

Irreversible Adsorption Governs the Equilibration of Thin Polymer Films

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We demonstrate that the enhanced segmental motion commonly observed in spin cast thin polymer films is a nonequilibrium phenomenon. In the presence of nonrepulsive interfaces, prolonged annealing in the liquid state allows, in fact, recovering bulk segmental mobility. Our measurements prove that, while the fraction of unrelaxed chains increases upon nanoconfinement, the dynamics of equilibration is almost unaffected by the film thickness. We show that the rate of equilibration of nanoconfined chains does not depend on the structural relaxation process but on the feasibility to form an adsorbed layer. We propose that the equilibration of the thin polymer melts is driven by the slow relaxation of interfacial chains upon irreversible adsorption on the confining walls.

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Polymers confined at the nanoscale level exhibit altered behavior with respect to the bulk, characterized by shifts in the phase transition temperatures and significant changes in other physical properties [1–3]. Interfaces play an active role on these confinement effects, due to the perturbation in intermolecular potential imposed by the confining medium (air, substrates, living cell membranes, etc.), which in turn affects chain configurations and the local monomer density [4]. The interfacial origin of nanoconfinement is also reflected in the increase in the deviations from bulk behavior at larger surface-to-volume ratios (e.g., upon reduction of the film thickness in 1D confinement).

A further contribution to confinement effects should be taken into account. Because of fast processing—thin polymer layers are obtained upon rapid evaporation of diluted solutions, typically within 1 min—polymer chains do not have time to equilibrate and form an entangled network as dense as in bulk melts [5,6]. As the energy difference in these conformational states is rather low, the probability to lock a polymer in a state different than that of equilibrium is nonzero [7]. Following the spontaneous evolution of nonequilibrium states, the properties associated to these higher-energy conformations evolve upon time. Manifestation of these equilibration kinetics is, for example, the reduced viscosity observed in spin-cast films [8,9]. Annealing in the liquid state, above the glass transition temperature T_g allows (partial) recovery of bulk low properties. Remarkably, this process occurs at time scales exceeding by far reptation, the relaxation mechanism capable to erase the memory of nonequilibrium conformations in bulk melts [10]. The reasons for the large difference between the bulk reptation time and the equilibration time in thin films are multiple. First, for long chains, the formation of an entangled network requires time scales much larger than those of reptation [11,12]. Second, in the proximity of nonrepulsive interfaces, reptation cannot take

place due to the high degree of confinement in the adsorbed layer [13].

Recent studies prove that also the deviation from the bulk glass transition temperature ΔT_g can have a finite lifetime; that is, the value of T_g shift is not univocally related to the film thickness and nature of the supporting substrate, but it evolves upon time. In some cases, bulk conditions ($\Delta T_g = 0$) are recovered after spin coating upon annealing the system sufficiently long. These intriguing features have been observed in both capped (two polymer-solid interfaces [14]) and supported films (one polymer-solid interface) of linear [15–17] and nonlinear polymers, e.g., in star-shaped polymers [18], of a broad range of molecular weights and functionality.

Intuitively, as spin-cast films exhibit larger interchain and intrachain distances [19,20], the variation of T_g upon annealing time could be attributed to concomitant changes in the free volume content [21] via a mechanism mimicking physical aging of bulk glasses. This hypothesis is supported by the linear correlation between ΔT_g and the interfacial free volume content [22,23].

Annealing a thin film in the conditions where densification can occur, e.g., via adsorption of chains onto the supporting substrate, should thus allow recovering the segmental mobility of a bulk melt. Previous measurements on the impact of annealing on segmental mobility [24,25] are qualitatively in line with this conjecture: The excess in segmental mobility with respect to the bulk gets reduced upon prolonged annealing in the liquid state. Those preliminary investigations provide a limited data set (e.g., after “short” and “long” annealing). A quantitative picture is, hence, still missing. This information on segmental mobility cannot be obtained via measurements of the thermal glass transition temperature, observed as a kink in the temperature dependence of the volume. Under nanoconfinement, segmental mobility and vitrification show, in fact, different size dependences [3,26]

and diverging activation energies [27]. These anomalies imply that the Frenkel-Kobedo-Reiner relation [28], ensuring a constant product of the cooling rate of vitrification and the value of τ at the thermal T_g , might not hold in confinement. A direct determination of the segmental time is thus necessary.

To unravel the underlying molecular mechanism that governs the equilibration of nanoconfined polymers in the liquid state, in this Letter, we discuss the impact of annealing on the segmental mobility of thin films of poly(4-chloro styrene), P4ClS, capped between Al layers. Our experimental results verify that the observed acceleration of segmental relaxation time τ refers to high-energy states out of equilibrium. Prolonged annealing above T_g , in fact, allows recovering bulk segmental mobility. We identify that the equilibration mechanism is enslaved to molecular rearrangements resulting in irreversible adsorption of chains onto the supporting interfaces. Owing to a tremendous difference in time scales—equilibration and adsorption are, for the investigated system, 10^9 times slower than segmental mobility—it was possible to measure the value of the segmental time in films of different thickness at different annealing times $\tau_{t_{\text{ANN}}}^{\text{film}}$, over a temperature range sufficient to determine the activation energy of the different processes. Remarkably, the equilibration rate is invariant with τ^{bulk} and does not depend on the film thickness. Based on the evidence that the equilibration process has the same activation energy of the segmental mobility of films of thickness comparable to that of an adsorbed layer, we propose that the equilibration of the whole thin polymer melt is driven by the relaxation of the interfacial chains.

We considered the system Al/P4ClS/Al for multiple reasons. P4ClS—whose segmental dynamics is very sensitive to volume perturbations, compared to that of its hydrogenated analogue and other polymers [29]—is an optimal candidate to test the validity of ideas on confinement effects focusing on the role of free volume. The capping geometry allows the application of small electric fields, necessary to investigate the dielectric response of the systems via an impedance analyzer (ModuLab XM MTS, Solartron Analytical) and, hence, determine $\tau_{t_{\text{ANN}}}^{\text{film}}$ (see Supplemental Material [30] for further details on materials and methods). To discard effects of solvent evaporation and correlated structure equilibration in the glassy state [42], samples were preannealed [43] at $T_g + 10$ K for a time $>10^4 \tau^{\text{bulk}}$ and kept in high-vacuum conditions overnight; we then set $t_{\text{ANN}} = 0$ at the instant in which we reached thermal stability at the final annealing temperature T_{ANN} . We have tested the response to annealing in a broad temperature range for P4ClS (and for P4BrS, where a Br atom replaces the Cl in the same position of the phenyl ring; see Supplemental Material [30]) and verified that the discussion on the perturbations in segmental time does not depend on the chosen annealing temperature. Hence, from now on we will refer only to the value of segmental

time at the annealing temperature $T_{\text{ANN}} = 433$ K ($T_g + 33$ K); further information on the effect of temperature is given in the last sections of this Letter. In Fig. 1, we plotted the dielectric loss as a function of the frequency at T_{ANN} at different intervals during an overall annealing time of ≈ 2 days. A broad asymmetric peak, attributed to the (α -) segmental relaxation [44], is present.

Regardless of the film thickness, the frequency of maximum of such a peak, f_{max} , provides a measurement of τ , as $2\pi f_{\text{max}} \tau = 1$ [45]. At short annealing times, the structural peak moves towards higher frequencies (see red arrows in Fig. 1) for thinner films, indicating an apparent increase in segmental mobility upon confinement; see Fig. 2 (red circles, $\log \tau_0^{\text{film}}$). Down to thicknesses on the order of 10 nm, the reduction in τ_0^{film} is monotonic within experimental errors, in line with the trend reported for its regioisomer poly(2-chlorostyrene) [46] and for other polymers in the same geometry [3].

Here, we have effectively tested whether τ_0^{film} corresponds to the equilibrium value of the segmental time in the confined geometry. This evaluation was possible by monitoring in isothermal conditions the structural relaxation process of thin films of different thickness, up to observation times of almost 2 days, that is, almost 2 billion folds

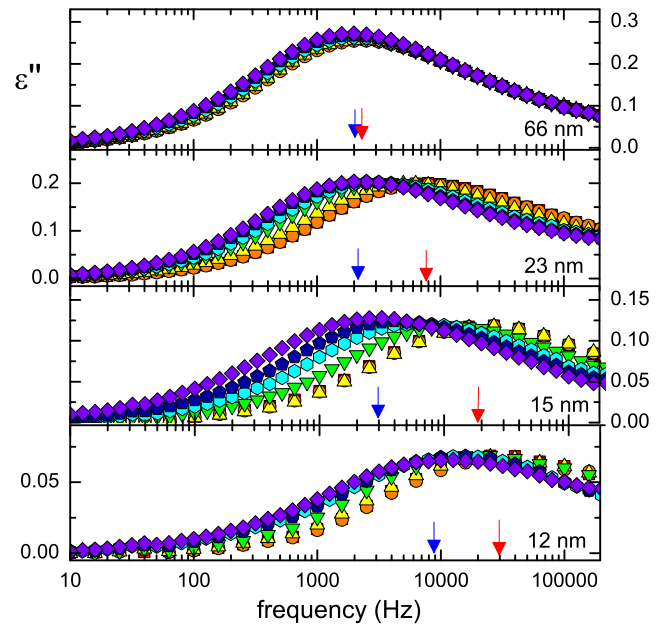


FIG. 1. The impact of thickness (indicated in the lower right corner of each panel) and annealing (red to violet curves were recorded at even intervals in a geometrical progression, while keeping the sample in isothermal conditions at $T = 433$ K) on the structural relaxation of thin films of poly(4-chloro styrene), visible as a peak in the frequency dependence of the dielectric loss, ϵ'' . Red arrows indicate the position of the peak maximum f_{max} at the onset of the experiment; blue arrows indicate the position of the peak after ≈ 2 days of annealing. The segmental relaxation time τ is given by $(2\pi f_{\text{max}})^{-1}$.

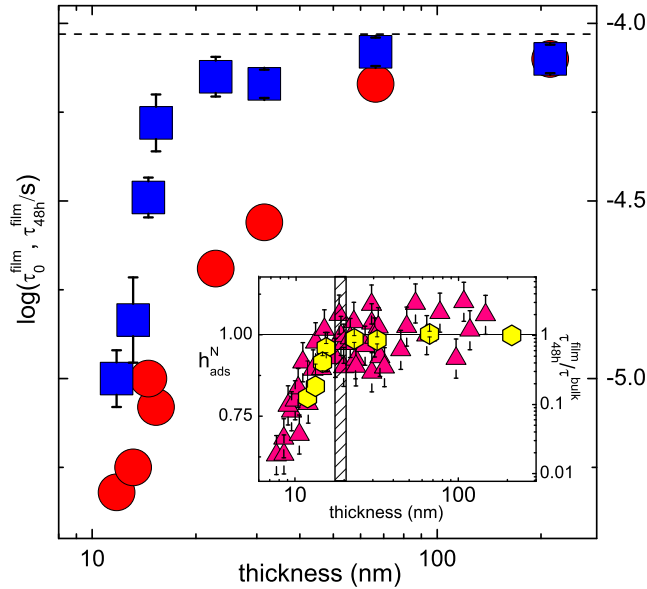


FIG. 2. Thickness dependence of the segmental relaxation time at $T = 433$ K for capped thin spin-casted films of P4CIS. Red circles indicate τ_0^{film} , the value of $\tau_{t_{\text{ANN}}}^{\text{film}}$ at the onset of the annealing (red arrow in Fig. 1), while the value after prolonged annealing in isothermal conditions (2 days, 433 K, blue arrows in Fig. 1) $\tau_{48\text{h}}^{\text{film}}$ is given by blue squares. The dashed horizontal line indicates the bulk value of the segmental time, τ^{bulk} . Inset: Comparison of the thickness dependence of the ratio $\tau_{48\text{h}}^{\text{film}}/\tau^{\text{bulk}}$ (yellow hexagons) and of the h_{ads}^N , the thickness of the adsorbed layer normalized to its bulk value (pink triangles). The dashed area indicates the onset of the confinement effect on the two independently determined quantities.

τ_0^{film} ($\approx 10^{-5}$ – 10^{-4} s). For all the samples investigated, during annealing the value of $\tau_{t_{\text{ANN}}}^{\text{film}}$ increases monotonically (see the shift of the relaxation peak towards lower frequencies in Fig. 1) till reaching an almost constant value (blue arrow in Fig. 1 and blue squares in Fig. 2) after an annealing time of 45–48 h.

The evidence of an annealing time dependence of $\tau_{t_{\text{ANN}}}^{\text{film}}$ implies that the measured value at the onset of the annealing is not associated to an equilibrium state. We remark that our results are compatible with the large literature showing a deviation from bulk behavior [1,2]. The thickness dependence of τ_0^{film} is in line with confinement effects observed in most of the previous measurements, which were performed on samples annealed for a time much shorter than that necessary to reach the steady state identified here. Importantly, our results are also in agreement with previous work by Kremer and co-workers on the segmental dynamics of supported films [47,48], where a bulklike response was measured in samples annealed in conditions similar to those used in this Letter.

Importantly, the occurrence of such an annealing time dependence opens to new processing strategies to tune $\tau_{t_{\text{ANN}}}^{\text{film}}$ and, hence, to tailor properties of nanoconfined systems

[49,50], e.g., friction [51] and crystallization ability [52,53], depending on segmental motion. To achieve such a goal, however, an adequate framework permitting one to understand the molecular origin of the time evolution in segmental mobility upon annealing in the liquid state should be introduced.

In order to further quantify the results, we considered the recovery function of the segmental time, $\Delta_\tau(t_{\text{ANN}}) = \log \tau_{t_{\text{ANN}}}^{\text{film}}/\tau_0^{\text{film}}$, that is, the variation in $\log \tau_{t_{\text{ANN}}}^{\text{film}}$ upon annealing; see Fig. 3. This quantity increases upon annealing (see the shift towards lower frequencies of the segmental peak in Fig. 1), reaching apparent saturation after 45–48 h.

Down to 30 nm, $\log \tau_{48\text{h}}^{\text{film}}$ (blue squares in Fig. 2), the value of Δ_τ after 48 h, eventually extrapolated using an analytical expression as that proposed by Housmans *et al.* [54,55], corresponds to the bulk value of the segmental relaxation time. This evidence means that annealing for $t_{\text{ANN}} \approx 10^9 \tau_0^{\text{film}}$ could erase the confinement effect on segmental mobility. For thinner films, the 2-day-long annealing procedure partially erased the increase in segmental mobility upon confinement, albeit not permitting full recovery of the value of τ for an unperturbed melt.

The character of these results urges us to define a new mechanism of equilibration that adequately treats these nonequilibrium phenomena. The physical mechanism in question should allow the reduction of free interfacial volume while decreasing free energy. We first considered a process mimicking the equilibrium recovery of bulk glasses, where the annihilation rate of free volume holes is dictated by segmental mobility [56]. This idea entails a

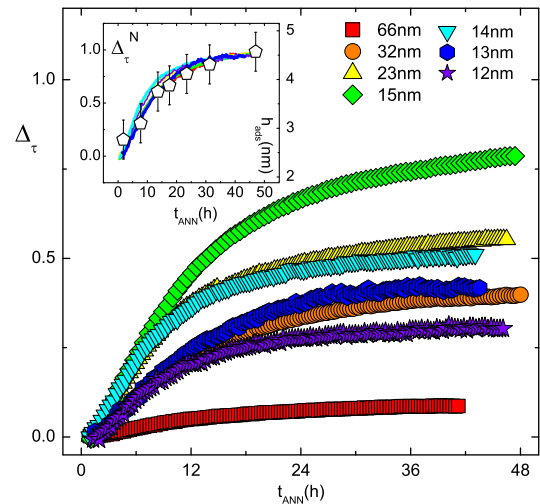


FIG. 3. Recovery of segmental relaxation time $\Delta_\tau(t_{\text{ANN}}) = \log \tau_{t_{\text{ANN}}}^{\text{film}}/\tau_0^{\text{film}}$ upon annealing time t_{ANN} . Inset: The same quantity normalized to $\tau_{48\text{h}}^{\text{film}}$. Inset: Comparison of the normalized recovery of segmental mobility, Δ_τ^N , and the kinetics of irreversible adsorption (see also Fig. S4 [30]); white pentagons indicate the thickness of the adsorbed layer formed within the same annealing conditions.

direct correlation between the kinetics of the equilibration [e.g., $\Delta_\tau(t_{\text{ANN}})$] and $\tau_{t_{\text{ANN}}}^{\text{film}}$. This hypothesis was promptly discarded, as τ_0^{film} (and the value of $\tau_{t_{\text{ANN}}}^{\text{film}}$ at each given annealing time) depends on the thickness, while the recovery functions follow a similar time evolution regardless of the extent of confinement.

Because of the latter property, we were able to construct a master curve for the kinetics of equilibration of all samples—see the inset in Fig. 3 (and Fig. S4 [30])—by simply normalizing the experimental data to $\log \tau_{48\text{h}}^{\text{film}}$. The results imply that the characteristic time of equilibration, t_{eq} , e.g., attributed to the time corresponding to 50%, or alternatively $(1 - 1/e) \approx 63\%$ of the total recovery, is thickness invariant; see Fig. S6 [30]. This result led us to speculate that the mechanism of equilibration should be related to an interfacial relaxation process, occurring in the same way regardless of the sample dimension.

We thus decided to test a possible correlation between the kinetics of adsorption and Δ_τ . As commonly observed, the kinetics of irreversible adsorption is by several orders of magnitude slower than the time scale of segmental motion [57]. For P4CIS at $T_{\text{ANN}} = 433$ K, apparent saturation is reached after an annealing period of almost 2 days ($\approx 10^9 \tau$), which is comparable to the annealing time where the increment in Δ_τ becomes smaller than the experimental error on this quantity. The values of the thickness of adsorbed layers, h_{ads} , against t_{ANN} —quantifying the kinetics of adsorption—superimpose, within experimental uncertainty, to the master curve of the kinetics of equilibration of τ , as shown in the inset in Fig. 3. The kinetics of adsorption is differentiated between two distinct regions, linear at short times and logarithmic upon further annealing [55], showing here a crossover at approximately 14 h. Importantly, the same kinetics applies to the equilibration of segmental relaxation.

Relating the equilibration process to irreversible adsorption implies that a depletion in adsorbable material would limit the recovery of bulk conditions. Such a limitation could be the reason for which thinner films exhibit only partial recovery of bulk behavior. To test this hypothesis, we compared the efficiency in recovery, $\tau_{48\text{h}}^{\text{film}}/\tau^{\text{bulk}}$, to the adsorbed amount after a long annealing time. The latter quantity is expected to decrease with the film thickness because of the reduced availability of adsorbable material. Results are shown in the inset in Fig. 2, where the two independent data sets are plotted as a function of the sample thickness. The striking agreement in the thickness dependence of the two independent parameters provides direct evidence that the limitation in the recovery in τ upon prolonged annealing is associated to an effective depletion of adsorbable material upon reduction of the film thickness.

To further elucidate the role of interfaces on the recovery kinetics, we performed annealing experiments of capped samples at different annealing temperatures and verified that, independently of the latter parameter, the kinetics of

equilibration always followed that of irreversible adsorption; that is, Δ_τ evolves in time as $h_{\text{ads}}(t_{\text{ANN}})$. Moreover, the analysis of the temperature and thickness dependence of the segmental time over a large thickness range revealed that the thermal activation energy of the equilibration process matches that of the segmental mobility of interfacial layers (5–10 nm, that is, when the whole film is occupied by adsorbed chains) rather than that of bulk melts; see Fig. 4. This evidence implies that the equilibration process and the segmental mobility in proximity of the adsorbing substrate share the same molecular origin [58].

This result supports the idea that the mechanism of equilibration does not involve the whole confined volume but is primarily related to the interfacial dynamics. Adsorption of new monomers would, hence, proceed as a perpetuated repetition of fluctuations in density, at the origin of the segmental relaxation [59], in those chains at the very interface with the supporting wall.

We anticipate that the mechanism of equilibration should be related to a molecular process that, after a large number of trials ($t_{\text{eq}}/\tau \approx 5 \times 10^8$), could allow the adsorption of new chains and annihilation of interfacial free volume; the latter phenomenon is responsible for the reduction in the acceleration in segmental mobility upon confinement. The existence of such a process is further supported by recent experimental [60] and *in silico* [61] investigations of relaxation mechanisms in adsorbed layers.

In conclusion, we have demonstrated that the enhanced segmental motion commonly observed in spin-coated

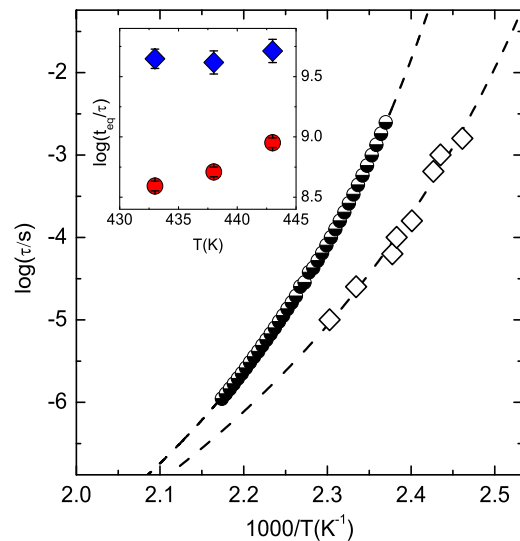


FIG. 4. Temperature dependence of the segmental relaxation time for a bulk melt (solid circles) and an 8-nm-thin film (empty diamonds). Fits of $\tau(T)$ to the Vogel-Fulcher-Tammann equation are shown by dashed lines. Inset: Temperature dependence of ratio of the equilibration time t_{eq} (see Supplemental Material [30]) and the value of τ for a bulk melt (red circles); blue diamonds indicate the ratio of t_{eq} and the value of τ for an 8-nm-thin film.

polymer film is a nonequilibrium phenomenon, ascribable to the presence of chains which do not relax at the time scale of reptation. We have shown that the excess in segmental mobility can be reduced and eventually totally erased via a mechanism of equilibration strongly differing from those of bulk melts (reptation, physical aging, etc.). The equilibration rate of spin-coated layers does not depend on the segmental mobility of the whole film but on ultraslow relaxation modes of interfacial chains permitting irreversible adsorption on the supporting walls. Our results challenge current theoretical work and *in silico* experiments treating spin-coated films as thin slabs of equilibrated polymer melts. New models and simulations aiming at predicting the behavior of 1D confined polymers should consider the metastable character of freshly spin-coated films.

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