Supporting information for

Can Thickness and Interfacial Interactions Univocally Determine the Behavior of Polymers Confined at the Nanoscale?

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A.   *Molecular weight dependence of the thickness of the irreversibly adsorbed layer at t*<<1*

B.   *Determination of the crossover and of the characteristic adsorption time*

A. *Molecular weight dependence of the thickness of the irreversibly adsorbed layer at t*<<1*
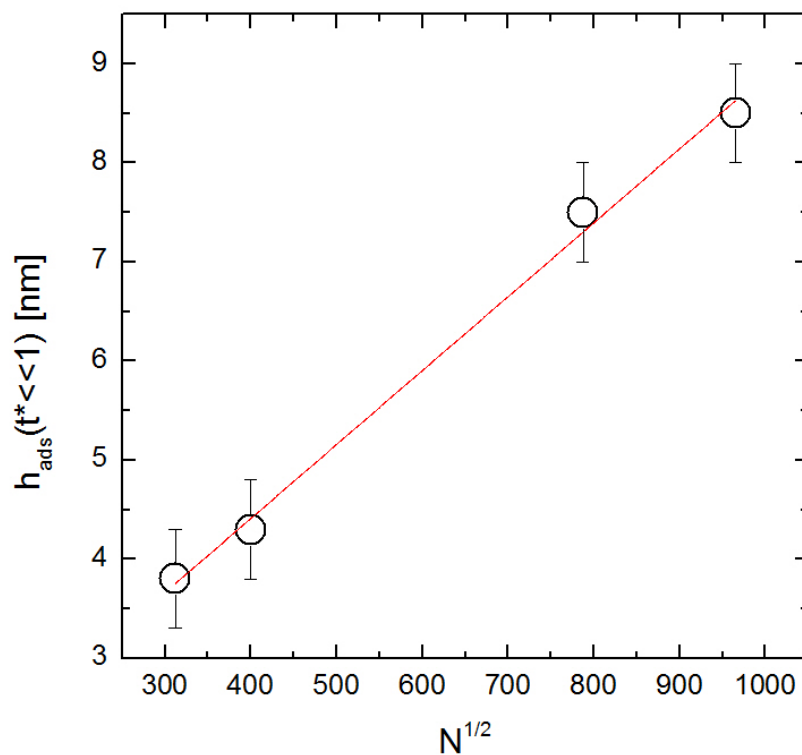

Figure S1   The thickness of the Guiselin brushes measured at short annealing times is plotted as a function of $N^{1/2}$, where N is the polymerization degree (here obtained as M_w/m_{mon}, where m_{mon} is the mass of one monomer). Such a correlation implies that the thickness of the irreversibly adsorbed layer (t*<<1) scales with the gyration radius ($\sim N^{1/2}$) and disproves the presence of croisslinking, which would instead result in $h_{ads} = const$.

B. *Determination of the crossover and of the characteristic adsorption time*
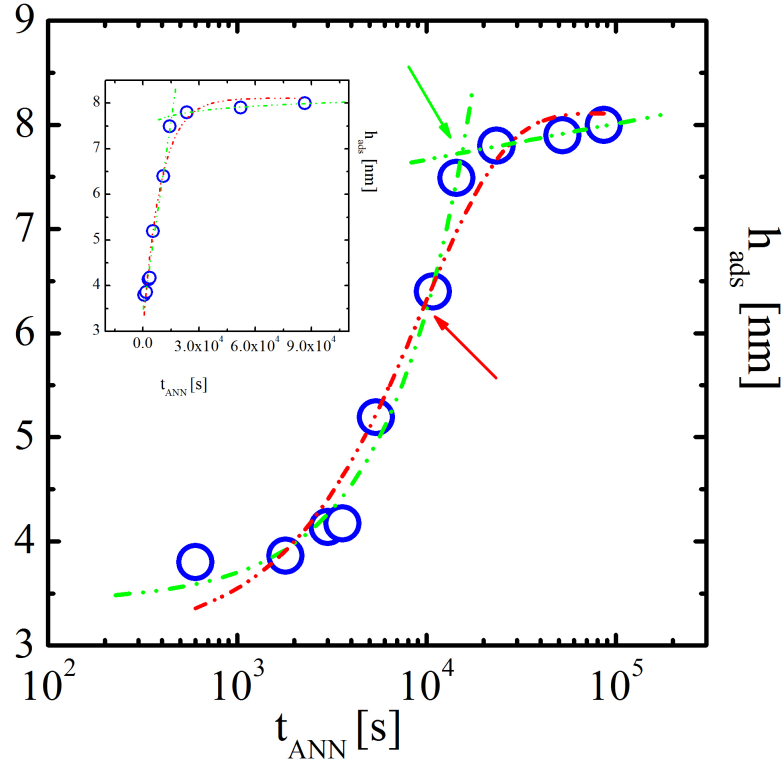

Figure S2   Comparison between an exponential fit (red line) an a power law/logarithmic fit (green line) for the data of PS97 in Figure 1, as a function of the time of annealing in a logarithmic scale. The red arrow indicates the characteristic adsorption time, t_{ads}, while the crossover time, t_{cross}, is indicated in green. The same data are plotted in the inset as a function of the time of annealing in a linear scale.

In line with the scaling predicted by Ligoure and Leibler [S1] and then Zajac *et al.* [S2], the thickness dependence of the adsorbed layer (and of the decay in dielectric strength [S3]) should formally be described in terms of a crossover between a power law and a logarithmic growth

$$h_{ads}(t) = \begin{cases} h(t=0) + gt^{\alpha} & t < t_{cross} \\ h(t=t_{cross}) + B\log t & t > t_{cross} \end{cases}$$

However, due to the large errors in the determination of h_{ads} (or of the adsorbed amount), several authors in the past preferred to use a simpler exponential form (see for example [S4]) of the type

$$h_{ads}(t) = h(t=0) + h_{ads}^{max}\left[1 - \exp\left(-t/t_{ads}\right)^{\beta}\right]$$

In the case that the slope of the logarithmic growth is not too large, it is not possible to distinguish between the "power law/logarithmic" and the "exponential" scenario, especially when the data are

plotted as a function of the time, and not its logarithm. The kinetics of irreversible adsorption of PS on Al presents such an ambiguity, see Figure **S2**. In addition to having less free parameters (4 vs 6), although less precise, the exponential fit permits to assign a characteristic time also in the case that the crossover to the logarithmic regime is not yet experimentally observed.

Fitting the data of Figure 1 with an exponential function, yielded $t_{ads} = (9.6 \pm 1.7)\ 10^3$ s, while the crossover fit gave $t_{cross} = (14 \pm 2)\ 10^3$ s. For the estimation of t* we used t_{ads} from exponential fits for PS97 and PS160; the constant value of h_{ads} for PS640 and PS932 (we checked the thicknesses at different annealing times but we did not perform the free volume experiments for these samples, as instead we did for PS160), implies that t*<<1 during the whole measuring time, which is in line with the scaling discussed in the text.

Following this formalism the transition between the power law regime and the logarithmic growth for PS97 occurs at t*=1.45 ± 0.46, i.e. t*~1. We stress that t* should not be interpreted as an absolute value, but just as an order of magnitude, which permitted us to define three regimes in the deviations from bulk behavior, i.e. t*<<1, t*~1 and t*>>1, see [S**5**] and [S**3**].

[S**1**] Ligoure, C.; Leibler, L. *Journal De Physique* **1990**, *51*, 1313

[S**2**] Zajac, R.; Chakrabarti, A. *Physical Review E* **1995**, *52*, 6536

[S**3**] Rotella, C.; Napolitano, S.; Vandendriessche, S.; Valev, V. K.; Verbiest, T.; Larkowska, M.; Kucharski, S.; Wubbenhorst, M. *Langmuir* **2011**, *27*, 13533

[S**4**] Durning, et al. Macromolecules **1999** 32, 6772

[S**5**] Napolitano and Wubbenhorst Nat Comm. **2011** 2, 260