Supporting Information

In Situ Monitoring the Imbibition of poly(*n*-butyl methacrylates) in Nanoporous Alumina by Dielectric Spectroscopy.

Chien-Hua Tu,¹ Martin Steinhart,² Hans-Juergen Butt,¹ and George Floudas* ^{3,1}

¹ Max Planck Institute for Polymer Research, D-55128 Mainz, Germany

² Institut für Chemie neuer Materialien, Universität Osnabrück, D-49069 Osnabrück, Germany

³ Department of Physics, University of Ioannina, 45110 Ioannina, Greece

*Author for correspondence: E-mail: gfloudas@uoi.gr (G.F.)

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I. Surface characterization (XPS)

XPS measurements were made to determine the surface characteristics of the electropolished Al disks coated with the thin native oxide layer in comparison to the AAO templates. An Axis Ultra DLD imaging X-ray photoelectron spectrometer was used utilizing a MgK α X-ray source (15 kV, 30mA (450W)). Spectra were recorded at an angle of 90 ° to the surface.



Figure S1. XPS high-resolution spectra from the electropolished Al disks coated with the thin native oxide layer. Spectra refer to oxygen (left), aluminum (center) and phosphorous (right) concentrations.

Figure S1 gives the oxygen, aluminum and phosphorous concentrations in the electropolished Al disks coated with the thin native oxide layer. The relative contributions of oxygen, aluminum and phosphorous is 69%, 9% and 1.5%, respectively. The O 1s spectrum provides information on the possible type of alumina. The main oxygen contribution is from oxidic oxygen (531.3 eV) (e.g., Al₂O₃) with a minor contribution from aluminum hydroxide (e.g., Boehmite AlO(OH), Gibbsite Al(OH)₃ or Augelite Al₂(PO₄)(OH)₃)).¹ On the other hand, the Al 2p spectrum shows two distinct contributions at 71.8 eV and 74.5 eV, corresponding to aluminum metal and aluminum oxide and/or aluminum hydroxides. Given the small contribution of hydroxide in the oxygen spectrum we conclude that the main contribution is from aluminum oxide.² Lastly a small contribution form phosphorous is found. These results on the surface characterization of the electropolished Al disks coated with the thin native oxide layer indicate similarities to surface properties of native AAO membranes. ³

II. Dielectric Spectroscopy



Figure S2. Dielectric loss curves at three temperatures for the two homopolymers (top): **PnBMA 5.5k** and (bottom): **PnBMA 100k**. The curves correspond to the separate α - and β -processes at the lower temperatures (293 K, 313 K) and to the merged $\alpha\beta$ -process at the higher temperatures (343 K, 373 K).

III. Rheology



Figure S3. Master curves for the storage (black triangles), the loss (red rhombi) moduli and the shear viscosity (green circles) all constructed at the same reference temperature (343 K).



Figure S4. (left) Shift factors for the homopolymers and their blends at the reference temperature (343 K). Solid lines represent fits to the WLF equation. (right) WLF coefficients as a function of blend composition, $\varphi_{PnBMA 5.5k}$, at the reference temperature.



Figure S5. Attempted use of time-temperature superposition for the PnBMA 5.5k (top) and PnBMA 100k (bottom) homopolymers and their symmetric blend (middle) at the same reference temperature .tTs does work because of overlapping processes with different temperature dependencies.





Figure S6. SEM images of a cross section from an AAO template with a 65 nm pore diameter showing a gold layer on the top surface and small gold particles in a maximum depth of 380 nm. (b) is a magnification of (a).



Figure S7. SEM image showing the presence of a meniscus (in yellow circles) at the tip of the advancing **PnBMA 5.5k** melt within an AAO template with a 400 nm pore diameter. The image refers to 5625 s of imbibition at 343 K.

V. Reflection optical microscopy (length calibration)



Figure S8. Imbibition lengths extracted by the two differed methods: (circles) from the evolution of the dielectric strength, (squares) from the equivalent circuit. The polymer is **PnBMA 5.5 k**, the templates have a diameter of 65 nm and the imbibition temperature is at 333 K. The image from reflection optical microscopy (inset) is obtained at the end of the imbibition process (corresponding yellow square point at 88 μ m).

VI. Dynamic contact angle



Figure S9. Fits of the dynamic contact angles of PnBMA 5.5k to the Cox model at three different temperatures; (top) T=343 K, (middle) T=333 K and (bottom) T=323 K.



Figure S10. Fits of the dynamic contact angle of the blends B1 (top) and B2 (middle) to the Cox model at T=343 K.

VII. AAO templates closed from one end vs open in both ends (free standing). Effect of trapped air.

The effect of trapped air was studied in AAO templates with nominal pore size of 65 nm. Figure S11, provides the imbibition length at 343 K for a AAO template with only one open end. It shows the expected increase as $t^{1/2}$ followed by a bending at longer times due to the pressure exerted by trapped air. To compare this with a AAO template with two open ends the following procedure was used. A 10% H₃PO₄ water solution was employed and the AAO template was put on top. In this way the closed side -which appears glossy- was in contact with the acid. As soon as the pore bottoms are opened, the solution flows through the pores to the upper AAO surface with the initial pore openings. Subsequently, the AAO template was removed from the acid solution and rinsed with water. As we can see from Fig. S11, this procedure inevitably results in pore widening especially from the template side in contact with the solution. This is shown in consecutive SEM images taken along the pore length indicating that the pore widening starts already from the middle region (B) all the way to the bottom (C). The pore widening process makes the comparison with the templates with one open end a difficult task especially for the longer imbibition times. The comparison of the two templates, one with one open end vs two open ends, is shown in Fig.S11. It shows comparable imbibition lengths at the beginning of the process. However, at longer times pore widening results to a further increase of the imbibition length without showing the bend over characteristic of trapped air. The Figure confirms that the origin of the non-linear dependence at long times for AAO templates with one open end is the pressure exerted by the trapped air at the bottom of nanotubes.



Figure S11. (Left) Comparison of the imbibition lengths at a temperature of 343 K for a template with one open end (red circles) and a template with two open ends (blue squares). The AAO template with the one open end had pore diameters (2R) of 65 nm. Calibration points from reflection microscopy are

shown with respective filled symbols. (Right) SEM images of the AAO template with two open ends taken at various positions along the nanopores: (A) 1.5 μ m, (B) 65 μ m and (C) 100 μ m from the top opening. The corresponding analysis with *ImageJ* reveals a widening of pores at the bottom.

VIII. Effective viscosity and dead layer thickness

According to a recent theory by M. Doi, the imbibition of entangled polymer melts is governed by the competition between two mechanisms. The first is the standard hydrodynamic flow. Under conditions of strong adsorption between the walls and the polymer a layer of immobile surface layer is formed (dead layer) reducing the pore radius, and leading to an increase in the effective viscosity. The second mechanism is the reptation of chains under a pressure gradient. The latter mechanism under strong confinement enhances the mobility of chains, leading to a faster imbibition (plug flow). According to the model the effective viscosity (η_{eff}) experienced by the polymer in confinement relative to the bulk (η_0) is:

$$\frac{\eta_{eff}}{\eta_0} = \left[\left(\frac{R_{eff}}{R} \right)^4 + \varphi \frac{8N_e^{\alpha} b^3 \eta_0}{3\zeta N R^2} \right]^{-1}, \ \eta_0 \approx \frac{\zeta b^2 N^3}{V_0 N_e^2}$$
(S.1)

The effective viscosity is of the form:

$$\frac{\eta_{eff}}{\eta_0} = [f(\Delta R, R) + g(\phi, N, R)]^{-1}$$
(S.2)

where the first function, f, is related to the dead-zone with thickness ΔR ,

$$f(\Delta R, R) = \begin{cases} \left(1 - \frac{\Delta R}{R}\right)^4 & \text{if } R > \Delta R\\ 0 & \text{if } R < \Delta R \end{cases}$$
(S.3)

The second function, g, is from the reptation model,

$$g(\phi, N, R) = \varphi \frac{8N_e^{\alpha}b^3\eta_0}{3\zeta NR^2} = \varphi \frac{8N_e^{\alpha-2}b^5N^2}{3V_0 R^2} = \phi \frac{N^2}{R^2}$$
(S.4)

Here φ is the fraction of free chains and *N* is the degree of polymerization. We have applied the model for **PnBMA 5.5k** in AAO at 343 K (Fig. 6) and the results for the effective viscosity relative to the bulk are included in **Figure S11**. Evidently, the dead layer effect is dominant for this molecular weight. From the fit to the model a dead layer thickness of about 2 nm was estimated.



Figure S12. The ratio η_{eff}/η_0 for the **PnBMA 5.5k** within AAO with different pore diameters (2R) plotted as a function of 1/R extracted. The effective viscosity is extracted from the slopes of Figure 6 (at 343 K). Lines are theoretical predictions (fraction of free chains $\varphi = 3 \times 10^{-5}$ nm², degree of polymerization, *N*=40) plotted for different values of the dead-zone thickness, ΔR . A dead zone thickness of approximately 2 nm is obtained.

Rerefences

1. Thissen, P.; Valtiner, M.; Grundmeier, G. Stability of phosphonic acid self-assembled monolayers on amorphous and single-crystalline aluminum oxide surfaces in aqueous solution. *Langmuir* **2010**, *26*, 156-164.

2. Strohmeir, B.R. An ESCA method for determining the oxide thickness of aluminum alloys. *Surface and Interface Analysis* **1990**, *15*, 51-56.

3. Selevou, A.; Papamokos, G.; Yildirim, T.; Duran, H.; Steinhart, M.; Floudas, G. Eutectic Liquid Crystal Mixture E7 in Nanoporous Alumina. Effects of Confinement on the Thermal and Concentration Fluctuations. *RSC Advances* (submitted).