Editors' Suggestion

Substrate Roughness Speeds Up Segmental Dynamics of Thin Polymer Films

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We show that the segmental mobility of thin films of poly(4-chlorostyrene) prepared under nonequilibrium conditions gets enhanced in the proximity of rough substrates. This trend is in contrast to existing treatments of roughness which conclude it is a source of slower dynamics, and to measurements of thin films of poly(2-vinylpiridine), whose dynamics is roughness invariant. Our experimental evidence indicates the faster interfacial dynamics originate from a reduction in interfacial density, due to the noncomplete filling of substrate asperities. Importantly, our results agree with the same scaling that describes the density dependence of bulk materials, correlating segmental mobility to a term exponential in the specific volume, and with empirical relations linking an increase in glass transition temperature to larger interfacial energy.

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Structural dynamics, the molecular mechanism associated with the vitrification of liquids, is altered by the presence of interfaces [1,2]. Because of the smaller number of neighbors (lower density ρ), molecules at the free surface with air are expected to experience faster dynamics [3–8].

Similarly, it has been reasoned that in proximity to rough substrates the structural relaxation time τ should increase [9,10], because of the larger number of contacts with the substrate. This phenomenon mimics an increment in interfacial interactions (larger ρ) [11,12].

Here, we confront the experimental reality that physical roughness, such as for example that of the surface of a homogeneous material, exists in the form of a random distribution of heights defining hills and valleys [13] that can be quantified by the root mean square deviation from a flat surface R_q. A polymer chain can make more contacts at the bottom of a valley (increase in interfacial density), which favors adsorption for enthalpic reasons, but based on entropic arguments, adsorption is more favorable at the top of a hill (reduction in interfacial density), because of the larger number of conformations a chain can adopt there [14,15]. The competition between these two opposing effects hints at the possibility to tune the density of a polymer coating, and hence segmental dynamics, by varying the physical and chemical nature of the interface. This is possible, for example, by altering the interfacial potential [16] or tuning the fractal nature of the surface [11].

We may consider another route: We take a system whose interfacial density increases upon adsorption, e.g., a polymer melt interacting with a rough substrate via van der Waals forces [16], and freeze its molecular conformations through adequate processing in a condition favoring migration to the hills. Such a case can be achieved by depositing an organic layer onto a rough substrate via spin coating [17,18], a technique that transforms—within a few seconds—a polymer solution into a melt. The related nonequilibrium conformations are known to persist for timescales exceeding those of technological interest [19]. Under these circumstances the interfacial polymer layer is expected to have lower density than the bulk and an enhancement of glassy dynamics—similar to that experienced in proximity of free surfaces—should be observed.

In this Letter, we present an experimental study on the structural relaxation of polymer thin films spincoated on layers of aluminum of different roughness. Our results show an enhancement in relaxation rate, that is faster dynamics, upon the increase of substrate roughness, in neat disagreement with conclusions from simulations that, in fact, are too simplified to capture the effects of truly rough substrates in equilibrated polymer melts. The deviation from bulk segmental time increases upon cooling, inducing a reduction—and not an increase—in glass transition temperature T_g. We demonstrate that this unexpected trend is due to a reduction in density in proximity of rougher substrates. The results are discussed in terms of very stable nonequilibrium conformations [20], and within the framework of recent models considering a perturbation in interfacial free volume content (molecular packing) at the origin of confinement effects on glassy dynamics [21,22].

In our experiment, aiming at controlling the substrate roughness, we evaporated aluminum onto glass substrates at different deposition rates [23]. R_q was evaluated by topography images obtained via atomic force microscopy. Analysis of the power spectral density (PSD) confirmed the

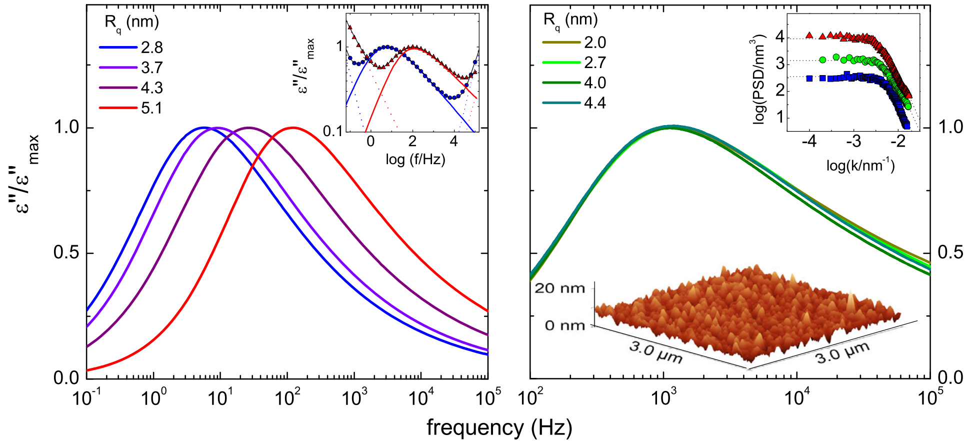

FIG. 1. Structural relaxation of 20 nm thin films of P4ClS at $T = 412$ K (left panel), and P2VP at $T = 403$ K (right panel) deposited on Al substrates of different roughness. To ease reading only the contribution of segmental mobility is given in the main panels, while in the inset of the left panel we plotted the raw dielectric signal of films of P4ClS on the smoothest and the roughest substrate, solid lines through the experimental data are fits to the HN function [29]. In the inset of the right panel, power spectral density of the surface of Al substrates (see an example of 3D view in the bottom of the panel) with different R_q values (blue squares 2 nm; green circles, 4 nm; red triangles, 9 nm) as a function of the wavelength k; dashed lines are fits to the k-correlation, ABC function [13]. More details on fitting are provided in the Supplemental Material [25].

random character of the heterogeneity in the roughness of each Al substrate, and that larger R_q values corresponded to a frequency independent increase in PSD [24], see Fig. 1 (and Supplemental Material [25]). Based on these findings, in the rest of the text we will refer to the R_q value to identify the roughness of our samples. We investigated glassy dynamics in polymer films capped between Al layers (the lower being varied in roughness) which allows for the application of small electric fields, necessary to investigate the dielectric response of the systems and, hence, determine the value of segmental relaxation time τ.

We have started our investigation with extensive work on samples of polystyrene, the most widely studied system in the thin films geometry. We noticed that polymer layers prepared on smooth substrates ($R_q < 2$ nm) dewet during the annealing step above T_g, and that measurements on samples prepared on rougher substrates ($R_q > 6$ nm) fail because of electric shortcuts.

Furthermore, due to the small dielectric signal of this system and the consequently low signal-to-noise ratio, we could not obtain reliable results for polystyrene. We, hence, focused on the roughness range $2 < R_q(\mathrm{nm}) < 6$ and on polymers of higher polarity and considered poly (2-vinyl pyridine), P2VP and poly (4-chloro styrene), P4ClS. The two systems, though differing just slightly in their chemical structure, have a different sensitivity to volume and temperature, the two main parameters controlling structural relaxation in glass forming materials [36]. The segmental dynamics of P4ClS is particularly affected by volume perturbations [31,33,37,38], while the structural relaxation of P2VP is more sensitive to temperature [39]. A comparison of how roughness affects τ in the two systems can thus help to discern the molecular origin of changes in segmental dynamics (that is, if the cause of such effect is or not related to a perturbation in specific volume) in the presence of nanostructured interfaces.

For each polymer, we deposited the same solution under identical spinning conditions (speed = 4000 rpm, time = 1 min, acceleration = 3000 rpm/s) onto substrates of different R_q. This procedure allowed the investigation of samples of constant thickness $h \approx 20$ nm. This thickness is sufficiently small to ensure that interfacial segmental dynamics have a relevant weight in the overall global response of the film and big enough to allow treating the effect of substrate roughness on the overall volume (<2%) as a perturbation [40]. The upper electrode was deposited simultaneously on all of the samples at constant evaporation rate (see Supplemental Material [25] for more information on sample preparation). We did not consider varying the evaporation rate of the upper metallic layer, because this parameter would not affect the polymer-metal interface. Al, in fact, forms via weak dispersive forces very sharp interfaces when evaporated onto polymers and it does not diffuse into the polymer during the measurement time [27]. The fabricated nanocapacitors were placed in a dielectric cell and stabilized in a thermostat in a dry He atmosphere before investigation via an impedance analyzer (ModuLab XM MTS, Solartron Analytical), in a broad temperature and frequency range.

In Fig. 1, the dielectric loss ϵ'' of samples of P4ClS (left panel) and P2VP (right panel) is plotted in isothermal conditions against frequency f at different R_q values. For both polymers, a broad asymmetric peak, attributed to the (α–) segmental relaxation, is present. The frequency of the maximum of such peak $f_{\max}$ provides a measurement of τ, owing to the model free relation $2\pi f_{\max}\tau = 1$. As a first observation, R_q has different impact on P4ClS than on P2VP. The position of the frequency of the maximum of the peak moves significantly to higher frequencies with increasing R_q for P4ClS, implying an acceleration of molecular mobility, while no apparent deviation of the peak position is evident for P2VP. The temperature dependence of segmental τ is presented in Fig. 2 (top panel), for both polymers, together with the values of τ for sufficiently thick bulklike films (open symbols).

The trend described earlier upon increasing R_q is verified throughout a broad temperature range. Regardless of the polymer and the R_q value, τ sharply increases upon cooling, following a trend in line with the Vogel-Fulcher-Tamman (VFT) equation, as expected for the temperature dependence of the α relaxation. The corresponding values of dynamic T_g, defined as the temperature at which $\tau = 100$ s are given in the lower panel of Fig. 2. While the T_g of P2VP appears roughness invariant, the dynamic glass transition temperature of P4ClS decreases by almost 10 K when R_q changes from 2.8 to 5.1 nm.

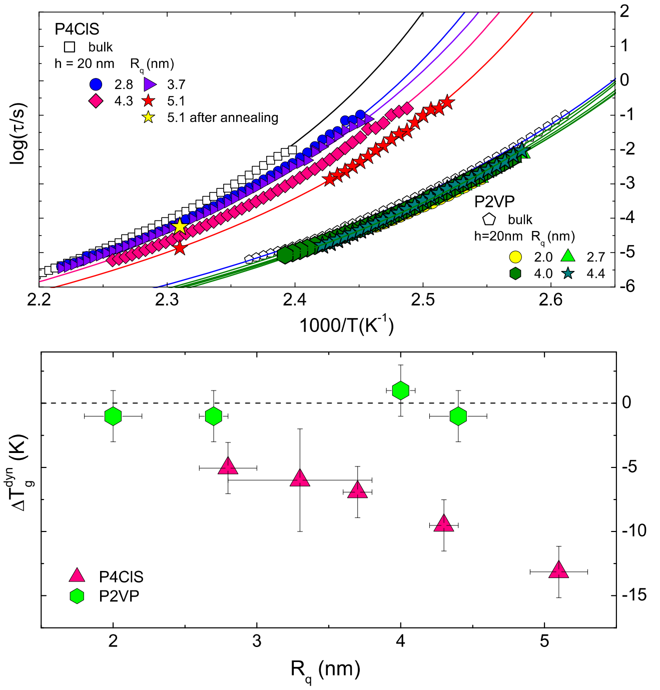

FIG. 2. Upper panel, temperature dependence of the structural relaxation time for thin films of P2VP and P4ClS on substrates of different roughness; data of films ($h > 300$ nm) sufficiently thick to exhibit bulk response are also given (open symbols). The value of τ for a 20 nm thin film of P4ClS ($R_q = 5.1$ nm) annealed for more than 48 h at 433 K is indicated by a yellow star. Solid lines through experimental data are fits to the VFT equation. Lower panel, shift in dynamic glass transition for 20 nm thin films of P4ClS (pink triangles) and P2VP (green hexagons) as a function of the substrate roughness.

We remark that because the segment length of the chains is in both cases smaller than the smallest R_q value considered, the differences in dynamics cannot be imputed to a trivial difference in packing within the roughness asperities.

To understand the origin of the apparent discrepancy between experiments and simulations, and to clarify at the molecular level the different response of the two polymers, we have performed a deeper analysis of the relaxation spectra and observed that the segmental process of P4ClS asymmetrically broadens towards higher frequencies at larger roughness. No significant change of the peak shape is detected for P2VP [41]. The α peak of bulk polymer melts will usually broaden at higher frequencies upon cooling, a trend that has been attributed to a larger hindrance in molecular motion at the length scale of segmental dynamics [42], e.g., to the reduction in free volume content. This interpretation would not stand in this case, as the broadening is accompanied by a concomitant acceleration of segmental dynamics (reduction in τ). Alternatively, in the case of confinement at the nanoscale level, broadening at higher frequencies might indicate the incorporation of faster relaxation modes in the distribution of relaxation times, due to geometrical constraints [43,44] or density variations upon packing frustration [45].

Based on all the trends here observed, and the peculiar sensitivities of the two systems to temperature and volume, we conjectured that the effect of substrate roughness on τ should be related to a perturbation in interfacial free volume. This reasoning, in line with recent work on low molecular weight glass formers [46] and polymers [37], permits clarifying the origin of the insensitivity of the segmental time of P2VP to R_q. As the dynamics of this polymer is more sensitive to a change in temperature than in a specific volume, a drop in density will not particularly affect the interfacial segmental mobility of P2VP.

To complete our demonstration, we considered if the acceleration in dynamics for P4ClS could be related to topological features of rougher substrates, permitting a larger access to free volume.

As the polymer solution wets the Al surface during spin coating, a fraction of the monomers might penetrate into the confining voids induced by roughness. This condition is, however, unfavorable. Following the Washburn theory of capillary flow [47], diffusion inside the voids is inhibited because of both the gradual reduction in pore diameter d, and the increase in viscosity upon solvent evaporation during and after spin coating. Furthermore, when surrounded by molecules of a good solvent (as that used for spin coating) an entropic force [48] opposes the diffusion of chains into narrower environments, because the energy penalty of confinement increases with d^{-2}. Placed in the proximity of the apex of an asperity, segments of a macromolecule will migrate towards more open sections of the cavity. These conditions imply that the specific volume occupied by the polymer in the nanopores soon after spin coating is lower than in bulk, which is in line with the large amount of experimental evidence indicating a reduction in density under 2D confinement [45]. For polymers such as P4ClS, where vitrification is more easily induced by densification than supercooling, confinement induced packing frustration is a source of fast dynamics. Because of the slow adsorption kinetics, it is possible to freeze P4ClS thin spin coated melts in a nonequilibrium state of low interfacial density for a time much longer than that required for measurements. While on moderately rough substrates ($R_q \approx 3$ nm) bulklike dynamics can be reached after annealing at 433 K ($T_g + 35$ K) for 48 h—the time necessary to complete the formation of an adsorbed layer [33]—on rougher substrates (≈5 nm) only ≈60% of initial deviation from segmental mobility could be recovered in the same annealing conditions. We remark that this processing protocol requires timescales exceeding by far those necessary to equilibrate a bulk melt, which indicates the extremely high stability of the nonequilibrium states achieved by spin coating thin films on rough substrates.

In these conditions, a film supported on a rough substrate could be modeled as a membrane of equivalent specific volume, freely suspended on pillars of equal height randomly distributed on a flat surface; an increase in roughness would correspond to a lower density of pillars, that is, to a larger freestanding surface per unit area. The high similarity in the confinement effects observed in the dielectric spectra of thin polymer layers on rough substrates and the response of freestanding and stacked films (reduction in relaxation time and asymmetric broadening towards higher frequencies) [49,50] supports these ideas.

To further test the robustness of our hypothesis, we considered methods to determine interfacial specific volume. Because of the heterogeneous structure of our samples, a direct determination of the density of the polymers in the pores is not possible. Nevertheless, the perturbation in specific volume is proportional to volume of the asperities per unit surface V_{void}, see Fig. 3. The latter parameter, promptly obtained by processing topography images is, hence, a measurement of the reduction in density in the presence of a rough substrate. We prepared a wider set of surfaces, covering R_q values extending below and above the roughness region where measurements of dynamics were possible. We observe a linear correlation between V_{void} and R_q [51], confirming that rougher substrates might induce a reduction in density at the interface.

To achieve a more quantitative picture, we extracted the value of the whole film specific volume V_{sp}, by means of the cooperative free volume (CFV) rate model [32,52] that has been successfully employed to describe the dynamics of thin films of P4ClS [31,34]. V_{sp} can be obtained (for both films and bulk) simply based on the experimentally determined value of τ and the corresponding temperature using the CFV $\tau(T, V_{sp})$ expression. (See the Supplemental Material [25] for details of the model implementation.) The perturbation induced by roughness leads to a change in the overall sample average density, and because this is still a relatively small change, the same physics can be used to characterize bulk and thin films [53].

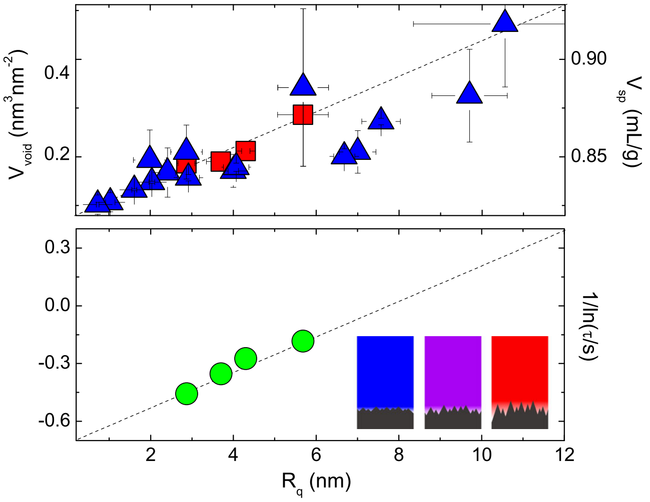

FIG. 3. Upper panel, the volume of voids determined via the Abbot method (blue triangles) and the specific volume of the polymer layer (red square) obtained via the CFV model are given as a function of the substrate roughness. Lower panel, the inverse of the segmental relaxation time is plotted as a function of the substrate roughness. Based on these results, we provided a series of sketches of the interface of a polymer with substrates of different roughness. By increasing R_q (left to right), the larger amplitude of the deviation from a flat substrate corresponds to a more pronounced reduction in density (pictured by less intense colors).

In Fig. 3, we also plotted the impact of roughness on V_{sp} and τ at 408 K. An increase in R_q from 2 to 6 nm resulted in a reduction in density by 2% and an increase in segmental mobility by a factor 100. The correlation between segmental time and the volume-related parameters is impressive, which supports the assumption that the observed acceleration of mobility in the presence of rough substrates originates from packing frustration in the pores.

The experimental data in Fig. 3 indicate a density dependence of the segmental time of the form $\tau \sim \exp(\rho)$, which is consistent with scaling functions describing the volume dependence of dynamics in bulk materials under isothermal conditions [54]. These results set a strong experimental proof for the validity of models of the glass transition which explicitly consider the role of volume and how density changes in confined geometries. Furthermore, considering a random (homogeneous) distribution of polymer-substrate contacts at the interface, the trend observed in density can be promptly extended to interfacial interactions, and to any measurement of the work of adhesion [55]. The results in Fig. 3 do provide, hence, a microscopic picture of the relation between glass transition temperature and interfacial free energy, empirically obtained in previous work [56].

In conclusion, we have shown that simple material processing—the deposition of thin polymer melts via spin coating—allows reaching a nonequilibrium regime where dynamics speeds up with increasing roughness, not otherwise achievable via equilibrium pathways [20]. Our results are in disagreement with the predictions of simulations that aim to treat rough substrates, largely because prior such work has failed to capture roughness on an experimentally relevant scale. We anticipate that our study will permit the fabrication of nanoconfined systems (thin coatings, nanotubes, nanocomposites, etc.) with tailored specific volume content, stable beyond timescales of technological interest, mimicking the condition of freestanding membranes also in the presence of attractive nanofillers and supporting interfaces.

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[25] See Supplemental Material at http://link.aps.org/supplemental/10.1103/PhysRevLett.124.027802 for further details on sample preparation, analysis of dielectric spectra and atomic force microscopy images, and calculations of specific volume via the CFV model, which also includes Refs. [26–35].

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