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# Dielectric relaxation studies of poly(propylene glycol) confined in vermiculite clay

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**Abstract.** The molecular dynamics of oligomeric poly(propylene glycol) (PPG) liquids ($M_w$ = 1200, 2000 and 4000 g/mol) confined in a two-dimensional layer-structured Na-vermiculite clay has been studied by broadband dielectric spectroscopy. In addition to the $\alpha$-relaxation, the normal mode relaxation process was studied for all samples both in bulk and confinement. For the normal mode process the relaxation rate in the clay is drastically shifted to lower frequencies compared to that of the bulk material in contrast to the $\alpha$-process whose relaxation time is only slightly affected by the confinement. Also the temperature dependence of the relaxation time for the normal mode process is strongly affected by the confinement. Moreover, in the clay the intensity of the normal mode is stronger than that of the $\alpha$-process, in contrast to the bulk samples where the opposite is observed.

**PACS.** 77.22.Gm Dielectric loss and relaxation – 68.35.Ja Surface and interface dynamics and vibrations – 61.25.Hq Macromolecular and polymer solutions; polymer melts; swelling

## 1 Introduction

During recent years the dynamics of molecules in confined geometries has gained a growing interest [1,2,3,4,5,6]. The influence of finite size effects on the structure and dynamics of matter is important both from a fundamental and an applied point of view. Of special interest is to understand the nature of the glass transition which is an unsolved problem of condensed matter physics [7,8,9,10,11]. By confining molecules in very small spaces, the existence or not of a length scale associated with molecular motions responsible for the glass transition can be established. Besides the $\alpha$-relaxation, the normal mode process, which is related to the diffusional properties of polymeric liquids, can be studied in some polymers [3]. These polymers have a dipole moment component parallel to the chain and, therefore, the total dipole vector is proportional to the end-to-end vector and so the overall chain dynamics can be measured by dielectric spectroscopy.

Various liquids in different confinements have been studied in recent years. Schüller *et al.* [1] found, for PPG confined in nanoporous glasses, a positive shift in $T_g$. This shift decreases as the $M_W$ increases. They also observed an additional relaxation process which they associated with a layer of molecules adsorbed at the pore surface. Huwe *et al.* [5] have studied the dynamics ethylene glycol confined to zeolitic host systems of different topologies and pore sizes. They observed a transition from a non-Arrhenius behaviour, for large pore sizes as well as the bulk liquid, to an Arrhenius one for single (or few) isolated molecules. Finally, the segmental dynamics of polymer films intercalated in polymer/silicate nanocomposites has also been investigated [6]. The authors found, for the polymer in the confinement, a new mode much faster than the segmental $\alpha$-relaxation of the bulk polymer and with a much weaker temperature dependence. The physical meaning of this new mode is still under discussion.

It is the aim of this work to analyze how $\alpha$- and normal mode relaxations are affected by the two dimensional vermiculite clay confinement.

## 2 Experiment

Poly(propylene glycol) (PPG) ($H[OCH(CH_3)CH_2]_nOH$) of different molecular weights ($M_W$ = 1200, 2000 and 4000 g/mol) have been used for this study as these are polymers showing a dielectrically active normal mode relaxation. The polymers were purchased from Polysciences Inc. and degassed by repeated freeze-dry cycles on a vacuum line. This procedure effectively eliminates water and any low $M_W$ residuals from the polymerization.

As confining host material, a vermiculite clay provided by Askania, Sweden, was used. Vermiculites are unique in the sense that they are able to provide two-dimensional geometries with extremely thin and well-defined layer thickness. The clays were washed and then treated for about three months with 1 M NaCl solution at room

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temperature, with regular changes of solution, to produce a pure Na vermiculite, with the chemical formula $Si_{6.13}Mg_{5.44}Al_{1.65}Fe_{0.50}Ti_{0.13}Ca_{0.13}Cr_{0.01}K_{0.01}O_{20}(OH)_4Na_{1.29}$.

Totally dry Na-vermiculite clays were obtained by drying at 150 °C in a vacuum oven, for 48 h, and their dielectric response was characterized. After the drying we carefully weighted the clay pieces and they were submerged in the respective polymer. The clays were left in bottles, at 70 °C for two weeks. Filling was carefully monitored by weighting the samples. A rough estimation of the density ($\rho_c$) of the intercalated PPG gave that $\rho_c \leq 0.20$ g/cm$^3$ for PPG2000 and $\rho_c = 0.47$ g/cm$^3$ for PPG1200 and PPG4000, which is lower than for bulk ($\cong 1$ g/cm$^3$). Thus, it is evident that the interlayer regions are not completely filled with polymer. This was further supported by X-ray diffraction measurements which showed that some of the interlayer spacings did not contain any polymer. The other observable Bragg-peak indicated a d-spacing of 12.4 Å for the polymer filled layers, giving an effective thickness of 3.8 Å for the polymer layer.

The dielectric measurements were performed on a high resolution Novocontrol system covering a broad frequency range ($10^{-2}$–$10^9$ Hz) over the temperature range 120–300 K. Isothermal (within ±0.02 K) frequency scans of the complex dielectric function, $\varepsilon^*(f) = \varepsilon'(f) - i\varepsilon''(f)$, were performed every third degree.

## 3 Results and discussion

In the case of the dry clay only one slow process, apart from the low-frequency dispersion, could be observed, and this was fitted with a Cole-Cole function [12]. The $\alpha$-parameter was temperature independent ($\cong 0.45$) and the relaxation time follows an Arrhenius temperature dependence with an activation energy of $E_A \cong 0.78$ eV. The physical origin of this process is not understood at present. However, since it is a very slow process, it is on the low frequency side of our experimental window and does not affect the main processes of PPG we are interested in as shown in Figure 1.

To parameterize the $\alpha$-relaxation we used an empirical frequency domain representation of the KWW equation [13]. The normal mode relaxation was described by a Cole-Cole function with the $\alpha$-parameter close to one. The temperature dependence of the relaxation times for both processes was found to closely follow the Vogel-Fulcher-Tammann (VFT) [14] equation, defined as:

$$\tau = \tau_0 \exp(DT_0/(T - T_0)) \quad (1)$$

where $\tau_0$ is the relaxation time at infinite temperature, D the fragility parameter (giving the curvature of the function) and $T_0$ the temperature where $\tau$ goes to infinity.

Figure 2 shows the Arrhenius plots for $\alpha$- and normal mode relaxations, both in bulk and confinement, for the three oligomers. In the figure it is clear that the dielectrically observed $\alpha$-relaxation is slightly faster in clay, while the normal mode shows a significant slowing-down.

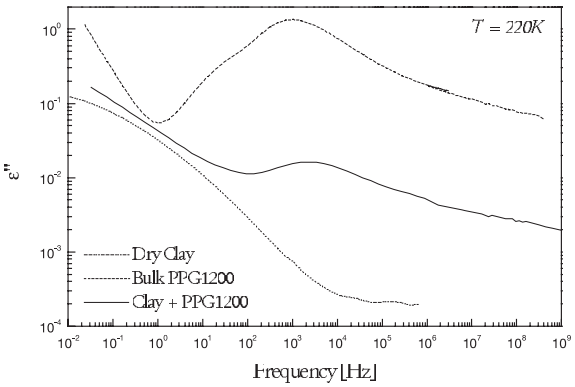


**Fig. 1.** Dielectric responses of the dry clay, bulk PPG1200 and the confined polymer is shown at $T = 220$ K.

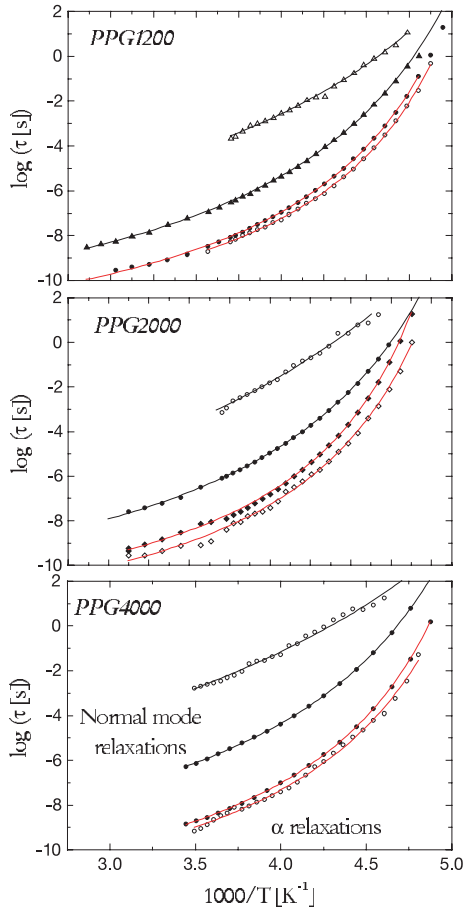


**Fig. 2.** Temperature dependence of the $\alpha$- and normal mode relaxation times in both bulk (solid symbols) and confined (open symbols) PPG's.

The same behavior is observed for all studied molecular weights. The speeding up of the $\alpha$-relaxation agrees with the findings for PPG in porous glasses by Schönhals and Stauga [4]. However a more significant variation of $T_g$, up to more than 10 K, was observed in their work. We found variations of $T_g$ within one degree between bulk and confined polymer. This fact suggests that the type of geometrical confinement as well as the strength of surface

interactions strongly affect the molecular dynamics. While porous glasses restrict molecular motion in all three dimensions, the present clays only restrict chain mobility in one dimension. Since the temperature dependence of the relaxation time is almost the same for the $\alpha$-relaxation in both bulk and our confinement it appears that the weak $\alpha$-peak in clays originates from regions where the confined polymer has a bulk like behavior, which further implies that the interactions with the clay surfaces are very weak.

The molecular weight dependence of the relaxation time for the normal mode process can be described by the Rouse theory [15]. We found for bulk PPG a $\tau \propto M^{1.96\pm0.16}$ dependence which agrees with the theoretical prediction ($\tau \propto M^2$) and with previous experimental data on PPG [16] and PI [17]. On the other hand, for confined polymer we obtained $\tau \propto M^{2.4\pm0.7}$. Within the experimental errors it seems that the Rouse theory is still appropriate to describe the molecular dynamics in this strong confinement. However, more data are necessary to give a definitive answer.

A significant difference in relative amplitude of the peaks between bulk and confined PPG's was observed for the three oligomers. The ratio of relative amplitudes between bulk and clay, defined as

$$\left.\frac{\dfrac{\Delta\varepsilon_\alpha}{\Delta\varepsilon_\alpha+\Delta\varepsilon'_\alpha}\Big|_{\text{Bulk}}}{\dfrac{\Delta\varepsilon_\alpha}{\Delta\varepsilon_\alpha+\Delta\varepsilon'_\alpha}\Big|_{\text{Clay}}}\right. \quad \text{and} \quad \left.\frac{\dfrac{\Delta\varepsilon'_\alpha}{\Delta\varepsilon_\alpha+\Delta\varepsilon'_\alpha}\Big|_{\text{Bulk}}}{\dfrac{\Delta\varepsilon'_\alpha}{\Delta\varepsilon_\alpha+\Delta\varepsilon'_\alpha}\Big|_{\text{Clay}}}\right. \tag{2}$$

for $\alpha$- and normal mode relaxations respectively, is plotted as a function of temperature in Figure 3. It is clear that the relative amplitude of the $\alpha$-relaxation is much larger in bulk than in clay for the three oligomers. The opposite behavior is observed for the relative amplitude of the normal mode, which is larger in clay compared to bulk. This fact indicates that the $\alpha$-relaxation is inhibited in parts of the clay. Since the normal mode relaxation is still present for the polymer within the clay, it means that the chains are not immobilized. We believe that the reason for the much lower relative amplitude of the $\alpha$-relaxation in the clay is due to that some interplatelet layers are only partially filled (or some even empty) as indicated by the lower polymer density in the clay and by X-ray diffraction experiments. In these layers, with only a few molecules, it is likely that the cooperative $\alpha$-relaxation can not occur. On the other hand, it is expected that the normal mode relaxation is promoted by the 2D geometry. According to Adachi and Kotaka [17,18,19], the dielectric strength of the normal mode process is proportional to the mean end-to-end ($\langle r^2\rangle$) vector of the chain. From the self avoiding random walk theory we know that $\langle r^2\rangle \propto M^{2\nu}$, with the exponent $\nu \cong 0.592$ in three dimensions and $\nu = 3/4$ for two dimensions. At constant molecular weight, a higher value of $\langle r^2\rangle$ is expected in the confinement and therefore a higher relaxation strength. We also observed that the molecular weight dependence for the relative relaxation strength of the normal mode in the clay is $\Delta\varepsilon \propto M^{0.21\pm0.05}$. This result agrees with that for dilute systems found by Ren *et al.* [18].

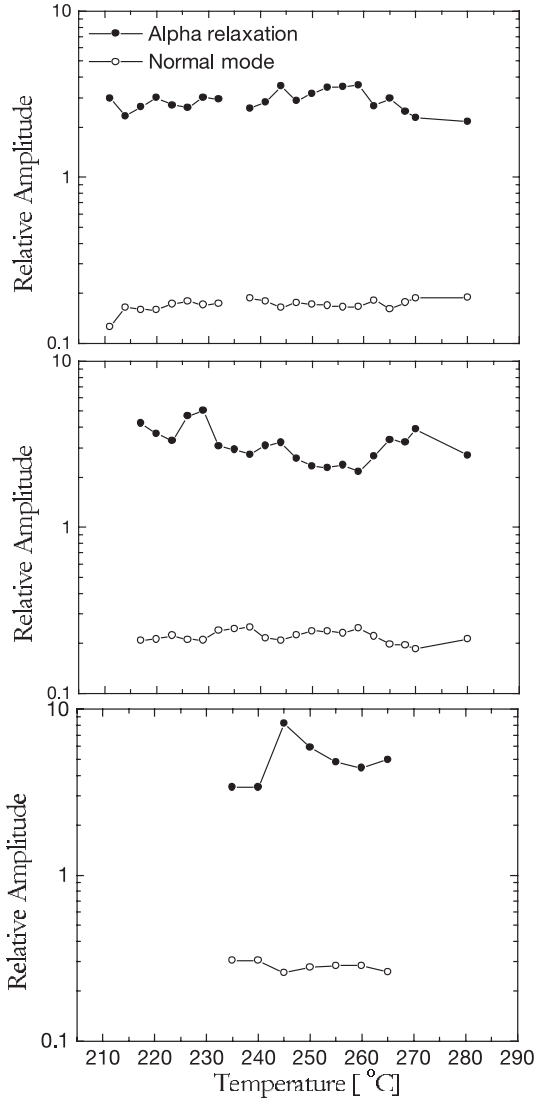


**Fig. 3.** Ratio of relative amplitudes between bulk and confined for the $\alpha$- and normal mode relaxations.

## 4 Concluding remarks

In this work we have analyzed the $\alpha$- and the normal mode relaxations both in bulk and in confined PPG of different molecular weights. We have found that the $\alpha$-process is only slightly speeding up in the confinement compared to bulk. Thus, the segmental dynamics of the polymer is almost unaffected by the 2D confinement. On the other hand, we have shown that the normal mode relaxation is strongly affected by the confinement. The increment of its relaxation strength in the clay has been related to the geometry of the confinement.

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## References


1. J. Schuller *et al.*, Phys. Rev. Lett. **73**, 2224 (1994)
2. M. Arndt *et al.*, Phys. Rev. Lett. **79**, 2077 (1997)
3. A. Schönhals, R. Stauga, J. Chem. Phys. **108**, 5130 (1998)
4. A. Schönhals, R. Stauga, J. Non-Cryst. Sol. **235-237**, 450 (1998)
5. A. Huwe *et al.*, Phys. Rev. Lett. **82**, 2338 (1999)
6. S.H. Anastasiadis *et al.*, Phys. Rev. Lett. **84**, 915 (2000)
7. P.W. Anderson, Science **267**, 1615 (1995)
8. C.A. Angell, Science **267**, 1924 (1995)
9. F.H. Stillinger, Science **267**, 1935 (1995)
10. M. Ediger, Annu. Rev. Phys. Chem. **51**, 99 (2000)
11. E. Donth, The Glass Transition (Springer, Heidelberg, 2001)
12. K.S. Cole, R.H. Cole, J. Chem. Phys. **9**, 341 (1941)
13. R. Bergman, J. Appl. Phys. **115**, 1405 (2000)
14. C.A. Angell *et al.*, Appl. Phys. Rev. **88**, 3113 (2000)
15. P.E. Rouse, J. Chem Phys. **21**, 1272 (1953)
16. M.E. Baur, W.H. Stockmayer, J. Chem Phys. **43**, 4319 (1965)
17. K. Adachi, T. Kotaka, Macromolecules **18**, 466 (1985)
18. J. Ren *et al.*, Polymer **44**, 847 (2003)
19. K. Adachi, T. Kotaka, Prog. Polym. Sci. **18**, 585 (1993)