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

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S *Supporting Information*

ABSTRACT: The behavior of polymers confined in ultrathin films (thickness < 200 nm) can sensitively differ from that observed in macroscopic samples. Based on the simple arguments of finite size and interfacial effects, film thickness, and surface interactions should be sufficient to univocally determine the deviation from bulk behavior. However, recent models suggest that a third key parameter, namely, the interfacial free volume, should also be considered. We describe a novel methodology that quantifies the volume available for structural relaxation at the interface between a thin polymer layer and its supporting substrate. Experiments performed at different annealing conditions verified that the shift in glass transition temperature, measured in thin films upon confinement, is proportional to the degree of adsorption and, thus, to the interfacial free volume.
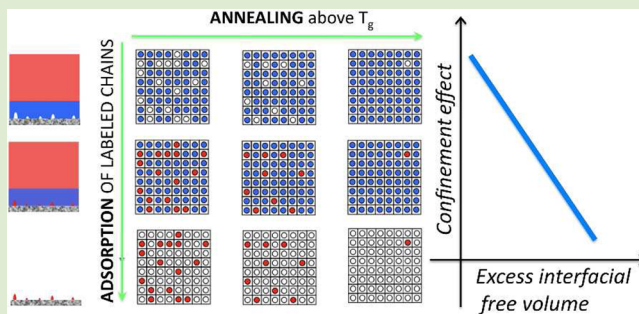
Confined at the nanoscale level, where the contribution of interfacial layers becomes relevant, polymers show a peculiar behavior characterized by a shift in the phase transition temperatures and dramatic changes in other physical properties with respect to the bulk.[1−9] Such confinement effects may be related to specific chain configurations, adopted by polymers in the attempt to reach thermodynamic equilibrium, minimizing their free energy under the perturbations in the intermolecular potential induced by interfaces.[10,11] In bulk, the exploration of the energy landscape requires times much shorter than τ_{REP}, the reptation time necessary to completely disentangle from the tube induced by screening of neighboring segments.[12] In confined geometries, on the contrary, equilibration might require much longer time scales, often larger than those of technological interest.[13,14] In fact, in proximity of nonrepulsive interfaces, reptation cannot take place due to the lack of space resulting from the monomer excess in the adsorbed layer.[15] In the case of ultrathin polymer films, we verified that the deviations from bulk behavior have a finite lifetime,[14] related to the kinetics of irreversible adsorption, which, for polystyrene (PS), significantly exceeds τ_{REP}. The separation increases with the molecular weight and it reaches 6 orders of magnitude for PS160 (where 160 indicates the molecular weight in kg/mol).

Sample preparation introduces further complications. Films prepared by spin-coating of dilute solutions suffer from fast evaporation of the solvent,[16,17] in the regime used for nanometers-thick films (typically ~1−10^{-2} w/w %) chains are, in fact, single entities not overlapping with each other. The memory of the configurations adopted in solutions persists in the dry film. Upon solvent evaporation, when the volume

fraction of the polymer reaches a critical value, vitrification takes place. Molecules are thus trapped in packing geometries where the overlap between chains is reduced (lower entanglement density), resulting in a lowered viscosity,[13,18] and influences dewetting.[19,20]

Furthermore, a recent investigation of the impact of solvent quality on the equilibration time necessary to recover bulk entanglement density,[21] suggests the existence of a correlation between the pinning density (degree of chain adsorption) at the polymer/solid interface and the viscosity of the whole film.

In our recent work,[14,22] we demonstrated the possibility of tuning the glass transition temperature (T_g) of thin films without altering the quality of the spin-coating solvent (same entanglement density), the nature of the substrate (same interfacial interactions), or the film thickness (constant surface/volume ratio). Instead, we showed that the time dependence of T_g corresponds to the thickening of the layer of chains irreversibly adsorbed onto the substrate (Guiselin brushes,[23] known also as residual layers[24]). We speculated that such a strong correlation between structure and dynamics in the adsorbed layer is due to the monomer density at the polymer/substrate interface, which acting as local free volume (here intended as space available for the molecular relaxation) alters the structural dynamics and, thus, T_g. Following this hypothesis, an increase in free volume, caused for example by packing frustration, might result in an acceleration of the segmental

dynamics and thus justify a reductions of T_g even in the presence of slower dynamics associated to chain adsorption.

In this Letter we present experimental evidence that the deviation from bulk behavior in ultrathin polymer films originates from the differences in free volume related to nonequilibrium conformations assumed by polymer chains in the irreversibly adsorbed layer. To prove our hypothesis, we developed an experimental approach that quantifies the effective local free volume, ζ, available at the interface between the polymer and the substrate, on the basis of the drop in the dielectric polarization of probe molecules allowed to diffuse at the adsorbed layers. Our ideas are finally supported by a strong correlation between the time evolutions of ζ and of T_g.

To achieve information on the interfacial layers (less than 10 nm) and to avoid the complications induced by film formation via fast evaporation of dilute solutions, samples were prepared in the configuration of Guiselin brushes. Thick films (thickness $\gg 4R_g$, typically 200 nm, where R_g is the radius of gyration) of neat polystyrene of different molecular weight (M_w) were spin-coated from a chloroform solution on thermally evaporated aluminum and then annealed for different times, t_{ANN}, at a temperature $T_{ANN} = T_g + 50$ K. Subsequent washing of the samples in the same good solvent (chloroform) used for spin-coating allowed removal of the nonadsorbed chains, and preserved the interfacial conformations.[23] Residual layers with thicknesses, h_{ads}, ranging from 3.8 to 8.5 nm were prepared by varying the annealing time t_{ANN} and M_w (97k < M_w < 932k, polidispersity < 1.11).

During annealing, the thickening of the irreversibly adsorbed layer of PS97 followed a power law ($h_{ads} \sim t^{0.9\pm0.1}$) until a crossover time $\approx 1.4 \times 10^4$ s indicated by a blue arrow in Figure 1, where the growth rate dropped and the kinetics became logarithmic (see Supporting Information for the procedure used to determine the crossover time). Such a transition, predicted by Ligoure and Leibler,[25] and by Monte Carlo simulations,[26] corresponds to the formation of highly stretched

brushes, limiting the insertion of new chains. Alternatively, in line with previous experimental reports on other physisorbed systems,[27] we could define a characteristic adsorption time by imposing an exponential growth $h_{ads} \sim 1 - \exp(-t/t_{ads})$, which permitted to build the dimensionless parameter $t^* = t_{ANN}/t_{ads}$, relevant in the following discussion on the impact of the structure on the deviation from bulk behavior.[14,28] At relatively short annealing times (for PS97, 5 min at $T_g + 50$K corresponds to more than 10^7 τ, where τ is the structural relaxation time, and to $t^* \ll 1$), h_{ads} is not zero, implying that adsorption already took place before reaching the annealing temperature. Considering the kinetics law involved, growth at $t^* \ll 1$ is slow; as a consequence, h_{ads} is constant, within experimental errors, up to an induction time $t_{on} \approx 2 \times 10^3$ s. Following our previous work,[29] we assigned t_{on} to the time the free chains need to diffuse through the first adsorbed layer. At $t > t_{on}$ chains can pin onto the available space at the PS/Al interface and continue the thickening of the Guiselin brush. This assumption implies that the increase in h_{ads} should be linearly proportional to the reduction of free volume at the polymer/metal interface

$$\zeta(t^*) \sim \text{const} - h_{ads}(t^*) \tag{1}$$

To verify the validity of the proposed scaling, we varied the thickness of the interfacial layer by annealing films of PS of different chain length at appropriate t_{ANN}, allowing direct comparison with the series of PS97, that is, this procedure permitted us to work with residual layers, annealed for the same time, having a comparable thickness ($\Delta h < 0.5$ nm) but different M_w, see Figure 1. The molecular weight dependence of the thickness of the first adsorbed layer, $h_{ads}(t^* \ll 1)$, agreed with a scaling of the type $M_w^{1/2}$ ($\sim R_g$), typical of the dry regime,[23] which verifies the effective removal of solvent molecules and the absence of cross-linking, see Supporting Information.

It was not possible to determine the local free volume at the interface PS/Al via scanning probe microscopy, due to the difficulty encountered by these approaches in characterizing buried interfaces and thin films and also because the fluctuations on the spatial distribution of these virtual holes created by the chain configurations on the time scale of the structural relaxation. Moreover, the extremely limited volume of the samples and the small density difference ($\leq 1\%$) that we aimed at measuring did not permit to use scattering techniques. To overcome this issue, we created a molding-like approach: we put the Guiselin brushes in contact with a reservoir of probe molecules, which, after diffusion inside the adsorbed layer, could finally irreversibly adsorb in the volume still free at the PS/Al interface (see Figure 2 for a scheme of the experiment). We obtained a measurement of ζ from the drop in probe amount after a long diffusion time.

For this purpose, we assembled multilayer films of a low molecular weight ($M_w \sim 20$k, thickness $h_{l-PS} = 50$ nm) polystyrene labeled with {4-[(4-cyanophenyl) diazenyl] phenyl}(methyl)amino, a highly polar side group (l-PS), on top of the irreversibly adsorbed layers of PS of different M_w listed in Figure 1. Metallization of the upper and lower surface of the bilayer PS/l-PS (aluminum 99%, pressure < 10^{-6} mbar, evaporation rate ≥ 10 nm s^{-1}, thickness ~ 50 nm; contact with air, before spin-coating, favors the formation of a layer of 2–3 nm of oxide on top of the metal, which enhances the affinity with l-PS), permitted the application of an AC electric field perpendicular to the surface of the polymers and the measure of
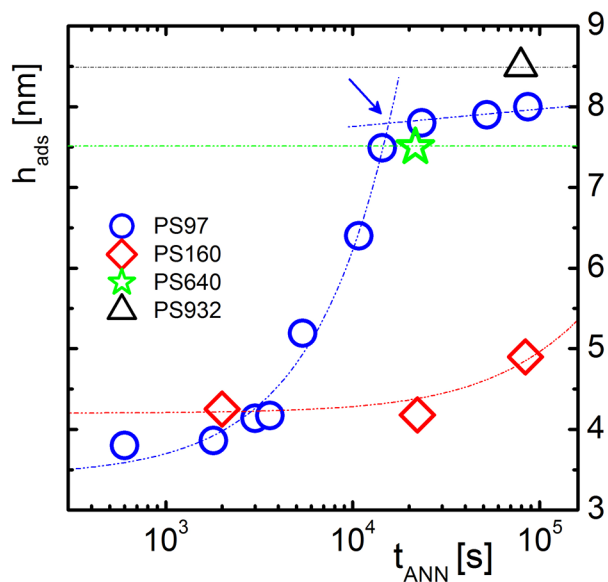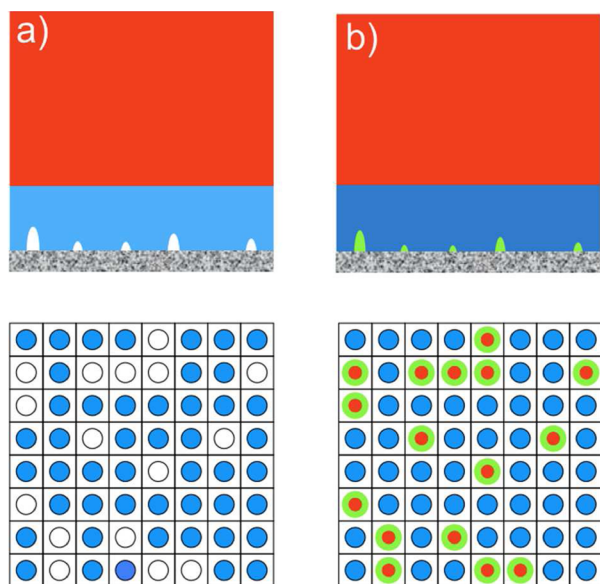

Figure 1. Time evolution of the thickness of the layer of polystyrene (PS, different molecular weights indicated in kg/mol) irreversibly adsorbed at 423 K on aluminum oxide. Dash-dotted lines indicate the kinetics of adsorption. An arrow indicates the crossover between power law and logarithmic regime for PS97.

Figure 2. Scheme (not in scale) of the molding approach used to determine the interfacial free volume ζ (white circles in the left lower panel), seen here as the opposite of the surface coverage of PS (blue circles). (a) To determine ζ, we placed a thick film of l-PS (a probe oligomer, red) on top of the interfacial layer of PS (blue). (b) The probes diffuse into the interfacial layer and finally occupy the free volume at the PS/Al interface, not yet occupied by PS (green). We follow the reduction of dielectric strength, while the probes irreversibly adsorb (green/red circles). The final drop in $\Delta\varepsilon$ is proportional to the number of probes immobilized and, thus, to the interfacial free volume.

Figure 3. Normalized interfacial free volume ζ (obtained via the procedure described in the text as the limiting value of $-\Delta\varepsilon_{high}$, the component in dielectric strength related to chain adsorption) as a function of the thickness of the irreversibly adsorbed layer for PS97 (blue circles), PS160 (red diamond), PS640 (green star), and PS932 (black triangle); to ease comparison, data were normalized to the value measured for Guiselin brushes of PS97 at $t_{ANN} = 17$ min. In the inset, time evolution of $-\Delta\varepsilon_{high}$ of l-PS during diffusion at 398 K in residual layers obtained from thick films of PS97 previously annealed at 423 K for 17 min (pink, top), 1.5 h (violet, middle), and 6.5 h (navy, bottom). The arrow indicates the thickness at the crossover time.

the current flow generated via an impedance analyzer. Film thickness was measured in single layers, by means of its electric capacitance, via a standard procedure.[14]

We monitored by dielectric spectroscopy the diffusion of l-PS in PS, followed by adsorption of the labeled chains onto Al. Measurements were performed at 398 K, where the adsorption of PS on Al is inhibited on the time scale of the experiment (t_{ads} increases upon cooling with an activation energy similar to that of the structural relaxation, so that $t_{ads}(398\ K)/t_{ads}(423\ K) \approx \tau(398\ K)/\tau(423\ K)$, that is, $t_{on}(398\ K)$ exceeds 10 days for PS97 and reaches almost 3 months for PS160). At the measuring temperature, the structural relaxation of l-PS appears as a peak in the dielectric loss of area corresponding to the dielectric strength ($\Delta\varepsilon$) and as a Kramers−Kronig correlated step in the real part of the dielectric function. Considering the intrinsically larger dipolar activity of l-PS ($\Delta\varepsilon_{l\text{-}PS}/\Delta\varepsilon_{PS} \approx 25$, $h_{l\text{-}PS}/h_{ads} > 5$), the contribution of PS to the total dielectric signal was negligible (<1%). Following a procedure that we described and validated elsewhere,[14,30] subtraction of a logarithmic background not related to the pinning of new chains permitted us to determine $\Delta\varepsilon_{high}$, the component of the dielectric strength proportional to the thickness of the adsorbed layer, see inset of Figure 3. Such proportionality arises from the link between the dielectric strength and the density number (N) of dipole moments (μ) participating in the orientational polarization ($\Delta\varepsilon \sim N\langle\mu^2\rangle$).[31] Pinning of chains onto a substrate, in fact, yields to a reduction of the solid angle where dipoles can reorient and the consequent drop in mean square dipole moment, justifying the strong correlation observed between $\Delta\varepsilon$ and the amount of adsorbed chains.
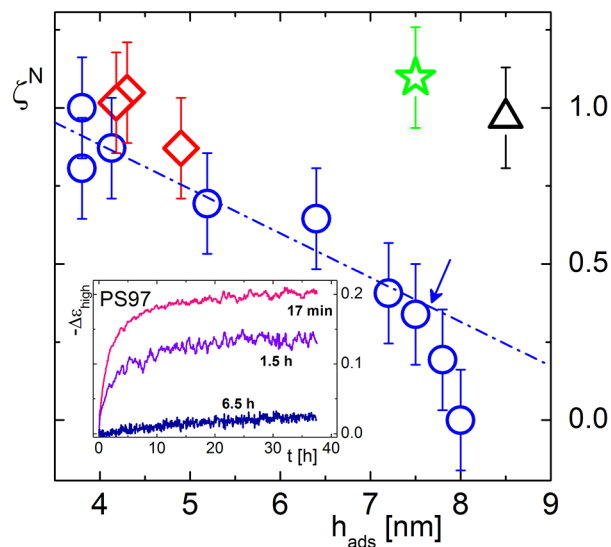
Similarly to what was discussed for $h_{ads}(t)$, the reduction rate of $\Delta\varepsilon_{l\text{-}PS}(t)$ increased after an induction time necessary for the diffusion of l-PS over the layer of PS, followed by adsorption onto Al. At much longer annealing times, $|d\Delta\varepsilon_{l\text{-}PS}(t)/d \log(t)|$ decreased to a value similar to the one at shorter times, implying that the adsorption process reached the final logarithmic stage, and almost all the available space at the PS/Al interface was finally filled by l-PS segments. The final drop in $\Delta\varepsilon_{high}$ is consequently proportional to the amount of segments of l-PS that could eventually adsorb. Because the adsorption of l-PS was possible only on the interfacial free volume not already occupied by chains of PS and because we kept constant the thickness of the l-PS layer (i.e., constant density of dipole moments), our molding-like approach permits the estimation of the local free volume as

$$\zeta \equiv \lim_{t \to \infty}\left[-\Delta\varepsilon_{high}(t)\right] \tag{2}$$

where the saturation value was obtained via an exponential fit of the experimental data. For interfacial layers of PS97 extracted from bulk-like samples annealed less than 14 h, ζ decreased with t_{ANN}, showing a strong correlation with the thickness of the interfacial layer up to the crossover between the power law and the logarithmic regimes ($t^* \sim 1$), see Figure 3, in line with our first hypothesis, see eq 1. The larger reduction in ζ at $t^* \sim 1$, see arrow, corresponds to the onset of a structural rearrangement[30] favoring more efficient packing in the adsorbed layer, as predicted by Monte Carlo simulations.[32]

The relation between the thickness of the residual layer and the limiting number of chains that can be pinned on the metallic surface and, thus, the surface coverage implies that thickening of the adsorbed layer mostly proceeds via an irreversible gradual filling of the empty spaces present at the

polymer/metal interface. Increasing the molecular weight did not influence the amount of adsorbed chains after long diffusion times, see Figure 3, suggesting that, at this stage of adsorption, that is, in the regime $t^* \ll 1$, the interfacial chain conformations are independent of the chain length. For these M_ws, investigations at larger t^* were not possible because of the risk of degradation upon exposure of such thin samples at elevated temperatures for the necessary experimental time (weeks, months, years, ...).

To complete the validation of our picture, we determined the value of the glass transition temperature of films of PS of constant thickness (∼20 nm) using the same molecular weight and annealing conditions as in Figure 1. We used capacitive dilatometry, that is, we exploited the direct proportionality between the electrical capacitance of the system and the inverse of the film thickness, an approximation valid in the geometry of parallel plates, as in our case.[33−35] The temperature dependence of the capacitance C(T) can thus be used to assign T_g to the temperature where dC/dT shows a discontinuity. Compared to bulk, we observed a faster dynamics, that is, reduction of T_g, in line with the experimental evidence collected by a large number of different techniques.[1] At annealing times much shorter than the adsorption time ($t^* \ll 1$), the difference between T_g of the film and bulk T_g (ΔT_g) is constant, regardless the molecular weight. On the contrary, for PS97, although the thickness was constant, ΔT_g changed with the annealing time and decreased until reaching zero, i.e. bulk T_g, where the local free volume approached zero. This evidence is in contrast with the commonly accepted ideas that surface/volume ratio (thickness) and interfacial interactions are sufficient to univocally determine the properties of ultrathin films and that the T_g of supported and capped films is molecular weight independent.[36] In fact, here we demonstrate that polymer films of the same thickness, prepared on the same substrate, from the evaporation of the same solvent, do show a significantly different T_g. This new experimental evidence cannot be adequately justified by the correlation between the thickness of the adsorbed layer and the shift in T_g[14,37] (see panel in Figure 4), whose validity is limited to each molecular weight data set, that is, the ratio $\Delta T_g/\Delta h_{ads}$ is a function of M_w. Combination of the values collected at different molecular weights and t_{ANN} supports instead the validity of a different scaling

$$\Delta T_g \sim -\zeta \qquad (3)$$

which directly correlates the perturbation in the glassy dynamics to a variation in the monomer density at the very interface between polymer and substrate, see Figure 4. Consequently, the faster dynamics modes should be related to localized excess in the volume that segments can explore during the conformational fluctuations, which manifest in the structural relaxation process. Such an idea is in line with reductions in glass transition temperature correlated to a higher specific volume,[38] larger interchain distances,[39] or a larger number of free volume holes at the interfaces.[40] Moreover, our results agree with the experimental observation that the enrichment in fast relaxation modes observed in as cast films (lower T_g), progressively extinguishes upon annealing.[14] The corresponding reduction in T_g vanishes upon an increase in the segment/surface ratio, that is, decreasing the value of ζ.

In conclusion, we introduced a new method permitting the determination of the local free volume at buried polymer/substrate interfaces. We found a strong correlation between
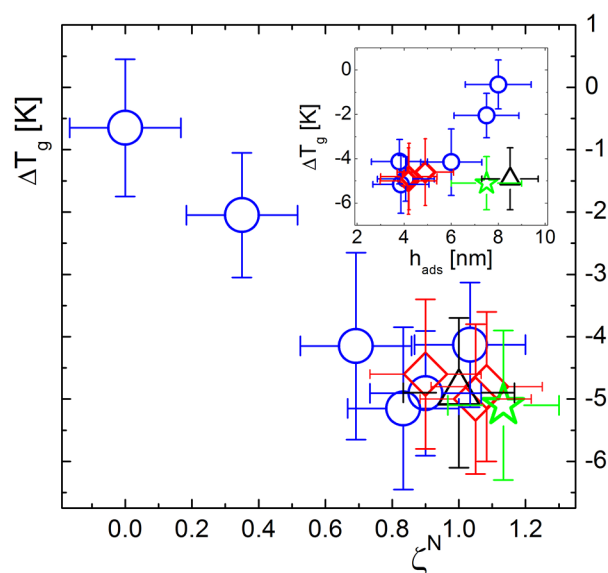

Figure 4. Correlation between the local free volume and the shift in T_g for PS97 (blue circles), PS160 (red diamond), PS640 (green star), and PS932 (black triangle). In the panel, a shift in T_g as a function of the thickness of the irreversibly adsorbed layer is observed.

such free volume and the changes in T_g in ultrathin film, which supports the idea that deviations from bulk behavior arise from the different nonequilibrium conformations assumed by polymers at the nanoscale,[4] that can eventually disappear after prolonged annealing.[41] Film thickness and interfacial interactions are not sufficient to fully predict the properties of macromolecules under confinement; models trying to describe the deviation from bulk behavior should consider also the perturbation in the free volume arising from chain adsorption.

■ ASSOCIATED CONTENT

S **Supporting Information**
Molecular weight dependence of the thickness of the irreversibly adsorbed layer at $t^* \ll 1$; determination of the crossover time and of the characteristic adsorption time. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes
The authors declare no competing financial interest.

■ ACKNOWLEDGMENTS

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