

Unique Behavior of Poly(propylene glycols) Confined within Alumina Templates Having a Nanostructured Interface

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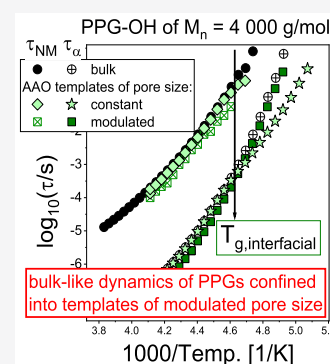
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ABSTRACT: Herein we show that the nanostructured interface obtained via modulation of the pore size has a strong impact on the segmental and chain dynamics of two poly(propylene glycol) (PPG) derivatives with various molecular weights ($M_n = 4000$ g/mol and $M_n = 2000$ g/mol). In fact, a significant acceleration of the dynamics was observed for PPG infiltrated into ordinary alumina templates ($D_p = 36$ nm), while bulklike behavior was found for samples incorporated into membranes of modulated diameter (19 nm $< D_p < 28$ nm). We demonstrated that the modulation-induced roughness reduces surface interactions of polymer chains near the interface with respect to the ones adsorbed to the ordinary nanochannels. Interestingly, this effect is noted despite the enhanced wettability of PPG in the latter system. Consequently, as a result of weaker H-bonding surface interactions, the conformation of segments seems to locally mimic the bulk arrangement, leading to bulklike dynamics, highlighting the crucial impact of the interface on the overall behavior of confined materials.

KEYWORDS: confinement effect, surface effect, interface roughness, aluminum oxide porous templates, dielectric spectroscopy, glass transition



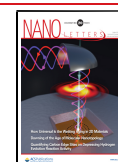
The confinement-induced enhancement of molecular dynamics and shift of the phase/glass transition temperatures of various glass formers were mainly assigned to the competition of two effects: finite size and surface interactions. However, as our understanding of the physical processes occurring at the nanoscale became better and deeper, special attention was focused on the properties of the molecules directly adsorbed to the substrate (the so-called interfacial layer). Numerous investigations have shown that the behavior of these molecules has a significant influence on the variation of the free volume,¹ negative pressure,² density fluctuations,^{3,4} and molecular conformations⁵ as well as the limited viscous flow⁶ of the material not directly attached to the interface (the so-called core molecules). In this context, it should be recalled that the deviation of segmental dynamics and shift of the glass transition of macromolecules deposited as thin films have a finite lifetime and strongly depend on the kinetics of the formation of an irreversibly adsorbed layer that further affects the packing density at the interface.^{3,4} On the other hand, positronium annihilation lifetime spectroscopy studies on 2-ethylhexanol infiltrated in silica pores revealed that as the sample was cooled below the vitrification point of the interfacial layer, the bulklike core molecules of the confined liquid enter the isochoric state, where the packing density remains constant.¹ Moreover, comprehensive studies on various soft materials incorporated within anodic aluminum oxide (AAO) membranes^{7,8} revealed that the difference between the glass transition temperatures, T_g , of bulk and

confined samples, ΔT_g , increases with the interfacial tension. This relationship was well-quantified by systematic measurements of the wettability, allowing calculation of the interfacial energy, γ_{SL} , and T_g of the spatially restricted polymers.^{7,8} Further studies indicated that higher γ_{SL} implies reduced mobility of the interfacial layers, which consequently leads to greater depression of T_g of core molecules in pores.⁹ Similar correlations were also reported in the case of the thin films.^{10,11} However, in some other cases the opposite effect was presented.¹² Interestingly, although these examples have demonstrated that interactions with the solid substrate are an important parameter controlling the behavior of soft materials confined at the nanoscale, this issue has been mainly explored by simple modification/functionalization of the solid substrate surface, including changes in its polarity, specific interactions (H-bonds), hydrophilicity, and hydrophobicity.^{10,12,11} However, another promising strategy to modify the strength of the interfacial interactions that is less investigated in the literature is to change the surface morphology (i.e., roughness). Molecular dynamics simulation studies pointed out that

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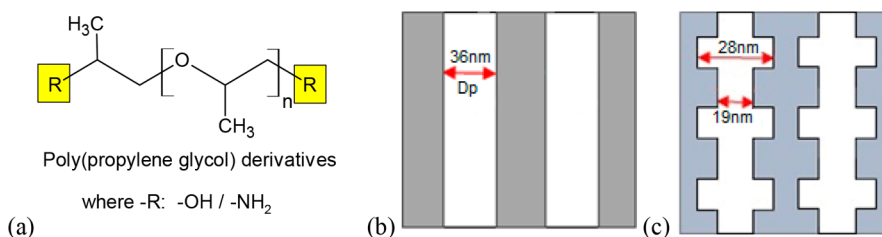


Figure 1. (a) Chemical structure of the investigated compounds and (b, c) schematic cross sections of the applied self-made alumina templates with (b) constant and (c) modulated pore diameter.

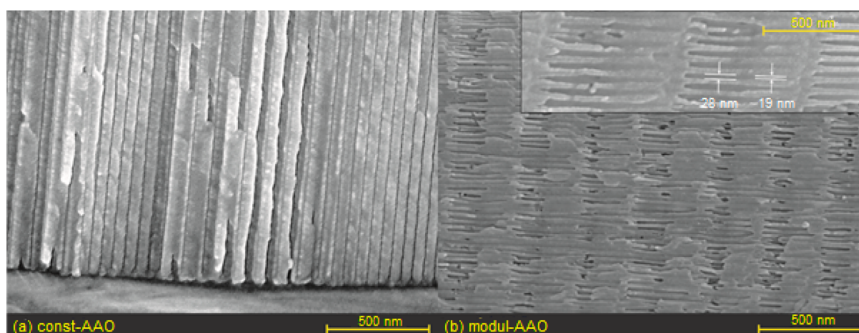


Figure 2. FE-SEM micrographs collected for the cross sections of applied (a) const-AAO and (b) modul-AAO.

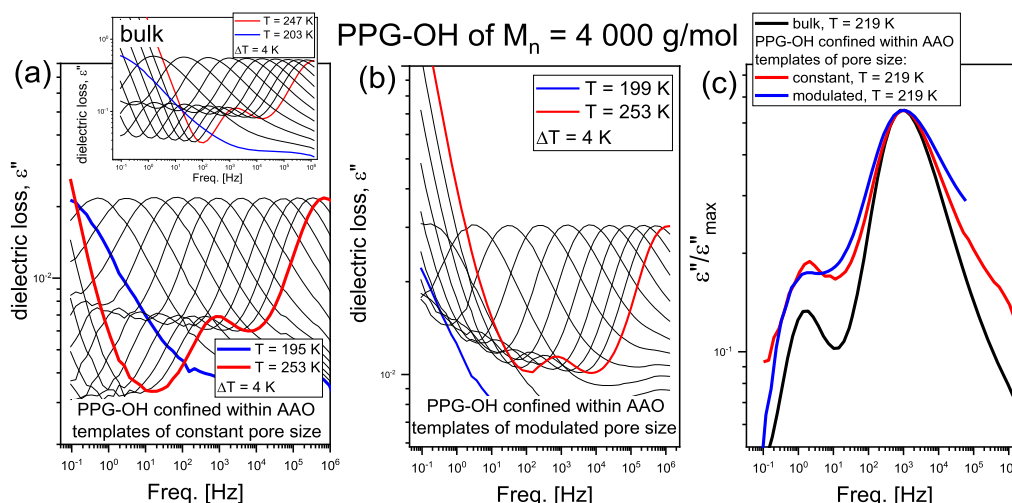


Figure 3. (a, b) Dielectric loss spectra measured for PPG-OH with $M_n = 4000\text{ g/mol}$ confined in (a) const-AAO and (b) modul-AAO membranes. The inset in (a) presents dielectric spectra of bulk PPG-OH. (c) Comparison of loss peaks recorded for bulk PPG-OH and sample infiltrated into pores at $T = 219\text{ K}$.

variation of this parameter has a strong influence on the mobility of adsorbed molecules and the dynamics of polymer films in general.^{13–15} Recently, this supposition was also confirmed by experimental data showing that the segmental dynamics of polymers supported as thin layers “prepared under non-equilibrium conditions” was enhanced near the rough interface because of the perturbation of the interfacial free volume and “noncomplete filling of surface asperities”.¹⁶

In this Letter, we examine the behavior of two poly(propylene glycol) (PPG) derivatives differing in the formation of H-bonds (terminated by $-\text{OH}$ and $-\text{NH}_2$ moieties; Figure 1a) infiltrated into two types of self-made AAO templates characterized by both constant (const-AAO) and modulated (modul-AAO) pore sizes having comparable average diameters ($D_p \sim 30\text{ nm}$) (Figure 1b,c) using dielectric and Fourier transform infrared (FTIR) spectroscopy, atomic force

microscopy (AFM), and differential scanning calorimetry (DSC). It should be pointed out that these are the first investigations where the dynamics of polymers infiltrated into porous templates of varying pore size, which in a rough approximation mimic a change in surface roughness, has been studied.

The materials under the investigation were two model glass-forming polymers, poly(propylene glycol) (PPG-OH) and poly(propylene glycol) bis(2-aminopropyl ether) (PPG-NH₂) of molecular weight $M_n = 4000\text{ g/mol}$ and $M_n = 2000\text{ g/mol}$ supplied by Sigma-Aldrich (with purity higher than 98%). As the constraining medium, we applied self-made alumina templates, const-AAO ($D_p = 36\text{ nm}$) and modul-AAO ($19\text{ nm} \leq D_p \leq 28\text{ nm}$), produced by well-established methods reported in the literature.¹⁷ The morphology of the cross sections of modul-AAO was confirmed by field-emission

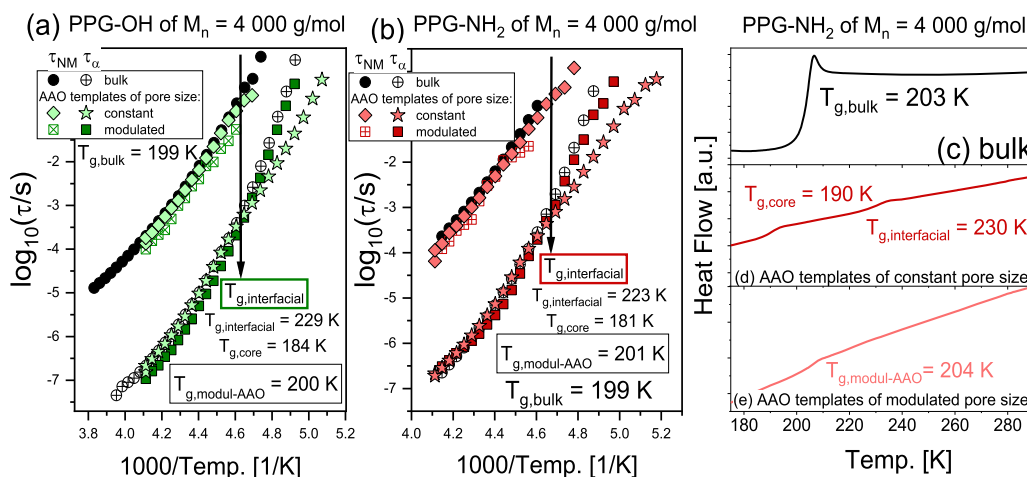


Figure 4. (a, b) Temperature dependences of τ_{NM} and τ_{α} of bulk and confined (a) PPG-OH and (b) PPG-NH₂. (c) DSC thermograms obtained for bulk PPG-NH₂ and samples infiltrated into const-AAO and modul-AAO templates.

scanning electron microscopy (SEM, Figure 2). The pore diameter ($D_p \sim 30$ nm) of the applied templates was selected for two reasons: (i) a strong confinement effect on the dynamics of PPG infiltrated in such membranes and (ii) successful production of AAO templates of comparable but modulated size ($19 \leq D_p \leq 28$ nm) with good accuracy. It should be noted that although the imbibition process for modul-AAO would not follow the classical Lucas–Washburn equation,^{18–20} the infiltration time was set as $t = 24$ h, as in the case of const-AAO. After that time, we found that the masses of both kinds of membranes were constant, indicating the imbibition process to be finished. For details regarding the experimental techniques, see the Supporting Information (SI).

Representative dielectric spectra obtained for the bulk and confined PPG-OH with $M_n = 4000$ g/mol and $M_n = 2000$ g/mol are shown in Figures 3 and S1. As illustrated, three different relaxation processes can be seen for all of the studied systems (also in PPG-NH₂), where apart from the dc conductivity, connected to the charge transport located at lower frequencies, and α relaxation, related to the cooperative motions of segments visible at the highest frequencies, the normal mode (NM) related to the fluctuations of the end-to-end vector can be detected as well. The NM process, which is dielectrically observed only in type-A polymers²¹ (e.g., PPGs), having dipole moment aligned along the backbone, reflects the global chain dynamics and provides information about polymer diffusion. Figure 3c compares dielectric spectra of the studied polymers (collected for constant segmental relaxation times). It was found that the broadest α -loss peak can be seen for PPGs within modul-AAO templates, indicating the larger dynamical heterogeneity of this sample with respect to the materials infiltrated into “standard” const-AAO membranes.^{22–24} It should be noted that the same scenario was also observed for PPGs with $M_n = 2000$ g/mol (Figure S1b).

Next, in Figures 4a,b and S1c we have plotted the temperature dependences of the relaxation times of the segmental process, τ_{α} , and normal mode, τ_{NM} , of the bulk and confined PPGs terminated with hydroxyl and amine moieties, which were determined from fits of the collected loss spectra to the superposition of the two Havriliak–Negami functions with an additional conductivity term.^{25,26} As shown for PPGs within the const-AAO templates, the T dependences (obtained upon measurements on heating) of τ_{NM} and τ_{α}

change from exponential (characteristic for the bulk sample) to Arrhenius-like behavior at comparable temperatures ($T_{g,interfacial}$). On the other hand, in the case of modul-AAO membranes, we found *bulklike* dynamics of both PPG derivatives irrespective of their M_n over the whole studied range of temperatures. Moreover, we also carried out annealing experiments at various temperatures to probe the variation of the segmental and chain dynamics of PPG infiltrated into const-AAO and modul-AAO templates. As shown in Figures S2 and S3, the maxima of the segmental and normal modes are either constant ($T = 245$ K) or shifted by around one decade toward lower frequencies ($T = 207$ K) depending on the temperature of the experiment for samples incorporated into the standard alumina templates. However, it should be noted that τ_{α} and τ_{NM} of the bulk material were not recovered even after longer annealing. For the PPG infiltrated in modul-AAO membranes, the effect of annealing on the dynamics was marginal. It is quite expected since $\tau_{\alpha}(T)$ and $\tau_{NM}(T)$ were bulklike over the whole studied temperature range. It should be noted that the same scenario was found for all of the studied PPGs independent of M_n . In addition, we also determined T_g for the investigated samples (for details, see the SI), and they are listed in Figure 4. As noted above, $T_{g,modul-AAO} \sim T_{g,bulk}$ while for const-AAO, $T_{g,interfacial} > T_{g,bulk} > T_{g,core}$. The results described above are interesting considering data reported to date for various PPGs (irrespective of molecular weight and terminal group) infiltrated within both alumina^{27–29} and silica^{30,31} pores that revealed deviations of τ_{α} from those measured for the bulk sample. Although a different interpretation of this finding has been proposed, previously such variation in the dynamics of confined PPGs has been assigned to the vitrification of the material adsorbed at the interface. One can recall that $T_{g,interfacial}$ corresponds well to the higher endothermic event (glass transition) detected in the collected thermograms (Figure 4).^{27–29} It should be noted that because of additional interactions of the substrate and adsorbed molecules, there is some heterogeneity in terms of density and mobility of the confined materials. Thus, there are at least two fractions of molecules (core and interfacial), characterized by various dynamics and glass transition temperatures ($T_{g,core}$ and $T_{g,interfacial}$, respectively) for liquid infiltrated in pores.³² On the other hand, the observed bulklike behavior and invariance of the segmental and chain dynamics

during annealing experiments of PPG in modul-AAO might be due to the absence of such dynamical heterogeneity as a result of weaker surface interactions.

To verify this supposition, we carried out additional DSC measurements (Figures 4c–e and S4). As can be observed, the representative thermogram of PPG-NH₂ within the modul-AAO template exhibits only one glass transition in the studied temperature range, while for the sample incorporated in the const-AAO membrane, two glass transitions can be detected³² (Figure 4d). It should be noted that the same scenario was found for all of the studied PPGs independent of M_n . It is worthwhile to stress that there is a good agreement between the T_g values determined from dielectric and calorimetric measurements.

To explain the peculiar behavior of polymers incorporated into modul-AAO, further AFM measurements were carried out along the cross-sections of empty and filled membranes to determine both the roughness of the nanochannel wall surface and the adhesion force between the tip and PPG of $M_n = 4000$ g/mol (for details, see the SI). It was found that the roughness of the const-AAO template was around ~ 2.5 nm, whereas for modul-AAO membranes it varied between ~ 1.7 and 6.2 nm (Table S1 and Figures S5–S9). Moreover, from AFM measurements we calculated that the material incorporated into the modul-AAO template is characterized by a lower adhesion force (~ 20 nN) compared with the one infiltrated to the “standard” alumina membrane (~ 40 nN). This means that the former system has a lower surface tension and most likely better wettability. Hence, similar to the case of glycerol,³³ we should also observe two T_g values in thermograms collected for PPGs within modul-AAO templates. Consequently, the confinement effect on the dynamics should be enhanced, not suppressed. Such a scenario has been recently reported for poly(4-chlorostyrene) deposited in the form of thin films on substrates differing in roughness.¹⁶ It was shown that the increase in surface roughness caused a perturbation in the interfacial free volume due to “noncomplete filling of surface asperities that lead to accelerated segmental dynamics”.¹⁶ The discrepancy between our data and those presented in ref 16 can be easily rationalized considering (i) the different geometries of the samples (1D vs 2D confinement), (ii) the varying molecular weights of the polymers, and mostly (iii) the different surface roughness modifications. It should be noted that varying the pore size is not a typical surface treatment applied to flat substrates to increase their roughness. Therefore, these parameters cannot be directly compared since modulation of the pore diameter may only in some way reflect a change in the morphology/roughness of flat surfaces. Herein, one can also consider the relationship between substrate roughness (quantified by RMS; see the SI), Kuhn segment, Kl, and the dynamics of PPG infiltrated in modul-AAO templates.³⁴ On the basis of the data reported in ref 34, one can expect a full recovery of the dynamics of the polymer incorporated into const-AAO pores when the RMS roughness is significantly larger than Kl (generally ~ 0.5 – 1 nm, depending on the polymer³⁵). This scenario should occur for PPG infiltrated in modul-AAO, where both the RMS roughness (1.7 – 6.2 nm; Table S1) and characteristic length of modulation, L (~ 9 nm since $19 \leq D_p \leq 28$ nm) are higher than Kl. Thus, this explanation fails to account for the unusual behavior of both PPGs infiltrated in AAO templates of varying pore size.

To finally address this problem, we carried out FTIR measurements for PPG-OH infiltrated into const-AAO and modul-AAO to verify whether a change in the surface morphology/roughness influences the surface interactions via H-bonds. It should be noted that the analysis of the obtained data was difficult because of the large thickness of the template and the additional contribution of vibrations of the OH units attached to the pore walls to the measured spectra. Nevertheless, the data obtained at either temperature and especially time-dependent measurements allowed us to extract the response of the sample and gain insight into the interactions between PPG-OH and the interface within both studied AAO membranes. It should be noted that the same kind of investigation of PPG-NH₂ infiltrated into these templates was inconclusive because of the much lower intensity of the amine vibrations with respect to the hydroxyl ones. The temperature-dependent FTIR spectra of bulk and confined materials revealed the broadening of the O–H stretching bands ($\nu_{O-H} \sim 3450$ cm⁻¹) toward lower frequencies under confinement, indicating an increasing population of stronger H-bonds formed within the two systems (Figure S10a). Surprisingly, however, the ν_{O-H} band of PPG-OH within the const-AAO membrane is narrower than that measured for the sample infiltrated into the membrane of the modified surface. This means that H-bonding interactions in the former system are less heterogeneous in terms of the strength of these specific intermolecular forces. Moreover, at T_g , an additional component appears as a shoulder on the low-frequency side of the ν_{O-H} band (~ 3250 cm⁻¹) in both confined materials. This new peak may indicate that additional strong H-bonds, most likely between the substrate and polymer, are created for the samples infiltrated into AAO membranes. It should be noted that the intensity of this component is significantly lower for PPG within templates of the modulated surface, suggesting a lower population of the strongly H-bonded polymer with the pore walls in this nanocomposite. Also, further time-dependent FTIR measurements at T_g revealed significant differences in the variation of the ν_{O-H} band spectral shapes for the two studied systems (Figure S10b). As can be observed, the intensity of the peak at ~ 3250 cm⁻¹ increased only slightly during the aging experiments at T_g in the case of PPG-OH within modul-AAO templates. On the other hand, this peak became much more intense over time in the case of const-AAO membranes. This suggests that the surface roughness, altered by the applied pore size modulation, in fact causes the perturbation in the H-bonding pattern of PPG-OH as a result of different orientations of –OH groups relative to Al–OH ones located at the porous walls. As a result, the interactions between the PPG-OH molecules and the surface of the modul-AAO membrane are weaker and more heterogeneous compared with those occurring in const-AAO membranes.

In conclusion, we have reported the bulklike behavior of both the segmental and chain dynamics of two PPG derivatives, independent of their M_n , due to the nanostructured interface enforced by the application of porous templates of modulated pore size. The unique behavior of PPGs infiltrated within modul-AAO templates points out the lack of a strongly interacting interfacial layer, characterized by reduced mobility, near the rougher pore walls. This has been confirmed by complementary DSC and FTIR measurements. Therefore, the weakly attached polymer chains seem to mimic the bulk arrangement. The presented data emphasize the crucial impact

of surface modulation, reflecting in some way a change in the roughness of the applied substrate (constraining medium), on the dynamics and phase transition of the confined liquids/polymers infiltrated into pores.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at <https://pubs.acs.org/doi/10.1021/acs.nanolett.0c01116>.

Experimental details and additional figures, including dielectric spectra collected for PPG-OH of $M_n = 2000$ g/mol infiltrated into both types of studied templates, DSC thermograms, membrane topologies measured by AFM techniques, SEM micrographs, and FTIR spectra (PDF)

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Notes

The authors declare no competing financial interest.

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