Letter

Experimental and Modeling Comparison of the Dynamics of Capped and Freestanding Poly(2-chlorostyrene) Films

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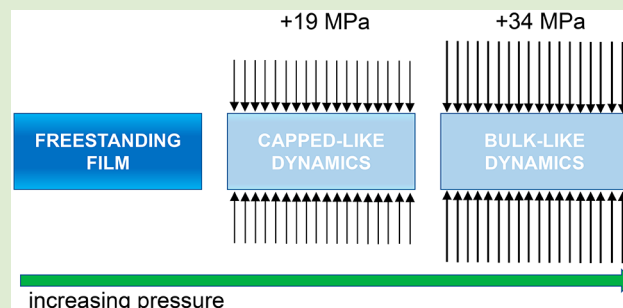
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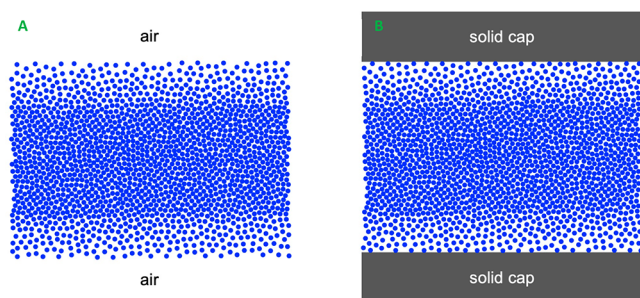ACCESS | Metrics & More | Article Recommendations | SI Supporting Information

ABSTRACT: Proximity to a nonrepulsive wall is commonly considered to cause slower dynamics, which should lead to greater relaxation times for capped thin polymer films than for bulk melts. To the contrary, here we demonstrate that Al-capped films of poly(2-chlorostyrene) exhibit enhanced dynamics with respect to the bulk, similar to analogous freestanding films. To quantitatively resolve the impact of interfaces on whole film dynamics, we analyzed the experimental data via the Cooperative Free Volume rate model. We found that the interfacial region adjacent to a cap contains an excess of free volume (relative to the bulk) about half of that proximate to a free surface. Employing a useful analogy between confinement and pressure effects, we estimated that the effect of capping an 18 nm freestanding film would be equivalent to applying a pressure increase of 19 MPa.

Polymer chains adjacent to a nonrepulsive wall have been long modeled as dead layers,[1,2] regions where thermal expansion is as small as zero and molecular relaxation would take place at extremely long time scales.[3] Experimental work has, on the contrary, shown that this ensemble of molecules can experience an enhancement in segmental dynamics,[4] attributed to nonequilibrium chain conformations arising from fast processing, e.g., spin coating.[5] This common method used to fabricate thin polymer layers consists of placing dilute solutions on a rotating plate that is covered with a solid material, e.g., vapor-deposited Al. This boundary material is sometimes referred to as a substrate or a wall; from this point on, we will refer to it as a cap. Figure 1 is a cartoon illustrating two kinds of interfacial regions, relative to the bulk, with Figure 1A showing it next to a free surface and Figure 1B showing it

proximate to a cap that has been placed either by spin coating, as described above, or via vapor deposition onto the remaining free surface of the film. While there is adsorption onto the capping interface, there is still a significant enhancement of free volume (relative to bulk) in the nearby region.

The rapid solvent evaporation which occurs during spin coating induces vitrification of polymer melts under conditions of a reduced entanglement density.[6,7] The corresponding imperfections in molecular packing lead to more free space and facilitate molecular motion. Dedicated experiments[4,8] have verified this excess of free space and then followed the interfacial repacking as the number of monomers directly adsorbed on the cap slowly increased. Ultimately, these initially nonequilibrium interfacial layers reorganize and densify upon time, leading to dynamics that become more bulk-like.[9−14] Such kinetics are extremely slow: though it can be accelerated by increasing the temperature, the formation of an equilibrium adsorbed layer can require several days even at temperatures well above the glass transition.[15]

The effective change in density is limited to molecules in close proximity to the interface (see ref 16) and falls below the sensitivity of most scattering techniques.[9,17,18] However, segmental dynamics, the molecular process coupled to

Figure 1. Schematics of free-standing (A) and capped (B) films. The difference in density at the interfaces was exaggerated for illustration purposes.
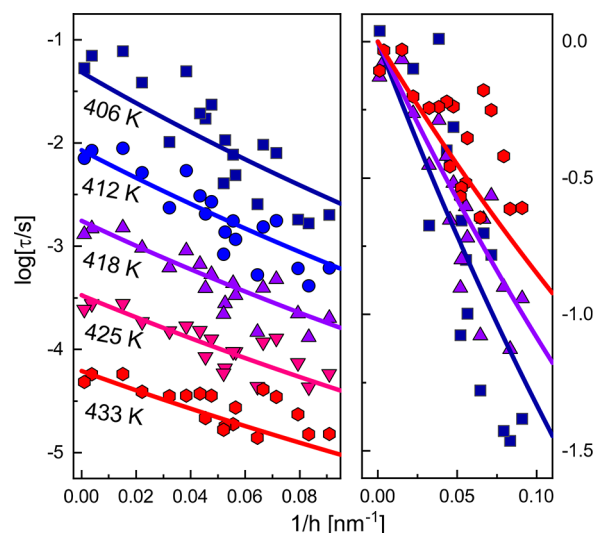
vitrification and glassy dynamics,[47] connects strongly and sensitively not only to the available thermal energy but also to density.[19,20] Knowing the time scale of this process, $\tau(T,V)$, e.g., via dielectric spectroscopy, provides a reliable way to measure the specific volume of both bulk and nanolayered material at any given temperature, T. By means of this approach,[21−23] it has been shown that poly(4-chlorostyrene) (P4ClS) thin films of about 20 nm are 1% less dense than an equilibrated bulk melt.

Based on these recent findings, rather than being associated with dead layers, interfacial chains proximate to a solid capping layer commonly show (at least before attaining full equilibrium adsorption) an unexpected resemblance to those at the free surface in proximity of air.[24] This comparison has until now, however, been limited to a merely qualitative description. While both types of interfacial layers (adjacent to caps and to free surfaces) do experience an enhancement in dynamics, the lack of experimental data (e.g., segmental relaxation times for films of the same polymer) and lack of appropriate analytical methods to characterize motion based on structural parameters severely limit our understanding of interfaces.

Here, we present an experimental and modeling comparison of the dynamics of films that are capped at both surfaces and films that are freestanding, both of poly(2-chlorostyrene) (P2ClS). By applying the Cooperative Free Volume (CFV) rate model,[21,22,25−28] we resolve the density-driven responses coming from the two kinds of interfacial regions. Our results confirm that these apparently different interfaces are both responsible for an enhancement in segmental dynamics of the whole film.

Figure 2 shows experimental data (symbols) and model curves (lines) for capped films of P2ClS plotted in the form of $\log \tau$ vs $1/h$ on several different isotherms. Details on the CFV model[21,22,25−28] and characterization to bulk P2ClS are in the Materials and Methods and SI. CFV expresses $\tau(T,V)$, so it is capable of resolving a material's response to density change 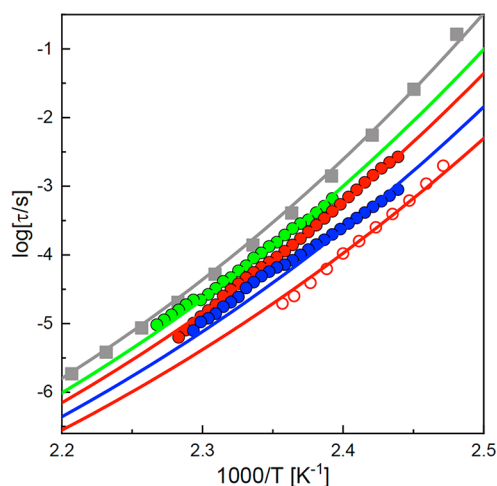(which we connect to interfacial effects) independently from its response to temperature change. In this application of the CFV model, we assume that each film has both an interfacial region and a bulk-like region. The specific volume for the whole film has weighted contributions from the bulk portion (at the same T,P) and the interfacial portion. The former comes from analysis of bulk pressure−volume−temperature (PVT) data. The excess in volume contributed by the latter portion is linearly proportional to the inverse film thickness, $1/h$. The strength of this interfacial term is characterized using a single temperature- and thickness-independent parameter, δ_{free}. This parameter, which characterizes how much the free volume in the interfacial region differs from the bulk, is easily obtained by analyzing a set of experimental measurements of the segmental time collected as a function of temperature, T, and thickness, h, as those in Figure 2.

The data in Figure 2 exhibit some scatter, due to the expected variance in metastable states following film formation.[5] However, given the large set of results (19 films in total) the average trends of interest can be clearly resolved. The model curves which track through the experimental results demonstrate how the trends with changing h and changing T can be captured by the CFV model by fitting just the single parameter, δ_{free}. Here, for capped P2ClS films, we find δ_{free} = 0.20 nm.

Next we turn to the comparison with freestanding films of P2ClS. In Figure 3 we show the results (experimental data and

Figure 3. Relaxation map, plot of $\log \tau$ vs $1/T$, of the segmental relaxation of thin-capped (filled circles) and freestanding (open circles) films of P2ClS along with the corresponding bulk (filled squares). For the case of capped films, three different film thickness values are shown corresponding to h = 31 (green), 18 (red), and 11 (blue) nm, chosen as representative values because they lie close to the average trends in Figure 2, and to better provide a comparison with the 18 nm thin freestanding film. Data for the P2ClS bulk and the freestanding film are from ref 29 and ref 30, respectively; see details on the comparison of these data in ref 31.

Figure 2. Left panel: Segmental (α-) relaxation time of capped P2ClS films as a function of the inverse thickness. Note that the data and model curves both show that the $\log \tau$ vs $1/h$ trend gets steeper as T decreases (see right panel). This confirms that the sensitivity to confinement is increasing with decreasing T, as predicted by the CFV.[28]

model curves) for films and corresponding bulk plotted in standard Arrhenius form, $\log \tau$ vs $1/T$. As expected, the deviation from the bulk trend increases with decreasing film thickness. In the same plot, the corresponding $\log \tau$ vs $1/T$ trend is shown for an 18 nm thick P2ClS freestanding film (open circles), from Fukao et al.[30] The CFV model curve for the data set on that freestanding film uses the same bulk characterization described above (and ref 31). As was done for the capped films, this data set has been best fit to obtain the

single δ_{free} parameter that characterizes the interfacial region for the freestanding film, yielding a value of $\delta_{\text{free}} = 0.46$ nm. Both δ_{free} values, for the capped and the freestanding film cases, are positive. Both kinds of interfacial regions exhibit an increase in free volume, which connects directly with an increase in the dynamics in both films, relative to a bulk sample. In contrast, if the capped systems had resulted in "dead zones" in the interfacial regions, their δ_{free} value would have been negative.

As an aside, we note here that the CFV bulk characterization, *alone*, has been successfully used to predict the implications of confinement when the material is a freestanding film.[31] In this paper, we use the CFV two-layer model both for freestanding and capped films, requiring a value for the parameter δ_{free}, in order to maintain consistency. While one should expect (at the detailed level) there to be a gradient in the locally averaged density, the simple two-layer model accounts for this by simply averaging over this gradient to produce an overall effective "interfacial layer". The resulting averaged density for this inhomogeneous region contributes, along with that from the homogeneous bulk layer, to the weighted average for the overall film sample, which will change with film thickness. The physical picture for this model has been described in detail in the appendix of ref 21.

To further understand these results, it is convenient to compare the dynamics of capped and freestanding P2ClS films at the same thickness ($h = 18$ nm). Here the dynamics data show that the shift in the log of the relaxation times compared to bulk is greater for the freestanding film; e.g., at $T = 423$ K, $\Delta \log \tau (/s) \approx 1.2$ and 0.5 for freestanding and capped films, respectively. This follows from the greater $\delta_{\text{free}} = 0.46$ nm value found for the freestanding film compared to the $\delta_{\text{free}} = 0.20$ nm value for capped films. We conclude that the free surface of a freestanding film evidently supplies a substantively greater increase in the overall sample free volume than arises from packing imperfections in material adjacent to a cap.
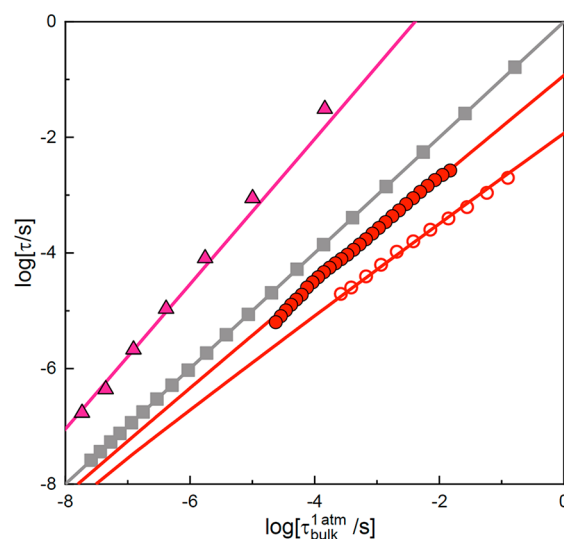
We emphasize that our analysis critically depends on an understanding of both the bulk form of the material as well as the *state* of the interfacial region in the film of choice (i.e., its density, as dictated by the degree of segment—substrate contacts). Being able to characterize the sensitivity of the bulk material's dynamics to volume change, e.g., as described by the b parameter in the CFV approach[21,26] or by the γ parameter in the density scaling approach,[19,20,32−36] is necessary because the confinement effect imparts a density change to the sample.[21−23,28,37−40,40,41] However, this density change from the interfacial region still remains to be quantified, and this (at least for capped films) cannot be predicted *a priori* based on a bulk characterization of the material.

To expand on the point made above, we take for comparison the case of P4ClS, an isomer of P2ClS. In comparing bulk samples, the segmental dynamics of the former is somewhat more sensitive to changes in specific volume, as revealed by the bigger shifts upon an isothermal increase in pressure; for example, at $T \approx 440$ K, the change in $\log \tau$ (/s) on going from $P = 1$ atm to 100 MPa is about 4.5 for P4ClS[23] and 3.9 for P2ClS.[29] However, the bulk material *sensitivity* to free volume, alone, still does not determine by *how much* the free volume changes in a capped sample. Experiments have shown that, depending on sample preparation, the δ_{free} at the P4ClS/Al interface can vary from 0.33[22] to about 0,[42] while of course the material's sensitivity to density stays invariant.

In the case of capped films, the sample preparation results in metastable states, and so it is expected that δ_{free} will ultimately change over long times, tending toward zero as the polymer reaches its final, fully adsorbed equilibrium state of adsorption. At that point, the density of the interfacial region achieves the bulk value. However, during the time frame of experimental interest, the density effect, via δ_{free}, must be quantified by analyzing data from dynamics measurements on the confined system itself, which is only feasible by having models that can connect dynamics (τ) to density, e.g., CFV and density scaling, both proven to capture pressure-dependent dynamics, $\tau(T,V)$.

Another insightful way to contrast the behavior of freestanding and capped films is to connect with the analogous pressure-induced effects in the bulk. The general CFV equation leads to a power—law relationship,[28,43] $\tau_2(T) \propto \tau_1(T)^c$, between any two isobars, "1" and "2", composed of the same material; these could be isobars of the bulk at two different pressures, or a film and bulk (e.g., both at ambient pressure), or two different films. The power—law exponent is determined by the free volume of one relative to the other, i.e., $c = V_{\text{free1}}(T)/V_{\text{free2}}(T) \approx$ constant.

Some examples of this power—law analysis are shown in Figure 4, where plots of $\log \tau_2$ vs the corresponding $\log \tau_1$

Figure 4. Relaxation times of P2ClS-capped and freestanding films and corresponding bulk at elevated pressure (50 MPa, pink triangles), plotted against relaxation times for the bulk at ambient pressure. The rest of the color scheme is the same as Figure 3.

value of the ambient bulk at the same temperature lead to the value of c from the linear slope. Data for both the 18 nm freestanding film and the 18 nm capped film form lines that fall below the diagonal (ambient bulk, $c = 1$). The freestanding film has the lowest value of c ($= 0.80$) which, again, indicates its greater free volume and lower activation energy compared to the capped film which has $c = 0.90$. Also shown in Figure 4 (pink triangles and line) is the result for the $P = 50$ MPa bulk isobar; this demonstrates the analogous "opposite movement" in density (an increase) relative to the ambient pressure bulk giving a c value of 1.16. The behavior shown here serves to emphasize that a material's response to an interface is connected to the way the material responds to a density (pressure) change in the bulk. The effect of the added free volume from interfaces of the sort discussed here causes a

response in dynamics that is very similar to the response to a decrease in pressure in the bulk.

We can quantify this explicitly by predicting how much pressure one would need to apply to a freestanding film in order to decrease its free volume to the point where it matches the material's bulk dynamics at the same temperature. Based on the CFV model (see SI), an 18 nm freestanding film would require a pressure increase of 19 MPa to obtain the same dynamics as the 18 nm capped film and a further increase of 15 MPa (i.e., an overall applied pressure of 34 MPa) to reach bulk dynamics. For comparison, these values are 3 orders of magnitude larger than the disjoining pressure[44] acting on the films (a quantity which has been held as one of the common metrics in the study of surface behavior).

In conclusion, we have presented a comparison study on capped and freestanding films of poly(2-chlorostyrene). We analyzed the experimental data within the framework of the two-layer CFV rate model, which rationalizes confinement effects in terms of both the material's sensitivity to volume (obtained through bulk data) and one single free parameter (δ_{free}), characterizing the interfacial effect on free volume content relative to the bulk. We determined that this quantity is positive for layers proximate to both capped and free surfaces. Based on this finding, we conclude that, as opposed to the commonly held view, the molecules in proximity to both capping (adsorbing) and polymer/air interfaces contribute to speeding up segmental dynamics. The larger shift in dynamics experienced by freestanding films is due to a larger gain in free volume associated with their proximity to free surfaces. Finally, we emphasize that a bulk material's inherent sensitivity to volume change (a characteristic property that is captured by the CFV and density scaling models) and the effect of an interfacial region on material free volume, as characterized by δ_{free}, are independent of one another. However, the latter can be understood by analyzing experimental data, such as obtained using dielectric spectroscopy, with models that have demonstrated success in illuminating pressure (density)-dependent dynamics.

MATERIALS AND METHODS

Thin films of P2ClS (M_{w} = 376 000 g/mol, PDI = 1.6, powder, from Polymer Source Inc.) were spin-coated at 3000 rpm for 30 s from chloroform (≥99.8%, from Sigma-Aldrich) solutions onto metallic electrodes, consisting of a thermally evaporated aluminum layer (≥99.9%, from Sigma-Aldrich, thickness ≈50 nm, evaporation rate ≈10 nm/s). Before evaporating the upper electrode in the same conditions as the lower one, the polymer layers were preannealed for >10^4 times of the segmental relaxation time at 10 K above bulk T_{g}. The obtained nanocapacitors allow the application of a weak electric field (<1 V/μm). Complex dielectric spectra were obtained from the measurement of the capacitance using an impedance analyzer (Solartron Analytical) under a helium environment in isothermal conditions as a function of frequency. The empirical Havriliak−Negami function[45] was used to extract the segmental relaxation time from the isothermal dielectric spectra. The CFV equation for relaxation times is $\ln(\tau/\tau_{\text{ref}}) = (V_{\text{hc}}/V_{\text{free}})(T^*/T)^b$, where for films $V_{\text{free}}/V_{\text{hc}}$ is equal to that of the bulk at the same T,P plus δ_{free}/h.[21,22] The parameters, b, T^*, τ_{ref}, and V_{hc} (where $V_{\text{free}} = V - V_{\text{hc}}$), were determined from bulk P2ClS PVT[46] and dynamics[29] data; see ref 31 and the SI.

ASSOCIATED CONTENT

Ⓢ Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acsmacrolett.1c00674.

Details on the CFV model, calculations for P2ClS films, and P2ClS bulk characterization (PDF)

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Notes

The authors declare no competing financial interest.

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(16) Note that because the density effect on dynamics is a cooperative, *intermolecular* phenomenon, defining quantities such as the free volume and density of inhomogeneous systems is more challenging than in the simpler case of bulk because the effective boundary of these systems must involve consideration of *intermolecular* scale (e.g., near-neighbor) distances beyond the outer molecular segments; see the discussion in refs 21−37.

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