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Effective Viscosity of Lightly UVO-Treated Polystyrene Films on Silicon with Different Molecular Weights

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Abstract: Recently, we found that a brief, 1-second exposure to ultraviolet ozone (UVO) can cause the effective viscosity, η_{eff} , of polystyrene films supported by oxide-coated silicon (PS-SiOx) to increase by more than 100 times. In this experiment, we study the phenomenon with different PS molecular weights, M_w , from 2.4 to 451 kg/mol. We found that η_{eff} was increased for all M_w 's when the film thickness, h_0 , was decreased below an onset thickness comparable to

the radius of gyration, R_g , of the polymer. For h_0 greater than the onset thickness, the η_{eff} versus h_0 dependence varies with M_w . Specifically, for $M_w \geq 60\text{K g/mol}$ η_{eff} was constant, equal to the bulk viscosity. For $M_w < 60\text{K g/mol}$, η_{eff} decreased with decreasing h_0 in the same way as that of the pristine counterparts. X-ray Photoelectron Spectroscopy (XPS) shows that oxygenated groups are formed in the films after the UVO treatment. We propose that the oxygenated groups can interact with the OH groups on the SiO_x surface to produce increases in η_{eff} . Correspondingly, we found that the η_{eff} data could fit well to a three-layer model containing a dynamically dead layer on the substrate. Results of the fit are consistent with a surface layer with a thickness of $\sim R_g$ and the following attributes. Below entanglement, the mobility of this layer is enhanced relative to the bulk polymer. Above entanglement, couplings between the surface chains and the chains in the inner, bulk-like region force the surface chains to flow as the inner chains. As a result, enhanced mobility can only be found in short-range, local motions over depths of the order of the average distance between entanglements. This picture explains a variety of surface relaxation phenomena reported in the literature.

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I. INTRODUCTION

Confining a polymer in nanoscale dimensions often results in changes in the properties of the polymer. Understanding the mechanism underpinning the changes is not only of practical value, but also fundamental interest. Nanometer polymer films have been excellent model systems for studying confinement effects due to their simplicity, namely they involve confinement of the polymer in one dimension only. The impacts of one-dimensional confinement on a variety of dynamic and mechanical properties of polymers have been investigated, including elastic modulus (E),¹⁻³ glass transition temperature (T_g),⁴⁻¹⁸ self-diffusion coefficient (D),¹⁹⁻²² and effective viscosity (η_{eff}),²³⁻²⁷ etc. It has been found that the confinement-induced alterations usually arise from interfacial effects that exacerbate with the interfacial area-to-volume ratio as the film thins. In supported films, there are two kinds of interfaces, namely polymer-air interface (or free surface) and polymer-substrate interface. The former has been reported to cause enhancement to the polymer mobility but reduction to the mechanical strength,^{2, 5, 8, 23} while the latter the opposites^{4, 20, 24} or no change if the polymer-substrate interactions are weak enough.^{6, 8,}

16

Torres et al.² found that the elastic modulus of entangled polystyrene (PS) films with thicknesses $< \sim 60$ nm supported by PDMS (PS-PDMS) changed from depressed to bulk-like after exposing the films to ultraviolet ozone (UVO) for ≥ 30 s. Similar exposures of unentangled PS-PDMS films, however, brought no change to the thickness dependence of the elastic modulus of the films. More recently, we studied the effective viscosity, η_{eff} , of UVO-exposed PS films with $M_w = 451$ kg/mol on silica (PS-SiOx).²⁸ Before exposure, η_{eff} of the films decreased strongly with decreasing film thickness, h_0 , attributable to promotion of substrate slippage by the

free surface.²⁵ Upon exposure to UVO even merely for 1.0 s, η_{eff} increased abruptly when h_0 was decreased below the radius of gyration, R_g , of the polymer.

To elucidate the origin of the noted rise in η_{eff} of the exposed 451 kg/mol PS-SiOx and to explore the phenomenon further, we study η_{eff} versus h_0 of similarly exposed PS-SiOx films for various M_w 's from 2.4k to 451k g/mol. We also perform X-ray Photoelectron Spectroscopy (XPS) to examine if new chemical groups may form in the films during UVO exposure²⁹ that could augment the interactions between the polymer and the substrate surface. Our result confirms the formation of such groups. Despite the presence of these groups, η_{eff} of the exposed films was the same as that of the pristine films for $h_0 > \sim R_g$, suggesting that impacts of these groups took place by their interactions with the substrate only. By fitting the η_{eff} versus h_0 data to the layer model,²⁴ we infer that the surface viscosity is comparable to the bulk viscosity for the entangled films, but much smaller than the bulk viscosity for the entangled films. We discuss implications of these results about the dynamic properties of the surface mobile layer.

II. EXPERIMENTAL SECTION

Sample Preparation. Single-crystal (100) silicon wafers covered by a 100 ± 5 nm thick thermal oxide layer or a native oxide layer were used as substrates (Si-TECH Inc., Topsfield, MA). Silicon slides (1×1 cm²) were cleaned in a freshly prepared piranha solution at 130 °C for 20 min., to remove organic contaminants. Before use, all the slides were rinsed in deionized water and dried by 99.99% nitrogen gas. The surface of oxide-covered silicon (SiOx) is predominantly covered by OH groups and hydrophilic³⁰. Hydrophilicity is confirmed by 0° water contact angle found of our substrate immediately after cleaning. To examine the effect of

polymer-substrate interactions on the η_{eff} of the UVO-exposed films, we also used silicon substrates that were HF-etched, prepared as follows. Immediately after the above cleaning process, the substrates were submerged in a 0.1% HF aqueous solution for 10 min. then dried by 99.99% nitrogen. Submersion in HF results in replacement of OH by Si-H surface groups ³⁰. Concomitantly, the water contact angle was measured to be $80^\circ \pm 2^\circ$, indicating the substrate surface to become more hydrophobic. Unless otherwise stated, SiOx were used as substrates.

Polystyrene (PS) with various weight-average molecular weights (M_w) between 2.4 and 451 kg/mol and polydispersity indices (PDI) of 1.01 – 1.1 were purchased from Scientific Polymer Products (Ontario, NY). According to the supplier, one end of the polymer is a butyl group and the other end is saturated styrene. Below we label different PS polymers by PSXXk, where XX is the M_w in kg/mol. To make the films, we dissolved the polymer in 99.8 % toluene (Fisher Scientific Co.) to produce solutions with different concentrations then filtered the solutions through a PTFE membrane with a nominal pore size of 0.1 μm (Fisher Scientific Co.). The filtered solutions are spun-cast onto cleaned substrates to make the films. A single-wavelength (633 nm) Stokes ellipsometer by Gaertner Scientific Corp. (Skokie, IL) was used to determine h_0 at multiple locations on the films. Deviations in the h_0 measurements were typically less than 0.3 nm.

Ultraviolet Ozone (UVO) Treatment. Ultraviolet ozone treatments were performed in a commercial UVO cleaner (ProcleanerTM Plus, BioForce Nanosciences Inc., Ames, IA) equipped with a mercury grid lamp with emission wavelengths between 185 and 450 nm and a maximum intensity at 253.65 nm. The nominal output of the UVO lamp was 19.39 mW/cm² at a distance of 11.1 mm. Before treatment, the UVO cleaner was turned on to allow the lamp to stabilize for 30 min. To treat a sample, the UVO cleaner door was opened and the sample placed quickly onto a

stage inside the chamber at a distance of 7.4 mm from the lamp before the cleaner door was closed. After the sample was exposed to UVO for 1.0 s (checked by using a stopwatch with a resolution of 0.1 s), the chamber door was reopened and sample removed. The whole sample-insertion process was conducted as quickly and consistently as possible. We checked that η_{eff} of the films treated by following this procedure was reproducible (Section I of SI). Moreover, when the exposure time was increased from 1.0 s to 3.5 s in steps of 0.5 to 1.5 s, the η_{eff} increased unequivocally (Figure S1). These results affirm that our treatment procedure is able to modulate the η_{eff} of our films with good control and repeatability.

X-ray Photoelectron Spectroscopy (XPS). The chemical composition of PS450k-SiOx with $h_0 = 110$ nm was characterized before and after 1.0, 5.0, 10.0, 20.0 and 90.0 s UVO exposure, respectively, by using high-resolution XPS. The value of h_0 was chosen as such to eliminate the impact of the substrate surface on the XPS signal, as confirmed by the absence of Si in the signal received. All the films were unannealed and let dry in air for at least 24 h before measurement. XPS spectra were recorded on an Axis Ultra DLD multi-technique system (Kratos Analytical, UK) equipped with a mono-chromated AlK $_{\alpha}$ radiation. A pass energy of 160 eV was used for the survey spectra and a pass energy of 40 eV was used for the high-resolution spectra. The high-resolution spectra were obtained at a take-off angle of 90°. The chemical shift data were obtained by using the center of the C-C/C-H peak at 285.0 eV as a reference. Surface chemical information was obtained by analyzing the carbon-1s peak after subtracting a linear background. Peak fit and area calculations were carried out by using the CasaXPS software. Elemental surface compositions (atomic %, excluding hydrogen) were calculated from areas of the carbon 1s peak and oxygen 1s peak and using the sensitivity factors provided by the instrument manufacturer.

Effective Viscosity (η_{eff}) Measurement. Effective viscosity, η_{eff} , (or equivalently, Mobility, M_{tot}) provides a measure for the resistance (or readiness) of a film to flow. In this experiment, η_{eff} or M_{tot} is determined by monitoring evolution of the surface morphology of the sample by using tapping-mode atomic force microscopy (AFM) followed by analyses based on hydrodynamic equations appropriate for the experiment.^{20, 23, 31} More specifically, time-sequenced AFM topographical images of the films were captured at various annealing times, t . The topographic data were then multiplied by a Welch function, Fourier-transformed and radial-averaged to produce the power spectral density (PSD).²³ The whole annealing process was conducted in nitrogen to protect the film from thermal degradation. We limited the annealing time to be sufficiently short so that the film roughness was much less than h_0 and no holes were detectable in the topographic image. It has been shown that the timed PSDs can be described by:

32

$$A_q^2(t) = A_{q,0}^2 \exp(2\Gamma'_q t) + \left[\frac{k_B T}{\gamma_s q^2 + G''(h_0)} \right] [1 - \exp(2\Gamma'_q t)], \quad (1a)$$

where $A_{q,0}^2 = A_q^2(0)$ and $\Gamma'_q = -M_{\text{tot}} q^2 [\gamma_s q^2 + G''(h_0)]^{-1}$ for unentangled films, (1b)

$$\text{or } A_{q,0}^2 = A_q^2(0) \left[\frac{3\mu_0 / (h_0^3 q^2)}{\gamma_s q^2 + 3\mu_0 / (h_0^3 q^2)} \right]^2 + \frac{k_B T}{\gamma_s q^2 + 3\mu_0 / (h_0^3 q^2)}$$

$$\text{and } \Gamma'_q = -M_{\text{tot}} q^2 \left[\left(\gamma_s q^2 + G''(h_0) \right)^{-1} + \left(\frac{3\mu_0}{h_0^3 q^2} \right)^{-1} \right]^{-1} \quad \text{for entangled films.} \quad (1c)$$

Here, q is the wave vector, k_B is the Boltzmann constant, T is the measurement temperature in degrees Kelvin, γ_s is the surface tension, M_{tot} is the mobility, μ_0 is the rubbery shear modulus of film if it is entangled, and $G(h_0) = -A/(12\pi h_0^2)$ is the interfacial potential, where A is the Hamaker constant.³³ We had also let A vary as a fit parameter and found that it had little impact

on the fit result. Equation (1a) portrays a dynamic process by which surface capillary wave modes with different q 's are excited in the film. By fitting the measured PSDs to equations (1a) and (1b) if the M_w is $< M_c \sim 31$ kg/mol - the characteristic molecular weight for entanglement in PS³⁴ - or equations (1a) and (1c) otherwise, we determined M_{tot} . Figure 1 shows a representative sequence of PSDs obtained from an entangled, UVO-exposed film and the respective best fit to our model. As seen, the fitted lines (solid lines) describe the data well. In determining the fit, we first fit the upper envelop of the data to $A_q^2 = k_B T / \gamma_s q^2$, which is the theoretical PSD of a bulk

Figure 1. Illustration of a representative set of PSDs obtained from a film (open circles) and the respective fit to equation (1). The data were obtained from a 23 nm thick 1-second UVO-exposed PS451k film annealed at 172 °C for various times as shown in the figure legend. The fit parameters are $\gamma_s = 0.030$ N/m, $\mu_0 = 2.5$ kPa and $M_{tot} = 1.1 \times 10^{-3}$ nm³Pa⁻¹s⁻¹, corresponding to $\eta_{eff} = 3.8 \times 10^6$ Pa·s. (solid lines). The dashed line denotes the theoretically predicted PSDs of a bulk liquid with surface tension $\gamma_s = 0.030$ N/m.

liquid with surface tension γ_s . By setting T equal to the measurement temperature, we determined γ_s (red dashed line). Then the entire data set was fit to equations 1(a) and 1(c) (or 1(b)) by using

M_{tot} and μ_0 (or M_{tot} only) as the fit parameters while assuming the experimental or previously determined values for the other parameters.

To interpret the result, we take note that M_{tot} is the steady-state unit-width current produced in the film upon application of a unit pressure gradient ∇P across it. Mathematically, $M_{\text{tot}} \equiv [-\int_0^{h_0} v(z) dz] / |\nabla P|$, where $v(z)$ is the velocity profile in the film.³² For polymer films supported by a solid substrate with no slip, if the viscosity of the film, η , does not vary with position, $M_{\text{tot}} = h_0^3 / (3\eta)$. However, various experiments show that η is usually a function of depth, z , due to perturbations to the polymer dynamics by the interfaces.^{20, 23-25, 28} In addition, the no-slip boundary condition does not always apply, especially when the films are ultrathin (namely $h_0 < \sim R_g$).²⁵ We thus define the effective viscosity η_{eff} by:^{23, 32}

$$\eta_{\text{eff}} \equiv h_0^3 / (3M_{\text{tot}}). \quad (2)$$

Under this definition, η_{eff} is the viscosity of a film if it is homogeneous and exhibits no slippage. Otherwise, η_{eff} is an effective viscosity measuring the overall resistance of the film to flow. In the recent past, we had measured $\eta_{\text{eff}}(h_0)$ of a variety of polymer films. By fitting the data to a layer model assuming a specific $\eta(z)$ and slippage condition, we inferred information about the dynamic heterogeneity^{20, 23-25, 28} and slippage condition of the films.^{25, 26}

III. RESULTS AND DISCUSSIONS

Figure 2(a) shows the η_{eff} versus h_0 of pristine (open symbols) and UVO-exposed PS-SiOx (solid symbols) with $M_w = 451$ and 13.7 kg/mol. For the pristine films of both M_w 's, as h_0 was decreased below ~ 30 to 60 nm, η_{eff} started to decrease from η_{bulk} (dashed lines in Figure 2(a)). The origin of this phenomenon is established. For PS13.7k, which is unentangled, it

Figure 2. (a) Effective viscosity, η_{eff} , versus h_0 of PS13.7k and PS451k, both pristine and after 1-s UVO exposure, supported by SiOx. The measurement temperature was 120 °C and 172 °C, respectively. The upper and lower dashed line indicates the bulk viscosity of PS451k and PS13.7k, respectively. The data of the 451k films were reproduced from Ref. ²⁵. (b) η_{eff} versus h_0 of PS451k films treated by UVO as in (a), but supported by HF-etched Si (Si-H).

is caused by enhanced mobility at the free surface. ^{23, 25} For PS451k, which is entangled, it is caused by promotion of interfacial slippage in the films by the free surface. ²⁵ For the UVO-exposed films, the $\eta_{\text{eff}}(h_0)$ dependence varies with M_w . For PS451k, on decreasing h_0 from 200 nm, η_{eff} first maintained the bulk value, then increased abruptly when h_0 was decreased past ~ 20 nm (c.f. $R_g \approx 18$ nm ³⁵). As for the PS13.7k films, η_{eff} first decreased with decreasing h_0 in the same manner as the pristine counterparts (open diamonds, Figure 2(a)), but when h_0 fell below R_g (≈ 3.1 nm ³⁵), evolution in the film surface became essentially halted. To show that the surface dynamics of exposed PS13.7k ultrathin films were indeed halted, we display the PSDs of one of these films, with $h_0 = 2.8$ nm annealed at 172 °C in Figure S2. (Note that 172 °C is much higher than the annealing temperature of 120 °C used to take the data of the PS13.7k films in Figure

2(a).) As Figure S2 shows, the PSD did not evolve even at this high temperature for ~ 3.5 d, except for an initial, abrupt rise characteristic of polymer films softening from the room-temperature glassy state to the rubbery state on heating above the T_g .³⁶ An evolution pathway as this is distinct from that of entangled polymer films, in which evolution of the PSD resumes after the entanglement time.³⁶ The prolonged stagnancy in growth exhibited by the PSD of this film is reminiscent of a polymer brush, which is elastic even in the melt state.³⁷ In fact, the shear modulus of this film (i.e., $\mu_0 = 450$ Pa) as determined by fitting the data to equations (1a) and (1c) is similar to that of a film constructed to mimic a Guiselin brush.³⁷ We thus surmise that UVO exposure introduces chemical groups to the PS polymer that promotes anchoring of their chains to the substrate surface. To explore this idea, we did two experiments. In the first experiment, we measured η_{eff} of UVO 1s-exposed PS451k films on HF-etched silicon. The result, displayed in Figure 2(b), shows that the rise in η_{eff} found at small h_0 ($< R_g$) is significantly reduced compared to that of the SiOx-supported films. (n.b. At $h_0 \sim 5$ nm, $\eta_{\text{eff}}/\eta_{\text{bulk}}$ was decreased from ~ 240 to ~ 1.8 when the substrate surface was changed from SiOx to HF-etched Si.) This strongly suggests that the increase in η_{eff} of the UVO 1s-exposed films is caused by enhancement in the polymer-substrate interaction. In the second experiment, we employ XPS to study any change in the chemistry of the polymer upon UVO exposure.

Figure 3(a) shows the XPS carbon-1s high-resolution spectrum of pristine PS, where the C-C/C-H peaks of the main chain and π - π^* shake-up peak of the phenyl rings can be seen. After exposure to UVO for 90.0 s, new peaks emerge, corresponding to the O=C-O, C=O C-OR and β C-C/C-H bonds. At the same time, the height of the π - π^* peak decreases suggesting breakage of phenyl rings. Oxygenated groups such as these had been found to form hydrogen bonds with

Figure 3. Peak-fit carbon 1s XP spectra of a pristine PS film (a) and a 90-s UVO-exposed PS film (b).

Figure 4. (a) Functional group distribution changes of UVO-exposed PS as a function of UVO exposure time (b) Concentration of oxygen atoms as a function of UVO exposure time.

the OH groups on the silica substrate surface,³⁸ which may account for the η_{eff} rise found in the UVO-exposed films. We have repeated the analysis on PS films subjected to various shorter

exposure times. The results are shown in Figure 4(a) and 4(b). As one can see, the extent of chemical modification decreases with decreasing UVO exposure time. At the exposure time used in this experiment (i.e., 1.0 s), the modification is $< \sim 1$ %.

In Figure 2(a), a correlation is apparent between R_g and the onset thickness for the η_{eff} rise. We examine this correlation more carefully by studying $\eta_{\text{eff}}(h_0)$ of UVO-exposed PS-SiOx films at the three additional M_w 's: 2.4k, 60k and 115k g/mol. Because η_{eff} varied significantly with h_0 , we had to use different measurement temperatures to complete this study, as listed in Table S1. The result of this study is shown in Figure 5 as $a_T \eta_{\text{eff}}/\eta_{\text{bulk}}$ versus h_0/R_g , where a_T is the shift factor calculated by using the data of $\eta_{\text{bulk}}(T)$ ³⁹ and 172 °C as the reference temperature. The normalization allows us to factor out the conventional influence of M_w on viscosity, and focus only on its effect on the $\eta_{\text{eff}}(h_0)$ dependence. From Figure 5, one sees that all the η_{eff} data rise above η_{bulk} when h_0/R_g is below ~ 1 . Furthermore, the slope of the η_{eff} rise increases with decreasing M_w . To quantify these observations, we fit the data to a model introduced earlier for PMMA films supported by silica.²⁴ In this model, the polymer film was assumed to be a tri-layer consisting of a surface layer with thickness h_t and viscosity η_t on top of a bulk-like layer in the middle, and a dynamically dead layer of thickness h_d at the bottom. It further assumes that when h_0 is decreased toward a threshold thickness, l_t , M_t (defined to be the contribution of the surface layer to M_{tot} and given by $h_t^3/3\eta_t$) begins to decrease with decreasing h_0 on a length scale of Δl_t . The following equations provide a mathematical description of this model:

$$M_{\text{tot}} = \left[\frac{(h_0 - h_d)^3}{3\eta_{\text{bulk}}} - \frac{h_t^3}{3\eta_{\text{bulk}}} \right] + M_t(h_0), \quad (3a)$$

$$\text{where } M_t(h_0) = \frac{M_t(\infty)}{1 + \exp[-(h_0 - l_t) / \Delta l_t]}. \quad (3b)$$

Figure 5. Normalized effective viscosity versus normalized film thickness of pristine and UVO 1s-exposed films with different M_w . Here, a_T is the shift factor calculated by using η_{bulk} of the polymers and 172 °C as the reference temperature. The thick solid lines are fits to the layer model (equation (3)).

In equation (3a), the quantity enclosed by the square bracket gives the mobility of the bulk-like layer, where h_t is the thickness of the surface layer. In applying these equations, we assume that $h_t = R_g$ considering that a polymer chain must move as a whole when it undergoes translational motion in fluid flow. Furthermore, when $h_0 - h_d$ is smaller than h_t , there can be no bulk-like layer and the surface layer is cut short by the dead layer. Therefore, we set $h_t = h_0 - h_d$ under this circumstance, which results in $M_{\text{tot}} = M_t(h_0)$. It is evident from equation (3b) that the parameter $M_t(\infty)$ is the asymptotic value of M_t when $(h_0 - l_t) \gg \Delta l_t$. Moreover, as h_0 is decreased to the point where $h_0 - l_t$ approaches or is less than zero, $M_t(h_0)$ decreases strongly with decreasing h_0 . We ascribe this reduction in $M_t(h_0)$ to the strong interactions between the UVO-treated polymer and the substrate surface and the cutting short of the surface layer by the dead layer mentioned above. As one can see, the model (thick solid lines, Figure 5) describes the data well. Table 1 summarizes the parameters obtained from the fits.³⁵

Next, we elaborate the fit result. Shown in Figure 6 is a plot of h_d as a function of R_g ⁴⁰. As seen, for $R_g > \sim 6$ nm, h_d is a constant ~ 2.23 nm, but decreases steadily toward zero with decreasing R_g for $R_g < \sim 6$ nm. We find that the small- R_g data can be described by $h_d = 0.37R_g$ (solid line). As for l_t and Δl_t , a transition near $R_g \sim 6$ nm can also be perceived from their variations with R_g shown in Figure 7(a) and 7(b), respectively. Below this transition, $l_t \approx R_g$ and $\Delta l_t \approx 0$. Above this transition, $l_t = 4.3 \text{ nm} + 0.55 R_g$ and $\Delta l_t = 0.074(R_g - 4.8 \text{ nm})$. From Figure 6, one may trace the transition R_g to be approximately 3 times the maximum value of h_d ($\cong 2.2$ nm,

Table 1. Summary of the tri-layer model fit result for UVO-1s PS films

Sample	R_g	h_d	l_t	Δl_t	$M_t(\infty)^a$	$\eta_t/\eta_{\text{bulk}}^b$	T/T_g^c
	(nm)	(nm)	(nm)	(nm)	($\text{nm}^3 \cdot \text{Pa}^{-1} \cdot \text{s}^{-1}$)		
PS451k	18	2.3 ± 1.3	14.0 ± 1.0	0.97 ± 0.13	$(5.4 \pm 1.6) \times 10^{-4}$	1.1	1.09
PS115k	9.1	2.2 ± 0.8	9.8 ± 0.8	0.42 ± 0.05	0.017 ± 0.009	0.65	1.12
PS60k	6.6	2.2 ± 0.5	7.5 ± 0.5	0.10 ± 0.01	0.063 ± 0.029	0.49	1.17
PS13.7k	3.1	$1.1 + 0.5/-1.0$	2.9 ± 0.5	0	1.32 ± 0.57	0.08	1.19
PS2.4k	1.3	$0.5 + 0.3/-0.4$	1.6 ± 0.3	0	4700 ± 2500	1.5×10^{-4}	1.15

- a) The values have been rescaled to that at a reference temperature of 172 °C using the data of $\eta_{\text{bulk}}(T)$.
- b) The values of h_t was obtained by assuming the surface layer thickness h_t to be R_g and the relation, $\eta_t = h_t^3/3M_t(\infty)$.
- c) The values of T (in K) are the measurement temperatures used for the exposed films with h_0 above the η_{eff} rise. The T_g (in K) are based on those published in Ref. ⁷.

Figure 6. Dead layer thickness, h_d versus R_g (open squares). The solid line is the best fit to the $R_g \leq 6.6$ nm data to $h_d = aR_g$ where a is a fit parameter found to be 0.37. The dashed line denotes $h_d = 2.23$ nm, which best fits the $R_g \geq 6.6$ nm data to a constant.

Figure 7. (a) l_t vs. R_g . (b) Δl_t vs. R_g . The dashed lines are the best linear fits to the data with $R_g \geq \sim 6$ nm. The solid lines are straight-line fits to the first three points passing through the origin.

Figure 8. Schematic drawings comparing R_g and the maximum dead layer thickness, $h_{d,max}$, with l_t and Δl_t (i.e., the onset thickness and decay length, respectively) that characterize the suppression of M_t due to proximity to the substrate surface. Two qualitatively different cases are identified, namely (a) $R_g > 3h_{d,max}$ (≈ 6.6 nm) and (b) $R_g < 3h_{d,max}$. The functional form of $M_t(h_0)$ in each case is shown by the red line.

denoted by $h_{d,max}$ below). Figure 8 shows schematic pictures summarizing these observations.

In our original report of η_{eff} increases by 1-second UVO exposure of PS-SiOx,²⁸ we introduced a slightly different model to describe the $\eta_{eff}(h_0)$ data. Specifically, the films were assumed to have no dead layer, and $M_t(h_0)$ was assumed to dominate M_{tot} when h_0 was $< l_t$. All else are the same as the current model. We find that within experimental uncertainty this model gives the same fit values of l_t and Δl_t as the current model (Figure S6), suggesting the two models to be equivalent. Several observations are noteworthy. Firstly, it would not be apparent from the earlier model what the physical origin is for the transition seen near $R_g \sim 6$ nm for $l_t(R_g)$ and $\Delta l_t(R_g)$ in Figure 7(a) and 7(b), respectively. But in the current model, one may correlate it to

an approach of R_g to where h_d saturates. Secondly, in both models, it is assumed that $M_{\text{tot}} \cong M_t(h_0)$ when h_0 is small enough. By introducing a dead layer, the assumption arises naturally as discussed above. By using equation (3b), one may explain why the two models give comparable fit results even though one has the dead layer and the other does not. Specifically, equation (3) suggests that $M_t(h_0)$, and hence M_{tot} , is significantly depressed (to ~5% of its maximum value) at $h_0 = l_t - 3\Delta l_t$. According to Table 1, all values of $l_t - 3\Delta l_t$ exceed h_d . Then as far as the total mobility is concerned, it would not matter whether the dead layer is present or not.

In a previous study, we found that the surface chains of PS2.4k-SiOx are much more mobile than those in the bulk polymer.²³ It is interesting to examine if the same holds for the UVO-exposed films. To this end, we estimate the relative surface viscosity, $\eta_t/\eta_{\text{bulk}}$ of these films by assuming that $\eta_t = h_t^3/3M_t(\infty)$, $h_t = R_g$ and the value of η_{bulk} found on fitting equation (3a) to experiment. The hence calculated $\eta_t/\eta_{\text{bulk}}$ are shown in Table 1. As seen, they are of the order of one for the films with $M_w \geq 60$ kg/mol, meaning that the mobility of the surface chains of these films are similar to the bulk chains. In contrast, the $\eta_t/\eta_{\text{bulk}}$ of the $M_w = 2.4$ and 13.7 kg/mol films are much smaller, equal to 0.015% and 8%, respectively. We contemplate that the bulk-like surface viscosity of the $M_w \geq 60$ kg/mol films are due to entanglements between the surface and the bulk-like, inner chains. As a result, the dynamics of the surface chains are dragged to be bulk-like. The fact that $\eta_t/\eta_{\text{bulk}}$ decreases appreciably as M_w is decreased below the characteristic M_w for entanglement supports this idea (Table 1).

In spite of the dramatic increase in η_{eff} found of the UVO-treated films for $h_0 < R_g$, our measurement result suggests that the UVO treatment may not have caused the intrinsic dynamics of the polymer to slow. In particular, the η_{eff} of the UVO-exposed PS2.4k and PS13.7k films

with $h_0 > \sim R_g$ is depressed and identical to that of the pristine films (Figure 5). We reason that the null change in the intrinsic dynamics from the UVO treatment is due to the short UVO exposure time of 1.0 s used in this experiment and the resulting low density of chemical modifications (Figure 4). It is remarkable that a previous study on the η_{eff} of high- M_w pristine PS-SiOx could not measure the value of η_t due to dominance of η_{eff} by surface-induced slippage in pristine films.²⁵ Upon introduction of oxygenated groups to the polymer by UVO, slippage is suppressed as the chains become more adherent to the substrate surface, enabling η_t to be determined.

The data of Figure 6 shows that the thickness of the dead layer, h_d , attains the maximum value ($h_{d,\text{max}} \sim 2.23$ nm) when R_g exceeds $\sim 3h_{d,\text{max}}$. But when R_g is smaller than $\sim 3h_{d,\text{max}}$, $h_d \sim 0.37R_g$. In an earlier experiment,²⁴ we studied the η_{eff} of PMMA-SiOx where we also found the existence of a near-substrate dynamic dead layer. In that work, PMMA with M_w 's of 2.7 and 12.4 kg/mol were studied, and h_d was found to be 2.2 ± 1.0 and 1.8 ± 1.0 nm, respectively. Because the R_g 's of these PMMA polymers were 1.4 and 3.0 nm, respectively, and the relative uncertainties of the h_d values were comparatively large, it could not be resolved whether those PMMA films belong to the $h_d \sim 0.37R_g$ regime or the $h_d \sim h_{d,\text{max}}$ regime identified above. We attribute the poor resolution of h_d in that work²⁴ to the lower density of thicknesses studied. Figures 2(a) and 5 show that it is imperative to take denser data points near and below $h_0 \approx R_g$ to obtain an accurate value of h_d , especially for the lower M_w films with $R_g < \sim 3h_{d,\text{max}}$.

The PSD evolution of the $h_0 = 2.8$ nm UVO-exposed PS13.7k film (Figure S2) shows that the film was essentially elastic throughout the annealing process from 150 s to 3.5 days at 172 °C. In contrast, a slightly thicker UVO-exposed PS13.7k film with $h_0 = 3.2$ nm evolved as a Newtonian liquid (Figure S3). A tempting attribute to the solid behavior of the $h_0 = 2.8$ nm film

is that all the polymer chains in this film were irreversibly adsorbed onto the substrate surface, mimicking a Guiselin brush.³⁷ According to Fujii et al.,⁴¹ upon extensively annealing thin films of PS-SiOx or PS on HF etched silicon above the T_g , an irreversibly adsorbed layer of the PS polymer developed on the substrate surface that could not be removed by vigorous rinsing with toluene even though toluene is a good solvent. To examine if the entire $h_0 = 2.8$ nm UVO 1s-treated PS13.7k film might have become adsorbed to the substrate, we rinsed the film with fresh toluene multiple times as in Ref.⁴¹. We found that the thickness of the residue film was $h_{\text{residue}} = 1.11 \pm 0.08$ nm. The fact that it is less than the thickness of the film suggests that a good fraction (up to $60\% = 1 - 1.11 \text{ nm} / 2.8 \text{ nm}$) of the polymer chains in the film were not bound to the substrate. Naively, one might think that some or all of the unbound chains should be able to contribute to M_{tot} to make it non-zero. We ponder the reason why this film and the near-substrate region within $0 < z < h_d$ of the $M_w \geq 60\text{K}$ g/mol films might appear dead. One possibility is that the motions of the unadsorbed chains are obstructed by the adsorbed ones, which act as barriers.

When the polymer chains are unentangled, this kind of obstructions is expected to take effect in the region where the adsorbed chains are physically present. For ultrathin films (defined to be ones with $h_0 < R_g$), the region should be $0 \leq z \leq h_0$, or the whole film. Within this region, if the density of the adsorbed chains is high enough, a percolation transition may take place whereupon the dynamics of the unadsorbed chains can be effectively jammed. As noted above, the fraction of adsorbed chains found of the $h_0 < 2.8$ nm UVO-exposed PS13.7k film is at least $\sim 40\%$. We consider this a lower limit because toluene rinsing could have pulled some of the adsorbed chains out. Furthermore, the adsorbed chains could entangle with the unadsorbed chains to make the effective area fraction of the “obstacles” to be larger. If the effective area fraction of the obstacles exceeds the percolation threshold for planar translational motions

(~68%)⁴² which we believe is likely in our films, the flow dynamics could halt as found in the $h_0 = 2.8$ nm (and thinner) UVO 1s-exposed PS13.7k films. For the thicker films with $h_0 > R_g$, the unadsorbed chains can pass the adsorbed ones from above. Then the thickness of the dead zone should be the thickness of the adsorbed layer, which is $(1.1 \text{ nm} / 3.1 \text{ nm})R_g = 3.5R_g$, which agrees with the relation, $h_d = 0.37R_g$ found above.

When the polymer is sufficiently entangled, a high areal density of stagnant, adsorbed chains may not be sufficient to completely stop the flow dynamics of the unadsorbed chains. It is because the unadsorbed chains may still slither through the entanglement network of the adsorbed chains as in bulk polymer. With this sort of motions, M_{tot} would depend on the conformation of the entanglement network of the adsorbed chains. It has been resolved that the thickness of the adsorbed layer is of the order of $\sim R_g$,⁴¹ consisting of a tightly bound layer of flattened chains and a loosely bound layer of loops.⁴³ The loops closer to the substrate surface are shorter and denser than those farther away. As a result, we surmise that the unadsorbed chains, upon entanglement with these loops, can have their dynamics strongly suppressed. This scenario can lead to a dynamically dead zone near the substrate surface. Considering that the dead zone is caused by shorter loops, its thickness might not depend on the M_w (or R_g) of the adsorbed chains, which would explain the finding that $h_d = \text{constant}$ in the $R_g > \sim 6$ nm regime of Figure 6. As one moves away from the dead zone, the average loop length increases and their density decreases, so the effectiveness of their drag on the unadsorbed chains lessens. Then the unadsorbed chains might need to reach deeper into the adsorbed layer to experience the same degree of drag from the adsorbed chains as those of films with a lower R_g do. This may explain why l_t continues to increase with R_g even after h_d becomes constant at $R_g \sim 6$ nm (Figures 7(a)

and 8(a)). It may similarly explain why Δl_t (namely the distance over which M_t varies by a factor of 2 from its value at $h_0 = l_t$) increases with R_g for large values of R_g (Figures 7(b) and 8(b)).

In this experiment, the distance over which the substrate influence on η_t persists is of the order of one R_g (Table 1). On the other hand, a tracer diffusion experiment reported that the persistence distance was somewhat longer, namely $\sim 3.5R_g$ to $6R_g$.⁴⁴ We ascribe the difference to η_{eff} and D being sensitive to different components of the dynamic spectrum (which arises from dynamic heterogeneity of the film) and the likelihood that the persistence distance is different for different dynamic components. We elaborate this idea as follows. The sort of dynamics that concern D should be more represented by the slow components because tracer diffusants naturally spend more time in the slow regions. Effective viscosity, on the other hand, should be more represented by the fast components. To perceive this, consider a film with a gradient of viscosity that increases with increasing depth from the free surface. Suppose we divide the film up into N layers labeled by $i = 1, 2, \dots, N$ with layer thicknesses of h_i and viscosities of η_i where $\eta_1 \ll \eta_2 \ll \eta_3 \ll \dots \ll \eta_N$. From Figure S7, one may perceive that

$$M_{\text{tot}} \approx \sum_{i=1}^N \frac{t_i^3}{3\eta_i}, \quad (4)$$

where $t_i = h_1 + h_2 + \dots + h_i$. Equation (4) shows that M_{tot} should be determined by the layers with the lowest viscosities. Our previous simulation result indicates that dynamic heterogeneity exists even within the first two segmental layers of the free surface⁴⁵. Given this and the assumption that $h_t \sim R_g$, a gradient of mobility should exist within the surface mobile layer. In entangled polymer films, it is established that the entanglement density, ρ_e , is reduced near the free surface.

⁴⁶ But on going deeper into the film ρ_e must return to the bulk value. We surmise that the gradient of ρ_e arising may contribute to heterogeneity in the surface mobile layer. By this view,

the fast component may correspond to the superficial chains that make the least entanglements with other chains; the slow component, on the other hand, may correspond to the chains that entangle with the deeper, bulk-like chains that are either in direct or indirect contact with the substrate surface. (For indirect contacts, we envision that they are facilitated through entanglements with other still deeper chains.) Such a scenario may explain why substrate influence can be more long-ranged for near-surface diffusivity, D , than for surface viscosity, η_t .

According to Table 1, the values of $\eta_t/\eta_{\text{bulk}}$ are $\geq \sim 0.49$ for $M_w \geq 60$ kg/mol, meaning that the surface viscosity, η_t , is bulk-like or almost bulk-like for these films. From first glance, a bulk-like surface viscosity for these films might seem contradictory to the noticeably enhanced surface relaxations deduced by Fakhraai and Forrest studying recovery of surface nanodeformations⁴⁷ and Ediger's group studying reorientations of fluorescent molecules.⁴⁸ We surmise that the different findings may be caused by different techniques probing different length scales of the dynamics: As noted above, while the surface chains may have enhanced dynamics up to a distance of $\sim R_g$ from the surface, when they entangle with the slow, bulk-like chains below, their translational motion becomes bulk-like. Given that the couplings between the surface and inner chains are facilitated by entanglements, the topmost surface region with thickness of the order of the average distance between entanglements or ~ 5 nm⁴⁹ should have few entanglements with the inner chains and thence be able to maintain fast local motions. At temperatures below the T_g , surface probes with sizes smaller than h_t such as nanodeformations (which had depths of $\sim 3 \pm 3$ nm⁴⁷) and fluorescent molecules might still sense significant polymer mobility even when translational motions of the polymer are arrested by entanglement with the bulk-like inner chains. We liken the situation to that of a hypothetical molten "Gueslin brush"³⁷ interwoven with a chemically identical "polymer solid" by entanglement, wherein the

fluffy brush corresponds to the mobile region and the polymer solid the bulk-like, inner region. This picture would account for the ~ 5 nm thick surface layer thickness found in the fluorescent probe reorientation experiment.⁴⁸ As temperature is increased above the T_g , the inner region begins to melt and flow. At the same time, the contrast in dynamics between the fluffy brush-like region and the bulk-like inner region decreases.²³ The dynamics sensed by the local probes becomes increasingly influenced by viscous flow (as opposed to the relatively local, viscoelastic relaxations probed in the $T < T_g$ regime). Then the viscous drag from the chains in the inner region might cause the measured dynamics to be bulk-like. This picture would explain the finding of $\eta_t/\eta_{\text{bulk}} \sim 1$ in this experiment, and the approaches to bulk-like relaxations found in the nanodeformations and fluorescent probe reorientation experiments as T increased toward T_g . It should be noted that the circumstances just discussed apply to entangled films only. In unentangle films, where the coupling between surface and inner regions is absent, the surface chains can move independently of the inner ones. As a result, enhanced surface mobility can take place even at $T > T_g$ as evident from the small values of $\eta_t/\eta_{\text{bulk}}$ ($< 8\%$) found here for the $M_w < 13.7$ kg/mol films (Table 1). It is noteworthy that similar enhancement was also found in the surface mobility of small-molecular glasses^{50, 51} and low- M_w ²³ or oligomeric PS.⁵⁰

IV. CONCLUSION

We have studied the influence of brief, 1-second treatment in a commercial ultraviolet ozone (UVO) cleaner on the dynamics of polystyrene films supported by oxide-covered silicon. For all the M_w 's studied (2.4 to 451 kg/mol), noticeably enhanced effective viscosity, η_{eff} , was found in the UVO-exposed films when the film thickness, h_0 , was decreased below an onset thickness of the order of the radius of gyration of the polymer, R_g . The enhancement in η_{eff} is attributed to

oxygenated groups found present in the UVO-exposed PS polymer, which are able to form strong hydrogen bonds with the OH groups on the substrate surface. This view is supported by the finding that the enhancement in η_{eff} became much reduced when the substrate surface was treated by HF etching. Most interestingly, just above $h_0 \approx R_g$, η_{eff} of the entangled films ($M_w \geq 60\text{k g/mol}$) were bulk-like, but those of the unentangled films ($M_w \leq 13.7\text{k g/mol}$) were depressed. The fact that the manner in which η_{eff} was depressed in the latter was identical to that of the pristine films shows that the UVO 1s treatment itself does not cause alteration to the intrinsic dynamics of the polymer. The observed increase in η_{eff} should then involve an extrinsic factor. We surmise that the extrinsic factor is the interaction between the oxygenated groups and the OH surface groups of the substrate. Increases in η_{eff} with thickness reduction also suggest that there is no slip in the films for otherwise the opposite thickness dependence should be found.²⁵ Because reductions in the η_{eff} of non-slipping polymers films originate from enhanced mobility at the free surface,²³ our result indicates that the surface mobility of the unentangled films is enhanced, but that of the entangled films is bulk-like. We attribute this finding to the viscous drag suffered by the surface chains of the entangled films due to entanglements with the bulk-like, inner chains, which are absent for the unentangled films. Because the concentration of UVO-induced chemical groups is extremely low ($< \sim 1\%$) and η_{eff} of the treated and pristine films are the same (except when they are ultrathin where the substrate effect sets in), we believe that the physical insights gained here about the surface mobile layer of our films are applicable to that of pristine PS films. Indeed, the picture arising from this result about the surface mobile layer is able to explain a variety of surface relaxation phenomena reported in the literature.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publication website at DOI: [10.1021/acs.chemmater.1c01111](#). Section I demonstrates the consistency of our UVO treatment method for the control of the η_{eff} of the sample films. Section II demonstrates the abrupt emergence in the viscoelastic character of the UVO 1s-exposed PS13.7k films when h_0 decreased from 3.2 to 2.8 nm. Section III provides information on the temperatures used to measure the η_{eff} of different films. Section IV demonstrates that the model used in Ref. ²⁸ for fitting the η_{eff} vs. h_0 data gives the same result as the layer model employed in this study. Section V shows how one may derive an approximate expression for the mobility of a multi-layer film with decreasing mobility toward the substrate surface.

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Effective Viscosity of Lightly UVO-Treated Polystyrene Films on Silicon with Different Molecular Weights

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SUPPORTING INFORMATION

Effective Viscosity of Lightly UVO-Treated Polystyrene Films on Silicon with Different Molecular Weights

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I. Consistency of our UVO treatment method for the control of the η_{eff} of the sample films

We have measured the effective viscosity, η_{eff} , of two sets of sample films treated by using our UVO treatment protocol and found that the η_{eff} values were reproducible within measurement uncertainty. Specifically, η_{eff} of two identically 1-second UVO treated PS13.7k films with $h_0 = 8.9 \pm 0.1$ nm were found to be $(1.3 \pm 0.4) \times 10^5$ and $(1.5 \pm 0.4) \times 10^5$ Pa·s at a measurement temperature, T , of 120 °C. Those of two 1-second UVO treated PS451k films with $h_0 = 10.9 \pm 0.1$ nm were $(1.2 \pm 0.4) \times 10^7$ and $(1.3 \pm 0.4) \times 10^7$ Pa·s, respectively, at $T = 172$ °C.

To demonstrate that the extent of modification to the η_{eff} of the films can be reliably adjusted by adjusting the UVO exposure time in steps of ≤ 1.0 s, we studied the η_{eff} of UVO-treated PS451k films with $h_0 = 11.0 \pm 0.2$ nm when the exposure time, t_{UVO} , was adjusted slightly from 1.0 s to values of 1.5, 2.0 and 3.5 s. The result, shown in Figure S1, reveals that η_{eff} increases unequivocally with t_{UVO} , testifying our 1-second treatment method.

We should also point out that the main result of this study (Figure 5) serves to affirm our treatment method as well. In particular, it shows that η_{eff} of the treated films varies in a systematic manner with h_0 and M_w . If the treatment procedure had been erratic and instilled random changes to the films, the noise that incurs should have obscured any systematic variations.

Figure S1. η_{eff} against t_{UVO} of PS451k films with $h_0 = 11.0 \pm 0.2$ nm measured at $T = 172$ °C. The blue dashed line indicates the bulk viscosity of PS451k. Without exposure to UVO, the η_{eff} is smaller than bulk viscosity (blue dashed line) due to surface-promoted slippage ¹.

II. Data showing emergence of viscoelastic behavior in the PS13.7k films upon reducing the film thickness from 3.2 to 2.8 nm

Figures S2(a) show that the viscoelastic film model (equations (1a) and (1c)) assuming $\eta_{eff} = 1.0 \times 10^9$ Pa·s and $\mu_0 = 450$ Pa is able to describe the data for times $t < 12,000$ s. Notice that $t = 12,000$ s is shorter than the viscoelastic time of the model ($\eta_{eff}/\mu_0 = 2.2 \times 10^6$ s). This means that the model is able to fit the data only when the film is in the rubbery elastic state. At longer times (for which the data are denoted by dijon and blue circles), the PSD decreases in amplitude with t , which is not predicted by the model. A possible reason for this decrease may be that the elastic modulus of the films increased with thermal annealing: By assuming the films to be elastic, we are able to fit the PSD's from $t = 60,000$ and $300,000$ s using $\mu_0 = 900$ Pa (fit result not shown), which is two times the value obtained for $t < 12,000$ s above. An increase in μ_0 with

Figure S2. PSDs (symbols) of an UVO 1s-exposed PS13.7 film with $h_0 = 2.8$ nm annealed at 172 °C for various times shown in the legend. In (a), the solid lines are calculations using the viscoelastic film model assuming $\eta_{\text{eff}} = 1 \times 10^9$ Pa·s and $\mu_0 = 450$ Pa. The color code of the lines follows that of the symbols. In (b), the solid lines are calculations using the liquid film model assuming $\eta_{\text{eff}} = 2 \times 10^8$ Pa·s.

thermal annealing could be caused by increases in the formation of anchors of the UVO exposed chains with the substrate surface. In light of the low estimated density of chemical modifications ($< \sim 1\%$) caused by the UVO-1s treatment, both the rate and drive for the anchoring process can be very low, and explain the slow evolution of μ_0 found. Figure S2(b) shows the fit result of the same PSD data using the liquid film model (equations (1a) and (1b)). As seen, the liquid film model predicts the amplitude of the PSD to increase continuously with time, which does not match the data at all. For comparison, we display the PSDs of an UVO 1s-exposed PS13.7K films with $h_0 = 3.2$ nm in Figure S3. It is noteworthy that this film is only 0.4 nm thicker than the film shown in Figure S2 and yet the PSDs evolve readily and can be fit by the liquid film model (solid lines). This shows that the elastic character emerges abruptly in the UVO-exposed 13.7K-SiOx films as the film thickness was decreased below the R_g of the polymer (~ 3.1 nm).

Figure S3. PSD of an UVO-1s exposed PS13.7k film with $h_0 = 3.2$ nm upon annealing at 120°C for various times labeled. The data fit well to the liquid film model (solid lines) assuming $\eta_{\text{eff}} = 1.7 \times 10^4$ Pa·s.

III. Measurement temperatures of the η_{eff} of different films

In taking the data of Figure 5, different measurement temperatures had been used as summarized below. For the values of l_t , see Table 1 of the main text.

Table S1. Temperatures used to measure the η_{eff} of different films

	T (°C) for $h_0 < l_t$	T (°C) for $h_0 > l_t$
Pristine PS2.4k	75	75
UVO-1s PS2.4k	172	75
Pristine PS13.7k	120	120
UVO-1s PS13.7k	172	120
Pristine PS60k	140	140
UVO-1s PS60k	172	140
Pristine PS115k	160	160
UVO-1s PS115k	172	160
Pristine PS450k	172	172
UVO-1s PS450k	172	172

IV. Demonstration that the layer model employed in Yu et al., Polymer **2017**, 116, 498-505 gives the same fit result as the layer model employed in the main text.

In our original report of η_{eff} enhancement in PS-SiOx by exposure to UVO,² we proposed the following model to describe the data:

$$M_{\text{tot}} = \begin{cases} M_t & (h_0 \leq l_t) \\ M_t + \left[\frac{h_0^3}{3\eta_{\text{bulk}}} - \frac{l_t^3}{3\eta_{\text{bulk}}} \right] & (h_0 > l_t) \end{cases} \quad (\text{S1a})$$

where

$$M_t(h_0) = \frac{M_t(\infty)}{1 + \exp[-(h_0 - l_t) / \Delta l_t]} \quad (\text{S1b})$$

In these equations, M_{tot} is the total mobility of the film and M_t is the surface mobility presumed to dominate M_{tot} when h_0 falls below the onset thickness, l_t , for the η_{eff} enhancement and Δl_t is the thickness range by which M_t decreases when h_0 is decreased below l_t . Physically, this model states that the film has a surface layer with mobility M_t and thickness l_t . When the film thickness is greater than l_t , it contributes to M_{tot} in the same manner as does by a liquid layer with the same thickness and a viscosity of $l_t^3/(3M_t)$. But when the film thickness is smaller than l_t , the film is devoid of any bulk-like region (mobility given by $[h_0^3/(3\eta_{\text{bulk}}) - l_t^3/(3\eta_{\text{bulk}})]$) whereupon $M_{\text{tot}} = M_t$. To account for the rise in η_{eff} for $h_0 < l_t$, we introduced the relation in equation (S1b) for M_t , which we had used before to model the data of PMMA and PiBMA films supported by oxide-coated silicon with success.^{3,4}

We have fit the η_{eff} vs. h_0 data of Figure 5 to equations (S1a) and (S1b) and obtained good agreement. (Please see Figure S4.) The fit values of l_t , Δl_t and $M_t(\infty)$ are shown in Table S2. Figure S5(a) and S5(b) displays the fit values of l_t and Δl_t , respectively, as a function of R_g . As one can see, they look similar to the corresponding data shown in Figures 7(a) and 7(b) obtained by using the model described in the main text (equations 3(a) and 3(b)).

To compare the fit results of the two models, we reproduce the data of Figure 7(a) and 7(b) in Figure S6(a) and S6(b) (symbols), respectively, and add the trend line shown in Figure S5(a) and S5(b), respectively therein (denoted by the red solid line). As one can see, the results of the two models agree within experimental uncertainties. The agreement justifies the explanation proposed in the main text for the transition seen near $R_g \sim 6$ nm in l_t vs. R_g and Δl_t vs. R_g to be caused by the existence of a dynamically dead layer with maximum thickness $h_{d,\text{max}} \approx 2.2$ nm, attained when R_g reaches $\sim 3h_{d,\text{max}}$.

Figure S4. The same normalized effective viscosity versus h_0 / R_g data shown in Figure 5, but different model lines (thick solid lines) as obtained by fitting the data to the model described by equations S1(a) and S1(b).

Table S2. Summary of the fit result using equations (S1a) and (S1b). ^{a)}

Sample	R_g (nm)	l_t (nm)	Δl_t (nm)	$M_t(\infty)^b$ (nm ³ ·Pa ⁻¹ ·s ⁻¹)	T/T_g^c
PS451k	18	13.1±1.0	0.95±0.13	(2.0±0.6)×10 ⁻⁴	1.09
PS115k	9.1	9.2±0.8	0.37±0.05	0.011±0.005	1.12
PS60k	6.6	8.0±0.5	0.14±0.10	0.053±0.022	1.17
PS13.7k	3.1	3.0±0.5	0	3.8±1.8	1.19
PS2.4k	1.3	1.6±0.4	0	5100±2600	1.15

^{a)} The values have been rescaled to that at a reference temperature of 172 °C using the data of $\eta_{\text{bulk}}(T)$.

^{b)} The values of T (in K) are the measurement temperatures used for the UVO exposed films with h_0 above the onset for the rise in η_{eff} to commence. The T_g values (in K) are based on those published in Ref. ⁵.

Figure S5. Plots of l_t vs. R_g (open squares) (a) and Δl_t vs. R_g (solid squares) (b). The dashed lines are the best linear fits to the data with $R_g > \sim 5$ nm. The solid black lines are the same guides-to-the-eye drawn in Figure 7(a) and 7(b), respectively.

Figure S6. (a) l_t vs. R_g (open squares). (b) Δl_t vs. R_g (solid squares) obtained by using the model described in the main text. The dashed lines are the best linear fits to the data with $R_g > 5$ nm. The solid red lines denote the best linear fit to the data shown in Figure S5(a) and (b), respectively. The solid black lines are the same guides-to-the-eye drawn in Figure 7(a) and 7(b), respectively.

V. Derivation for the Mobility of a multi-layer film with a mobility gradient

Consider a film consisted of an integer number of layers, N , where the local viscosities of the layers are η_i , and the layer thicknesses are h_i ($i = 1, 2, \dots, N$). Let $\eta_1 \ll \eta_2 \ll \eta_3 \ll \dots \eta_N$. Figure S7 shows the normalized velocity profile, $-v(z)/\nabla P$, in a film like this with $N = 3$ upon application of a uniform in-plane pressure gradient ∇P . Mobility is defined to be the area under this curve. From Figure S7, one can perceive that provided $\eta_1 \ll \eta_2 \dots \ll \eta_N$, this area can be approximated by the sum of the areas of the parabolas labeled in the figure that we refer to as the mobility of layer i . Mathematically, this corresponds to the approximation:

$$M_{tot} \approx \sum_{i=1}^N \frac{t_i^3}{3\eta_i}, \quad (S2)$$

where $t_i = h_1 + h_2 + \dots h_i$.

Figure S7. Normalized velocity profile, $-v(z)/\nabla P$, of an $N=3$ multilayer film described in the text, where ∇P is the uniform, in-plane pressure gradient that causes the velocity profile. The height of individual layer i is given by $t_i = h_1 + h_2 + \dots h_i$.

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