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Anomalous behavior of secondary dielectric relaxation in polypropylene glycols

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Abstract

A surprising slow down in the dielectric secondary γ -relaxation with temperature increasing near the glass transition is confirmed for several polypropylene glycols. The peculiar behavior diminishes as the molecular weight grows. The minimal model (Dyre and Olsen 2003 *Phys. Rev. Lett.* **91** 155703) is applied successfully to describe the temperature dependences of the γ -relaxation times. The minimal model parameters are analyzed for different molecular weights. A molecular explanation of the γ -process anomaly for polypropylene glycols is proposed on the basis of the minimal model prediction.

1. Introduction

Secondary dielectric relaxations were first observed both in small rigid and in flexible molecules by Johari and Goldstein more than three decades ago [1]. These processes are still investigated intensively because they are a basic source of information about relaxation phenomena in the glassy state where the structural α -relaxation times become too long to be registered experimentally. Unfortunately, in spite of all efforts, an origin of the secondary relaxation has not been fully recognized. Finding the actual temperature dependences of dielectric secondary relaxation times can facilitate understanding molecular phenomena near the glass transition. From dielectric measurements, we can easily obtain secondary relaxation times below the glass transition temperature T_g . However, secondary relaxation times determined above T_g are usually less reliable due to strong coupling of the structural and secondary processes. For many years it has been suspected that the temperature dependences of secondary relaxation times obey the Arrhenius law, with the same apparent activation energy below as well as above T_g [2]. Some recent studies have shown that other scenarios are also possible. The difficulties mentioned in determining secondary relaxation times in the merging region have led researchers to find different descriptions for the temperature dependence of secondary relaxation times above T_g even for one material, e.g. for sorbitol [3]. Tanaka, in his discussion about the origin of secondary relaxation [4], suggested that secondary relaxation

times in the merging region should have a temperature dependence of Vogel–Fulcher–Tammann (VFT) type, reflecting the cooperative nature of this process in the coupling region. Another scenario has been observed by Corezzi *et al* [5] for two glass-forming epoxy resins. They have noticed that the temperature dependence of secondary relaxation times deviates from the Arrhenius law above T_g , i.e. just above T_g the apparent activation energy of the process decreases significantly in the narrow temperature range, and then at higher temperatures it increases and seems to return to its value for the glassy state.

Recently, Dyre and Olsen [6] showed that the well-resolved secondary relaxation for tripropylene glycol (TPG), denoted herein by the γ symbol, reveals more interesting and peculiar behavior. They found a minimum in the temperature dependence of the γ -relaxation times near T_g . Moreover, they have proposed the minimal model (MM) of the secondary relaxation, which assumes that the process can be described by an asymmetric double-well potential. The potential parameters in liquid—a barrier U and an asymmetry Δ —are temperature functions. These dependences are linear (equation (1)) because the MM applicability is limited to a narrow temperature range in a liquid state. Both of the potential parameters are fixed (equation (2)) below some fictive temperature T_f at which one regards a glassy state as fully reached when

$$U = U_0 + akT, \quad \Delta = \Delta_0 - bkT, \quad \text{for a liquid state,} \quad (1)$$

$$U = U_0 + akT_f, \quad \Delta = \Delta_0 - bkT_f, \quad \text{for a glassy state.} \quad (2)$$

Taking into account these minimal assumptions, Dyre and Olsen have derived formulae which can be reduced to temperature functions of the γ -relaxation time (equation (3)) and the maximum loss of the γ process (equation (4)),

$$\tau_\gamma = \tau_0 \exp\left(\frac{2U + \Delta}{2kT}\right) \operatorname{sech}\left(\frac{\Delta}{2kT}\right), \quad (3)$$

$$\varepsilon''_{\max\gamma} = \frac{T_0}{T} \operatorname{sech}^2\left(\frac{\Delta}{2kT}\right), \quad (4)$$

where k denotes the Boltzmann constant, as in equations (1) and (2). In order to exploit the MM capabilities fully, the seven parameters U_0 , Δ_0 , a , b , T_f , τ_0 and T_0 need to be found in the fitting procedure, but three of them, Δ_0 , b and T_f , are shared by equations (3) and (4), making the procedure more reliable.

Dyre and Olsen [6] have successfully applied their MM to describe the peculiar behavior of the secondary process in TPG. However, they have been forced to make some assumptions to find the loss γ -peak frequencies of TPG in the relaxation merging region. To increase the separation between primary and secondary relaxations, we have performed high-pressure broadband dielectric measurements on TPG at 1.8 GPa [7]. In this manner we have claimed that the temperature dependence of the γ -relaxation times for TPG undoubtedly exhibits a minimum in the vicinity of the glass transition. We have also found [8] new MM parameters for the γ process which have turned out to be more appropriate than those determined earlier by Dyre and Olsen [6]. Applying these new parameters, we have been able to describe the temperature dependence of γ -relaxation times for TPG at ambient pressure in the whole temperature range where the process is observed. Other experimental evidence for the interesting behavior has also been presented for the γ relaxation of PPG 400 [8].

In this work we examine several compounds belonging to the homologous series of propylene glycol in order to get answers: whether the materials generally reveal the mentioned peculiar behavior of the γ relaxation near the glass transition and how the molecular weight of polypropylene glycol (PPG) influences the behavior of secondary processes. Moreover, we apply the MM to describe the temperature dependence of τ_γ for the materials investigated.

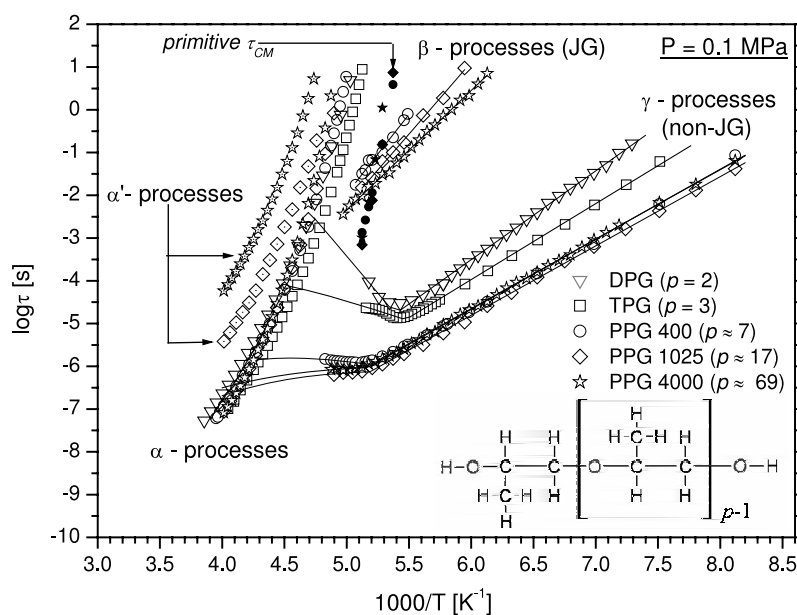


Figure 1. Dielectric relaxation map for the PPGs studied. Dielectric data for DPG [9], TPG [6, 8], and PPG 400 [8] have been published previously. In the case of the β process, the solid lines represent the fits of the experimental data to the Arrhenius law, whereas in the case of the γ relaxation the solid lines indicate approximations of the dependences $\log \tau_\gamma(1000/T)$ obtained by using the MM (equation (3)) with its parameters collected in table 1. Solid symbols denote the primitive relaxation times τ_{CM} derived from equation (6).

2. Experimental details

Herein we consider dipropylene glycol (DPG) and PPGs of molecular weights of 1025 g mol⁻¹ (PPG 1025) and 4000 g mol⁻¹ (PPG 4000) in comparison with TPG and PPG 400 studied earlier by us [8] and also analyzed in terms of the MM. We used dielectric spectra of DPG published previously by us [9]. The other materials, PPG 1025 and PPG 4000, were purchased from Aldrich. Isobaric measurements of the complex dielectric permittivity, $\varepsilon^*(\omega) = \varepsilon'(\omega) - i\varepsilon''(\omega)$, were made using the Novo-Control Alpha dielectric spectrometer at ambient pressure in the broad band from 10⁻² to 10⁹ Hz. The sample temperatures in the range from 123.15 to 249.15 K were controlled by a Quatro System using a nitrogen gas cryostat. The temperature stability was better than 0.1 K.

3. Results and discussion

The PPGs that were investigated exhibit several relaxation processes at ambient pressure depending on their molecular weight (figure 1). The processes are denoted in order of increasing relaxation peak frequency by the following symbols: α' —the low-frequency process, the so-called normal mode; α —the primary, structural relaxation; and β and γ —the secondary relaxations. However, herein we focus our attention on the secondary processes, especially on the peculiar behavior of the faster of them (γ) near T_g . In order to obtain the correct relaxation times of the secondary processes, it is necessary to find the best fits of entire dielectric spectra. The dielectric spectra of PPGs after subtraction of the dc conductivity

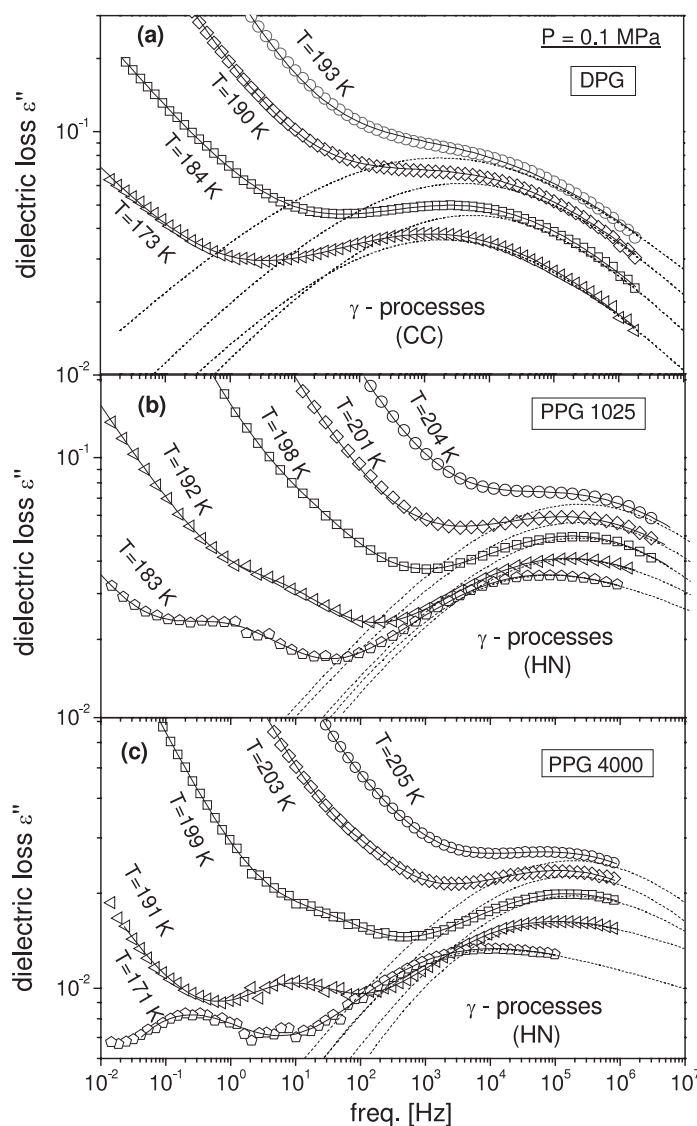


Figure 2. Selected dielectric loss spectra of the γ relaxation near the glass transition at ambient pressure and at different temperatures for DPG (a), PPG 1025 (b), and PPG 4000 (c). The solid lines indicate the fits of the dielectric spectra. The dotted lines represent the fits of the γ processes.

are described by superpositions of commonly used Havriliak–Negami (HN), Cole–Cole (CC), and Debye functions. The asymmetrically broadened α -peaks are fitted to the HN functions. The secondary processes are usually fitted by the CC functions, such as in the case of the β relaxation. However, similarly to PPG 400 [8], the γ processes in PPG 1025 and PPG 4000 are better approximated by the HN function (figures 2(b) and (c)).

The secondary β -relaxation, well resolved for PPG of larger molecular weight, reveals Arrhenius behavior. The interesting regularity is established for the apparent activation energy of the β process ΔE_β . The energy obtained by fitting $\tau_\beta(T)$ to the Arrhenius law (solid straight lines in figure 1) decreases as the molecular weight of PPG grows. The values ΔE_β are equal

Table 1. Fitting parameters of the minimal model obtained for the γ process in the analyzed PPG. Values of the MM parameters for TPG and PPG 400 are taken from our earlier paper [8]. The potential parameters U and Δ are calculated from equation (2).

Fitting parameters	DPG	TPG	PPG 400	PPG 1025	PPG 4000
$\log \tau_0$	-16.19	-14.89	-14.66	-14.76	-14.70
U_0/k (K)	-8100	-2237	-1044	-11	52
Δ_0/k (K)	2958	3039	3371	2893	2532
a	69.38	34.56	24.80	19.33	19.10
b	12.00	12.77	14.54	12.67	10.87
T_0 (K)	111	130	48	22	8
T_f (K)	186	183	192	193	194
U/k (K)	4774	4079	3730	3716	3747
Δ/k (K)	732	705	572	449	429

to 71.4 kJ mol⁻¹, 64.2 kJ mol⁻¹ and 53.4 kJ mol⁻¹ for PPG 400, PPG 1025 and PPG 4000, respectively.

In contrast to the β process, the faster secondary relaxation (γ) exhibits very intriguing non-Arrhenius behavior observed for each analyzed PPG in the vicinity of T_g (figures 1 and 3(a)). The special feature of the phenomenon is a slow down in the γ relaxation with increasing temperature near T_g in comparison with the γ -relaxation behavior predicted by extrapolating the low-temperature Arrhenius dependence to higher temperatures. The minimum in the dependence $\tau_\gamma(T)$ is clearly formed and surprisingly deep for oligomers DPG and TPG (figures 2(a) and 3(a)) and becomes shallower as the molecular weight of PPG increases (figures 2(b), (c) and 3(a)). It should be emphasized that the peculiar behavior for small PPGs, which exhibit strong coupling of the α and γ processes in the merging region, has been confirmed irrefutably by pressure measurements [7]. The separation of the processes for larger PPGs increases significantly [10]. We have established that it is about three decades larger for PPG 4000 in relation to that for DPG (figure 4). The greater separation observed for larger PPGs (400, 1025 and 4000) considerably facilitates finding the actual dependences of $\tau_\gamma(T)$ near T_g . Therefore, we can claim that the interesting behavior of the γ relaxation is a common property of PPGs.

The temperature dependences of the relaxation time (figure 3(a)) and the maximum loss for the γ process (figure 3(b)) can be successfully fitted to the MM formulae (equations (3) and (4)). The MM parameters are collected in table 1. R -squared measures of goodness for the MM approximations of the dependences $\log \tau_\gamma(1/T)$ are satisfactory, from 99.78% for DPG to 99.96% for PPG 4000. As can be seen in the inset of figure 3(a) the MM parameters yield the consistent MM predictions in spite of putting only necessary constraints on the fitting procedure (i.e. sharing the parameters Δ_0 , b , and T_f by equations (3) and (4) and enabling only the parameter U_0 to be negative). The analysis of the potential parameters U and Δ calculated from equations (1) and (2) with the MM parameters (U_0 , Δ_0 , a , b , T_f) leads to several conclusions.

At first it can be easily seen in the figure 5 that the potential parameters U and Δ have fixed values in glass (equation (2)) where the barrier U is lowest and the asymmetry Δ is highest. Heating above the fictive temperature T_f indicates that, in accordance with equation (1), the barrier increases linearly, whereas the asymmetry decreases and reaches its minimal value, $\Delta = 0$. However, the linear dependence $\Delta(T)$ given by equation (1) seems to be insufficient to predict the exact temperature of merging of the α and γ relaxations [8]. Moreover, the splitting temperatures T_s , derived from the condition $\Delta = 0$, correspond roughly to the temperatures

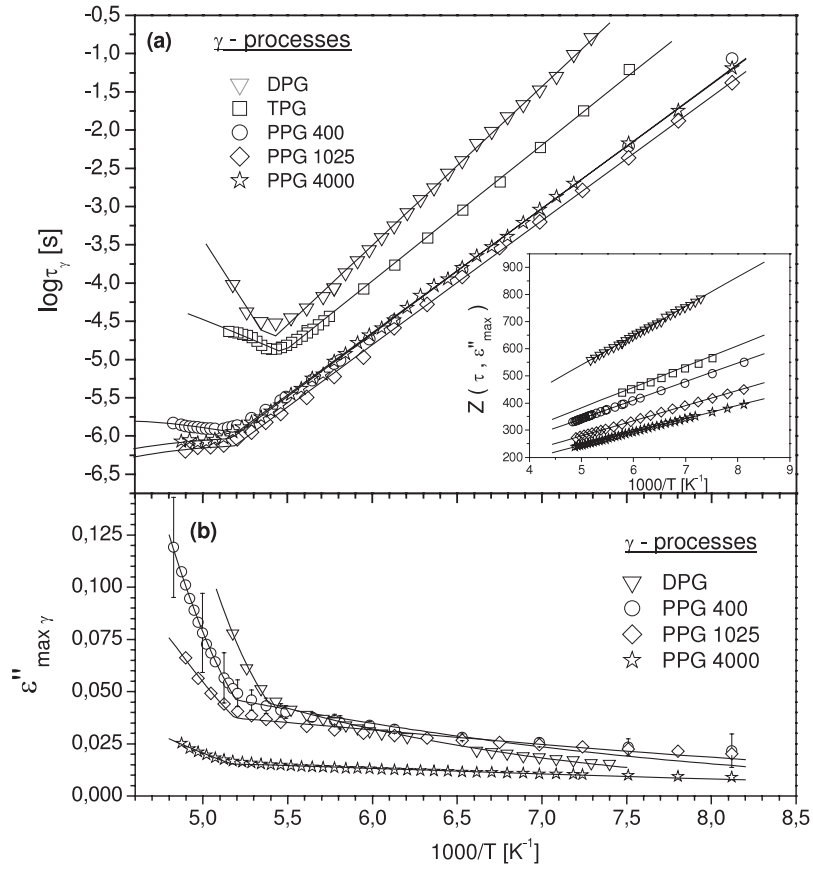


Figure 3. The temperature dependences of the relaxation times (a) and the loss peak maxima (b) are depicted for the γ process in PPG. Solid lines indicate their fits obtained from the minimal model (equations (3) and (4)). The inset of (a) shows a test of the MM predictions. Open symbols denote values of the expression $Z(\tau_\gamma, \epsilon''_{\max \gamma})$ calculated from its definition given by equation (6) in [6] using our experimental temperature data for the γ -relaxation time τ_γ and the maximum loss of γ process $\epsilon''_{\max \gamma}$. Solid lines represent the MM predictions, $Z = (a\Delta_0 + bU_0)/T$ (also given by equation (6) in [6]), established using our MM parameters.

T_{is} at which the MM extrapolations of $\log \tau_\gamma(1/T)$ intersect the dependences $\log \tau_\alpha(1/T)$, e.g. $T_s = T_{is} + 35$ K for DPG. Their accordance becomes better for PPGs of larger molecular weight, e.g. $T_s = T_{is} - 10$ K for PPG 4000.

Analyzing the potential parameters found for the γ relaxation in the glassy state (see table 1) in the order of the molecular weight of PPG, one can observe some regularity. Both U and Δ decrease as the molecular weight of PPG grows (figure 6). The parameters vary slightly for PPGs of higher molecular weights. A comparison between the double-well potentials for PPGs of extreme molecular weights, which are plotted in the inset of figure 6, shows that the barrier U and the asymmetry Δ for DPG are about 30% and 70%, respectively, which are larger than those for PPG 4000.

It is worth noting that the logarithm of τ_γ derived from equation (3) can be expressed as the Arrhenius term diminished by $f(\Delta, T) = \log_{10}[1 + \exp(-\Delta/kT)]$. In glass, the exponent Δ/kT is relatively large and $f(\Delta, T)$ varies slowly with temperature. Then, the term $f(\Delta, T)$ can be neglected and equation (3) tends to the Arrhenius law. As can be seen in figure 6, the

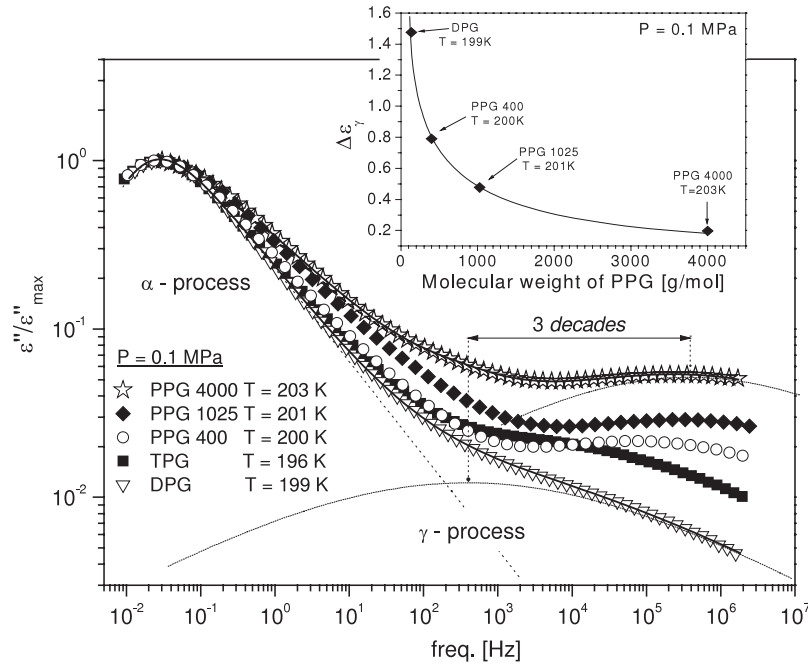


Figure 4. Selected dielectric loss spectra of DPG, TPG, PPG 400, PPG 1025, PPG 4000 with the same α -peak frequency show that the separation between the α - and γ -processes increases as molecular weight of PPG grows. The solid lines represent the fits of the dielectric spectra. The dashed line indicates the fit of the α -process for DPG, whereas the dotted lines denote the fits of the γ -processes for DPG and PPG 4000. The inset shows the dielectric strength of the γ relaxations for the selected spectra versus molecular weight of PPGs.

Arrhenius activation energies ΔE_γ below T_f are really close to the barriers U for all the PPGs that were studied. The relative deviations of the barrier U from the energy ΔE_γ do not exceed 2%. Therefore, the minimal model can be treated as some generalization about the Arrhenius law.

On the basis of the MM and extended coupling model (CM) [11] predictions, some hypothesis concerning a molecular origin of the γ relaxation can be formulated. Using the Ngai and Paluch criterion [12] based on the extended CM we can classify the secondary relaxations exhibited by PPGs as: (i) a Johari–Goldstein (JG) process originating from the motions of entire molecules or essentially all molecular parts, even in the case of nonrigid molecules; and (ii) a non-Johari–Goldstein (non-JG) process reflected in the rotations of some atom groups in molecules. The genuine JG relaxation is considered to be a precursor of structural relaxation, therefore its relaxation time τ_{JG} should correspond well to the primitive relaxation time τ_{CM} of the CM [12], i.e.

$$\tau_{JG} \approx \tau_{CM}. \quad (5)$$

The primitive relaxation time at any temperature can be calculated from the parameters τ_α and $\beta_{KWW} = 1 - n$ of the Kohlrausch–Williams–Watts (KWW) function [13], $\phi(t) = \exp[-(t/\tau_\alpha)^{\beta_{KWW}}]$, where $0 < \beta_{KWW} \leq 1$, used to fit the α -loss peak at the same temperature, by the CM equation

$$\tau_{CM} = (t_c)^n (\tau_\alpha)^{1-n} \quad (6)$$

where t_c is equal to 2 ps for small molecular and polymeric glass formers [14].

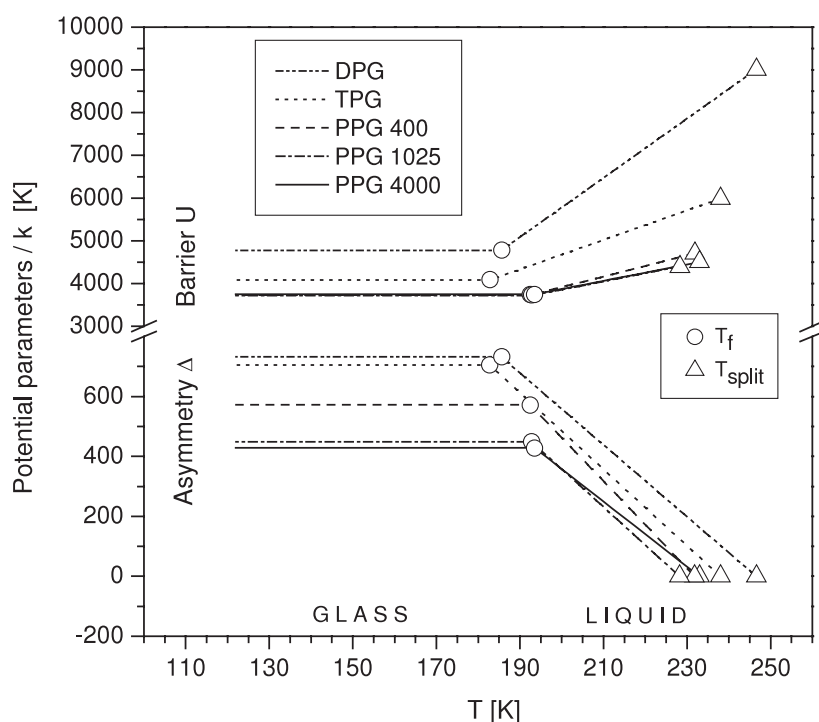


Figure 5. Analysis of the asymmetric double-well potential parameters, U and Δ , for the γ processes in studied PPGs. The temperature dependences of the potential parameters are calculated using equations (1) and (2). Open circles indicate the fictive temperatures T_f whereas open triangles represent the splitting temperatures T_s .

Comparing the primitive relaxation times τ_{CM} calculated at several temperatures (solid symbols in figure 1) with the β -relaxation times τ_β found at the same temperatures, one can classify the β relaxations of PPGs as the JG processes. As shown for DPG [9], TPG [12] and PPG 400 [8], and as established similarly for PPG 1025 and PPG 4000,¹ the γ relaxations of the materials do not meet the criterion (equation (5)), i.e. the processes can be treated as non-JG relaxations. In accordance with this CM prediction, one can assume that the γ relaxation of PPG originates from some full or partial rotations of hydroxyl groups or some motions of terminal molecular units containing OH groups. This assumption is reinforced by decreasing the dielectric strength of the γ process, $\Delta\epsilon_\gamma$, with increasing molecular weight of the PPG (see the inset of figure 4) which can reflect the decrease in the number of OH groups as the molecular weight of PPG grows. It seems that application of the minimal model to the description of the non-JG γ relaxations of PPGs is not false, especially since the reorientations of terminal OH groups are not simple intramolecular motions, but they are strongly coupled with intra- and intermolecular hydrogen bonding (between the OH groups as well as between the ether and OH groups). Consequently, the motions of terminal units of PPG molecules are dependent on the structure, which is affected by the thermodynamic conditions. Moreover, the minimal model was first applied to the secondary relaxation of TPG at ambient pressure by Dyre and

¹ To calculate τ_{CM} (equation (6)) we used the Kohlrausch stretch exponent $1 - n = 0.55$ for PPG 4000 published in [10], as well as $1 - n = 0.57$ for PPG 1025 obtained by fitting the loss α -peak at $T = 204.15$ K taken from among our experimental data to equation (10) in [11] which transforms the time-dependent KWW function to the frequency domain.

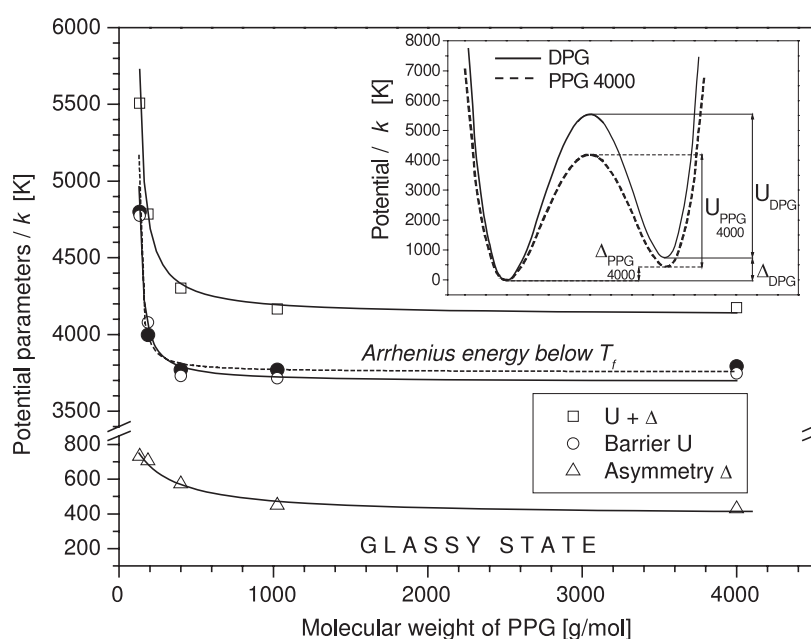


Figure 6. The potential parameters in the glassy state versus molecular weight of PPG. Solid circles indicate the activation energies obtained by fitting the γ -relaxation data below T_f to the Arrhenius law. Comparison of the asymmetric double-well potential for two analyzed diols of extreme molecular weights (DPG and PPG 4000) is presented in the inset.

Olsen [6]. This secondary process, called γ by us, has been classified as not the genuine JG relaxation [12], whereas a new, additional secondary process [15], which emerges from the excess wing under high pressure, has been recognized as true JG relaxation [12].

In the glassy state the motions of OH groups require relatively low constant activation energy in the wide temperature range. When the temperature is sufficiently high, near the glass transition and further in the liquid state, molecular motions become more and more chaotic and the degree of molecular collisions grows considerably. Then the reorientations of OH groups are hindered in the liquid state, and consequently they require higher activation energies which are dependent on temperature. The proposed molecular scenario corresponds to the temperature dependence of the potential barrier U determined in accordance with the MM (see figure 5). Moreover, it is possible that H bonds formed by PPG additionally influence the slow down in the γ relaxation near T_g . In the case of PPG the OH groups are mainly responsible for hydrogen bonding. The number of OH groups per volume unit rapidly decreases as the molecular weight of PPG grows, because each of the compounds possesses only two OH groups. Therefore, the larger depth of the minimum in $\tau_\gamma(T)$ as well as the higher barrier U observed above T_f for oligomers DPG and TPG compared to those found for larger PPG (see figures 3(a) and 5) can reflect a stronger suppression of the reorientations of OH groups by H bonds in the case of smaller PPG. However, further investigations are required to confirm the hypothesis.

4. Conclusions

The molecular dynamics of low-molecular-weight dipropylene glycols (DPG) as well as poly(propylene) glycols (PPG 1025, PPG 4000) were studied by dielectric spectroscopy.

Secondary relaxations were at the center of our attention. The results that were obtained are compared to those reported for TPG and PPG 400 [8]. The most important results of our analysis can be summarized as follows:

- Dielectric investigations performed at both atmospheric and high pressures show that the anomalous behavior of γ relaxation near the glass transition is the real physical phenomenon characteristic for poly(propylene) glycols (DPG, TPG, PPG 400, PPG 1025, and PPG 4000). This implies that the secondary γ relaxation of PPG reflects some molecular motions which are sensitive to the liquid–glass transition.
- These motions are rather intramolecular, e.g. some reorientations of OH groups, because the analysis based on the extended coupling model showing that the γ relaxation is not a genuine JG process. However, the motions of OH groups are affected by a hydrogen-bonded network. Thus the sensitivity of the non-JG relaxation to the glass transition can be related with the effect of thermodynamic conditions on the degree of H bonds.
- The behavior of the γ processes changes with the molecular weight of PPGs. The minimum in the dependence of $\tau_\gamma(T)$ becomes shallower as the molecular weight of PPG grows. This can be related to stronger interactions between the molecules of smaller oligomers of propylene glycol by hydrogen bonding (between the terminal OH groups as well as between the ether and hydroxyl groups) than in the case of PPGs of larger molecular weight.
- The temperature dependences of the γ relaxation times for all PPGs that were studied can be described successfully by Dyre and Olsen's minimal model. The double-well potential parameters, the barrier U and the asymmetry Δ decrease as the molecular weight of PPG grows, which can reflect the smaller number of H bonds per unit volume in the case of polymers.

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