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Enthalpy and dielectric relaxation in the glass transition region of polypropylene glycol

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Abstract

We investigated enthalpy and dielectric relaxation behaviors in the glass transition region of polypropylene glycol of molecular weight 1000 and 4000 by measuring both dynamic heat capacity and dielectric susceptibility as a function of frequency and temperature. The data at each temperature were fitted to the Kohlrausch–Williams–Watt (KWW) relaxation function, and the relaxation time, the shape parameter β, and the relaxation strength were extracted. The relaxation times follow the same Vogel–Tammann–Fulcher (VTF) equation for both enthaply and dielectric responses, while β of the KWW relaxation function showed different temperature dependences. β of the enthalpy relaxation shows a linear temperature dependence, whereas it stays constant in the dielectric relaxation. Significant molecular weight dependence occurs only in the relaxation strength. We discuss the temperature dependence of the shape parameter in terms of broadening of the relaxation time distribution associated with cooperative molecular rearrangements. © 2001 Elsevier Science B.V. All rights reserved.

Keywords: Enthalpy; Enthalpy relaxation; Dielectric relaxation; Polypropylene glycol

1. Introduction

The most important relaxation process governing the glass transition is the structural rearrangements, often called α process. Two prominent features of the α process may be summarized as follows: firstly, the temperature dependence of the relaxation time τ is expressed by the Vogel–Tammann–Fulcher (VTF) form in various glass systems [1]

$$\tau = \tau_0 \exp\left[\frac{D}{T - T_0}\right], \tag{1}$$

where T_0 is typically 30–60 K below the glass transition temperature T_g at which τ becomes about 100 s, is usually identified with the Kauzmann temperature T_K [2] or an ideal glass transition temperature in connection with the hypothetical second order phase transition [3]. Secondly, the relaxation dynamics is described by a nonexponential relaxation function. Most experimental data can be well fitted to the Kohlrausch–Williams–Watt (KWW) relaxation function with the stretch exponent β:

$$\phi(t) = \exp\left[-\left(\frac{t}{\tau}\right)^{\beta}\right], \quad 0 < \beta < 1. \tag{2}$$

Some time ago Adam and Gibbs (AG) derived the VTF equation by considering temperature variations of the size of cooperative rearranging regions (CRRs)

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and the associated configurational entropy [3]. More recently Ngai et al. developed the coupling model by incorporating mutual interactions between CRRs of the AG theory, and they derived the KWW relaxation function from the model [4]. There also exists a theory, the mode coupling theory (MCT), which interpret the glass transition as a dynamic phenomenon. MCT predicts the existence of a critical temperature T_c, typically 30–80 K above T_g, above which the relaxation time is characterized by a power-law behavior, i.e. $\tau \sim (T - T_c)^{-\gamma}$ for $T > T_c$ [5]. Though a substantial number of experimental data seem to support the MCT, [6,7] a clear explanation of the dynamics below T_c is yet to be given. In addition, recent experimental results have suggested a possibility that the characteristic length scale associated with the glass transition may diverge at T_0, not at T_c [8–10].

It is generally believed that there exists some kind of a dynamic cross-over at a temperature near T_c, and a change from the Arrhenius temperature dependence (or the power-law behavior) to the VTF form occurs in the relaxation times [11,12]. However, detailed analysis of many glass forming materials indicates that this simple picture may not be true [13,14]. Nevertheless, the existence of a cross-over is beyond doubt, and is supported by the various experimental evidences such as a breakdown of the Stokes–Einstein relation [8,15,16], decoupling of the Johari–Goldstein (β_{JG}) process [17] from the α process [15,18]. We denote this cross-over temperature as T_A.

Since the slow dynamics in the supercooled state is at the center of glass transition phenomenon as cited above, various dynamic probes have been used to investigate the glass dynamics. Dielectric susceptibility measurements, in particular, have been a tool of choice in the field due to its wide dynamic range, high sensitivity, and ease of use. Recent development of dynamic calorimetry, however, has offered researchers another dynamic tool with similarly wide dynamic range. Since different tools employed in probing the glass dynamics would couple to different degrees of freedom in the system, the comparison of dynamic data obtained with the various tools may not be straightforward. To isaddress this question, we attempted a comparative study on the glass transition dynamics by carrying out simultaneous measurements of dynamic heat capacity and dielectric susceptibility of a glass-forming liquid.

The major aim of this paper is to critically compare dielectric and enthalpy relaxation spectrums occuring in the supercooled state of polypropylene glycol (PPG) [19]. PPG is known to have a complex dielectric relaxation spectrum, [9,20–23] which includes the conductivity effect, α' (normal mode), α, and β_{JG} processes, [24] and therefore it would be of interest to seek for the corresponding counterparts in the enthalpy relaxation spectrum. One expects that the features of enthalpy relaxation would be rather different from those of dielectric relaxation because heat capacity measurements probe all degrees of freedom, while dielectric susceptibility is sensitive to the orientation of local dipole moments. One may also expect a situation where some of the dielectric modes may not carry enough entropy to be calorimetrically detected.

2. Experimental

PPG samples of molecular weight 1000 (PPG-1000) and 4000 (PPG-4000) were obtained from Aldrich Chemicals and used without further purification. Dielectric susceptibility was measured using the standard three terminal method with parallel-plate sample cells and a lock-in amplifier in the frequency range from 10^{-2} to 10^5 Hz. Dynamic heat capacity was measured using a fully automated dynamic calorimeter based on the 3ω method, the details of which was described before [25,26]. The amplitude of the temperature modulation was kept less than 0.1 K in all the measurements, and the frequency range covered was from 10^{-2} to 10^4 Hz. A platinum resistance thermometer calibrated against the standard one from Omega Engineering Inc., was used to measure the absolute temperature. It should be stressed that the dynamic heat capacity measurements were carried out in the linear response regime, and therefore the data reflect the characteristics of the samples in equilibrium.

3. Results and discussion

In Fig. 1 plotted are the dielectric relaxation spectrums of PPG-1000 and PPG-4000, which were normalized with respect to the permittivity of free space ϵ_0. In the case of PPG-1000, only ionic conductivity

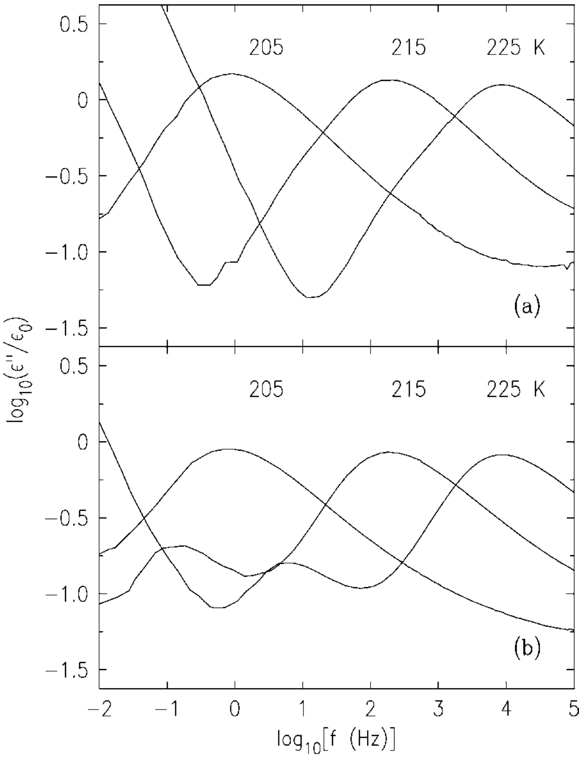

Fig. 1. The imaginary part of the normalized dielectric constant ϵ of polypropylene glycol (PPG) at labeled temperatures: (a) molecular wieght of 1000 and (b) 4000.

shoulders and α peaks are present in the spectrum, while an additional peak (normal mode α') is seen between the ionic conductivity shoulder and the α peak for PPG-4000. Peaks associated with the β_{JG} process do not show up in both samples because its time scale is outside our experimental window. Only the high frequency part of the spectrum corresponding to the α relaxation was used in the data analysis. Both real and imaginary parts of the dielectric constant ϵ were simultaneously fitted to the following equation [27] using the KWW relaxation function of Eq. (2):

$$\epsilon(\omega) = \epsilon_0 + \mathrm{i}\omega\,\Delta\epsilon \int_0^\infty \phi(t)\exp(\mathrm{i}\omega t)\,\mathrm{d}t, \qquad (3)$$

where ω is the angular frequency ($\omega = 2\pi f$), ϵ_0 the static dielectric susceptibility, $\Delta\epsilon$ the dielectric relaxation strength defined by $\Delta\epsilon = \epsilon_0 - \epsilon_\infty$. The fitting results are shown as solid lines in Fig. 2 and the quality of the fitting indicates that the KWW function properly describes the dielectric α relaxation within our frequency window. Since the exponent β of the KWW function determines the shape of the function (imaginary part in particular) in the frequency domain, β will be called the shape parameter. It is noted that the dielectric β does not change as a function of temperature or molecular weight and has a fixed value of 0.50.

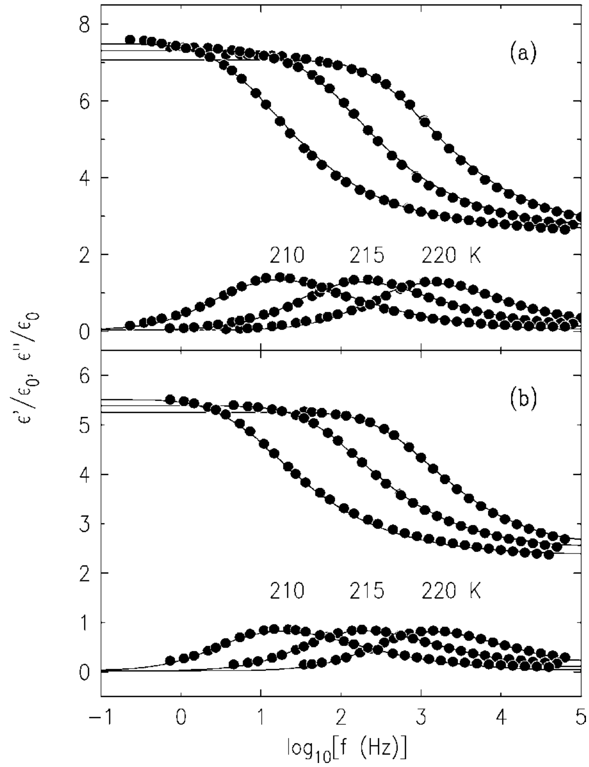

Fig. 2. The real and imaginary parts of the dielectric α relaxation of PPG at labeled temperatures: (a) PPG-1000 and (b) PPG-4000. The solid lines denote the fitting results using the KWW relaxation function. The shape parameter β of the KWW function has a fixed value of 0.50 at all temperatures for the dielectric constant of both materials.

The data from the dynamic heat capacity measurements are displayed in Fig. 3. Although the 3ω method measures only the product of heat capacity C_{p} and thermal conductivity κ, no attempt was made to separate them and instead the measured quantity, κC_{p}, was directly used in the data analysis. ($\sqrt{\kappa C_{\mathrm{p}}}$ is often called thermal effusivity in the literature.) This was motivated by the fact that no appreciable change in thermal conductivity was discovered in the glass transition region of supercooled liquids in previous

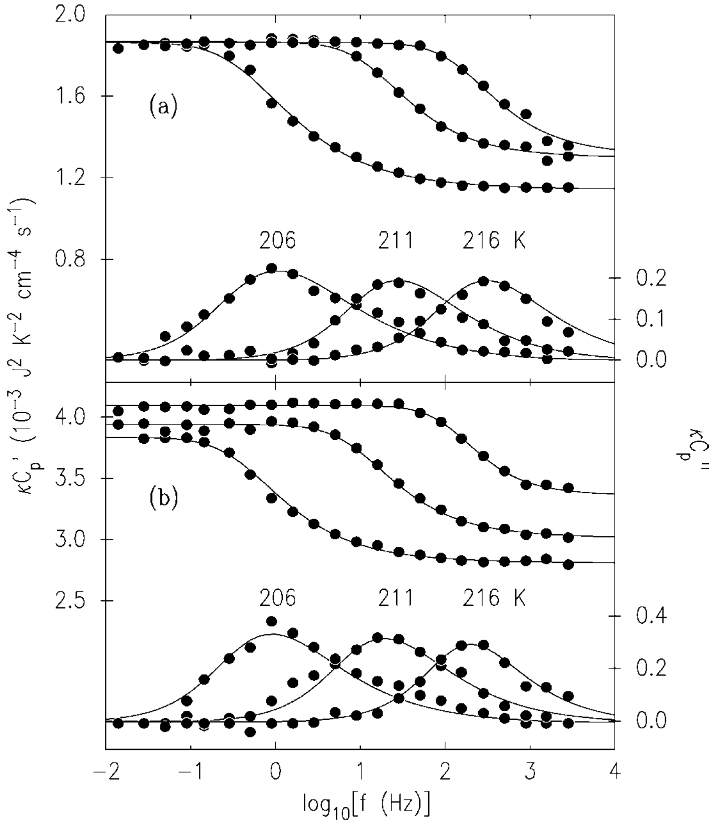

Fig. 3. The real and imaginary parts of κC_p of (a) PPG-1000 and (b) PPG-4000. The solid lines denote the fitting result using the KWW relaxation function. The shape parameter β of the KWW function for enthalpy relaxation varies linearly as a function of temperature (see Fig. 5 for details).

studies [25,28,29]. Thus, any frequency dependence in κC_p should be equivalent to that in C_p caused by enthalpy relaxation. The enthalpy relaxation data were then fitted to Eq. (3) with κC_p in place of ϵ. Here again the KWW function seems to properly describe the relaxational behavior within our frequency window. However, the enthalpic β of both PPG-1000 and PPG-4000 decreases as temperature decreases (see Fig. 5). It should be noted for the comparative purpose that the enthalpy relaxation spectrum of PPG-4000 exhibits neither a conductivity shoulder nor an normal mode α' peak in contrast to the dielectric constant of the same material. This may be interpreted to indicate that the normal modes related to the α' process carry too little amount of entropy to be calorimetrically detected. Of course, it is not surprising to find that the entropy associated with the conductivity effect is rather small. The absence of these corresponding effects in the calorimetric data also indicates that calorimetry as an experimental probe is less sensitive than dielectric spectroscopy.

In Fig. 4, the temperature dependence of the peak frequency f_p. The α peak frequency values were converted from the fitted values of τ using the relationship between f_p and τ, $\log_{10}(f_p) = 0.2598(1-\beta) -\log_{10}(2\pi\tau)$, which holds for the KWW function [30]. Also shown in the figure are the dielectric peak frequencies associated with the α' process and the β_{JG} process [24]. The present result for the α' peak in PPG-4000 is consistent with the previous report [9]. As we focus our attention on the α relaxation in the figure, we find a general agreement between dielectric and enthaply relaxation times (or peak frequencies). On closer inspection, however, it is seen that the enthalpy α relaxation time of PPG-4000 is slightly slower than that of PPG-1000, and no molecular weight

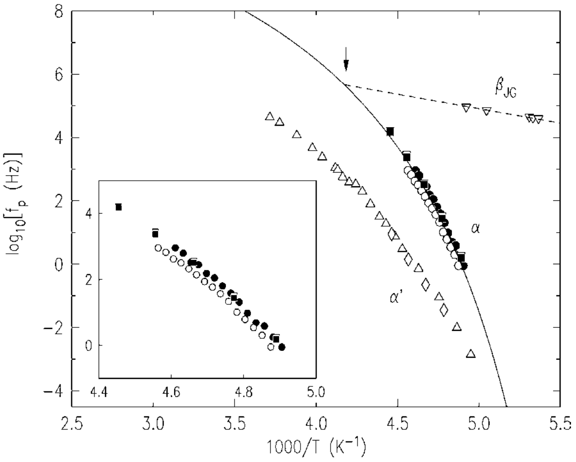

Fig. 4. Arrhenius plot of the peak frequencies. For the α relaxation, the filled symbols represent the data points for PPG-1000, and the open symbols for PPG-4000. Enthalpy and dielectric relaxation peaks are displayed by circles (C_p) and squares (ϵ), respectively. The α' peaks in ϵ of PPG-4000 (diamonds) show a good coincidence with the dielectric data of [9] (up triangles). The solid line represents the fitting results of all the α relaxation data to a single VTF equation with $T_0 = 163$ K, while the broken line does an Arrhenius fit to the β_{JG} relaxation data. The arrow in the figure denotes the decoupling temperature T_A (239 K). In the inset, the α relaxation data from this work are plotted on a larger scale to compare the enthalpy relaxation with the dielectric relaxation.

dependence is found in the dielectric case. Regarding the dielectric relaxation, it was proposed before that the lack of a molecular weight dependence is caused by the fact that the α relaxation is dominated by transient entanglement driven by hydrogen-bonding between OH end-groups of PPG [21–23]. Then, it follows from the molecular weight dependence of enthalpy relaxation times that the enthalpy relaxation also involves other type of motion such as segmental motion than the hydrogen bond kinetics.

The solid line in the figure was drawn using the fitting parameters; all the data points of the α relaxation peaks were fitted to a VTF equation, i.e. $f_p = f_0 \exp[-D/(T - T_0)]$. The fitting parameters extracted from the fit are $f_0 = 10^{12\pm0.3}$ Hz, $D = 1174 \pm 80$ K, and $T_0 = 163 \pm 2$ K. The effect of the slower enthalpy relaxation of PPG-4000 on the fitting parameters turned out to be negligible except that it may change f_0 within the error bar. Now turning to the β_{JG} process, one may define the decoupling temperature, designated as T_A, where the α and β_{JG} processes separate. By extrapolating the peak frequencies of the β_{JG} process in PPG-4000, T_A was obtained to be 239 K as shown by a arrow in Fig. 4. Such extrapolation is justified by the fact that the β_{JG} processes are well known to show the Arrhenius behavior. Possible types of decoupling were discussed before in terms of molecular cooperativity [31–34]. The significance of T_A in the distribution of relaxation times will be discussed shortly.

The temperature dependence of β, the shape parameter of the KWW function, is presented in Fig. 5. As was noted above, β of the dielectric relaxation does not show either temperature or molecular weight dependence; it has a fixed value of 0.50 in accordance with the previous results [22,23,35]. β of the enthalpy relaxation also lacks the molecular weight dependence. However, the enthalpy relaxation data shows a rather different behavior as a function of temperature; β varies linearly with T. It should also be pointed out from Fig. 5 that the enthalpic β has larger values than the dielectric β has. These results for PPG are in contrast to the case of glycerol in many ways: in glycerol, for example, the enthalpic β does not change as a fucntion of temperature. Furthermore, the value of

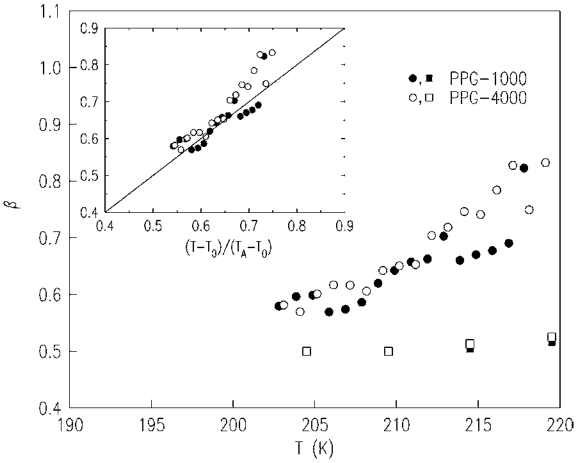

Fig. 5. The shape parameter β of the KWW function of PPG-1000 (filled symbols) and PPG-4000 (open symbols) is plotted as a function of temperature. The enthalpic β (circles) varies linearly with temperature, while the dielectric one (squares) stays constant at 0.50. The inset displays β against the normalized temperature, $(T - T_0)/(T_A - T_0)$. The solid line represents $\beta = (T - T_0)/(T_A - T_0)$. T_0 (163 K) and T_A (239 K) are the VTF temperature and decoupling temperature, respectively.

the enthalpic $\beta = 0.65$ is smaller than the dielectric value of 0.70 [36,37]. One conclusion we may draw from these observations may be that the shape of the α relaxation function associated with the glass transition is quite sensitive to the type of probes one adopts, while the average relaxation time follows more or less the same pattern regardless of the type of probes. This then brings up the question on what probe is the most fundamental one in the study of glass transtion phenomena. While the answer to this old question is yet to be given, we would maintain the position that the measurements of dynamic heat capacity should be regarded as the prime method in the investigation of glass transition, because it deals with fundamental quantities such as entropy and enthalpy.

In the inset of Fig. 5, we show the variation of the enthalpic β of PPG as a function of temperature normalized in a particular way to emphasize the role of two distinct temperatures, T_0 and T_A. It is easily seen that the data coincide reasonably well with a solid line of $\beta = (T - T_0)/(T_A - T_0)$ [38]. Although the measurements were unable to cover the whole temperature range of interest, one may still infer that the shape parameter β takes the value zero at T_0 and becomes 1 for $T \geq T_A$. Considering the fact that a universally accepted theory of relaxation for the KWW function is still lacking, one may resort to the distribution of relaxation times in interpreting the value of β. As a matter of fact, it is quite reasonable that the distribution of relaxation times (or energy barriers) follows from the size distribution of CRRs in the context of the original or extended AG theory [3,4]. Then, the inset suggests that the system would relax with a single relaxation time above T_A. Below T_A the distribution of relaxation times starts to appear and gets broader as temperature decreases. It appears that both the nonexponential relaxation and the decoupling between α and β_{JG} processes are initiated by the formation of CRRs at T_A. Below T_A the broadening of the distribution continues until the distribution width would diverge at T_0, where τ is also supposed to diverge to infinity.

In order to emphasize that the variation of relaxation times in PPG as a functioin of temperature described above is not an isolated event, we may cite a few other examples: The same behaviors of the distribution of relaxation times were found in the enthalpy relaxation of a material belonging to a different class, an ionic glass-forming liquid $[Ca(NO_3)_2]_{0.4}(KNO_3)_{0.6}$ [27,39]. Also experimentally found was a divergence at T_0 in the width of the relaxation time distribution in *o*-terphenyl and salol [28,30,40]. Again similar features were noted from a treatment based on the AG theory by Moynihan and Schroeder [41]. From the theoretical side, it may be of value to point out that there exist models predicting such features as a linear temperature dependence of β and exponential relaxation at high temperatures [42–44]. More convincingly, recent molecular dynamics simulation of a model glass-forming liquid found the same kind of exponential–nonexponential cross-over, accompanying an Arrhenius–nonArrhenius cross-over in relaxation time, at a temperature above T_g, and this cross-over was caused by the variation in potential energy barrier heights in the energy landscape of the system [45].

Fig. 6 shows the temperature dependence of the relaxation strengths. It is seen from the figure that the

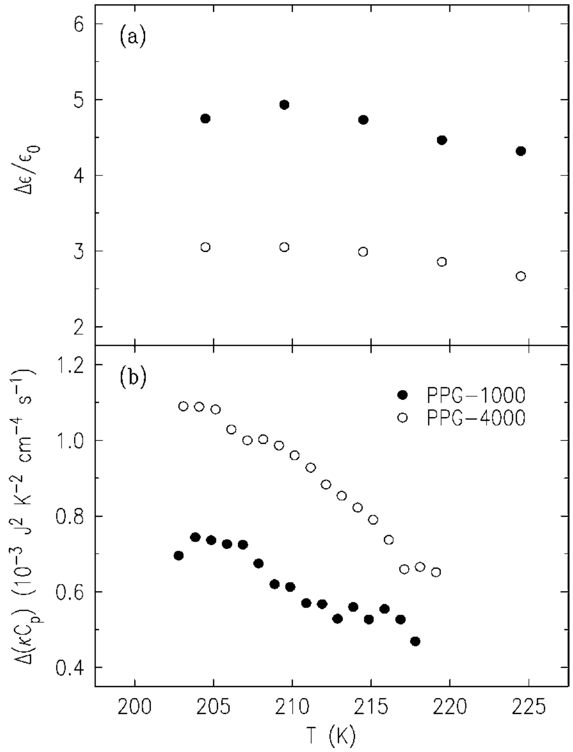

Fig. 6. The dielectric and enthalpy relaxation strengths are plotted against temperature: (a) $\Delta\epsilon$ normalized with ϵ_0 and (b) $\Delta(\kappa C_p)$ of PPG-1000 (filled symbols) and PPG-4000 (open symbols).

dielectric strength of PPG is very weakly temperature dependent, whereas the enthalpic strength is a strong function of temperature. The dielectric strengh of PPG-1000 is about twice larger than that of PPG-4000. As for the enthalpy relaxation, it is not possible to directly compare ΔC_p's of PPG-1000 and PPG-4000, because κ was not measured in this investigation. However, if we take into account the fact that thermal conductivity is generally proportional to $M_w^{1/2}$, where M_w is molecular weight, in polymers of low molecular weight, [46] the ΔC_p difference between PPG-1000 and PPG-4000 should be less than the $\Delta\epsilon$ difference. It may be of interest to note that if we linearly extrapolate ΔC_p in temperature, it approaches zero in the vicinity of T_A [47].

4. Conclusion

From the present investigation it became clear that the characteristics of the dielectric and enthalpic relaxations in the supercooled state of PPG are not the same except the behavior of the relaxation time τ. While τ follows the same pattern as a function of temperature and shows no (or little) molecular weight dependence in both cases, the shape parameter β and the relaxation strength of the two relaxations behave differently as a function of either temperature or molecular weight. β of the enthalpy relaxation decreases, or the width of the relaxation time distribution broadens, as temperature decreases; on the other hand, β of the dielectric α relaxation remains constant. The relaxation strength also remains constant as a function of temperature for dielectric relaxation, while the enthalpic strength increases as temperature is reduced. A molecular weight dependence appears strongly only in the relaxation strength.

At this stage, it appears that a comprehensive understanding of both dielectric and enthalpy relaxations in various glass-forming materials including PPG would be difficult to achieve. Nevertheless, it should be pointed out that the different behaviors of the two relaxations revealed in the present study of supercooled PPG suggest that the whole dielectric degrees of freedom of the system do not participate in the enthalpy relaxation or vice versa. This then in turn casts a doubt on any conclusion drawn from the measurements using a single dynamic probe.

Acknowledgements

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