Dynamics of propylene glycol and its oligomers confined in clay

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Abstract. The dynamics of propylene glycol (PG) and its oligomers 7-PG and PPG, with $M_W = 4000$ (about 70 monomers), confined in a Na-vermiculite clay have been investigated by quasi-elastic neutron scattering and dielectric spectroscopy. The liquids are confined to a single molecular layer between the clay platelets, thus giving a true 2D liquid. The results show that the average relaxation time $\langle \tau \rangle$, deduced from neutron scattering at a momentum transfer Q of about $1\,\text{Å}^{-1}$, is in perfect agreement with the dielectric α-relaxation time, although neutron scattering does not only probe the main (α-) relaxation, but all motions of hydrogens on the experimental time scale. At room temperature $1/\langle \tau \rangle$ is proportional to Q^2, indicating that the relaxations are mainly due to ordinary translational diffusion. The most unexpected finding is that $\langle \tau \rangle$ (or the dielectric α-relaxation time) is almost unaffected by the 2D confinement, in contrast to the dielectrically active normal mode of PPG which is substantially slower in the confinement. Only the 7-mer has a significantly slower segmental translational diffusion in the clay. The results suggest that the interactions to the clay surfaces are weak and that the present 2D confinement has a very small influence on the time scale of all our observed relaxation processes, except the normal-mode relaxation.

PACS. 61.25.Em Molecular liquids – 68.35.Ja Surface and interface dynamics and vibrations – 61.12.-q Neutron diffraction and scattering

1 Introduction

The dynamics of molecular liquids and polymers have been studied widely over several decades. More recently, there is also a growing interest in thin polymer films due to their many technological applications in areas such as microelectronics, biomaterials and medicine, where, for example, the polymers are used to achieve certain wanted surface properties. An increased understanding, on the microscopic level, of polymers at surfaces and in confined geometries would thus greatly assist in the development and improvement of new technologies. Furthermore, the structure and dynamics of polymers confined into a true 2-dimensional geometry (such as the here used Na-vermiculite clay) is interesting from a more theoretical point of view since it gives an opportunity to test various models and theoretical predictions for a reduced dimensionality.

The aim of this work is to elucidate how the molecular diffusion and glass-transition–related main (α-) relaxation of propylene glycol (PG) and its oligomers are affected by the 2D geometry that is obtained by trapping the liquids between vermiculite clay platelets. In recent years,

many similar investigations have been performed on similar [1–3] and other geometrical confinements [4–12]. In most of these studies porous glasses, with pore dimensions in the range 2–10 nm, have been used to obtain geometrically controlled confinements. The experiments, however, have often led to contradictory results and the conventional explanation of this is that there is a competitive balance between confinement and surface effects. These depend on different experimental conditions, such as the temperature, the size of the cavity compared to the cooperativity length of the molecular rearrangements, the density of the confined liquid compared to bulk and the nature of the surface interactions (*e.g.*, hydrophilic or hydrophobic). As a function of these parameters, the relaxational motions in the system will either slow down or speed up. In order to discriminate between, for instance, the confinement and surface effects it is often necessary to study the dynamics of chemically different liquids in different geometrical confinements with various surface properties. However, despite such systematic studies having been performed, the exact influence of the different parameters is still controversial. Some authors [4–6] have argued that the confinement effect itself causes a slowing-down of the dynamics whereas other authors [7–12] have proposed that geometrical confinements always speed up the dynamics

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and that only surface interactions can give rise to slower relaxational motions compared to the corresponding bulk system. In favour of the latter opinion are both the dramatic decrease of the glass transition temperature T_g observed for free-standing polymer films [13,14] and, in the case of polymers intercalated in clays, the simultaneous slowing-down of polymer segments which interact with the clay surfaces and the speeding-up of other polymer segments in the centre of the approximately 20 Å thick polymer layers [2,3].

In this study PG, its 7-mer and PPG with $M_W = 4000$ (about 70 monomers) were confined in the 2D galleries of a Na-vermiculite clay to obtain ultrathin layers of the liquids. The thickness of the liquid layers were only 5.5 Å in the case of PG and 3.7 Å for 7-PG and PPG [15]. This implies that the oligomers must form a flat monolayer with their methyl groups pointing in the direction of the clay surfaces. In contrast, the monomers are likely to be orientated either perpendicular to the clay layers or parallel to the layers, but with the methyl groups pointing towards a clay surface. One should also note that the densities of the intercalated liquids are considerably lower than for bulk. By comparing the weights of the submerged and vacuum dried clay crystals we were able to estimate the macroscopic densities of the intercalated PG, 7-PG and PPG to approximately 0.15, 0.28 and 0.47 g/cm^3, which were the maximum densities we were able to obtain. Furthermore, it is clear from the diffraction measurements [15] that the molecules are very inhomogeneously distributed (with large free volumes), which makes it difficult to estimate the effective microscopic densities, which are of interest for the present results, of the intercalated liquids. The reason for the inhomogeneous distribution of the molecules is most likely that the clay crystals are naturally occurring minerals with an inhomogeneous distribution of different ions (and therefore also of the charge density) in the clay layers.

In order to follow all the relaxation processes over a wide temperature range, it is important to cover a wide dynamical time window. Therefore, this study is carried out on three different quasi-elastic neutron scattering (QENS) instruments; IN16 at ILL, Grenoble, France (resolution 1 μeV), IRIS at ISIS, Rutherford-Appleton Laboratory, UK (resolution 15 μeV) and FOCUS at SINQ, PSI, Switzerland (resolution about 0.2 meV), as well as on a broadband dielectric spectrometer (Novocontrol) covering the frequency range 10^{-2}–10^9 Hz. The results from the IRIS measurements on the bulk and confined monomers and 7-mers have been published previously in reference [16] (and Ref. [17], in the case of the bulk samples). However, the combination of these techniques allow us to study dynamics over a considerably broader time range of 10^{-13}–10^2 s. The wide dynamical window of dielectric spectroscopy in combination with the possibility of using QENS to study dynamics on different length-scales, which is essential in order to be able to elucidate the nature of the motions (*i.e.* how the molecules are actually moving), gives a powerful experimental approach to study dynamics in liquids and polymers. Different kinds of molecular motions are normally present at widely different time scales. However, in this paper we focus on the temperature dependence of the main (α-) relaxation process and the related high-temperature translational or segmental diffusion. More detailed results are, or will be, presented elsewhere (see, *e.g.*, Refs. [15–19]), where also the sample preparation and experimental procedures are described.

Our dielectric studies have shown the remarkable result that the present confinement has basically no influence on the α-relaxation and the secondary β-relaxation times, although the intensity of the α-relaxation decreases dramatically [19,20]. Only the relaxation time of the dielectrically active normal mode, which is associated with the motion of an entire chain (see Ref. [9] for more details), is strongly affected by the present confinement [19,20].

In the current system the methyl group prevents the bulk liquids from crystallising in the supercooled regime, and the structural properties can be systematically varied from a hydrogen-bonded network structure of PG [21] to a characteristic polymer structure of PPG [22] by simply increasing the number of connected monomer units. Furthermore, the vermiculite clay is ideal for producing truly two-dimensional liquids and polymers which are possible to investigate with conventional experimental techniques due to the fact that each macroscopically sized sample consists of nearly a million of such ultrathin parallel layers.

2 Results and discussion

The QENS studies (see Refs. [16] and [17]) show that, at least, three dynamical processes are present at room temperature on a pico-nanosecond time scale. Two of them are weakly temperature dependent and Q-independent, where the faster one, with an estimated correlation time of about 4 ps from the measurements on IRIS, arises from a local motion of hydrogens in the backbone of the monomers and the about ten times slower one is due to the methyl group rotation [16,17]. The fast process is not affected by the confinement, whereas the methyl group rotation tends to speed up in the clay, most likely due to the reduced density. However, in this paper we will focus on the dominating third process, which describes the more long-range translational or segmental motion of single or connected monomers. This diffusive motion is strongly related to the α-relaxation observed in the dielectric measurements, which means that the present QENS measurements allow us to make a rough estimation of the α-relaxation at high temperatures where it is too fast to be observed with our dielectric equipment.

A combination of the three QENS experiments shows that the neutron data (*i.e.* all the three processes are here included) can, to a good approximation, be described by the Kohlrausch-Williams-Watts (KWW) stretched exponential relaxation function [23,24]

$$S(Q,t) = (1-B)\exp\left[-\left(\frac{t}{\tau}\right)^{\beta_{KWW}}\right] + B,$$
$$0 < \beta_{KWW} < 1, \tag{1}$$

where τ is a typical relaxation time, β_{KWW} a stretching parameter, and B is the "background level" at long times (which is zero for our bulk samples and about 0.45 for the clay samples, where we have immobile atoms in the clay platelets). The results show [18] that the present confinement tends to reduce β_{KWW} whenever the time scales of the translational (or segmental) motion and the methyl group rotation are similar (or if the contribution from the methyl group rotation is removed before the fitting procedure). Thus, the translational (or segmental) motions seem to have a slightly wider time distribution in the clay, in qualitative agreement with findings from NMR [2] and dielectric experiments [1] as well as molecular-dynamics (MD) simulations [3] of polymers intercalated in other types of natural or synthetic clays. However, in general β_{KWW} could be as low as 0.4 for all the samples since $S(Q,t)$ is a superposition of three processes on normally different time scales. The separation in time between the three processes, and thus the value of β_{KWW}, depends on the momentum transfer (Q) and temperature in the experiment. An attempt to separate the processes and provide more details on the momentum transfer (Q) and temperature dependences of β_{KWW} will be given in reference [18]. Here, we have avoided to make the assumptions that are necessary for such a separation and instead performed a direct calculation of the average relaxation time $\langle\tau\rangle$ of the three processes (although dominated by the translational or segmental motions), which was obtained from the KWW fits through the relation (see Ref. [25])

$$\langle\tau\rangle = \frac{\tau}{\beta_{KWW}}\Gamma\left(\frac{1}{\beta_{KWW}}\right), \qquad (2)$$

where Γ is the gamma-function.

Figure 1 shows the Q-dependence of the so-obtained average relaxation times, plotted as $1/\langle\tau\rangle$ as a function of Q^2, for PG, 7-PG and PPG in bulk as well as confined in clay. Two important findings emerge directly from the figure; firstly, the inverse of the relaxation time is approximately proportional to Q^2, which is typical for continuous translational diffusion, and, secondly, the relaxation time is almost unaffected by the confinement, except for the 7-mer which is slowed down a factor 4 in the clay. The former observation is partly in contrast to the preliminary indications we got from fitting the IRIS data with Lorenzian functions, where it was found [16] that the translational or segmental diffusion in the clay was best described by the Gaussian jump length distribution model [26]. It is also interesting to note in Figure 1 that the relaxation time of the confined liquids is basically independent of the chain length. In fact, the only significant difference between all the investigated samples is that the dynamics in bulk 7-PG is considerably faster than in the other samples. One would expect the dynamics to become slower with increasing chain length and a possible explanation for the fact that the dynamics of the 7-mers is faster than for the single monomers may be that the OH endgroups of the monomers are linked together forming a network, and, as a result, slow down the diffusion at temperatures low enough to keep the network structure intact [17]. In
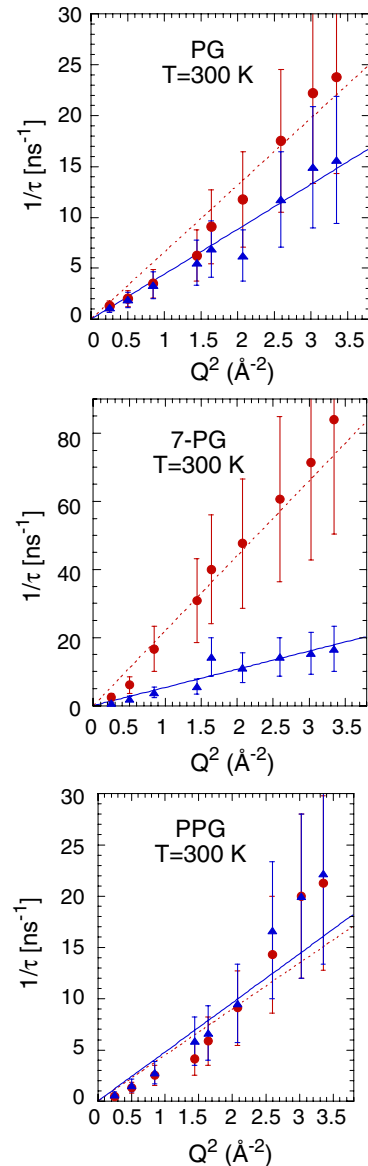

Fig. 1. $1/\langle\tau\rangle$ as a function of Q^2, for PG, 7-PG and PPG in bulk (circles) and confined in clay (triangles). The lines indicate the approximate Q^2-dependence of $1/\langle\tau\rangle$.

support of this interpretation is the less fragile behaviour of PG [21].

The small effect of the present confinement is also observed in the dielectric α-relaxation (and the more local β-relaxation process [19]). This is evident in Figure 2, which shows the temperature dependence of the average relaxation time from neutron scattering as well as the dielectric α-relaxation time of PG and PPG in bulk and confined in clay. The estimated glass transition temperatures T_g of bulk PG and PPG, based on the temperature where the α-relaxation time is 100 s, are 169 K and 200 K, respectively, in good agreement with values reported in the literature (see, *e.g.*, Ref. [5]). For the confined liquids T_g is shifted downwards less than 2 K. On the other hand, the normal mode of PPG is considerably slower in the confinement
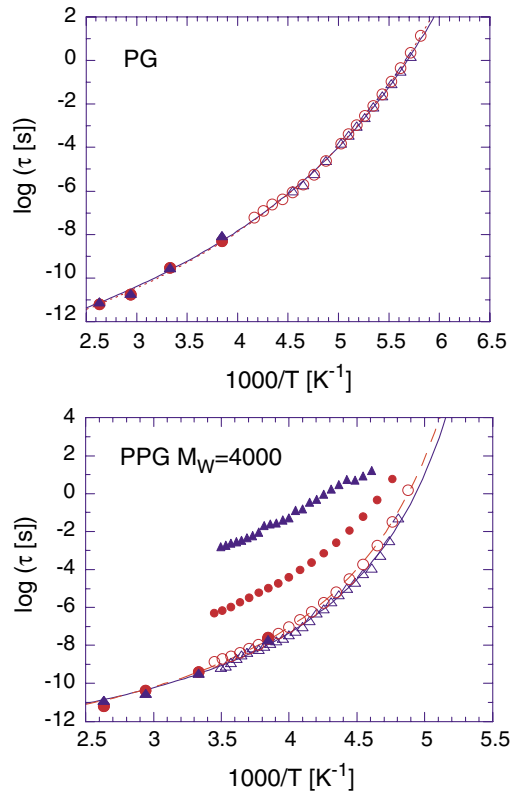
Fig. 2. Temperature dependence of the average relaxation times for PG and PPG in bulk (circles) and confined in clay (triangles). The dielectric α-relaxation is given by open symbols whereas both the average relaxation time from neutron scattering and the dielectric relaxation time of the normal mode of PPG are marked with filled symbols (smaller symbols for the normal mode). Note the excellent agreement between the average relaxation time from neutron scattering and the dielectric α-relaxation time, evident from the simultaneous fitting with the Vogel-Fulcher-Tamman (VFT) [27] equation (dashed line for bulk and solid line for confined liquid).

(see Ref. [20] for more details), as also indicated in Figure 2. In fact, Kojio *et al.* [28] observed a slowing-down of the normal mode of PPG (containing about 1% LiClO$_4$), confined between parallel insulating mica surfaces, even for a film thickness as large as 30 nm. Thus, it is an interesting observation that the different relaxation processes are so differently affected by the confinement, and it is especially amazing that the relaxation time of the α-process, which is generally accepted to be a result of the cooperative motions in the material, is so little affected by both the confinement to a single molecular layer as well as the interactions with the clay surfaces. A possible explanation is, of course, that the two effects cancel out by working in opposite directions, although that appears to be a too improbable coincidence to occur for both PG and PPG.

The present experimental results are in support of molecular-dynamics (MD) simulations by Baschnagel and Binder [29], where they studied polymer melts confined between two parallel non-interacting smooth hard walls. It was found that the diffusion coefficient in a direction

parallel to the walls was almost indistinguishable from that of the bulk. On the other hand, if we instead have a liquid–hard-wall interface then both an attractive force to the walls (provided that the thermal energy is lower than the attraction energy) as well as rough surfaces are likely to slow down the dynamics [11]. This is supported by MD simulations of simple diatomic liquids confined between two parallel smooth interacting walls [6] or in a pore surrounded by the same, but frozen, liquid [30]. In both studies the dynamics was dramatically slowed down close to the walls due to surface interactions in the former case and the rough interface in the latter case. Furthermore, a slowing-down of segmental motions of polymers intercalated in other types of clays has been observed for polymer segments interacting with the clay surfaces [2,3].

It has also been suggested that both pure geometrical confinement effects and surface interactions cause a slowing-down of the dynamics. This has been indicated from dielectric studies of PG and its oligomers confined in porous glasses [4,5]. A possible explanation for the apparently contradictory results in the literature was proposed by Huwe *et al.* [12], where the density of the confined liquid was pointed out to be a key parameter. Thus, if the geometrical confinement gives rise to a reduced density compared to the bulk liquid, as is the case in the present study, the dynamics is expected to be accelerated, whereas the opposite behaviour might be the case for an increased density. The importance of having a low density for fast dynamics was also pointed out by Manias *et al.* [3] who showed that the dynamics was strongly enhanced in regions of low density. In the present study it is likely that the microscopic density is generally lower than in bulk, but, on the other hand, we have an extreme confinement where all the monomer units interact with the clay surfaces. Thus, since the different effects have different influences on the dynamics it is difficult to make a definite statement about how they affect the dynamics, although the small change of translational and segmental motions as well as the dielectric α-relaxation suggests that none of the effects have particularly strong influence on the time scale of such motions. This is, however, not the case for the dielectrically active normal mode, which is considerably slower in the clay. This might be a result of surface interactions, but can also be caused by the completely different chain conformation in two dimensions, compared to three dimensions. The reduced dimensionality increases the end-to-end distance of the polymer chains, which, in turn, is expected to increase the relaxation time of the normal mode.

3 Concluding remarks

By comparing data from quasi-elastic neutron scattering and dielectric spectroscopy it is evident that the average relaxation time from neutron scattering (at $Q \approx 1\,\text{Å}^{-1}$) is almost identical to the dielectric α-relaxation time. It is also clear that this relaxation process corresponds to molecular motions of translational character and that it is almost unaffected by the present true 2D confinement, in

contrast to the dielectrically active normal mode of PPG which is substantially slower in the confinement. Thus, there is no indication, for none of the confined liquids, that the OH endgroups should form strong hydrogen bonds to the clay surfaces. In fact, the rather small effect of the present confinement on the diffusive dynamics and the main relaxation time suggest that the surface interactions are considerably weaker than in many other model systems (*e.g.*, unmodified Vycor glasses and zeolites) commonly used to confine liquids and polymers.

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