

# Does the Johari-Goldstein $\beta$ -relaxation Exist in Polypropylene Glycols?

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## Abstract

Secondary relaxations with properties closely related to the  $\alpha$ -relaxation have fundamental importance in glass-forming substances including polymers. To distinguish these secondary relaxations from those involving intra-molecular degrees of freedom, they are called the Johari-Goldstein (JG)  $\beta$ -relaxations. Acting as the precursor of the  $\alpha$ -relaxation, the JG  $\beta$ -relaxation is supposedly ubiquitous in all glass-formers, a thesis supported by experiments on a variety of glass-formers. Notwithstanding, the JG  $\beta$ -relaxation has not been identified definitively in the hydroxyl-terminated polypropylene glycols (PPGs) with various molecular weights, despite these polymers have been intensively studied experimentally in the last several decades. The difficulty of finding the JG  $\beta$ -relaxation is due to the presence of a faster intramolecular  $\gamma$ -relaxation and a slower relaxation originating from residual water. This is demonstrated in two recent papers by Gainaru, C. et al. *Macromolecules* **2010**, *43*, 1907, and Kaminski, K. et al. *Macromolecules* **2013**, *46*, 1973. In this paper we show the presence of the JG  $\beta$ -relaxation in the PPGs from the dielectric relaxation data by using the time honored criterion derived from the Coupling Model in conjunction with the observed anomalous temperature dependence of the  $\gamma$ -relaxation caused by merging with the JG  $\beta$ -relaxation, and

new experimental data obtained by applying pressure on PPG4000 before and after drying the sample to remove the residual water. From the results we conclude that the behavior of the PPGs is no different from the other glass-formers as far as the omnipresence of the JG  $\beta$ -relaxation is concerned.

## 1. Introduction

Starting from the simplest molecule, propylene glycol, oligo-propylene glycols and poly(propylene glycol) are formed by bonding together more of the same basic molecular units. These materials have the chemical formula,  $\text{H}-(\text{C}_3\text{H}_6\text{O})_N-\text{OH}$ , where  $N$  is the number of repeat units. Although the chemical structures are similar, the character of intermolecular interactions changes with  $N$ . In case of oligomers (low value of  $N$ ), the H-bond interactions play important role whereas for higher values of  $N$  they become less important. In the last case, van der Waals interactions become dominant. The only change is the size (chain length) of the molecule (polymer). Thus, this family of glass-forming substances is ideal for studying the dependence of the molecular dynamics on the size or chain length, which may give insight into the fundamental mechanism of glass transition.<sup>1-20</sup> From now on we denote members of this family by  $\text{PG}_N$ . Propylene glycol, the dimer, and the trimer correspond to  $N=1$ , 2, and 3 respectively. The better known PPG400 and PPG4000 have respectively molecular weights of about 400 and 4000, and corresponds to  $N=7$  and  $N=68$ . We shall consider also data from samples with  $N=52$  and  $N=315$ . The entanglement molecular weight of the hydroxyl-terminated PPG was estimated to be equal to  $M_w=5500$  g/mol.<sup>19</sup> Hence the sample with

$N=315$  is well entangled. Although we follow many of the previous papers in using the term poly(propylene glycol) for PPG400 and PPG4000, but more appropriately they should be called the poly(propylene oxide)s or PPOs according to the IUPAC recommendation. The correct terminology, PPO-425 and PPO-4000), was used in the pioneering dielectric studies by Johari and coworkers with or without added water<sup>21-23</sup>. All  $PG_N$  have large dipole moment, and the dynamics are easily probed by broadband dielectric relaxation spectroscopy<sup>1,5-16,18-20</sup>. The structural  $\alpha$ -relaxation and a secondary  $\gamma$ -relaxation appear prominently in the dielectric spectra in all  $PG_N$ , except in propylene glycol ( $PG_{N=1}$ ) the  $\gamma$ -relaxation is absent. The spectral width of the  $\alpha$ -dispersion increases monotonically with  $N$  and levels off after  $N$  becomes large. The same trend holds for the fragility measured by the steepness index,  $m = d\tau_\alpha(T_g/T)/d(T_g/T)$  evaluated at  $(T_g/T) = 1$ , where  $\tau_\alpha$  is the  $\alpha$ -relaxation time, and  $T_g$  is the glass transition temperature.

In recent years, much attention is focused on the secondary relaxation belonging to a special class which distinguishes itself from other secondary relaxations by bearing various strong relations to the  $\alpha$ -relaxation in properties found by experiments and simulations.<sup>24-28</sup> The relations are anticipated by the Coupling Model (CM)<sup>24-26</sup> from the analogy of its primitive relaxation to this secondary relaxation. From the analogy, this secondary relaxation is supposedly universally present in all glass-formers. In totally rigid molecular glass-formers, the only one secondary relaxation discovered by Johari and Goldstein<sup>29-31</sup> is such an example. To honor the two researchers for their important discovery, all secondary relaxations belong to the special class, even the glass-formers are not rigid and can be polymeric, inorganic and metallic, are summarily called the Johari-Goldstein (JG)  $\beta$ -relaxation.<sup>24-27</sup>

While indisputable evidences of the existence of the JG  $\beta$ -relaxation abound in many different kinds of glass-formers, the situation remain unclear in the family of  $PG_N$ . The relaxation time,  $\tau_\gamma$ , of the well resolved  $\gamma$ -relaxation in  $PG_N$  with  $N \geq 2$  turns out to be pressure insensitive, in contrast to the strong pressure dependence of  $\tau_\alpha$ . Hence this particular absence of relation with the  $\alpha$ -relaxation indicates that it is not the JG  $\beta$ -relaxation according to one of several criteria.<sup>27</sup> Notwithstanding, there are attempts to uncover the JG  $\beta$ -relaxation in the  $PG_N$ . The efforts with results seemingly suggesting the presence of the JG  $\beta$ -relaxation include the following.

(i) By long term physical aging of propylene glycol, the excess wing on the high frequency side of the  $\alpha$ -relaxation was transformed into a shoulder<sup>32</sup>.

(ii) A secondary relaxation slower than the  $\gamma$ -relaxation shows up by application of elevated pressures to the dimer,  $PG_2$  and trimer  $PG_3$ .<sup>9</sup>

(iii) The appearance of a slower secondary relaxation than the  $\gamma$ -relaxation in the glassy states of PPG400 and PPG4000<sup>13</sup>, and in  $PG_N$  with  $7 \leq N \leq 315$ .<sup>19</sup>

On the other hand, findings potentially dashing the hope of ever finding the JG  $\beta$ -relaxation include the following items.

(iv) The slower secondary relaxation of a sample with  $N=315$  mentioned in (iii) disappears after heating treatment at 150 and 200 C, indicating that it originates from residual water in the sample.<sup>19</sup> Moreover its strength was enhanced by exposing the sample to air at room temperature for times longer than about 1 day. Its activation energy of about 6400 K is similar to that found in many hydrated hydrophilic glass-formers.<sup>33</sup> All these observations suggest that it originates from residual water in all the  $PG_N$  with  $7 \leq N \leq 315$ .

(vi) A slower secondary relaxation than the  $\gamma$ -relaxation in the glassy state of a sample of amino- ( $\text{NH}_2$ -) terminated polypropylene glycol with  $N=68$  disappears by annealing.<sup>20</sup>

The last two experimental observations suggest that the slower secondary relaxation is not an intrinsic property of the PPGs, and definitely not the JG  $\beta$ -relaxation we are looking for.

From the account given in paragraph above, the question of whether the JG  $\beta$ -relaxation exists or not in the PPGs remains unanswered. One way or the other, the answer will have serious repercussion on the thesis that the JG  $\beta$ -relaxation is ubiquitous and fundamentally important in acting as the precursor of the structural  $\alpha$ -relaxation.<sup>24-27,34</sup> The purpose of this paper is to answer the question on the presence of the JG  $\beta$ -relaxation in the PPGs positively by providing other evidences, as well as presenting new experimental data at elevated pressures in PPG4000 before and after drying the sample.

## **2. Evidences for the presence of JG $\beta$ -relaxation in the PPGs**

There are two proven ways to test if a resolved secondary relaxation is the JG  $\beta$ -relaxation or not. One is the application of elevated pressure  $P$  in the equilibrium liquid state. One criterion is the significant increase of the relaxation time,  $\tau_\beta$ , of the secondary relaxation on elevating pressure, mimicking the property of  $\tau_\alpha$ .<sup>27</sup> A further confirmation is the invariance of the ratio,  $\tau_\alpha(T,P) / \tau_\beta(T,P)$ , to variations of  $P$  and  $T$  while keeping  $\tau_\alpha$  constant.<sup>34-38</sup> This criterion is impractical for the 2PG, 3PG, and PPG400 because the structure changes at high pressure and temperature by breaking hydrogen bonds. Moreover, the secondary relaxation slower than the irrelevant  $\gamma$ -relaxation was observed only in the glassy state, which is insensitive to pressure.

As mentioned before, PPG with  $N=315$  has a slower and resolved secondary relaxation, but since it vanishes on heating, it is likely contributed by residual water. Hence, experiment at elevated pressure needs to be carried out on dried sample. This study performed on PPG4000 before and after the sample had been thoroughly dried will be reported in Section 4.

The other test proven in many glass-formers since 1998 is that, if the  $\beta$ -relaxation is the JG  $\beta$ -relaxation, its  $\tau_\beta(T)$  should be approximately equal to the primitive relaxation time,  $\tau_0(T)$ , of the Coupling Model (CM), i.e.

$$\tau_{\text{JG}}(T,P) \approx \tau_0(T,P). \quad (1)$$

This prediction is based on the similarity in properties of the primitive relaxation and the JG  $\beta$ -relaxation. Both are precursors of the  $\alpha$ -relaxation, with properties connected to that of the  $\alpha$ -relaxation including the invariance of  $\tau_\alpha(T,P)/\tau_\beta(T,P)$  at constant  $\tau_\alpha$ . For  $\tau_0(T,P)$ , these properties are direct consequence of the time honored CM equation,<sup>26,39-41</sup>

$$\tau_\alpha(T,P) = [t_c^{-n} \tau_0(T,P)]^{1-n}, \quad (2)$$

where  $t_c=1$  to 2 ps for molecular glassformers, and  $(1-n)$  is the fractional exponent of the Kohlrausch function,

$$\phi(t) = \exp[-(t/\tau_\alpha)^{1-n}], \quad (3)$$

which fits the contribution of the  $\alpha$ -relaxation to the susceptibility,  $\varepsilon^*(f) = \varepsilon'(f) - i\varepsilon''(f)$ , after Fourier transformation to frequency space.

There is another phenomenon in the PPGs which can help in locating the JG  $\beta$ -relaxation. This is the observation of anomalous behavior of the  $\gamma$ -relaxation at temperatures in the vicinity of  $T_g$ . Its relaxation time  $\tau_\gamma$  decreases on cooling from the equilibrium liquid state down to the glassy state.<sup>11-16,42,43</sup> This unexpectedly  $T$ -dependence of  $\tau_\gamma$  on cooling continues until a minimum is reached and thereafter  $\tau_\gamma$  reverts to its normal behavior of

monotonic increase in the glassy state. Such anomaly was reported in hydrogen-bonded glassformers including 2PG, 3PG, PPG400, PPG1025, and PPG4000,<sup>11-14</sup> the van der Waals liquid di-*n*-octyl phthalate (DOP),<sup>43</sup> and the epoxy resins DGEBA and PPGE.<sup>16</sup> As explained in ref.[16], the anomalous behavior of  $\tau_\gamma(T)$  is caused by the encroachment of  $\tau_{JG}(T)$  towards it at temperatures near and above  $T_g$ . This effect is inferred from the behavior of  $\tau_0(T)$  calculated from eq.(2), and the approximate equality (1) between  $\tau_{JG}(T)$  and  $\tau_0(T)$ . The encroaching slower JG  $\beta$ -relaxation (involving the motion of the entire basic unit)<sup>27</sup> hybridizes with the faster  $\gamma$ -relaxation (involving part of the basic unit), resulting in a shift of  $\tau_\gamma$  to longer times. Since encroachment increases with increasing temperature, the shift of  $\tau_\gamma$  towards longer times increases correspondingly, and this effect gives rise to the minimum in  $\tau_\gamma$  as observed. Thus a supplementary evidence of the presence of the JG  $\beta$ -relaxation is the encroachment of  $\tau_0(T) \approx \tau_{JG}(T)$  towards  $\tau_\gamma(T)$  within the temperature range where the anomalous  $T$ -dependence of  $\tau_\gamma(T)$  is observed.

In the next section we gather the kind of evidences described in the above from the experimental data of PPG400, PPG4000, and PPG<sub>*N*</sub> with  $N=52$  and  $N=315$  to show the presence of the JG  $\beta$ -relaxation in all these PPGs.

### 3. Results

#### (A) PPG400

The dielectric loss spectra,  $\varepsilon''(f)$ , of PPG400 in a wide temperature range from the glassy state to above  $T_g$  are shown in Fig.1. The chain normal modes observed at lower frequencies than the  $\alpha$ -relaxation are not the concern of this paper, and hence their contributions to  $\varepsilon''(f)$  at lower frequencies are not shown except for one temperature (blue closed triangles). The

broadening of the  $\alpha$ -loss peak on its low frequency flank is evident. Also some data in the figure are omitted to enhance visibility, particularly for the sake of the slower secondary  $\beta$ -relaxation with weak strength found only in the glassy state. The green open squares were taken at  $T=177$  K. The prominent  $\alpha$ -relaxation loss peaks were fitted by the Fourier transforms of the Kohlrausch function (3) with  $n=0.37$  which is nearly constant for all the data shown. As an example, the dashed line is the fit at one temperature. The values of  $\tau_\alpha(T)$  determined from the Kohlrausch fits (blue open squares) together with the Vogel-Fulcher fit can be found in the relaxation map (Fig.2). Since the frequency dispersion of the  $\alpha$ -loss peak is constant at temperatures near and below  $T_g$ , we can shift the data having the  $\alpha$ -loss peak at a temperature above  $T_g$  to lower frequencies to overlap the  $\alpha$ -loss peak data at temperature below  $T_g$  in Fig.1. In this way, the master curve (not shown) obtained enables determination of the peak frequency  $f_\alpha(T)$  and  $\tau_\alpha(T)$  at lower temperatures. The values of  $\tau_\alpha(T)$  obtained in this manner are shown by open green squares in Fig.2. There is good agreement between these values of  $\tau_\alpha(T)$  and the Vogel-Fulcher-Tammann fit to data of  $\tau_\alpha(T)$  obtained at higher temperatures.

Also entered into Fig.2 are the values of  $\tau_0(T)$  calculated via eq.2 from the data of  $\tau_\alpha(T)$  as well as the Vogel-Fulcher-Tammann fit of  $\tau_\alpha(T)$  extended to lower temperatures (line) and  $n=0.37$ . The locations of the primitive frequencies,  $f_0(T)\equiv 1/2\pi\tau_0(T)$ , in Fig.1 are indicated by the vertical arrows pointing at the corresponding loss spectra. These values of  $\tau_0(T)$  or  $f_0(T)$  should be approximately the same as  $\tau_{JG}(T)$  or  $f_{JG}(T)$  according to the criterion of  $\tau_{JG}(T)\approx\tau_0(T)$  or  $f_{JG}(T)\approx f_0(T)$  for identification of the JG  $\beta$ -relaxation.<sup>24-27</sup> Suggested by the presence in the glassy state of a secondary  $\beta$ -relaxation slower than the  $\gamma$ -relaxation in Fig.1,



its relaxation time  $\tau_\beta(T)$  together with  $\tau_\alpha(T)$  and  $\tau_\gamma(T)$  was deduced in the past<sup>14</sup> by the fits of the spectra in Fig.1 to the sum of three independent contributions from the  $\alpha$ -,  $\beta$ -, and  $\gamma$ -relaxations. The  $\gamma$ -relaxation is not only extremely broad but also asymmetric. However it is commonly observed for various materials that the secondary relaxation processes have symmetric shapes and can be well described by CC function. Thus, the asymmetry of the  $\gamma$ -relaxation peak is the consequence of coalescence of two secondary relaxation processes, and the slower one could be the JG  $\beta$ -relaxation. A fit of  $\varepsilon''(f)$  at 177 K by the sum of a Cole-Cole function for the  $\beta$ -relaxation and the  $\gamma$ -relaxation by either a Havriliak-Negami or Cole-Cole function is shown in Fig.3. The value of  $\tau_\beta(T)$  at  $T=177$  K determined from the fits is illustrated by the closed diamond in Fig.2. It is clear by inspection of Fig.2 that the values of  $\tau_\gamma(T)$  are distinctly different from  $\tau_0(T) \approx \tau_{JG}(T)$ , and hence the  $\gamma$ -relaxation is definitely not the JG  $\beta$ -relaxation of PPG400. The  $\beta$ -process in PPO-425 found dielectrically by and Johari<sup>23</sup> has relaxation times comparable to  $\tau_\gamma(T)$  in Fig.2, and hence it is also not the JG  $\beta$ -relaxation. On the other hand the values of the calculated  $\tau_0(T)$  shown by the line in Fig.2 appears to meet the values of  $\tau_\beta(T)$  at lower temperatures, supporting the possibility that slower  $\beta$ -relaxation can be the JG  $\beta$ -relaxation. Notwithstanding, another possibility is that the  $\beta$ -relaxation of PPG400 comes from residual water as pointed out by Gairaru et al.<sup>19</sup> and Kaminski et al.<sup>20</sup> since  $\tau_\beta(T)$  in the glassy state have activation energy of the same size as water in hydrophilic systems.<sup>33</sup>

The JG  $\beta$ -relaxation cannot be uncovered in the equilibrium liquid state at temperatures above the glass transition temperature  $T_g$  either. Indicated by the vertical arrow pointing at the data at each temperature is the calculated value of  $\log f_0(T)$ . The proximity of  $f_{JG}(T) \approx f_0(T)$  to

the extremely broad  $\gamma$ -relaxation (see Fig.1) makes the JG  $\beta$ -relaxation difficult to be resolved in the spectra. Nevertheless, on the high frequency side of the  $\alpha$ -loss peak, the data are in excess of the fit by the Fourier transform of the Kohlrausch correlation function. The excess, called the excess wing, is found in many glassformers and is actually the unresolved JG  $\beta$ -relaxation hidden under it<sup>32,43,44</sup>. Thus the  $\varepsilon''(f)$  spectra at temperatures above  $T_g$  lend support to the presence of the JG  $\beta$ -relaxation in PPG400. An additional support of the JG  $\beta$ -relaxation times  $\tau_{\text{JG}}(T)$  are well approximated by  $\tau_0(T)$  in Fig,2 comes from the anomalous temperature dependence of  $\tau_\gamma(T)$  occurs in the temperature range where  $\tau_0(T) \approx \tau_{\text{JG}}(T)$  is seen to encroach  $\tau_\gamma(T)$ . A minimum exhibited by  $\tau_\gamma(T)$  in Fig.2 occurs at temperatures above  $T_g$  where the calculated  $\tau_0(T)$  approaches and crosses  $\tau_\gamma(T)$ . The encroachment of  $\tau_0(T) \approx \tau_{\text{JG}}(T)$  towards  $\tau_\gamma(T)$  leads to hybridization of the intramolecular  $\gamma$ -relaxation (libration of the  $\text{CH}_3\text{C-OH}$  end group<sup>20</sup>) with the slower JG  $\beta$ -relaxation, and the process causes  $\tau_\gamma(T)$  to exhibit the anomalous increase with increasing temperature, and in turn the minimum. The minimum of the relaxation time  $\tau_\gamma(T)$  of an intramolecular secondary relaxation is found in 2PG, 3PG, PPG400, PPG1025 and PPG4000 as well as in the van der Waals glassformer DOP, and the epoxy resins DGEBA and PPGE.<sup>16</sup> In all cases the phenomenon can be explained by the encroachment of the JG  $\beta$ -relaxation. This explanation of the apparently general phenomenon is another evidence of the presence of the JG  $\beta$ -relaxation in PPG400 and the others of the same family.

The aging of some glass-formers showed that relaxation strength of the JG  $\beta$ -relaxation decreases, whereas the relaxation time changes slightly as shown in a review by Vij and Power<sup>45</sup>. Another attempt to determine  $\tau_{\text{JG}}(T)$  of the PPGs via  $\tau_{\text{JG}}(T) \approx \tau_0(T)$  was made by

Kaminski et al. by an aging experiment.<sup>20</sup> The so called iso-structural  $\alpha$ -relaxation times,  $\tau_{\text{age}}$ , deep in the glassy state was deduced from the change with time at a fixed temperature at a frequency near the maximum of the  $\gamma$ -process. The amplitude of the  $\gamma$ -loss decreases with aging time, and its time dependence was fitted by the equation derived by Leheny and Nagel.<sup>46</sup> The  $\tau_{\text{age}}$  obtained by this method at two temperatures and represented the two open circles in Fig. 2 are much shorter than  $\tau_{\alpha}(T)$  of PPG400 at equilibrium expected from the extrapolation of the Vogel-Fulcher-Tammann fit. The temperature dependence of  $\tau_{\text{age}}$  is so weak such that its activation energy is comparable to  $\tau_{\gamma}$  and significantly smaller than the  $\beta$ -relaxation associated with residual water. These extraordinary attributes of  $\tau_{\alpha}(T)$  do not support it as the relaxation times of any physical meaningful measure of  $\tau_{\alpha}(T)$  in the glassy state. The cause of this situation can be traced to the nature of the  $\gamma$ -relaxation. It is an intramolecular relaxation having no connection to the  $\alpha$ -relaxation unlike the primitive relaxation/JG  $\beta$ -relaxation. Its relaxation time  $\tau_{\gamma}(T)$  is not sensitive to applied pressure, and hence also insensitive to change in density on physical aging. Thus, on aging PPG400, the decrease of the amplitude of the  $\gamma$ -loss reflects neither the structural  $\alpha$ -relaxation or the JG  $\beta$ -relaxation. Basically, the  $\gamma$ -relaxation is the wrong choice to apply the Leheny and Nagel method unlike the case of polyvinylethylene (PVE)<sup>47</sup> and telmisartan<sup>48</sup>, where the time dependence of the amplitude of the JG  $\beta$ -relaxation is used to deduce  $\tau_{\alpha}(T)$  in the glassy state. Incidentally, this difference in change with time on aging between JG  $\beta$ -relaxation and intramolecular relaxation can be used as another criterion to distinguish the former from the latter.

## **(B) PPG4000**

The isothermal spectra of the dielectric loss  $\varepsilon''(f)$  measured in PPG4000 are presented in Fig.4. In addition to the prominent  $\alpha$ -loss peak are two secondary relaxations. The slower  $\beta$ -relaxation is only evident in the glassy state. The faster  $\gamma$ -relaxation is very broad and seen at temperatures above and below  $T_g$ . The fits to the  $\alpha$ -loss peaks at two temperatures by the Fourier transform of the Kohlrausch functions are shown by the lines in Fig.4. The value of  $n$  in the stretch exponent of the Kohlrausch function is 0.49, and is nearly constant for the data shown. The values of  $\tau_\alpha(T)$  are entered into the relaxation map of Fig.5 together with the Vogel-Fulcher-Tammann fit, and the  $\tau_0(T)$  calculated via eq.2 from  $\tau_\alpha(T)$  and  $n=0.49$ . Appearing also in Fig.5 are the values of  $\tau_\beta(T)$  and  $\tau_\gamma(T)$  determined by fitting each spectrum to the superposition of the contributions from the  $\alpha$ -,  $\beta$ -, and  $\gamma$ -relaxation, but without taking into consideration of the possible presence of the JG  $\beta$ -relaxation.<sup>13</sup> The inset of Fig.4 compare the values of  $\tau_\beta(T)$  reported in two publications<sup>13,20</sup>. Again judging from the similarity of the activation energy  $\approx 50$  kJ/mol of  $\tau_\beta(T)$  to that of water in hydrophilic systems, the  $\beta$ -relaxation may originate from residual water in PPG4000. It is worth pointing out that the  $\beta$ -relaxation observed by Johari<sup>21</sup> in PPO-4000 has relaxation times of similar size as  $\tau_\gamma(T)$  in Fig.5, and hence is not the JG  $\beta$ -relaxation.

In Fig.4, the locations of the primitive frequencies,  $f_0(T) \equiv 1/2\pi\tau_0(T)$ , are indicated by vertical arrows pointing at the corresponding loss spectra. These values of  $f_0(T)$  or  $\tau_0(T)$  should be approximately the same as  $f_{JG}(T)$  or  $\tau_{JG}(T)$  according to the criterion of  $\tau_{JG}(T) \approx \tau_0(T)$  or  $f_{JG}(T) \approx f_0(T)$  used to identify the JG  $\beta$ -relaxation. It can be seen in Fig.4 that  $f_{JG}(T) \approx f_0(T)$  is on the low frequency side of the broad secondary relaxation loss peak previously attributed entirely to the  $\gamma$ -relaxation. This is likely the cause of why the JG  $\beta$ -relaxation has not been

resolved. Moreover, the extremely broad secondary loss peak at all temperatures near and below  $T_g$  suggests that it is composed of the JG  $\beta$ -relaxation and the  $\gamma$ -relaxation. This is supported by the proximity of the calculated  $\tau_0(T) \approx \tau_{JG}(T)$  to the values of  $\tau_\gamma(T)$ . As can be seen by inspection of the relaxation map (Fig.5), on increasing temperature,  $\tau_0(T) \approx \tau_{JG}(T)$  is encroaching  $\tau_\gamma(T)$ , and eventually the two merge together. The encroachment causes  $\tau_\gamma(T)$  to level off instead of continuing its monotonic decrease with temperature. The effect found is another evidence of the presence of the JG  $\beta$ -relaxation with its relaxation time  $\tau_{JG}(T)$  well approximated by  $\tau_0(T)$  in Fig.5.

Kaminski et al.<sup>20</sup> deduced the iso-structural  $\alpha$ -relaxation times,  $\tau_{age}$ , of PPG4000 deep in the glassy state from the decrease of the amplitude of the  $\gamma$ -loss with aging time by the same method as described in subsection A. The  $\tau_{age}$  obtained at three temperatures and represented by the three closed circles in Figure 5. The temperature dependence of  $\tau_{age}$  is so weak such that its activation energy is comparable to  $\tau_\gamma(T)$  or  $\tau_\beta(T)$  and cannot be  $\tau_\alpha(T)$  in the glassy state. The problem is due to  $\tau_\gamma(T)$  not sensitive to applied pressure, and hence also to change in density on physical aging. Thus, on aging PPG4000, the decrease of the amplitude of the  $\gamma$ -loss does not reflect the structural  $\alpha$ -relaxation or the JG  $\beta$ -relaxation. Nevertheless the values of  $\tau_{age}(T)$  were considered to represent the iso-structural  $\tau_\alpha(T)$  in Ref.20 and the CM relations (1) and (2) were used to calculate  $\tau_0(T) \approx \tau_{JG}(T)$  from  $\tau_{age}(T)$ . These results do not represent  $\tau_0(T) \approx \tau_{JG}(T)$ . Nevertheless, they are shown in Fig.4 by the three open circles in Fig.5. Their very weak temperature dependence is sufficient to indicate that the results are unphysical, and do not represent  $\tau_0(T) \approx \tau_{JG}(T)$ .

#### 4. PPG4000 At Elevated Pressures

Since the relaxation time of JG  $\beta$ -relaxation increases with pressure while the relaxation time of secondary relaxation of intramolecular origin is insensitive to pressure, the expedient way to separate apart the two processes possibly making up the very broad and asymmetric  $\gamma$ -relaxation of PPG4000 is to measure  $\varepsilon''(f)$  by increasing the applied pressure at constant temperature. If the  $\beta$ -relaxation in PPG4000 is contributed by the residual water, it will disappear from the loss spectrum when measurements of  $\varepsilon''(f)$  is made in a thoroughly dried sample. Surprisingly measurements at elevated pressure have not been carried out on PPG4000 despite many studies have been done on PPG4000. For this reason, we have made these measurements on sample before and after it had been dried, and the results are presented in subsections (A) and (B) as follows.

##### (A) Nominal Sample

Isothermal measurements of  $\varepsilon''(f)$  at elevated pressures were made on the same sample of PPG4000 used to make isobaric measurements presented before in Fig.4. The isothermal data at  $T=0$  C and over a range of applied pressure  $P$  from 600 to 1037 MPa are shown in Fig.6. The  $\alpha$ -loss peak shifts to lower frequency significantly on increasing pressure, while the loss peak frequency of the  $\gamma$ -relaxation,  $f_\gamma$ , remains unchanged. The absence of pressure dependence of  $f_\gamma$  is concrete proof of the intramolecular nature of the  $\gamma$ -relaxation.

On the other hand, elevated pressures do not make the  $\beta$ -loss peak disappear even though the temperature has to be raised to counter the elevated pressure in maintaining the same value of  $f_\alpha$ . This behavior of the  $\beta$ -process is consistent with it originating from residual

water in the sample. We performed additional isothermal measurements at a higher temperature of 20 C and pressures from 818 to 961 MPa. Presented in Fig.7, the  $\beta$ -loss peak frequency  $f_\beta$  does not change much with pressure, and thus it is an intramolecular process whether it originates from residual water or not.

### **(B) Dry Sample**

The only way to ascertain residual water as the origin of the  $\beta$ -relaxation is to remove it by heating the sample at higher temperature as done by Gainaru et al.<sup>19</sup> Therefore we dried the sample thoroughly for 12 hours under vacuum at 80 C. Measurements of  $\varepsilon''(f)$  at elevated pressures were made on the dry sample. The isothermal spectra at  $T=20$  C and pressures ranging from 804 to 1197 MPa are presented in Fig.8. The  $\beta$ -loss peak is no longer visible in the dry sample, indicating that it is associated with local relaxation of residual water in the nominal sample. The  $\alpha$ -loss peak of the dry sample is narrower, reflected by the smaller value of  $n=0.42$  in the Kohlrausch function to fit it than the value of 0.49 for the nominal sample.

Having succeeded in removal the extrinsic  $\beta$ -relaxation due to residual water, the spectra in Fig.7 make possible a clear perception of the intrinsic dynamics and processes in pure PPG4000. Present in the spectra are the  $\alpha$ -relaxation accounted for by the fit with the Fourier transform of the Kohlrausch function, the excess wing (EW) defined as the excess of the measured  $\varepsilon''(f)$  over the Kohlrausch fit on the high frequency side of the  $\alpha$ -loss peak, and the intramolecular  $\gamma$ -process. The EW is a recurrent feature in many glassformers having no resolved JG  $\beta$ -relaxation. By various means including physical aging,<sup>24,29,43,44,49-51</sup> the JG  $\beta$ -relaxation hidden under the EW was resolved. Thus the EW is basically the unresolved JG  $\beta$ -relaxation. This is confirmed in the present case of pure PPG4000 by the shift of the EW to

lower frequencies on increasing the applied pressure in concert with the  $\alpha$ -relaxation (see Fig.7), which is a property of the JG  $\beta$ -relaxation.

## 5. Conclusions

As a good glass-forming system, the dynamics of polypropylene glycols and oligomers of propylene glycol (PPGs) have been extensively studied in the past number of decades and continued to the present time. In recent years, search for the fundamental mechanisms leading to glass transition has been an active research field. Experimental investigations in many kinds of glass-forming substances and systems have shown the presence of a secondary relaxation with properties bearing strong connection to the structural  $\alpha$ -relaxation. It is the precursor of the  $\alpha$ -relaxation and hence is fundamentally important for glass transition. To distinguish it from other irrelevant secondary relaxations, it is called the Johari-Goldstein (JG)  $\beta$ -relaxation. It is supposed to be universal process in all glass-formers because without it the  $\alpha$ -relaxation cannot come to fruition. However, despite many studies of the dynamics of polypropylene glycols and oligomers of propylene glycol, the JG  $\beta$ -relaxation had either not found or wrongly identified as the  $\beta$ -relaxation originating from residual water or the  $\gamma$ -relaxation involving the libration of librational fluctuations of the polar COC moiety. The unfortunate situation in the PPGs causes doubt of the universal existence and fundamental importance of the JG  $\beta$ -relaxation.

In this paper we have analyzed the dielectric relaxation data of two archetypal PPGs to elucidate the reason why it is impossible to resolve the JG  $\beta$ -relaxation. In nominal samples the spectra is complicated by the presence of two prominent secondary  $\beta$ - and  $\gamma$ -relaxations,. Notwithstanding, the anomalous temperature dependence of the  $\gamma$ -relaxation time and the



explanation by the Coupling Model provide evidence of the presence of the JG  $\beta$ -relaxation. The new experimental results obtained by applying elevated pressure on the nominal sample and thoroughly dried sample of PPG4000 give definitive proof that the  $\gamma$ -relaxation is of intramolecular nature, and the  $\beta$ -relaxation comes from the local relaxation of residual water. The excess wing showing up in the spectra of the dry PPG4000 sample shifts to lower frequencies with increasing pressure is the hidden JG  $\beta$ -relaxation that has eluded identification in past studies.

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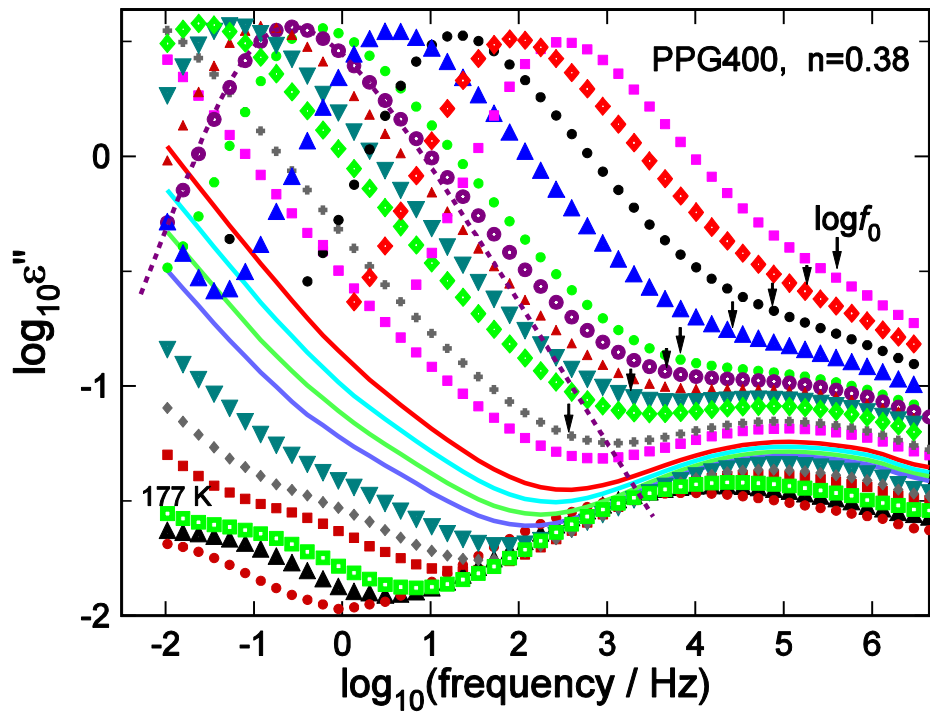


Figure 1. Isothermal dielectric loss spectra of PPG400 at temperatures (from right to left) 216, 213, 210, 207, 204, 203, 202, 201, 200, 198, 197, 195, 194, 193, 192, 189, 183, 177, 173, and 167 K. The dashed line is the Kohlrausch fit of the  $\alpha$ -relaxation with  $n=0.38$ . The locations of  $\log f_0$  are indicated by the arrows.

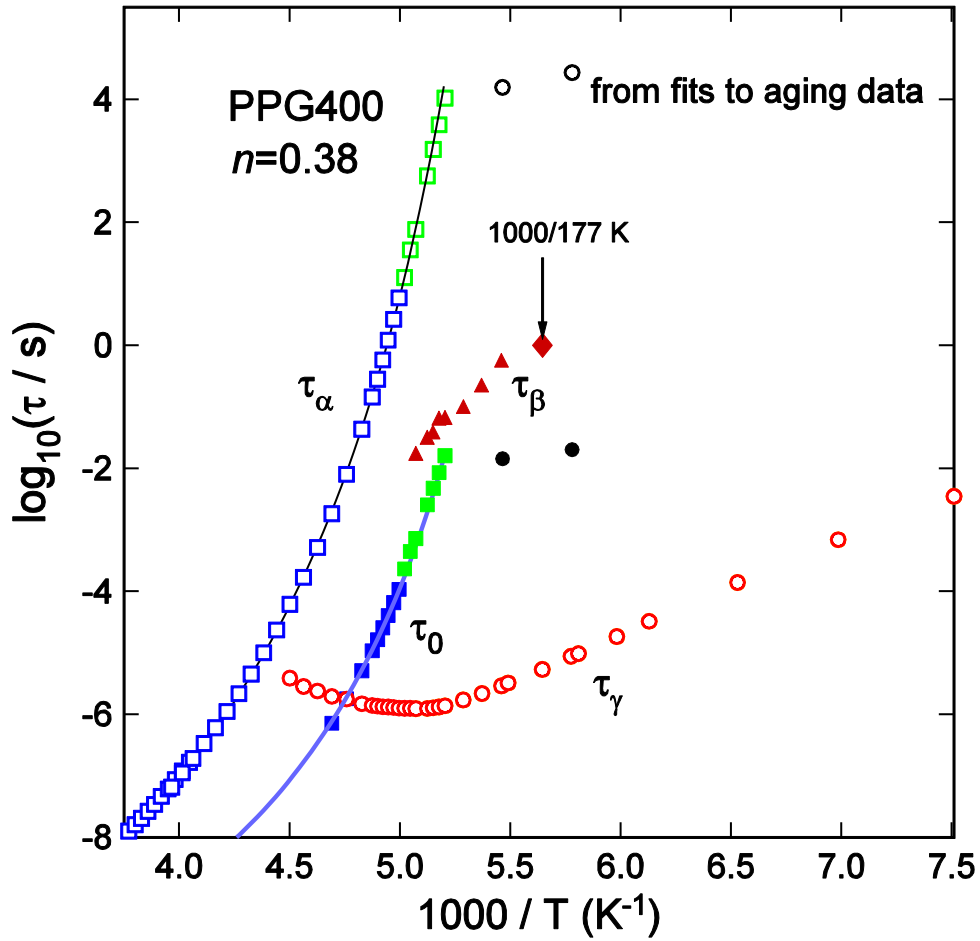


Figure 2. Relaxation map of PPG400 showing encroachment of  $\tau_0(T) \approx \tau_{\text{IG}}(T)$  towards  $\tau_\gamma$  (open red circles) at the region where  $\tau_\gamma$  exhibits the anomaly. Open blue squares are  $\tau_\alpha(T)$  determined from the fits to the isothermal spectra in Fig.1. The thin black line is the VFT fit, The green open squares are extrapolated values of  $\tau_\alpha(T)$  by the VFT dependence. The closed blue and green squares are  $\tau_0(T)$  calculated using eq.2 with  $n=0.38$  and the values of  $\tau_\alpha(T)$  (open blue and green squares). For the two black open circles on top and the two black closed circles below, see text for description.

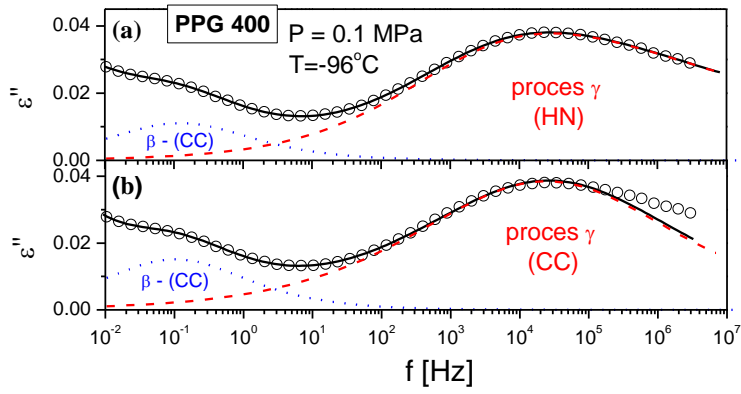


Figure 3. the asymmetry of the  $\gamma$ -relaxation loss peak at 177 K is fitted by the sum of a Cole-Cole function for the  $\beta$ -relaxation and the  $\gamma$ -relaxation by either a Havlilak-Negami function (a), or a Cole-Cole function (b).

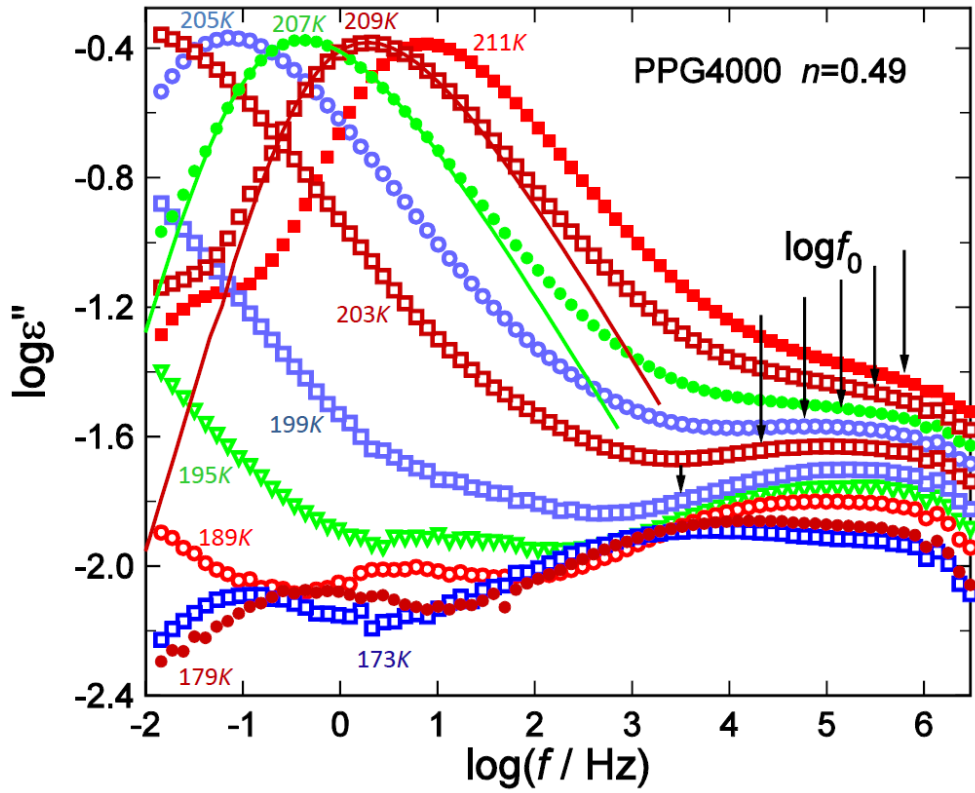


Figure 4. Dielectric loss spectra at ambient pressure of PPG4000 at various temperatures from 173 to 211 K as indicated. The lines are fits to the  $\alpha$ -relaxation by the Fourier transform of the Kohlrausch function with  $n=0.49$ . The vertical arrows indicate the locations of the calculated  $\log f_0$  by eq.(2) with  $n=0.49$ .



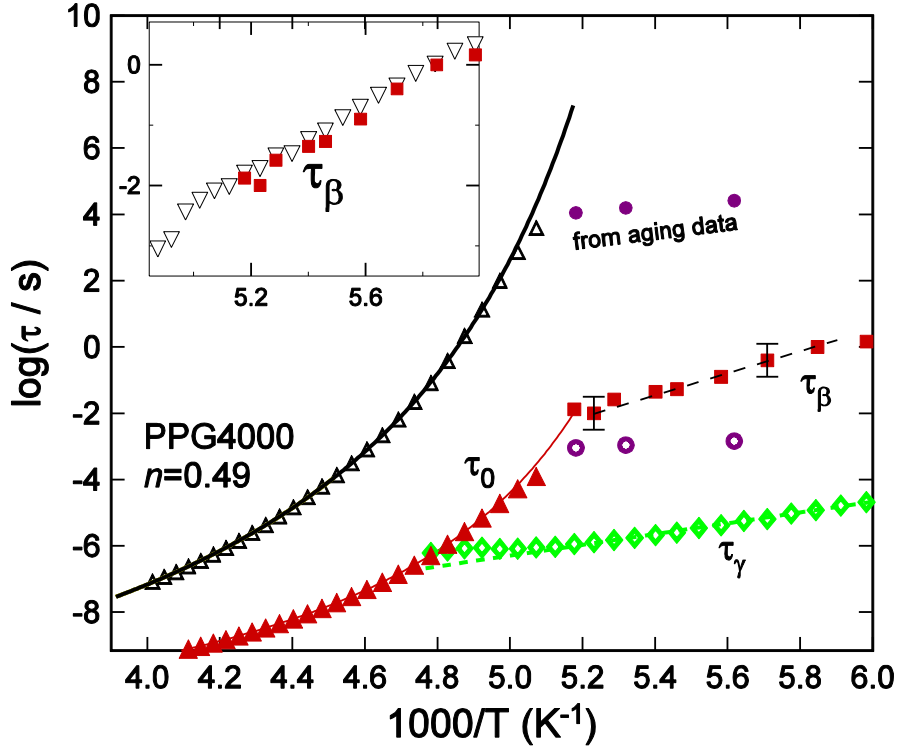


Figure 5. Relaxation map of PPG4000 showing encroachment of  $\tau_0(T) \approx \tau_{JG}(T)$  towards  $\tau_\gamma$  (open green diamonds) at the region where  $\tau_\gamma$  exhibits the anomaly. Open black triangles and closed red squares are  $\tau_\alpha(T)$  and  $\tau_\beta(T)$  respectively determined from the fits to the isothermal spectra in Fig.4. The black line is the VFT fit to  $\tau_\alpha(T)$ . The closed red triangles are  $\tau_0(T)$  calculated using eq.2 with  $n=0.49$  and the values of  $\tau_\alpha(T)$ . For the three purple closed circles on top and the three purple open circles below, see text for description. The inset shows  $\tau_\beta(T)$  taken from ref.20 (open inverted triangles) and ref.13 (closed red squares).

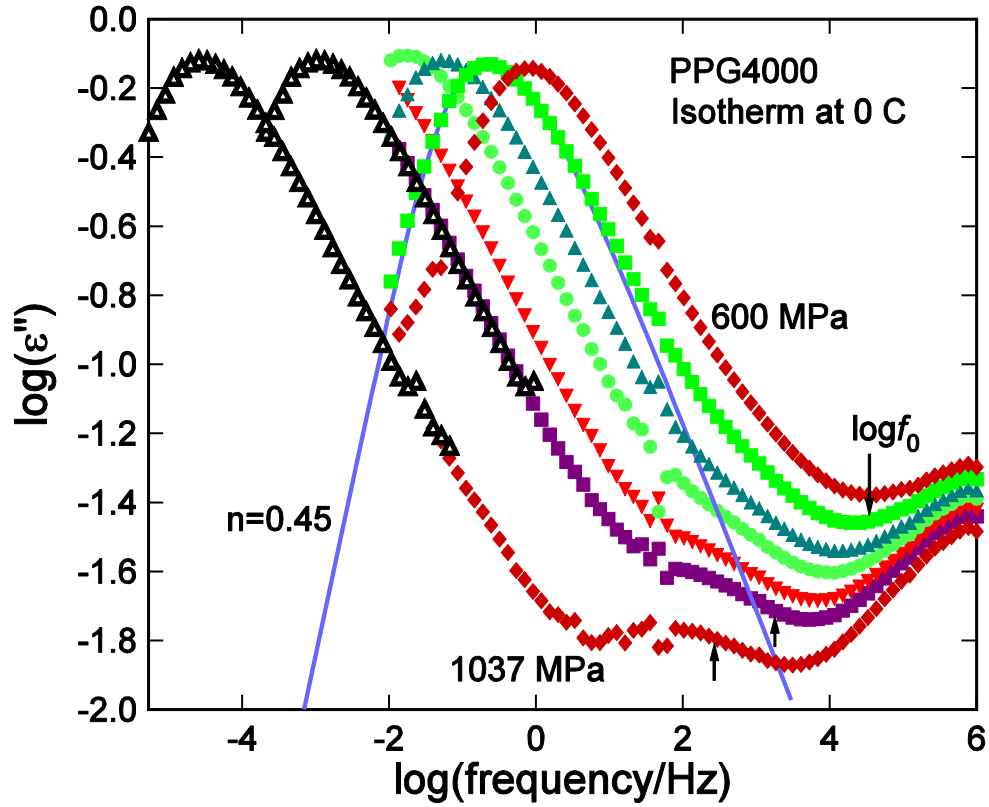


Figure 6. Dielectric loss data of nominal PPG4000 at 0 C and increasing applied pressure from 600 MPa to 1037 MPa, showing the  $\gamma$ -relaxation are insensitive to pressure. The line is fit to the  $\alpha$ -relaxation by the Fourier transform of the Kohlrausch function with  $n=0.45$ . The vertical arrows indicate the locations of the calculated  $\log f_0$  by eq.(2) with  $n=0.45$ .

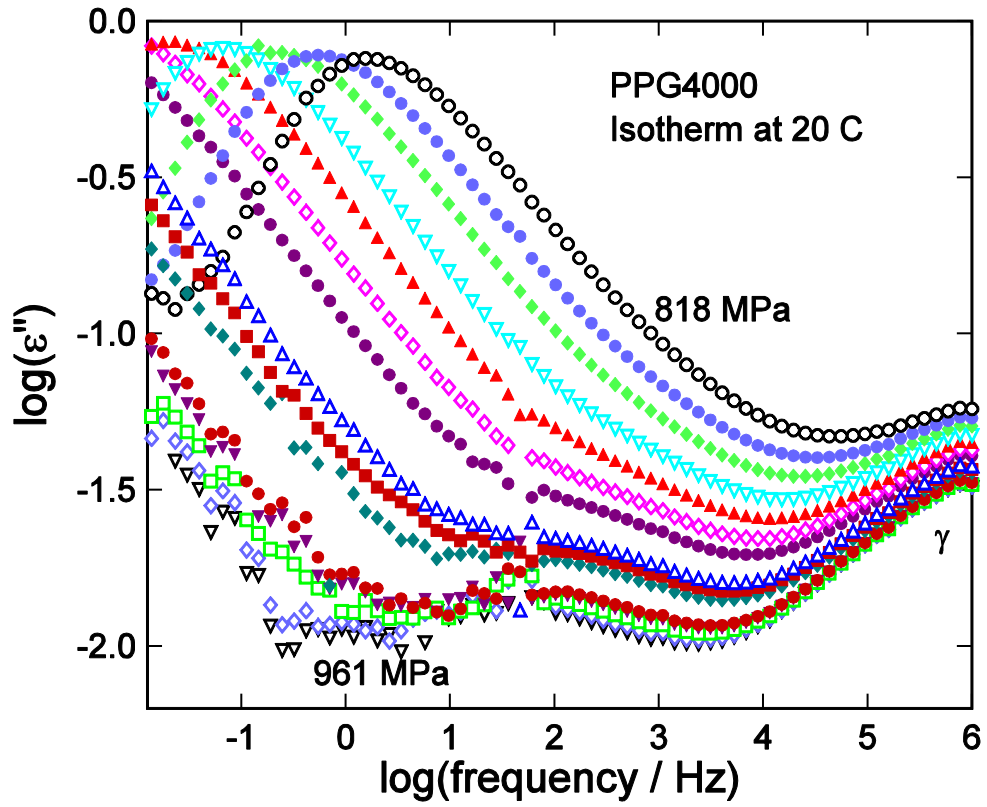


Figure 7. Dielectric loss data of nominal PPG4000 at 20 C and increasing applied pressure from 818 MPa to 961 MPa, showing the  $\beta$ - and the  $\gamma$ -relaxation are insensitive to pressure.

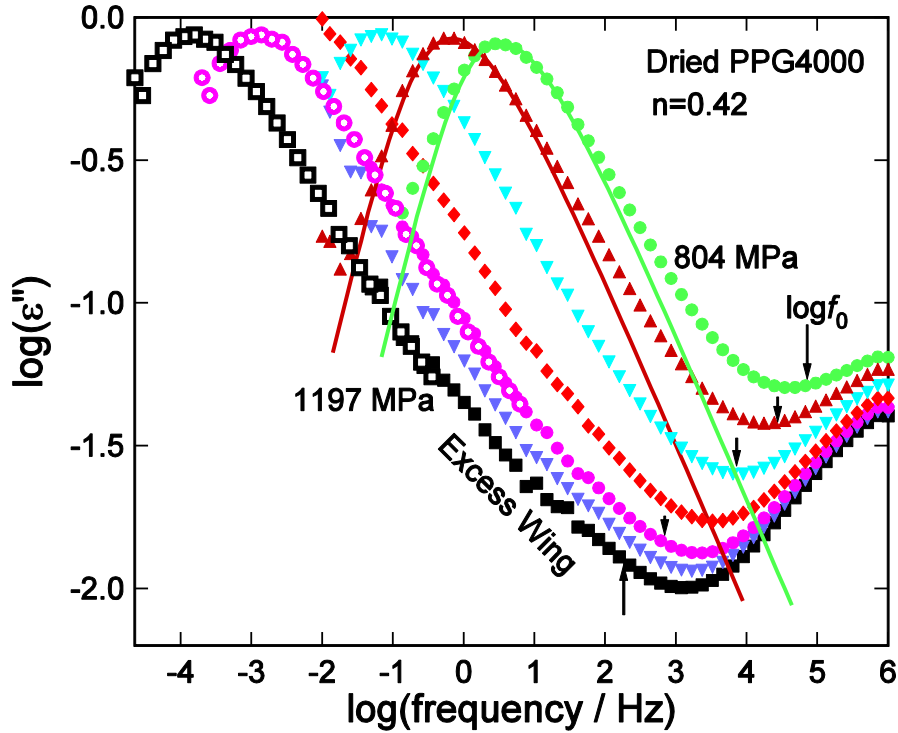


Figure 8. Dielectric loss data of dried PPG4000 at 20 C and increasing applied pressure from 804 MPa to 1197 MPa, showing the excess wing instead of the  $\beta$ -process. This excess wing shifts in concert with the  $\alpha$ -loss peak to lower frequencies on increasing pressure. In contrast, the  $\gamma$ -relaxation is sensitive to compression.