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# Influence of Molecular Characteristics on Dielectric Relaxation of Propylene Glycol Oligomers

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**Summary:** The relaxation dynamics of polypropylene glycol oligomers having different end groups was studied by broadband dielectric spectroscopy (10 mHz to 10 GHz) in the temperature interval 110-350 K, above and below the glass transition. The effects produced on structural and secondary relaxations by the different end groups are discussed.

**Keywords:** glass transition; oligomers; relaxation; structure-property relation; terminal groups

## Introduction

The relaxation dynamics of a polymeric system is characterised at least by two processes, generally labelled as main or structural (α) and secondary (β). The relation between molecular motions, both of the whole molecule and of chain segments or terminal groups, and the response to an external electric field, i.e. dielectric permittivity, is described by the correlation function of the dipole moment resulting from the sum of the microscopic dipoles contained in a correlation sphere [1]. Consequently, the influence on the permittivity of the detailed microscopic structure is averaged by the complex interactions of a relative large number of molecules. However, since dielectric spectroscopy can investigate the dynamics of polar complex systems in the liquid and glassy state over a frequency interval of 15 decades, and it senses directly the molecular motion through the changes of the charge distributions, it is a powerful spectroscopic technique and it can be used for this type of investigation.

Here we analyse some aspects of the dynamics of some propylene glycol oligomers having the same polar repeating unit but different polar groups at the end of the molecular chain. Besides our experimental data, the results reported in the literature have been also considered [2,3,7-10] in order to provide a more general picture of the observed phenomenology.

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## Experimental

Commercial samples of poly(propyleneglycol) diglycidyl ether, PPGDE, with different average number of monomer units, *N*=4.3 and *N*=8.8 (molecular weight M.W.=380 and M.W.=640, respectively for PPGDEI and PPGDEII, by Aldrich), of poly(propyleneglycol) PPG with *N*=7 (M.W.=400, by Fluka), poly(propyleneglycol) dibenzoate, PPGDB, with N=3 (M.W.=400 g/mol by Aldrich) and poly(propyleneglycol) dimethyl ether, PPGM, with N=2 (M.W. 162 g/mol) were measured without further purification. Each investigated system is composed by oligomers with the same repeating unit (- $OCH(CH_3)(CH_2)$-), but different terminal groups. In particular, end groups were chosen with different dipole moment value, μ, and different steric hindrance.

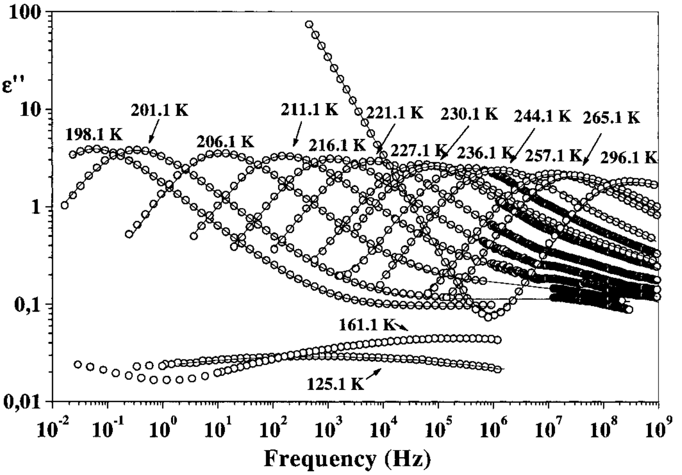

Figure 1. Dielectric loss spectra for PPGDE2 (open symbols) at some temperatures above and below $T_g$. The line are the fit performed as described in the text.

Dielectric measurements were performed in the frequency interval ($10^{-2}$-$10^{10}$ Hz) by employing three different experimental techniques: gain-phase frequency response analysis, by means of the Alpha spectrometer by Novocontrol; impedance spectroscopy, by the autobalanced bridge HP4194A impedance analyser (by Hewlett-Packard); reflectometric technique, with the network analysers HP8753E and. The temperature of the sample was controlled by a conditioned flux of dry nitrogen and isothermal measurements in the interval 110-350 K at temperatures stabilised within ± 0.1 K were performed.

## Results

Dielectric spectra of the studied systems show the existence of two main relaxation peaks (Fig.1): an asymmetric one (structural or α- relaxation peak) and a second one located at higher frequency (secondary or β- relaxation peak). The first peak is very sensitive to temperature changes, and moves quickly toward lower frequencies as the glass transition is approached; the second one is less temperature dependent and remains detectable in the frequency interval above $10^{-2}$ Hz also below $T_g$. In the spectra no signs of normal-mode relaxation process are shown, whereas below $T_g$ in PPGDE2, PPG, and PPGDB spectra a further relaxation process occurring in the frequency interval between the α- and β- processes is present. The characterisation of this last process is out of the scope of this work and consequently is not reported here.

Dielectric relaxation spectra were fitted by the superposition of two Havriliak-Negami (HN) functions:

$$\varepsilon(\omega)-\varepsilon_\infty=\frac{\Delta\varepsilon_\alpha}{\left[1+(i\omega\tau_\alpha)^{1-\alpha_\alpha}\right]^{\beta_\alpha}}+\frac{\Delta\varepsilon_\beta}{\left[1+(i\omega\tau_\beta)^{1-\alpha_\beta}\right]^{\beta_\beta}} \qquad (1)$$

where $\varepsilon_\infty$ is the unrelaxed permittivity, $\Delta\varepsilon_i$, $\tau_i$, $\alpha_i$, and $\beta_i$ are the dielectric strength, relaxation time and shape parameters related to the *i*-process (i=α, β), respectively. Moreover, to take into account for the low frequency contribution at high temperature due to the ionic conductivity, the term $\sigma/(i\omega\varepsilon_0)$ (where $\varepsilon_0$ is the vacuum permittivity) was added to Eq. 1 (see Fig.1 for loss spectra of PPGDE2 with the fit curves). Finally, a further HN function was added to fit the relaxation process appearing in PPGDB, PPG, and PPGDE2 spectra below $T_g$. For each process the frequency of the loss peak, $\nu_m$, was chosen as characteristic dynamic variable and was calculated by the HN parameters

$$\nu_m=\frac{1}{2\pi\tau}\cdot\left\{\frac{\sin\left[\frac{(1-\alpha)\pi}{(2+2\beta)}\right]}{\sin\left[\frac{(1-\alpha)\beta\pi}{(2+2\beta)}\right]}\right\}^{\frac{1}{1-\alpha}} \qquad (2)$$

The temperature dependence of the relaxation frequency of the α- loss pea, $\nu_m^\alpha$, (Fig.2a) is well reproduced by the Vogel Fulcher Tamman (VFT) equation

$$\nu_m^\alpha = \nu_0^\alpha \exp[-DT_0/(T-T_0)] \qquad (3)$$

where $\nu_0^\alpha$ is the frequency in the high temperature limit, $T_0$ is the Vogel temperature, D is the so-called strength parameter. The parameters obtained by fitting the relaxation time data with the VFT equation are reported in Tab. 1. The glass transition temperature, $T_g$, is determined as the temperature at which the relaxation is 100s. We observe that PPG and PPGDE samples have very similar values of $T_g$, whereas the $T_g$ value of PPGM is smaller for about 60 K, and that of PPGDB is greater of about 30 K. Accordingly, also $\nu_0^\alpha$ value changes a lot from PPG to PPGM or PPGDB samples, whereas the $\nu_0^\alpha$ values for PPG and PPGDE samples are similar.

In Fig. 3a the dielectric strength data of the α- relaxation, $\Delta\varepsilon_\alpha$, versus $T_g/T$ are reported: the greatest values of relaxation strength value are those of PPGDE1 and the smallest are those corresponding to PPGM and PPGDB.

In Fig. 2b we report the frequency of the maximum of the loss peak of the β- relaxation process, $\nu_m^\beta$, which is well described by the Arrhenius equation

$$\nu_m^\beta = \nu_0^\beta \exp[-\Delta E_\beta/(RT)] \qquad (4)$$

where R is the molar gas constant, $\nu_0^\beta$ is the relaxation frequency in the high temperature limit, and $\Delta E_\beta$ is the activation energy. The values of the activation energy and of $\nu_0^\beta$ are

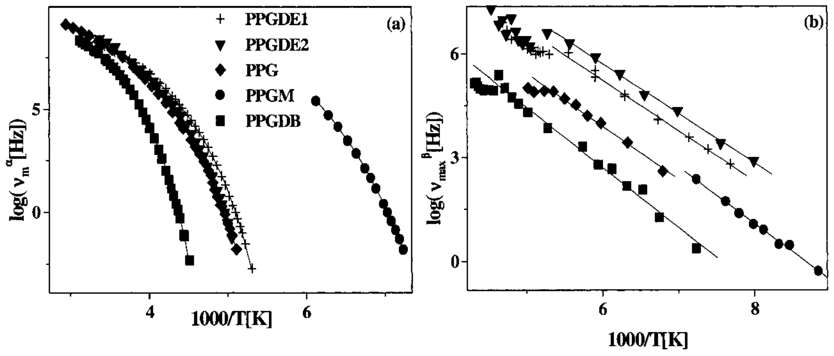

Figure 2. (a) Frequency of the loss peak for (a) structural and (b) secondary processes. Symbols refer to the same systems in both figures.

Table 1. Characteristic parameters of structural and secondary relaxation processes (see text).

| | $\nu_0^\alpha$ | D | $T_0$ | $T_g$ | $\nu_0^\beta$ | $\Delta E_\beta$ | $\Delta E_\beta/(RT_g)$ |
|---|---|---|---|---|---|---|---|
| | [THz] | | [K] | [K] | [THz] | [kJ/mol] | |
| PPG400 | 1.9±0.3 | 8.5±0.2 | 156±1 | 194±3 | 10±4 | 29±1 | 18±0.9 |
| PPGDE1 | 1.4±0.5 | 7.8±0.23 | 153.6±0.7 | 189±5 | 90±40 | 27.9±0.6 | 17.7±0.7 |
| PPGDE2 | 0.9±0.3 | 6.7±0.1 | 162.1±0.4 | 194±5 | 200±60 | 27.5±0.6 | 17±0.6 |
| PPGM | 64±20 | 9.5±1 | 109±6 | 136±6 | 1000±500 | 31.26±1 | 27.6±0.9 |
| PPGDB | 27±9 | 8.2±0.2 | 181.4±0.9 | 221±5 | 10±3 | 32±1 | 16.8±0.3 |

reported in Tab. 1. All the systems show activation energy of about 30 kJ/mol, in agreement with previous studies on PPG oligomers [2,3], while the value of $\nu_0^\beta$ changes by one order of magnitude from PPG to PPGDE2. Around $T_g$, the temperature dependence of $\nu_m^\beta$ seems to depart from the Arrhenius behaviour, since $\nu_m^\beta$ shows a weak temperature dependence just below $T_g$, which is enhanced just above $T_g$. Really, in the region near $T_g$ it is difficult to take information on the β- relaxation since it is often hidden under the high frequency tail of the α- relaxation peak. For our samples, β-relaxation is quite not detectable for PPG and PPGM and it appears as a shoulder at high frequency for PPGDB and PGDE. When the relaxation are very close to each other, different fitting equations have been proposed [4-6], which provide appreciable different results in the merging region, where the relaxation peaks are closer than two frequency decades. However, since for PPGDE and PPGDB samples the α- and β- relaxation peaks in the region around the glass transition are separate for more than 2 decades, we

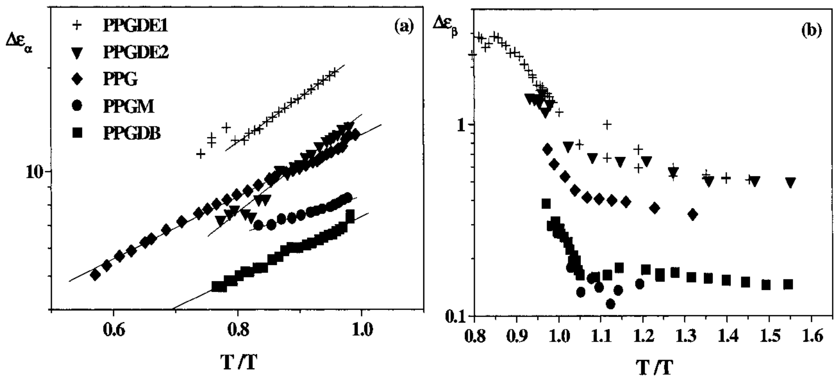

Figure 3. Relaxation strength of the (a) structural and (b) secondary relaxation process.

have confidence that the behaviour $\nu_\beta$ vs. temperature near $T_g$ is a true physical feature. In agreement with the above remarks recent findings on two polyalcohols showed that in these systems the Arrhenius dependence of secondary relaxation times is no longer valid [11]. Concerning the dielectric strength of the β- relaxation, $\Delta\varepsilon_\beta$, versus $T_g/T$ (Fig. 3b) we observed a smaller value of relaxation strength in the case of PPGDB and PPGM, and the same relaxation strength for the two samples of PPGDE.

## Discussion

*α- relaxation*

The relaxation strength is related to different microscopic features such as the value of the mean square dipole moment involved, intermolecular interactions, and molecular packing [1]. Therefore, the value of $\Delta\varepsilon_\alpha$ and its temperature dependence are different for each system (Fig. 3a). However, it is not easy to single out the effect of each microscopic feature. Evidences for the influence of end group on relaxation dynamics, also called finite size effects, have been reported for PPG of low molecular weight [12]. In fact, in PPG compounds, the dielectric contribution from the hydroxyl end dipoles cannot be neglected in comparison with the dipole moment in the polymeric backbone. Nicolai and Floudas found such a contribution by evaluating the so-called temperature corrected total strength, $T\Delta\varepsilon_T$, an average quantity proportional to the mean square dipole moment per unit volume [12]. In fact, they found that $T\Delta\varepsilon_T$ is almost constant at high molecular weights, where the contribution from the dipoles of the end groups is less significant, whereas it increases at low molecular weights where the influence of end groups is more significant. In our system we revealed finite size effects by analysing two different relaxation parameters, the relaxation strength of structural relaxation, $\Delta\varepsilon_\alpha$, and the Vogel temperature, $T_0$. In particular, we found that $\Delta\varepsilon_\alpha$ for the two PPGDE compounds decreases as molecular weight increases, according to the minor role that end group have in relatively long oligomers. In fact, in the hypothesis that molecules do not fold up, the contribution from the strong dipole moment, μ, of the epoxy groups to the mean square dipole moment per unit volume becomes less important as the number of the repeating units increases. Interestingly, the ratio of $\Delta\varepsilon_\alpha$ of PPGDE1 to $\Delta\varepsilon_\alpha$ of

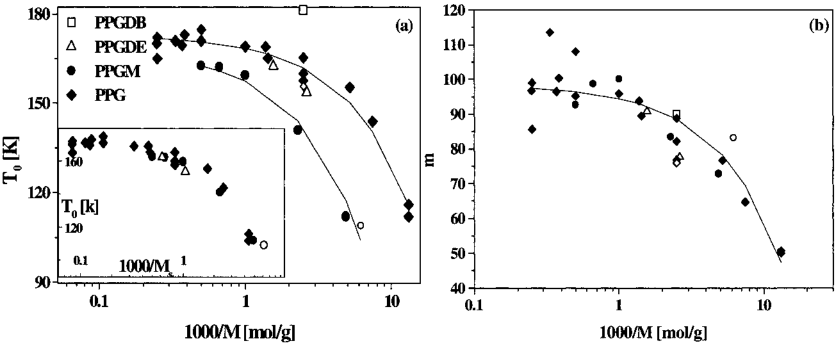

Figure 4. (a) $T_0$ versus 1000/M. The lines are the fit with the law $T_0$*-K/M. (b) Fragility as function of 1000/M. In both graph the lines are the fit with the law C-K/M. Inset: values of $T_0$ as a function of rescaled value of molecular weight, $M_s$ (see text). Correspondence between symbols and systems is the same in all figures. Closed symbols refer to literature data [2,3,7-10].

PPGDE2 is about 1.45 and the ratio of the density of the end groups of the two systems is about 1.56, which confirms the influence of end groups.

Moreover, also the value of the Vogel temperature $T_0$ is influenced by the molecular structure and in particular by finite size effects (Fig. 4a). In fact, $T_0$ depends on the molecular weight, M, according to the Fox-Flory relation [13]

$$T_0 = T_0^* - K / M \tag{5}$$

where $T_0$* is the temperature in the limit of infinite molecular weight, and K is a constant. In particular, we can compare the behaviour for the compounds with methyl (PPGM) and hydroxyl (PPG) end groups over a wide interval of molecular weight values. For these systems we obtain comparable values of $T_0$*, 173 for PPG and 168 for PPGM, respectively, but the values are of K is different as K is 4330 for PPG and 10300 for PPGM, respectively. This result means that $T_0$ of PPG approaches the asymptotic value $T_0$* for lower molecular weight with respect to $T_0$ of PPGM. A possible explanation is that PPG compounds behave as they have an effective greater value of molecular weight, due to the strong and directional H- bond interaction. In fact, the H-bond interaction can be the cause of a strong correlation between different PPG molecules, which behave as they have a greater molecular weight. However, comparing the results of PPG compounds to those of PPGDE we note that the value of $T_0$ for PPG of molecular weight 400 is similar to that of PPGDE1 (M.W. 380), being the difference within the experimental error (Tab. 1). This result leads to the conclusion that, besides H-bonds interaction, also strong dipolar interactions among the end result in an effective greater molecular weight. The effective molecular weight of PPG and PPGDE can be estimated. In fact, for PPGM the effective and real molecular weight coincides as it has weakly polar end groups, and consequently weak dipolar interaction between them. Then, provided that differences in the $T_0$ values of the studied systems can be explained in terms of effective molecular weight, molecular weight values of PPG and PPGDE can be scaled in order to shift $T_0$ data of PPGDE and PPG and superimpose them over those of PPGM. Indeed, this is possible by multiplying the molecular weight of PPG by a factor 3 (inset in Fig. 4a). The new values of molecular weight for the compounds of PPG correspond to their effective molecular weights, in other terms this means that on average three molecules of PPG are strongly co-ordinate due to H-bonds among end groups. For PPGDE a similar analysis is not completely reliable since only two values of $T_0$ are available; however, a shift factor of the same order of magnitude of that of PPG is sufficient to superimpose the data of PPGDE over those of PPGM. Finally, the analysed sample of PPGDB, which has a relatively low molecular weight (400 g/mol), has the greatest value of $T_0$ which is even greater than the value of $T_0^*$ of PPG and PPGM. Since the differences of the polar characteristics of the end groups of PPGDB and PPG or PPGDE cannot justify the result for PPGDB, we conclude that the different behaviour is of intramolecular nature, originating from the greater size of the benzoate group with respect to the others.

In Fig. 4b the value of the parameter, $m=d(\log\tau)/d(T_g/T)\,|_{T=T_g}$, which is a measure of the „fragility“ of the system [14], is shown as a function of 1000/(M). The fragility of glass former is a characteristic that has been related to the capability of the system of maintaining short range order against temperature effects (see [14] and reference therein), or equivalently it has been related to the number of configurations that the system can assume [15]. In Fig. 3b, a clear dependence of fragility on the inverse of molecular weight is observed; in particular, the fragility increases with molecular weight, i.e. with the number of repeating units. Since increasing the number of repeating unit in a chain increases also the number of their possible arrangement (configurations), as a consequence a greater fragility can be expected for longer oligomers. In the determination of the molecular configurations also intermolecular interactions, which in our case can be varied by changing end groups, have to play a role. Anyway, no systematic differences on the fragility values can be observed by changing the end groups. However, we know that the role of end groups is more important for lower molecular weights but unfortunately in this conditions we have only a few and scattered data points not sufficient for reliable conclusions.

### *β- relaxation*

The characteristic frequency of β- relaxation process below $T_g$ shows an Arrhenius behaviour (Eq. 4), related to activated processes over an energy barrier, $\Delta E_\beta$, to be overcome from the relaxing units. The activation energy has the same values for the two PPGDE samples, and it is a little greater for the other compounds; in particular the greatest value is observed in PPGDB. For almost all compounds the differences in the value of the activation energy can be explained with the hypothesis that the β- relaxation reflects the motion of the end groups. In fact, the two compounds of PPGDE have the same end group and the same activation energy; in PPG the existence of H-bonds between end groups can explain the greater value of activation energy with respect to that of PPGDE; for PPGDB the great inertia of the benzoate group can explain the greatest value of $\Delta E_\beta$. However, for PPGM we have a large value of activation energy, which is not supported by considering the β- relaxation due to the motion of the almost free methyl end group. Moreover, considering the ratio $\Delta E_\beta/(RT_g)$, which is the activation energy normalised to the thermal energy at the glass transition, a great difference appears in the value of the ratio for PPGM and the others systems (Table 1). Again, this result suggests for the origin of the β- relaxation of PPGM a microscopic mechanism, which is different to those of the other systems.

Some interesting conclusions can also be drawn from the values of the relaxation strength for the β- process (Fig. 3b). $\Delta\varepsilon_\beta$ below $T_g$ is the same for the two samples of PPGDE, insensitive to the change of molecular weight, and is smaller for PPG, PPGM and PPGDB. Since the means square dipole moment of the epoxy group is larger than for hydroxyl group, again these results can be explained considering the motion of the end group as the origin of the β- relaxation. An exception is PPGDB, which though having a great value of mean square dipole moment associated to the end group has the lowest value for $\Delta\varepsilon_\beta$ like PPGM.

## Conclusion

The nature of the end group in low molecular mass oligomers affects the relaxation dynamics. Concerning the $\alpha$- relaxation it was found that end group characteristics influence both the value of $T_0$ and dielectric strength; moreover, an increase of fragility with molecular weight is found. The analysis of the dependence of $T_0$ on molecular weight for PPGDE and PPG indicates that molecules are strongly interacting, and these systems exhibit an apparent greater value of molecular weight. In particular, it has been estimated that about three molecules of PPG correlate each other due to the strong interaction between the hydroxyl end group. Concerning the secondary relaxation process, the observed differences in relaxation strength and activation energy for the different systems were coherently explained considering the dielectric and structural characteristics of the end groups. PPGM is one exception, as its great value of $\Delta E_\beta$ cannot be related to molecular characteristics of the methyl end group. Thus it can be supposed that for PPGM secondary relaxation dynamics is more related to the motion of the whole molecule.

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