

Surface Dynamics of “Dry” Homopolymer Brushes

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ABSTRACT: The dynamics of the surface height fluctuations on layers of covalently tethered, nearly monodisperse polymer chains synthesized by atom transfer radical polymerization were studied using X-ray photon correlation spectroscopy. The data reveal that both polystyrene and poly(*n*-butyl acrylate) “brushes” have structure at the surface with length scales in the region of 620–3100 nm, but the surface features show no relaxation in a time window of 0.1–1000 s, even at temperatures more than 130 °C above the glass transition temperature of the corresponding untethered chains. This remarkable alteration of the dynamics is compared with the suppression of fluctuations on this length scale anticipated by thermodynamic theories. The alteration of surface dynamics by tethering has implications for wetting, friction, and adhesion.

Introduction

The dynamics of surface fluctuations have been studied experimentally for polymer solutions,¹ gels,² melt films of untethered polymer chains,^{3,4} and polymer brushes in solvent,^{5–8} but not for melt polymer brushes. Harden et al.⁹ predicted that when one moves from pure solvent to increasingly concentrated polymer solutions to melts, the onset of viscoelastic behavior brings important changes in the surface modes. For a dilute solution, only capillary wave modes, for which the restoring force is surface tension, are present. For sufficiently concentrated solutions, Rayleigh waves, for which elasticity of the bulk solution is the primary restoring force, can be present. Solution viscosity, which dissipates the surface modes, also plays a role. Various wave modes can coexist on a concentrated solution or gel. Several of these predictions have been experimentally verified.¹ Recently,^{3,4} it has been demonstrated that at temperatures far above the glass transition temperature, T_g , the surface height fluctuations on a film of undiluted, untethered polymer chains of thickness greater than $4R_g$, where R_g is the unperturbed chain radius of gyration, can be understood using an overdamped capillary wave theory.¹⁰ At thicknesses less than $4R_g$ films begin to manifest effects of an appreciable elastic modulus.⁴ Pinning of the chains closest to the substrate creates behavior that is somewhat “brushlike”, displaying suppression of surface dynamics. The resulting changes in the characteristic surface relaxation time have been successfully modeled⁴ by modifying the equation for characteristic time, $\tau_0(q_{||})$, in the

model of a viscous liquid film to account for the film elastic modulus, μ

$$\tau(q_{||}) \cong \frac{\tau_0(q_{||})}{1 + \tau_0(q_{||})(\mu/\eta)} \quad (1)$$

where η is the viscosity of the film and $q_{||}$ the in-plane wave vector. Equation 1 and the expression for $\tau_0(q_{||})$ have been derived in earlier work.^{3,4}

No full theoretical treatment of the surface dynamics of densely grafted brushes has been published. Thermodynamic theories^{11–13} that draw on an analogy with an elastic layer predict that if chains are covalently end-grafted with a distance between tethering points smaller than R_g of the unperturbed chain, the resulting stretching from Gaussian conformations in the “polymer brush” (shown schematically in the inset of Figure 1) leads to dramatic changes in film surface dynamics. For surface modes with wavelengths $\lambda = 2\pi/q$ much larger than the equilibrium brush height, h_0 , the entropic cost to stretch the chains the necessary amounts varies strongly with $q_{||}$ so that modes with $\lambda \gg h_0$ are predicted to be suppressed. Competition between an elastic restoring force at long wavelengths and a surface tension penalty at shorter wavelengths should lead to an energetically preferred wavelength of the order of h_0 . Fredrickson et al.¹¹ further argue that while the fluctuation spectrum of equal-time correlations is governed only by thermodynamics, what may be observed in time-resolved scattering measurements is very sensitive to two time scales of motion of the surface elastic waves. One time scale is the wave frequency of the Rayleigh-like surface modes, ω . The second is a time τ_r for entanglements in a melt brush to relax. Those authors remark that theoretical work by Obukhov and Rubinstein¹⁴ suggests that τ_r is a very large time that grows at least exponentially with the length of the brush chains. In practical situations it could be that $\omega \gg \tau_r^{-1}$, and the chain entanglements are unable to relax during the time required for a wave to travel

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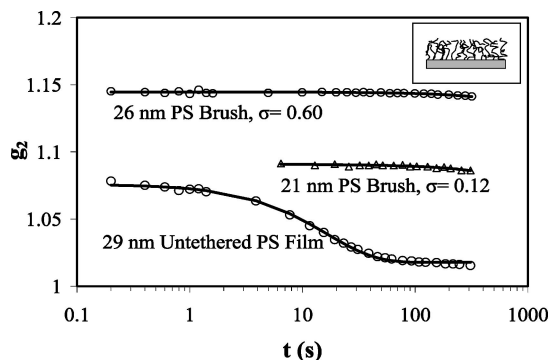


Figure 1. Intensity-normalized time autocorrelation function vs delay time at $q_{||} = 5.3 \times 10^{-3} \text{ nm}^{-1}$ for a 26 nm thick PS brush ($M_n = 28 \text{ kg/mol}$) with σ (chains/ nm^2) = 0.60, 29 nm thick film of untethered PS chains ($M_n = 65 \text{ kg/mol}$) measured at 170 °C and 21 nm thick PS brush ($M_n = 115 \text{ kg/mol}$) with $\sigma = 0.12$ measured at 225 °C. A schematic of a polymer brush is shown in the inset.

a distance of order $2\pi/q_{||}^*$, the wavelength of the most probable thermally excited mode of the melt brush. The observation, in static scattering measurements, of correlation between the roughnesses of the top and bottom interfaces of a diblock copolymer brush¹⁵ and a self-affine structure at the surface of homopolymer brushes¹⁶ has offered indirect evidence that long wavelength fluctuations are suppressed in densely grafted brushes,¹⁵ but it remains to demonstrate this suppression directly with a measurement of surface dynamics.

The collective dynamics of polydisperse ($M_w/M_n \approx 2$) “wet” (solvent swollen) polymer brushes synthesized by conventional free radical polymerization has been studied using evanescent wave dynamic light scattering (DLS) with visible light.^{5–8} These experiments revealed that fast cooperative diffusion is characteristic of the good solvent regime, whereas in a Θ solvent fast diffusion is accompanied by a slower mode. To study surface dynamics of melt (“dry”) brushes, however, smaller length scales must be reached. X-ray photon correlation spectroscopy (XPCS) performed in a reflection geometry achieves surface sensitivity, probes the necessary length scales, and has proven useful for investigating the surface dynamics of smectic liquid-crystal membranes,¹⁷ opaque magnetic colloidal systems,¹⁸ block copolymer vesicles,¹⁹ liquid surfaces,²⁰ and films of untethered chains.^{3,4,21–25} Here we show that when chains are densely tethered in a dry brush, the dynamics of surface fluctuations at length scales exceeding the thickness of the brush are dramatically altered, even more than in ultrathin films of untethered chains.⁴ While the thermodynamic theories anticipate suppression of the fluctuations,^{11–13} the observed behavior may be alternatively rationalized as resulting from a freezing or tremendous slowing of the surface dynamics. The samples are well-defined, dense brushes with low chain polydispersity (PDI) very similar to the brushes envisioned in theoretical studies.

Experimental Section

Materials. Styrene (Aldrich, 99%),²⁶ *n*-butyl acrylate (Aldrich, >99%),²⁶ *N,N,N',N'*-pentamethyldiethylenetriamine (PMDETA, Aldrich, 99%),²⁶ and ethyl 2-bromoisobutyrate (E2Br-iB, Aldrich, 98%)²⁶ were passed through a column of activated basic alumina. CuBr (Aldrich, 98%)²⁶ was purified as described in the literature.²⁷ Dodecyltrichlorosilane (DTS, Aldrich, 99%)²⁶ was vacuum-distilled prior to use, and anhydrous anisole (Aldrich)²⁶ was used as received. Silicon wafers (100), having thicknesses of $500 \pm 50 \mu\text{m}$, were purchased from the Semiconductor Processing Co.²⁶ All other reagents were purchased from either Aldrich²⁶ or Fisher Scientific²⁶ and used as received.

Substrate Preparation. Silicon wafers ($15 \text{ mm} \times 30 \text{ mm} \times 0.5 \text{ mm}$) were cleaned by treatment with a freshly prepared

“piranha” solution²⁸ (70/30, v/v, concentrated H_2SO_4 /30% aqueous H_2O_2) at 90–100 °C for 1 h and were then rinsed with distilled water and dried with a stream of technical grade nitrogen gas.

General Procedure for Deposition of Surface-Bound Initiator. A 20 mL glass vial was placed in a drybox, and a freshly cleaned silicon wafer was placed in the vial. The (11-(2-bromo-2-ethyl)propionyloxy)undecyltrichlorosilane was synthesized according to literature precedent²⁹ and utilized as a surface-bound initiator. For every 5 mL of anhydrous toluene, 0.1 mL of 25% by volume solution of the trichlorosilane initiator was added to the vial via syringe. The vial was sealed with a glass cap and heated at 60 °C for 4 h in the drybox. The silicon wafer was then removed, sequentially washed with toluene, ethanol, and methylene chloride, and then dried in a stream of technical grade nitrogen gas. To vary grafting densities of the brushes, first DTS was deposited using various deposition times to yield different packing densities, and then the empty spaces were backfilled by depositing the trichlorosilane initiator. This procedure decreases the density of initiating sites on the substrate for the preparation of brushes with targeted lower grafting densities.

Procedure for Surface ATRP from an Initiator-Covered Silicon Substrate. Polystyrene (PS) and poly(*n*-butyl acrylate) (PnBA) brushes ($\sigma = 0.12$ – 0.6 chains/nm^2) were synthesized by atom transfer radical polymerization (ATRP). CuBr, anisole, and monomer were added to a 100 mL Schlenk flask with a magnetic stir bar, sealed with a rubber septum, and degassed by purging with technical grade nitrogen for 2 h. Three vacuum/purge cycles were applied to the flask, and it was left under a nitrogen atmosphere. PMDETA was added to the mixture via a syringe, and the solution stirred at reaction temperature until it became homogeneous ($\approx 5 \text{ min}$). An initiator-modified silicon wafer was placed in a separate 100 mL Schlenk flask and sealed with a rubber septum. The flask was degassed and backfilled with nitrogen at least three times and left under a nitrogen atmosphere. The solution was then transferred to the flask containing the silicon wafer via a cannula, followed by the addition of free initiator (E2Br-iB) via a syringe. The polymerization was allowed to proceed at 90–100 °C for a period of time depending on the thickness targeted, after which the silicon wafer was removed. The final concentrations were as follows: $[d_8\text{-S}]_0 = 3.9 \text{ M}$, $[\text{PMDETA}]_0 = 25 \text{ mM}$, $[\text{CuBr}]_0 = 12 \text{ mM}$, and $[\text{Br-iB}]_0 = 5 \text{ mM}$ or $[\text{n-BA}]_0 = 2.3 \text{ M}$, $[\text{PMDETA}]_0 = 25 \text{ mM}$, $[\text{CuBr}]_0 = 12 \text{ mM}$, and $[\text{Br-iB}]_0 = 10 \text{ mM}$. To remove untethered polymer chains, the silicon wafer was placed in a Soxhlet extractor and extracted exhaustively with tetrahydrofuran (THF) for 24 h followed by sonication in toluene for 2 h. The brushes were annealed in high vacuum for 18 h at 150 °C to remove residual solvent. The chain length PDI was less than 1.2 except for samples PS-21 and PS-107 (PDI = 1.6), for which additional monomer was added to the reaction flask at high conversions to achieve thicker brushes while maintaining lower grafting density. The thickness (h), calculated grafting density (σ), molecular weight, distance between anchoring points (d), R_g , and h/R_g values for selected samples are shown in Table 1.

X-ray Reflectivity. Brush thicknesses were determined using X-ray reflectivity (XR) measured using a spectrometer mounted on a rotating anode source³⁰ (Rigaku, 12 kW RU200)²⁶ with Cu K α radiation ($\lambda = 0.154 \text{ nm}$) or at the 8-ID-I beamline ($\lambda = 0.126 \text{ nm}$) at the Advanced Photon Source. Reciprocal space resolutions q_z in both instances were about 0.01 nm^{-1} . To correct the experimentally measured specular reflection intensity, the background scattering was estimated by performing longitudinal diffuse scans in which the detector and incident angles were increased simultaneously, but with the incident angle offset by 0.1° from the specular condition. This background intensity was then subtracted from the experimentally measured specular intensity.

XPCS. XPCS data were collected after equilibration at the temperature of interest. The XPCS experiments were performed at beamline 8-ID-I at the Advanced Photon Source using X-ray energy of 7.5 keV and experimental geometry described previously.³ An incidence angle of $\alpha_i = 0.14^\circ$ (below the critical angle of PS, $\alpha_c = 0.17^\circ$) ensured the penetration depth was $\approx 9 \text{ nm}$. Scattering from

Table 1. Characteristics of Polymer Brushes

sample	thickness (nm) ^a ± 0.2	M_n^b (kg/mol)	σ^c (chains/nm ²)	d^d (nm) ± 0.03	R_g^e (nm)	h/R_g
PS-9	9	10 ± 0.5	0.6 ± 0.03	1.4	2.8 ± 0.1	3.2 ± 0.1
PS-21	21	115 ± 5.7	0.12 ± 0.05	2.9	9.2 ± 0.4	2.3 ± 0.1
PS-26	26	28 ± 1.4	0.6 ± 0.03	1.3	4.6 ± 0.2	5.6 ± 0.2
PS-39	39	34 ± 1.7	0.6 ± 0.04	1.3	4.9 ± 0.2	8.0 ± 0.3
PS-48	48	50 ± 2.5	0.6 ± 0.03	1.3	6.0 ± 0.3	8.0 ± 0.4
PS-107	107	115 ± 5.8	0.58 ± 0.05	1.3	9.2 ± 0.5	11.6 ± 0.6
PnBA-30	30	25 ± 1.3	0.8 ± 0.04	1.1	3.6 ± 0.2	8.3 ± 0.5

^a Thickness (h) values from XR. ^b Number-averaged molecular weights measured using gel permeation chromatography (GPC) for free chains in solution created at the same time the brush was synthesized. ^c Grafting density (σ) calculated using $\sigma = N_A \rho h / M_n$, where M_n is the number-average molecular weight, N_A is Avogadro's number, and ρ is the bulk mass density. ^d Distance between the anchoring points. ^e Radius of gyration for corresponding unperturbed chain.

the film/substrate interface was negligible, and only fluctuations at the polymer/vacuum surface were probed for all samples except a 9 nm thick PS brush. For the range of in-plane wave vector, $q_{||}$, accessed (10^{-3} – 10^{-2} nm⁻¹) van der Waals interactions are negligible. A direct-illumination charge coupled device (CCD) camera, located 3545 mm downstream of the sample, recorded the off-specular diffuse scattering. The beam dimensions were 20 μ m by 20 μ m with a typical flux of $\approx 3 \times 10^9$ photons/s. The X-ray exposure time of any point on the sample was limited to reduce beam damage. The results were confirmed by repeating measurements during a later, independent series of experiments and by correlating different portions of a data set to prove that the correlation function was independent of the portion of the overall data set chosen for correlation.

Under conditions of partial beam coherence, the scattering pattern will exhibit interferences, called “speckles”, which will vary in time if the surface relaxes in the experimental time window in response to thermal fluctuations. Analysis of the normalized intensity–intensity time autocorrelation function,³¹ g_2 , of a speckle pattern yields the characteristic relaxation times of the surface. The intensity–intensity time autocorrelation function is

$$g_2(q, t) = \frac{\langle I(q, t') I(q, t' + t) \rangle}{\langle I(q, t') \rangle^2} \quad (2)$$

where $I(q, t')$ is the scattering intensity at wavevector transfer q at time t' , the angular brackets refer to averages over time t' , and t is the delay time.

Results and Discussion

That the fluctuations at the surface of a film of polystyrene chains are remarkably altered by tethering is clear from the comparison in Figure 1 in which $g_2(\tau)$ at $q_{||} = 5.3 \times 10^{-3}$ nm⁻¹ is plotted for three films at temperatures far above T_g : a 26 nm thick film of tethered PS chains with $\sigma = 0.6$ chains/nm², a 21 nm thick film with $\sigma = 0.12$ chains/nm², and a 29 nm thick film of untethered chains of similar molecular weight made by spin-casting, drying, and annealing.

The surface relaxation for the film of untethered chains is clearly observed and fitting with a single exponential, $g_2 = 1 + \beta \exp(-2t/\tau)$, where β is the speckle contrast, yields a relaxation time of 32 s. In contrast, g_2 for each brush is greater than unity and exhibits no relaxation within the experimental window. The fact that the value of g_2 remains above unity reflects that there is structure at the surface of the brush, but this structure does not relax, on the length scale probed, in the time window investigated. If the brush had a surface relaxation on this length scale with single exponential shape and a relaxation time of ca. 10 000 s or smaller, at least the beginning of the relaxation would be visible within this time window. Data collected for 26 nm (Figure 1) and 48 nm thick brushes (data not shown) demonstrated that there was no relaxation at times as short as tenths of a second. Comparison of line cuts through the speckle patterns of a brush sample and a film of untethered chains, shown in Figure 2, also makes clear that the brush surface has structure that is static over the time scales

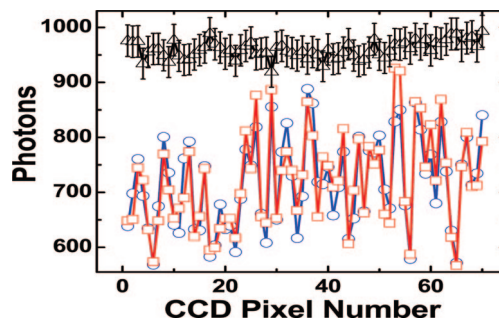


Figure 2. Comparison of speckle data for a brush and a film of untethered chains for $q_{||} = 0.01$ nm⁻¹. Bottom curves: photons as a function of CCD pixel along a line in the speckle patterns measured for brush PS-21: averaged over the first 441 s or 70 frames (open circles) and averaged over last 441 s (open squares). Error bars are given as square root of the photon counts (i.e., ± 25 – 30). Top curve (triangles): same, but for 100 nm thick film of untethered 36K PS chains at 150 °C averaged over 280 s (100 frames) and shifted up by 150 photons for clarity. Error bars are given as square root of the photon counts (i.e., ± 30 – 32).

investigated. Error bars in Figure 2 represent ± 1 “standard deviation”. A line cut averaged over 441 s at the beginning of a measurement for brush PS-21 shows detailed structure arising from scattering of the coherent beam. The same line cut averaged over the same period of time (or number of frames) at the end of the run (126 s later) shows the same detailed scattering pattern, to within experimental uncertainty. In contrast, the same line cut made for the data from a film of untethered chains and averaged over 280 s (100 frames) is simply flat within the uncertainties because the surface structures relax within that period of time.

The XPCS data provide information on surface fluctuations with a range of characteristic wavelengths, according to the range of $q_{||}$ probed. No relaxation was seen for lengths scales from 620 to 3100 nm, as shown in Figure 3. The lack of surface relaxation was seen for brushes with h varying from 9 to 107 nm, corresponding to values of h/R_g from 3 to 11.6, a value of h/R_g much larger than those for which Jiang et al.⁴ found suppression of surface fluctuations in films of untethered chains. It would be interesting to test the behavior of still thicker brushes, but it is not currently possible to make thicker brushes with chains of molecular weight as well controlled as for the brushes studied here. Even to reach the thickness of 107 nm required relaxing the molecular weight control relative to our standard ATRP synthesis protocol. Data collected at much shorter times for the 26 and 48 nm thick brushes demonstrated that there was no relaxation at times as short as tenths of a second.

No relaxation was seen for any brush at any temperature investigated, as highlighted by Figure 4, which presents data for the PS-48 brush at temperatures up to 230 °C. The highest temperature is about 130 °C above the T_g of untethered chains of the same molecular weight ($T_g \approx 100$ °C). For the PnBA-30

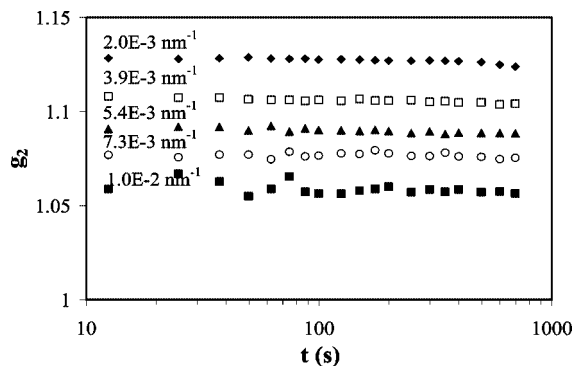


Figure 3. $g_2(t)$ for the 39 nm thick PS brush at 190 °C at $q_{||} = 0.002, 0.0039, 0.0054, 0.0073$, and 0.01 nm^{-1} . The data for the $q_{||} = 0.0039 \text{ nm}^{-1}$ film has not been offset. For clarity, the other curves have been vertically offset by -0.01 (0.002 nm^{-1}), -0.01 (0.0054 nm^{-1}), -0.015 (0.0073 nm^{-1}), and -0.035 (0.01 nm^{-1}), respectively.

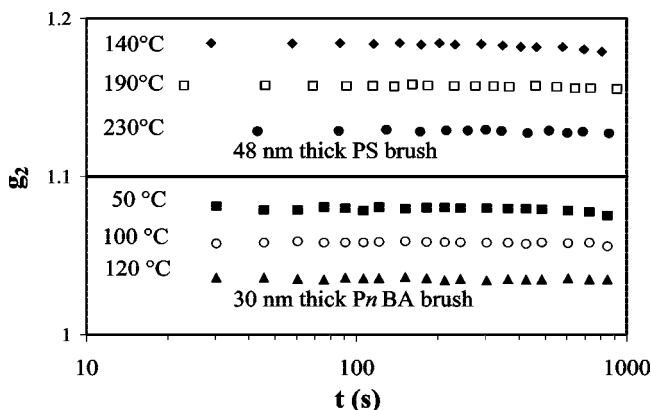


Figure 4. Intensity autocorrelation functions for (top) a 48 nm thick PS brush and for (bottom) a 30 nm thick PnBA brush at three temperatures. For clarity, curves for the PS brush have been offset by 0.07 (140 °C), 0.04 (190 °C), and 0.018 (230 °C); curves for the PnBA brush have been offset by -0.08 (50 °C), -0.07 (100 °C), and -0.12 (120 °C).

brush no surface relaxation was seen for temperatures up to 170 °C above the T_g of untethered chains, which is ≈ -50 °C, so the phenomenon is also not peculiar to PS brushes.

All of these observations may be compared with the predictions of Fredrickson et al.¹¹ and Milner et al.¹² that long wavelength surface modes should be suppressed. Unfortunately, the scattering intensity falls off so quickly with $q_{||}$ that even at this state-of-the-art facility it is not currently possible to reach the values of $q_{||}$ comparable to $2\pi/h$ where relaxations are predicted to become evident. One anticipates that for sufficiently large h/R_g as the grafting density is decreased one should begin to see surface relaxation in the experimental time and $q_{||}$ window. However, for a grafting density of 0.12 chains/nm^2 ($h/R_g = 2.3$) still no relaxation is observed.

Application of eq 1 to the brushes suggests that their viscosities could be very high. Estimates of moduli for these brushes using the theory of Fredrickson et al.¹¹ are of order 2 MPa for grafting density of 0.6 chains/nm^2 . This is 3 orders of magnitude higher than the values of moduli seen by Jiang et al.⁴ for thin films of untethered chains. If the viscosity of the brush were the same at 170 °C as that of the 65 kg/mol chains in the 29 nm film of untethered chains in Figure 1, eq 1 predicts the surface relaxation time would be of order 0.01 s, which is too short to be seen in the XPCS experiment. For the relaxation time of a film of this viscosity to be so large that it falls beyond the XPCS window on the high side the viscosity would have to

be at least 5 orders of magnitude higher than that of a corresponding film of untethered chains.

It is certain that the suppression or freezing of fluctuations seen here is not due to an increase in the T_g of the film. Reflectometry measurements of change in thickness with temperature of the 42 nm thick PS brush revealed that the brush has a glass transition temperature within a few °C of the bulk T_g .

Conclusion

In summary, XPCS measurements have revealed that the surface fluctuations seen in a particular time and $q_{||}$ window for films of untethered chains are absent on homopolymer brushes with grafting densities in the range of $0.12\text{--}0.6 \text{ chains/nm}^2$. In fact, no relaxation at all can be observed in the time and wavevector space currently accessible. This is consistent with thermodynamic theories^{11–13} to the degree that they anticipate fluctuations should be suppressed on the brush and with the suggestion of Obukhov and Rubinstein¹⁴ that chain relaxations in the brush could be very slow. Whether the fluctuations are truly suppressed or rather slowed dramatically is not yet clear because the surface does have some sort of structure. This remarkable change in surface dynamics is more profound than that seen in ultrathin films of untethered chains and is a result of covalent tethering. The ability to alter surface dynamics by tethering could be used to tailor wetting, friction, and adhesion of polymer surfaces.

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