

## Hydrogen bonding and secondary relaxations in propylene glycol trimer

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Broadband dielectric spectroscopy was employed to study the behavior of propylene glycol trimer (Tri-PPG). Measurements for different conditions of temperature and pressure allowed the effect hydrogen bonds on the complicated relaxation behavior to be clarified. We find that both the  $\alpha$  and  $\beta$  processes are affected by changes in the degree of hydrogen bonding, an indication of their correlation and consistent with their intermolecular character. On the other hand, the faster  $\gamma$  process is relatively unaffected by hydrogen bonding. To corroborate this interpretation, the H-bonding was altered by mixing the Tri-PPG with water. The behavior of the mixture was very similar to that of neat Tri-PPG under high pressure.

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### I. INTRODUCTION

The dynamics of glass-forming materials includes various processes, from the slow translational motions to the very fast vibrations giving rise to the Boson peak. These processes are associated with different types of molecular motions, which may or may not be related. A longstanding problem in condensed matter physics is to understand how the dynamics at the microscopic or mesoscopic levels underlies the macroscopic relaxation properties.

Upon approach to the glass transition, many relaxation times change drastically with changes in temperature, and, interestingly, the different relaxation processes exhibit different temperature dependences. For the glass transition process *per se* (e.g., the dielectric  $\alpha$  process), the temperature dependence is described in the vicinity of the glass temperature ( $T_g$ ), by the divergent Vogel-Fulcher equation,<sup>1,2</sup>  $\log(\tau_\alpha) = A + B/(T - T_0)$ , where  $A$ ,  $B$ , and  $T_0$  are constants. Higher-frequency secondary relaxations are usually less sensitive to temperature, and below  $T_g$  exhibit Arrhenius behavior. However, their  $T$  dependence changes above  $T_g$ , an intriguing feature of the glass transition.<sup>3-7</sup>

Secondary processes, first observed in polymers,<sup>8</sup> are now recognized as being essentially universal.<sup>9,10</sup> Although the local motion of pendant side groups in polymers does give rise to peaks in the relaxation spectrum, a more fundamental process, involving every atom in the molecule (or the entire repeat unit in a polymer chain), is present in all glassformers. This relaxation has come to be referred to as the Johari-Goldstein (JG) relaxation, which refers specifically to cooperative secondary relaxations, rather than motion of an isolated moiety.<sup>11</sup> In recent years, another feature of the relaxation spectrum, the so-called “excess wing” (EW), has attracted considerable research interest.<sup>12-17</sup> The EW appears as a second power law on the high-frequency flank of the  $\alpha$  peak, and typically does not separate from the  $\alpha$  peak as the temperature is varied; that is, the EW does not become a distinct peak. Since glassformers associated with EW behavior usually lacked the usual JG process, a classification

scheme of type A liquids (having a JG relaxation) and type B (having an EW) was proposed.<sup>18</sup> However, aging experiments<sup>14</sup> and measurements at high pressure<sup>19</sup> have shown that the EW does become a well-resolved peak, under appropriate conditions, and therefore should be considered as simply an unresolved JG.

Another important aspect of secondary relaxations under high pressure is the sensitivity of the relaxation times to pressure.<sup>19,20</sup> Some secondary processes are almost insensitive to pressure, while others have a pressure dependence nearly equal to that of the  $\alpha$  peak. Included among the latter are those having the form of an EW. In an analogous fashion, during physical aging, the relaxation time of some secondary processes varies, while for others it is invariant to aging.<sup>21</sup> These experimental findings are consistent with the idea that only some secondary relaxations are intermolecular (i.e., JG processes), and such a distinction must be made to understand the dynamics of supercooled liquids.

A theoretical tool valuable in distinguishing the two types of secondary relaxations is the coupling model (CM).<sup>11</sup> The primitive relaxation time  $\tau_0$  of the CM can be calculated as

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

where  $\tau_\alpha$  is the  $\alpha$ -relaxation time,  $t_c$  ( $\sim 2$  ps<sup>22</sup>) is a characteristic time for the onset of intermolecular cooperativity, and  $n$  is the coupling parameter, equal to one minus the value of the stretch exponent,  $\beta_{\text{KWW}}$ , of the Kohlrausch-Williams-Watts (KWW) relaxation function.<sup>23</sup> It has been observed that  $\tau_0$  is correlated with the JG secondary relaxation time,<sup>24-26</sup> and the correlation is maintained under high pressure<sup>11,27</sup> Accordingly, conformance to  $\tau_\beta \sim \tau_0$ , with  $\tau_0$  determined from Eq. (1), provides a test of whether a secondary relaxation should be considered as a true JG.

In this paper we discuss the influence of hydrogen bonding on the relative pressure dependence of the JG and  $\alpha$  processes in the trimer of propylene glycol (Tri-PPG). In particular, using the fact that the number of hydrogen bonds depends on both T and P, we show that apparently different behaviors can be observed in the same material. We also

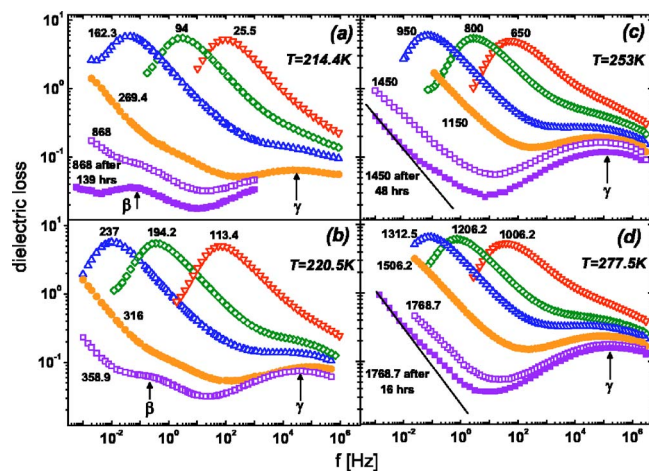


FIG. 1. (Color online) Dielectric loss spectra of Tri-PPG measured at the four indicated temperatures and various pressures (given in MPa in the figure). Also shown (as filled squares) are the spectra for three temperatures after aging for several hours. Lines in (c) and (d) are guides for the eye evidencing deviations from a power law behavior. Arrows indicate the  $\beta$  and  $\gamma$  peaks.

show how blending Tri-PPG with water can alter the degree of H bonding, yielding results analogous to those induced by T and P.

## II. EXPERIMENTAL

Propylene glycol trimer was obtained from Sigma-Aldrich Co., and used as received. A mixture was prepared with 4% by weight of deionized water (15 mole% H<sub>2</sub>O). The dielectric spectra measured at NRL (isotherms at  $T=214.4$  and  $220.5$  K) were obtained with a parallel plate geometry using an IMASS time domain dielectric analyzer ( $10^{-4}$  to  $10^3$  Hz) and a Novocontrol Alpha Analyzer ( $10^{-2}$  to  $10^6$  Hz). For high-pressure measurements, 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). The sample assembly was contained in a Tenney Jr. temperature chamber, with control of  $\pm 0.1$  K at the sample.

Measurements at higher pressure (at Silesian University) employed a technique similar to that of Johari and Whalley.<sup>28</sup> The liquid sample and parallel plate capacitor were placed in a Teflon bellows mounted in the high-pressure chamber. This technique enables the generation of pressures as high as a few GPa. Pressure was measured by a Nova Swiss tensometric meter, which had an accuracy of 10 MPa. Temperature was controlled to within 0.5 K by means of liquid flow from a thermostatic bath.

## III. RESULTS

The dielectric loss spectra for Tri-PPG measured at various pressures at each of four fixed temperatures are shown in Fig. 1. The expected slowing down of the  $\alpha$  peak with in-

creasing pressure is observed, a manifestation of an increasing glass transition temperature. At the lowest temperature (Fig. 1(a)), this slowing down of the  $\alpha$  process causes the appearance of a secondary peak at higher frequency ( $f_{\max} \sim 10^5$  Hz). At even higher pressure, another secondary process emerges, closer to the  $\alpha$  peak; this lower frequency secondary relaxation only becomes a distinct peak at very high  $P$ . In the following, we refer to these as the  $\gamma$  and  $\beta$  processes respectively. Interestingly, in measurements limited to atmospheric pressure, the  $\gamma$  process behaves similar to at high pressure, while the  $\beta$  relaxation is hard to detect, never appearing as a separate peak but only a difficult to resolve excess wing.<sup>19,26</sup>

Thus, we have the intriguing situation that in the lowest-temperature/ambient pressure condition, only the  $\alpha$  and  $\gamma$  processes are resolved as distinct peaks. A moderate increase of pressure/temperature allows the additional observation of the  $\beta$  peak (Figs. 1(a) and 1(b)). However, with a further increase of pressure/temperature, the spectra return more to the form seen at ambient pressure, with the  $\beta$  process no longer resolved as a separate peak (Fig. 1(c) and 1(d)). For the isotherms at the higher temperatures, aging brings forth an excess wing. The straight lines in panels (c) and (d) are the fits to the high-frequency flank of the  $\alpha$  peak. In (d) a departure from linearity (i.e., an excess wing) is noted. The spectrum in each panel denoted by filled circles represents the dielectric loss curve that attains a value of  $\sim 2$  at  $10^{-3}$  Hz. The maximum of the  $\alpha$  peak is at too low a frequency to be visible in these spectra; however, the shape parameters in Tri-PPG are relatively insensitive to changes in thermodynamical conditions, so these spectra should have comparable  $\tau_\alpha$ .

If we compare the pressure dependences of the  $\beta$  and  $\gamma$  processes, it is evident that the latter is almost unaffected by pressure, while the  $\beta$  process has a sensitivity very similar to that of the  $\alpha$  peak. This can be quantified by calculating the activation volumes,

$$\Delta V(T) = RT \left. \frac{\partial \ln(\tau)}{\partial P} \right|_T. \quad (2)$$

It was previously reported that  $\Delta V_\beta$  is about half of  $\Delta V_\alpha$ , while  $\Delta V_\gamma$  is two orders of magnitude smaller.<sup>29</sup>

At an increasingly higher temperature, the pressure necessary to significantly slow down the  $\alpha$  peak becomes larger. This has two causes: the larger increase in the glass transition required at higher  $T$  (for a given change in  $\tau_\alpha$ ) and the progressive decrease of  $\Delta V_\alpha$  with increasing temperature. Thus, comparing Figs. 1(a) and 1(d), a temperature increase of 63.1 K means that an eightfold larger pressure change is necessary to obtain the same relaxation time  $\tau_\alpha$ . Since Tri-PPG is a hydrogen-bonded liquid, and the H-bonding concentration is known to depend on  $T$  and  $P$ , we expect the degree of association of the liquid to be rather different for these two cases. Comparing the spectra at different  $T$ , it is evident that while the frequency of the  $\gamma$  process is virtually the same at any temperature, the  $\beta$  and  $\alpha$  peaks become less distinguishable with increasing  $T$ . In fact, for the spectra at the two

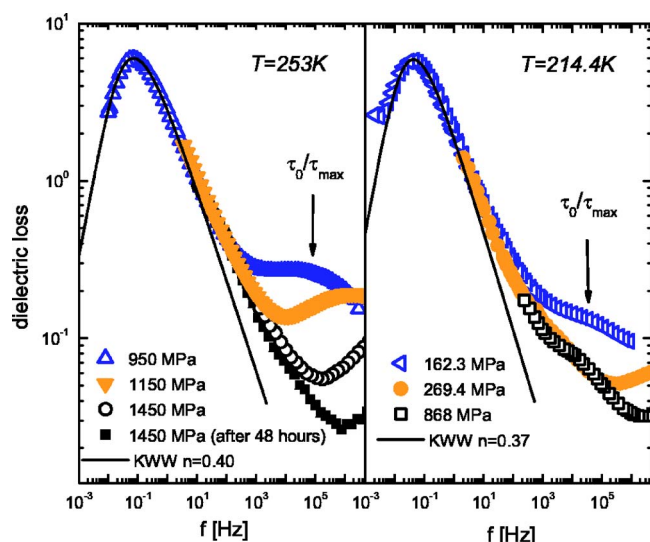


FIG. 2. (Color online) A comparison of dielectric loss spectra for Tri-PPG measured at two different temperatures. The spectra at higher pressure were shifted horizontally (no vertical shifts) so that their low-frequency side superimposes with the high-frequency flank of the two spectra at lower pressure. The solid line is the fit of the  $\alpha$ -peak to the KWW relaxation function. The arrow indicates the  $\tau_0$  (normalized by  $\tau_{\alpha}$ ) calculated from Eq. (1).

higher temperatures, the  $\beta$  relaxation has more the form of an EW.

In Fig. 2, we show spectra at high pressure for two of the temperatures in Fig. 1. For the higher pressures, the maxima in the  $\alpha$  peak are out of the frequency range; these spectra were shifted horizontally so that their low-frequency side superimposes with the high-frequency flank of the lower-pressure spectrum (chosen arbitrarily to be the reference spectrum). At comparable values of  $\tau_{\alpha}$ , the  $\alpha$  peak has essentially a constant shape. Fitting to the KWW function, we find that the breadth of the  $\alpha$  peak is sensibly independent of temperature ( $n=0.39\pm 0.02$ ). The  $\tau_0$  calculated from Eq. (1), shown by arrows in Fig. 2, correlate with the position of the  $\beta$  process, even when the latter is submerged under the  $\alpha$  peak.

In Fig. 3 are displayed spectra of Tri-PPG with 4% by weight-water. The presence of the water induces a small change in  $T_g$  (defining the glass transition as the temperature at which  $\tau_{\alpha}=100$  s,  $T_g=192$  K for neat Tri-PPG versus 188 K with 4 wt.% added water). As is also the case for high pressure, the  $\gamma$  process of the hydrated Tri-PPG is essentially invariant to pressure. Again, the  $\beta$  process has a  $P$  dependence closer to that of the  $\alpha$  process. At both low- and high-temperature/pressure conditions, for which only the  $\alpha$  and  $\gamma$  processes were visible as distinct peaks in the spectra of neat Tri-PPG, one can now clearly observe the  $\beta$  process. Comparing the spectra with and without water at about the same value of  $\tau_{\alpha}$  (Fig. 4), the principal observation is a reduced  $\gamma$  peak height.<sup>30</sup> Differences in the  $\alpha$  peak are negligible, except that below  $T_g$  the  $\beta$  relaxation emerges as a well-separated peak (Fig. 3).

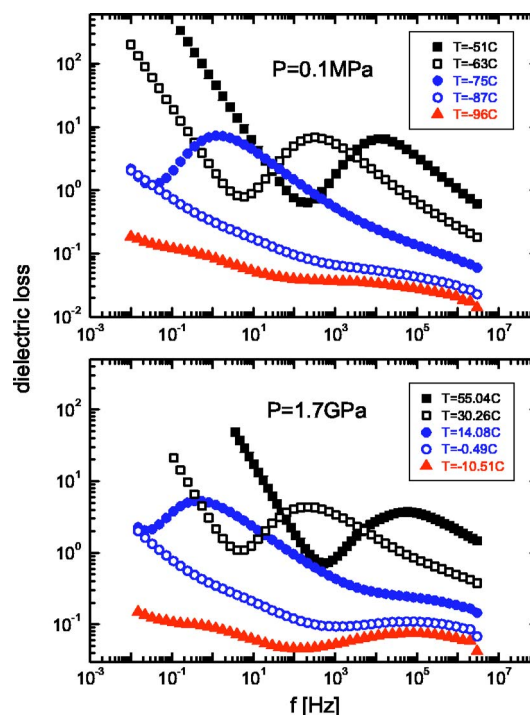


FIG. 3. (Color online) Dielectric loss spectra at ambient (a) and elevated (b) pressure at the indicated temperatures for Tri-PPG mixed with 4% by weight of water.

#### IV. DISCUSSION AND SUMMARY

The most interesting aspect of this work is the peculiar behavior of the  $\beta$  process, which we believe reflects the nature of the intermolecular interactions in Tri-PPG. This compound is an associated liquid, and having both ether and hydroxyl groups Tri-PPG can form different structures, involving H bonding of different strengths and geometries.<sup>31,32</sup>

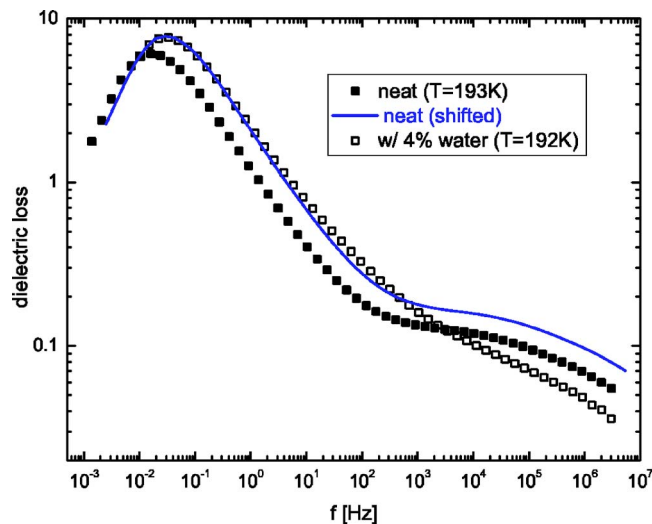


FIG. 4. (Color online) A comparison of the dielectric loss spectrum obtained for neat Tri-PPG and for the mixture of Tri-PPG and water at ambient pressure and the indicated temperatures. The solid line is the data for neat Tri-PPG after multiplying the frequencies by 1.8 and  $\epsilon''$  by 1.28.

Due to its thermally labile nature, the strength of hydrogen bonding decreases with temperature. The effect of pressure on hydrogen bonding is more complicated. There are experimental data<sup>33,34</sup> and molecular simulations,<sup>35</sup> which indicate that pressure promotes the formation of hydrogen bonds, while other experiments<sup>36,37</sup> and Monte Carlo simulations<sup>38</sup> suggest no effect or a reduction in H bonds. For water, the best-studied case, pressure clearly reduces the degree of H bonding<sup>39,40</sup>. Generally, it seems clear that the concentration of hydrogen bonds at low temperature and low pressure will be larger than at high temperature and high pressure.

It is well established that for hydrogen-bonded glassformers, temperature tends to be the dominant variable governing the dynamics; pressure (or density) exerts a much smaller effect.<sup>41–43</sup> Accordingly, we can ascribe the different behavior for the isotherms in Fig. 1 to different extents of hydrogen bonding. At higher temperature, H bonding is weaker, and there are smaller differences in respective activation volumes for the  $\beta$  and  $\alpha$  peaks. Thus, the  $\alpha$  and  $\beta$  peaks have different activation volumes and can be resolved when Tri-PPG behaves more like an associated liquid (low  $T$ , high  $P$ ). However, when the majority of the H bonds are dissociated, Tri-PPG behaves more like a van der Waals liquid. The activation volumes of the  $\alpha$  and  $\beta$  processes becomes comparable, so that the  $\beta$  process is not readily resolved (high  $T$ , higher  $P$ ). This is consistent with the dielectric spectra of materials having an EW: The  $\beta$  peak can be resolved (at least partially) for H bonded materials, especially under high pressure, but not for van der Waals liquids<sup>16,44</sup> since only for the former are the intermolecular interactions strongly affected by  $T$  and  $P$ . Of course, this does not mean that for Tri-PPG at  $\sim 1$  GPa H bonds have no role at all. The associated structure is complex, since the hydroxyl groups of Tri-PPG can interact with other hydroxyl groups or with the ether oxygen, leading to different intra- and intermolecular complexes. For a given condition of  $T$  and  $P$ , some structures are preferred over others, based on both geometry and energy considerations.

The results for the blend of Tri-PPG with water (Fig. 3) corroborate these ideas. Water molecules have a strong pro-

ensity for H-bond formation, thus tending to participate in complexes with the Tri-PPG, potentially decreasing the extent of H bonding between Tri-PPG molecules. Consequently, even at the lowest and highest  $T$ - $P$  conditions a resolved  $\beta$  peak is present in the dielectric spectrum.

Interestingly, a decrease is also observed in the amplitude of the  $\gamma$  process upon the addition of water. This may reflect that fact that in neat Tri-PPG, a small fraction of molecules are not involved in H bonding,<sup>32</sup> and these would preferentially interact with the water. If motion of the unbonded Tri-PPG were giving rise to the  $\gamma$ -process, its intensity should decrease upon addition of the water. However, this would not account for the insensitivity to temperature and pressure of the  $\gamma$ -relaxation times in Fig. 1. This decrease is also due at least in part to the dilution of the Tri-PPG. The larger amplitude of the  $\alpha$  relaxation could be attributed to a decrease of the intermolecular H bonds due to the presence of water, which increases the orientability of the Tri-PPG molecules (note that the relaxation of the water itself is at much higher frequencies). Thus, it seems more likely that the  $\gamma$  peak reflects (local) motion of those end groups not involved in H bonding; that is, the  $\gamma$  process is a non-JG secondary relaxation. (See Fig. 4)

In conclusion, the peculiar changes in the  $\beta$  relaxation of Tri-PPG for different conditions of  $T$  and  $P$  can be explained in terms of the variation in the degree of hydrogen bonding. Tri-PPG behaves more like a van der Waals liquid at high  $T$  and like a strongly H-bonded liquid at low  $T$ . The dependence of both the  $\alpha$  and  $\beta$  peaks on the extent of hydrogen bonding is a further indication of the correlation between these two processes. Both are cooperative in nature, as confirmed by the agreement with the CM prediction. This can be contrasted with the properties of a faster  $\gamma$  peak, which is uncorrelated with the primary  $\alpha$  relaxation.

#### ACKNOWLEDGMENTS

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