

Pressure effect on sorbitol

Sorbitol is a well-studied glass former which has a distinct secondary process.[52–55] The effect of pressure on the α and β relaxations of sorbitol has been studied recently.[44] Due to the presence of H bonds, the structural relaxation for sorbitol, similar to that for PPG, has a rather small sensitivity to pressure ($dT_g/dP=40$ K/GPa). At low pressure, the relaxation time of the β process is much less sensitive to pressure than the α relaxation.[44] The ratios of the activation volumes $\Delta V_{\beta}^{\#}/\Delta V_{\alpha}^{\#}$ at the two temperatures measured in Ref. 44 are 7.7×10^{-2} and 0.11. This indicates that the β relaxation in sorbitol has properties more similar to that of the secondary relaxation than of the EW in di-PPG or tri-PPG. This raises the question of whether an EW could be observed is sorbitol, simultaneously with the β peak. The dielectric loss spectra for sorbitol measured at 270 K and 288 MPa are shown in Fig. 7. At low frequency, ionic conductivity is observed, which is found to be insensitive to pressure. At high frequencies, there is a well-resolved peak, which has been identified as a JG process.[53–55] The low-frequency contribution was fitted to a power law $[\varepsilon''(\omega)=A\omega^{-n}]$ and the β peak with a Cole-Cole function (Fig. 7). Comparing the experimental data with the sum of these two fits, it is evident that there is an extra contribution. By subtracting the fit of the β peak from the experimental data, a second power law $[\varepsilon''(\omega)=A\omega^{-m}]$ becomes apparent, having an exponent $m\sim0.2$. This exponent is much smaller than for the α relaxation ($n\sim0.5$), but quite close to literature values for the EW in

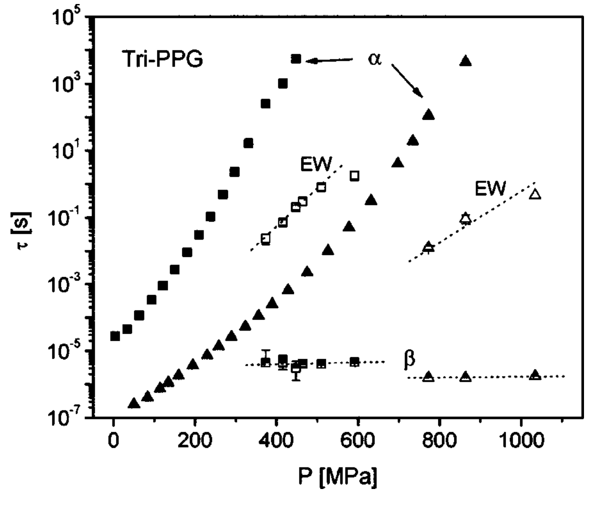

FIG. 6. Relaxation times obtained from fitting the tri-PPG spectra at $T=218.4$ (squares) and 245.2 K (triangles).

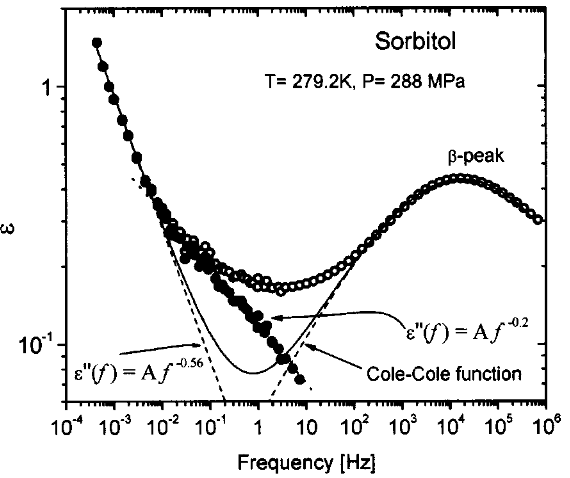

FIG. 7. Dielectric loss spectra for sorbitol measured at high pressure (open symbols). The dashed lines are the fit of a Cole-Cole function to the β relaxation and of a power law to the loss at low frequency, respectively. The solid line is the sum of these two fits. The solid symbols are the differences between the data and the Cole-Cole fit to the β relaxation.

other liquids.[56] This is at least an indication that an EW may be present in the dielectric loss of sorbitol.

DISCUSSION

Comparison with the CM predictions

As described in the Introduction, the EW for PG has been found to have a temperature dependence in good agreement with the τ_0 of the CM.[18] In light of the fact that in the spectra in Fig. 1 the α relaxation and EW are only slightly separated by pressure, we infer that the connection between the EW relaxation time and τ_0 [Eq. (1)] is maintained under high pressure. We can assess whether this agreement is found for di-PPG and tri-PPG. To do this, we note that if Eq. (1) is satisfied, then from the definition of the activation volume [Eq. (3)],

$$\Delta V_{\alpha}^{\#}=\beta_{\mathrm{KWW}}(T,P)\Delta V_{\tau_0}^{\#}, \tag{4}$$

where $\Delta V_{\tau_0}^{\#}$ is the activation volume of τ_0. Equation (4) implies that, if $\tau_{\mathrm{EW}}\sim\tau_0$, then the ratio $\Delta V_{\mathrm{EW}}^{\#}/\Delta V_{\alpha}^{\#}$ should be equal to β_{KWW}. As shown in Figs. 3 and 5, $\beta_{\mathrm{KWW}}=0.67$ and 0.63 for di-PPG and tri-PPG, respectively, independent of pressure and temperature.[34] These are in rough agreement with the corresponding ratios of $\Delta V_{\mathrm{EW}}^{\#}/\Delta V_{\alpha}^{\#}$ (Table I) for the dimer and trimer. On the other hand, the ratios of $\Delta V_{\beta}^{\#}/\Delta V_{\alpha}^{\#}$ for di-PPG, tri-PPG, and sorbitol are all very much smaller than β_{KWW}, indicating that the β peak in these liquids is not a JG, at least according to the CM criterion. This conclusion is at odds with a recent interpretation of the secondary process in sorbitol as a JG relaxation.[53,55]

What is the β process in PPG and sorbit ol?

The very small activation volume of the β process in di-PPG and tri-PPG indicates that the motion is very localized. Together with the fact that (i) this motion is not present in the monomer PG and (ii) it has been found to have a different relaxation time for PPG having different end groups,[57] this suggests that this relaxation is related to the reorientation of the end groups. Such motion may be only weakly intermolecular, contrary to the views of other authors.[6,53,55,58] However, the amplitude of the secondary peak and its dependence on temperature indicate some degree of sensitivity to ‘‘intermolecular surroundings.’’ [52,59,60] While we believe restricting the definition of JG relaxation to molecular motions that involve intermolecular interactions[4,12] is correct, confusion arises because of the difficulty in making this assessment solely on the basis of relaxation measurements at atmospheric pressure. As has been suggested by other authors,[12] one approach to distinguish these processes is by analysis of their sensitivity to pressure, as well as the use of Eq. (1) from the CM. Such information is especially required for the interpretation of the dynamics of glass formers exhibiting multiple secondary processes in their relaxation spectra.[60,61]

What is the EW?

The results herein and in our previous paper,[42] together with the results discussed in the Introduction, strongly suggest that the EW is not a wing, but rather a separate, albeit often submerged, process. Identifying the EW as a JG process can be problematic, primarily, as discussed above, because of the somewhat vague definition of a JG process. However, from the results it can be inferred that (i) the EW has an intermolecular origin and (ii) its characteristic time is very close to that predicted for the primitive relaxation of the CM (i.e., the relaxation time for the escape of molecules from their liquid-structure cages[24]), similarly to what is observed for an intermolecular β process. The verification that this process is the precursor of the α relaxation would make it of fundamental interest for understanding the structural relaxation process in glasses, but this requires further investigation.

CONCLUSIONS

Dielectric relaxation spectra for PG, di-PPG, and tri-PPG were studied under high pressure. The data for di-PPG and tri-PPG reveal the simultaneous presence of an EW and a secondary process (the latter having been identified in prior work as a JG relaxation). In the trimer, the EW evolves into a distinct peak at sufficiently high pressures. For all three liquids, the EW exhibits an activation volume having the same order of magnitude as $\Delta V^{\#}$ for the α relaxation, but (for di- and tri-PPG) much larger than the activation volume of the β process. Measurements on sorbitol similarly indicate the presence of an EW, which is masked at low pressure; however, the loss contribution from conductivity precludes resolution of this EW.

From these results, we conclude that (i) the EW is a submerged secondary peak, and (ii) some secondary relaxations have been erroneously classified as JG processes, at least if the criteria described herein are adopted. In particular, a large difference in activation volume appears to be a facile method to distinguish between the two types of secondary processes, intermolecular versus intramolecular, with the former including the EW for the liquids herein. Moreover, since (by definition) the JG relaxation involves the entire molecule, it must be the slowest secondary process. Accordingly, the EW must be the JG relaxation. A comparison with the prediction[20,21] of the CM suggests that those secondary relaxations that are intermolecular serve as precursors to the α relaxation. The implication is they are of fundamental importance for the vitrification process.

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