Supporting Information

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

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I. EXPERIMENTAL SECTION

1.1. Materials
Poly(propylene glycol) (PPG-OH) and poly(propylene glycol) bis(2-aminopropyl ether) (PPG-NH₂) with purity higher than 98% and molecular weights, Mₙ = 4 000 g/mol and Mₙ = 2 000 g/mol, were supplied by Sigma-Aldrich. The nanoporous aluminum oxide membranes used in this study are self-made templates composed of uniaxial channels (open from both sides) with a well-defined pore diameter of the constant (const-AAO) or modulated (modul-AAO) value of comparable length scale, Dₚ ≈ 30 nm. AAO membranes with the constant pore diameter of Dₚ = 36±3 nm were prepared by two-step anodization of aluminum in stirred 0.3 M H₂C₂O₄ at 25 °C; whereas those of modulated pore size (19≤Dₚ≤28 nm; Dₚ ~ 19 nm (MA mode) and Dₚ ~ 28 nm (HA mode)).

1.2. AAO membrane preparation
Anodic alumina membranes (AAOs), both const-AAO and modul-AAO, were prepared via two-step anodization of aluminum in acidic electrolytes. A high purity aluminum foil (99.999%, GoodFellow) was degreased in acetone and ethanol and electrochemically polished in a mixture of ethanol and perchloric acid (3:1 vol.) at 20 V and 0 °C, for 2 min. Two types of AAO membranes were prepared with (i) a straight pore diameter (const-AAO) and (ii) modulated pore diameter (modul-AAO). The anodization of aluminum was performed in a two-electrode electrochemical cell in an (i) 0.3 M H$_2$C$_2$O$_4$ and (ii) 0.3 M H$_2$SO$_4$ aqueous solution at a constant voltage of (i) 45 V and (ii) 25 V, and the temperature of (i) 25 °C and (ii) 5 °C. The duration of the first step was (i) 1 h and (ii) 12 h. After that, the unordered porous layer was etched away in a mixture of 6 wt% H$_3$PO$_4$ and 1.8 wt% H$_2$CrO$_4$ for 1 h at 60 °C. The second step of anodization was performed at a constant (const-AAO) or pulse (modul-AAO) potential modes. The anodization at a constant potential (const-AAO) was performed at the same conditions as the first step, except anodization duration, which was t = 4 h. While during the pulse anodization (modul-AAO), a series of 50 potential pulses comprising a mild anodizing (MA) pulse (25 V for 3 min) and hard anodizing (HA) pulse (35 V for 1 s) was applied.

1.3. Samples preparation

As first, the applied AAO templates were dried in an oven at T = 423 K under a vacuum (10$^{-2}$ bar) for at least t = 24 h to remove any volatile impurities from the nanochannels. After cooling, they were used as a constrain medium. For that purpose, AAO templates were placed in a small glass flask containing PPG. The whole system was maintained at T = 298 K in a vacuum (10$^{-2}$ bar) for t = 24 h to let all compounds flow into the nanocavities. After completing the infiltration process, the surface of the AAO membrane was dried, and the excess sample on the surface was removed by the use of a metal blade and a paper towel. Note that although the imbibition process of the modul-AAO would not follow the classical Lucas-Washburn equation$^2,3,4$, the infiltration time was set as t = 24 has in case of const AAO. After that time, we found that the mass of both kinds of membranes was constant, indicating the imbibition process to be finished. Before the measurements, samples were annealed at T = 353 K for t = 1 h and 12 h. Importantly, there was no impact of the time of annealing on the segmental and chain dynamics of PPGs incorporated within the porous alumina templates of constant and modulated pore sizes. For the AFM experiments, samples were fractured, and produced cross-section was investigated. In the experiment, we used membranes of comparable pore diameters, $D_p \sim 30$ nm.

1.4. Methods
Broadband Dielectric Spectroscopy (BDS). Isobaric measurements of the complex dielectric permittivity $\varepsilon^*(\omega) = \varepsilon'(\omega) - i\varepsilon''(\omega)$ were carried out using the Novocontrol Alpha dielectric spectrometer over the frequency range from $10^{-2}$ to $10^6$ Hz at ambient pressure. The temperature stability controlled by Quatro Cryosystem using a nitrogen gas cryostat was better than 0.1 K. Dielectric measurements of bulk PPG were performed in a parallel-plate cell (diameter: 10 mm, gap: 0.1 mm) immediately after preparation of the amorphous sample. AAO membranes filled with PPG were also placed in a similar capacitor (diameter: 10 mm, membrane thickness: 0.05 mm)\(^5,6\). Nevertheless, the confined samples are a heterogeneous dielectric consisting of a matrix and an investigated compound. Because the applied electric field is parallel to the long pore axes, the equivalent circuit consists of two capacitors in parallel composed of $\varepsilon^*_{\text{compound}}$ and $\varepsilon^*_{\text{AAO}}$. Thus, the measured total impedance is related to the individual values through

$$\frac{1}{Z^*_{\text{c}}} = \frac{1}{Z^*_{\text{compound}}} + \frac{1}{Z^*_{\text{AAO}}},$$

where the contribution of the matrix is marginal. The measured dielectric spectra were corrected according to the method presented in Ref.\(^7\).

To determine the mean relaxation times of the normal and segmental modes, $\tau_{NM}$ and $\tau_\alpha$, the obtained experimentally dielectric spectra were further analyzed by the superposition of two Havriliak-Negami (HN) functions with an additional term related to the dc conductivity\(^8\):

$$\varepsilon^*(\sigma) = \frac{\sigma_{dc}}{\varepsilon_0\sigma} + \text{Im} \sum_{i=1}^{2} \left( \varepsilon_{\infty} + \frac{\Delta\varepsilon_i}{1 + (i\sigma\tau_{\text{HN}_i})^{\alpha_{\text{HN}_i}}} \right)^{\beta_{\text{HN}_i}},$$  \hspace{1cm} (1)

where $\alpha_{\text{HN}}$ and $\beta_{\text{HN}}$ are the shape parameters representing the symmetric and asymmetric broadening of given relaxation peaks, $\Delta\varepsilon$ is the dielectric relaxation strength, $\tau_{\text{HN}}$ is the HN relaxation time, $\varepsilon_0$ is the vacuum permittivity and $\sigma$ is an angular frequency ($\sigma = 2\pi f$). Note that $\tau_{NM}$ and $\tau_\alpha$ were estimated from $\tau_{\text{HN}}$ accordingly to the equation given in Ref.\(^9\).

To determine the glass transition temperatures of all examined materials (bulk and confined), the estimated segmental relaxation times were fitted by a combination of the Vogel-Fulcher-Tammann (VFT) and Arrhenius equations. It should be mentioned that both functions were applied only for the PPG incorporated into const AAO membranes due to the observed deviation in the slope of $\tau_\alpha(T)$-dependences at $T_{g,\text{interfacial}}$. Note that the VFT equation was used only for an accurate determination of a point (temperature), at which the slope changes; while, the glass transition temperatures of confined samples (in this case of the core molecules) were estimated from the extrapolation of Arrhenius fits. In turn, for the bulk samples and PPG infiltrated into const-AAO, only a single VFT equation was applied\(^10,11,12\):

$$\tau_\alpha = \tau_\infty \exp\left( \frac{D_\alpha T_0}{T - T_0} \right),$$  \hspace{1cm} (2)
where $\tau_\alpha$, $D_T$ and $T_0$ are fitting parameters. The Arrhenius equation was used as follows:

$$\tau_\alpha = \tau_\infty \exp\left(\frac{\Delta E}{k_B T}\right),$$  

(3)

where $k_B$ is the Boltzmann constant, and $\Delta E$ is the activation energy. Determined values of $T_g$ were added to Fig. 4. Note that $T_g$ is defined as a temperature at which $\tau_\alpha = 100$ s and the glass transition temperature of core molecules of examined confined materials, determined from the extrapolation of the Arrhenius fit, is denoted as $T_{g,\text{core}}$.

Fig. S1. (a) Dielectric loss spectra measured for PPG-OH of $M_n = 2,000$ g/mol confined in modul-AAO membranes. As an inset, dielectric spectra of the bulk are presented. (b) Comparison of loss peaks recorded for bulk and infiltrated PPG-OH of $M_n = 2,000$ g/mol at $T = 219$ K. (c) Temperature dependences of $\tau_{NM}$ and $\tau_\alpha$ of bulk and infiltrated PPG-OH of $M_n = 2,000$ g/mol.
Fig. S2. Time evolution of the loss spectra measured for PPG-OH of Mn = 4 000 g/mol confined into const-AAO of $D_p = 36$ nm (a) and modul-AAO of $19 \leq D_p \leq 28$ nm (b) nanochannels at indicated temperatures. As insets, the shift of $\alpha$-peak upon the annealing at higher temperature are presented. (c,d)Temperature dependencies of segmental relaxation times before and after the performed annealing experiments.
Fig. S3. Time evolution of the loss spectra measured for PPG-OH of $M_n = 2\,000$ g/mol confined into const-AAO of $D_p = 36$ nm (a) and modul-AAO of $19 \leq D_p \leq 28$ nm (b) nanochannels at indicated temperatures. (c,d) Temperature dependencies of segmental relaxation times before and after the performed annealing experiments.

**Differential Scanning Calorimetry (DSC).** Calorimetric measurements were carried out using a Mettler–Toledo DSC apparatus (Mettler–Toledo International, Inc., Greifensee, Switzerland) equipped with a liquid nitrogen cooling accessory and an HSS8 ceramic sensor (heat flux sensor with 120 thermocouples). Temperature and enthalpy calibrations were performed by using indium and zinc standards. Measurements were carried out on bulk and the crushed membranes filled with the examined compound. The samples were contained in sealed crucibles, with a heating rate of 10 K/min over a temperature range from 170 K to 300 K.
Fig. S4. DSC thermograms of bulk (a) and confined (b,c) PPG-OH of $M_n = 4\,000\, g/mol$.

**Atomic Force Microscopy (AFM).** Surface topography and mechanical parameters (adhesion) were measured using a NanoWizard®3 BioScience (JPK Instruments, Berlin, Germany) AFM. Images were acquired using ultra-sharp Si tips with a diamond-like spike with different force constants ($3 - 5\, N/m$) and the resonant frequencies ($75 - 150\, kHz$). Statistical analysis and mechanical parameters were estimated using JPK software and Gwyddion package. These investigations were performed along the cross-section of both empty and polyalcohol filled membranes.

The AFM technique can be directly implemented for the measurement of the adhesion force between the sample and the cantilever tip. To do that, the tip is brought into contact with the sample at a constant velocity until the maximum load is obtained. Afterwards, the movement is reversed, and the sample and the tip are separated. However, due to the interaction between the tip and the surface, a certain force has to be applied to separate them again. This force is described as the adhesion force in our experiments, and it can be defined as the total force that is exerted by a liquid on the AFM tip. This force depends on several parameters. The most important one is a linear function of the liquid surface tension $\gamma_L$.

Thus, by measuring several force-curves in a raster, one can generate an adhesion map. This map can be further analyzed.
and compared to the sample topography. Typical topography along with the adhesion map of a cross-section of a membrane are presented in Fig. S5.

![Fig. S5](image1.png)

**Fig. S5.** Typical AFM results for a cross-section of AAO modulated membrane (a) topography (b) adhesion map.

It is crucial to mention that the presented adhesion map is a result of the analysis of a number of curves, 65536 per image (typical force-distance curve is shown in Fig. S6).

![Fig. S6](image2.png)

**Fig. S6.** Typical force-distance curve measured on the empty AAO membrane.

One can notice a slight correlation between the topography and adhesion force maps most probably stemming from the increase of the adhesion inside the pore due to the presence of residual water. This fact shows that to obtain reliable values of the adhesion between the AFM tip and the PPG other factors, such as the presence of water, has to be factored. Thus, the data from tens of images for each sample was gathered (more than 300k curves) and compiled into
single histogram showing contribution from different components. Typically only 2 or 3 distinctive components were found; 1) adhesion between AFM tip and the AAO membrane material, 2) adhesion between AFM tip and the thin layer of residual water, 3) adhesion between the AFM tip and PPG. Further, to avoid any influence from any tip-surface related parameters (contact size, tip material etc.), we decided to analyze only the difference between adhesion force of PPGs within nanochannels and the adhesion force of the empty AAO templates.

The AFM technique is also well suited for the analysis of the determination of root mean square error (RMS). However, in the case of AAO membranes simple approach of gathering RMS value from the whole image is problematic. First, during large fracturing surface of the pore material is revealed, while our sole interest lays in the roughness inside the nanometer-sized pores, not between them. Second, the measurement of the RMS on the curved surface with such small curvature is very difficult. Third, the fracturing can open pores not only in one layer but in several, thus increasing the roughness for the whole image as shown in Fig. S7. In this case, we have decided to measure the RMS along certain paths (lines). We have gathered data from each revealed pore centre and averaged it over tens of pores; a typical path is showed in Fig. S8. The results can be found in Table S1.

| sample    | pore size (nm) | line RMS (nm) |
|-----------|----------------|---------------|
| modulated | 19             | 1.7           |
| reference | 28             | 6.2           |
|           | 36             | 2.5           |

Table S1. The line RMS (the roughness measured along with pores) for the different AAO membranes.
It is worthwhile to mention that the modulated AAO membranes consisted of $19 \leq D_p \leq 28$ nm, pores sizes with the volume ratio of 1:1. Thus the average line RMS for modulated AAO membrane was approximately 4.0 nm, thus giving value almost twice as the reference pore.

**Fig. S8.** The typical path along which we have investigated the line RMS values.

**Scanning Electron Microscopy (SEM).** A field-emission scanning electron microscope (FE-SEM Hitachi S-4700, Tokyo, Japan) was used to study the morphology of cross-sections of anodic aluminum oxide (AAO). Before FE-SEM examination, the samples were broken and pre-etched in 5 wt% $\text{H}_3\text{PO}_4$ at 25 ºC for ca. 7 min. Subsequently, the samples were attached to the holder and sputter-coated with a thin (~12 nm in thickness) conductive Au layer using a vacuum sputter coater (Emitech K575X). The imaging was performed at accelerating voltage of 20 kV, emission current of 9 µA, the working distance was 12.8 mm, and the lens mode was normal.

The length of each segment, $L$, is $L = 429 \pm 49$ nm and $L = 347 \pm 25$ nm of narrower and wider pore size, respectively. Note that this parameter was calculated from 50 different places in the taken SEM picture, see **Fig. S9**.
**Fig. S9.** FE-SEM micrographs collected for the cross-section of applied anodic aluminum oxide (AAO) of modulated pore size. Light and dark fragments represent narrower and wider pore size, respectively.

**Fourier Transform Infrared Spectroscopy (FTIR).** FTIR spectra were collected on a Thermo Scientific Nicolet iS50 spectrometer in the range of 4000-1300 cm\(^{-1}\). 32 scans were averaged for each spectrum at a spectral resolution of 4 cm\(^{-1}\). The measurements were carried out at room temperature (\(T = 293\) K) and the glass transition temperature (\(T_{g,\text{bulk}} = 201\) K and \(T_{g,\text{core}} = 183\) K of PPG-OH within const-AAO). Each AAO membrane was placed into a Linkam THMS 600 (Surrey, UK) heating/cooling stage and cooled to the glass transition temperature, in an atmosphere of nitrogen, at a constant cooling rate of 10 K min\(^{-1}\). The desired temperature was measured with an accuracy of ±0.1 K. The time-dependent IR spectra were recorded at equal intervals, i.e., every 1 minute after the temperature stabilization at \(T = 183\) K.
Fig. S10. (a) FTIR spectra of bulk and confined PPG-OH of $M_n = 4\,000$ g/mol within AAO membranes of constant (red dash line) and modulated (solid blue line) pore sizes normalized to the $\nu_{O-H}$ band at $T=293K$ and $T=T_g$; (b) Comparison of the $\nu_{O-H}$ peaks recorded for confined PPG-OH at $T = 183$ K at initial times ($t = 1$ min) and after $t = 30$ min.

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