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Tuning the Effective Viscosity of Polymer Films by Chemical Modifications

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Abstract: We report controllable adjustment of the flow dynamics of polystyrene (PS) films supported by oxide-covered silicon by using a combination of ultraviolet ozone (UVO) treatment of the polymer and variable treatments of the substrate that adjust the contents of Si-OH and Si-H groups on the surface. The latter were achieved by submerging the substrates in a piranha solution then deionized water (leading to enrichment of Si-OH), or an aqueous HF solution (leading to enrichment of Si-H), or both (leading to intermediate surface chemistry). X-ray Photoelectron Spectroscopic (XPS) chemical analyses showed that the UVO treatment produced oxygenated functional groups in the polymer. Alongside, effective viscosity (η_{eff}) of the films became enhanced. However, the degree of enhancement increases (decreases) with the content of Si-OH (Si-H) groups on the substrate surface, ascribable to the resulting increases in the attractive

interactions between the UVO-induced oxygenated groups in the polymer and the Si-OH on the substrate surface. Likewise, η_{eff} of the pristine films displayed increases with the Si-H content on the substrate surface, corresponding to increases in the polymer-substrate interaction. Our observations pave the way for strategic tuning of the dynamics of polymer films by modulating the polymer-substrate interactions by chemical modifications.

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INTRODUCTION

Polymer thin films are broadly used in applications owing to their versatility and ease of fabrication. As technology advances, demand for polymer films with nanoscale features or thicknesses increases. Recent studies have shown that the properties of polymers under nanoconfinement are usually different from those of the bulk materials, and the differences can sometimes be quite large. In the case of nanometer polymer films, glass transition temperature (T_g)¹⁻¹¹, elastic modulus (E)¹²⁻¹⁴, and effective viscosity (η_{eff})¹⁵⁻²¹ have all been reported to demonstrate non-bulklike behaviors.

One popular postulate for confinement-induced changes in properties is that they are caused by perturbations to the mobility of polymers by an interface.^{1, 6, 16, 22-26} At the free surface (i.e., the polymer-air or polymer-vacuum interface), polymer segments are frequently found to be more mobile than those in bulk.^{6, 15, 22, 27-31} Accordingly, reductions in T_g ^{1-3, 32}, E ^{13, 14, 33} or η_{eff} ^{15, 17, 18} of polymer films are usually attributed to the mobility-enhancing effect of the free surface. Conversely, polymer segments tend to be less mobile near a substrate surface.^{16, 19, 26, 34} In that order, enhancements in T_g , E or η_{eff} of polymer films are usually ascribed to the mobility-suppressing effect of the substrate surface with the extent of enhancement increasing with the polymer-substrate interactions.^{1, 16, 23, 35} Based on these ideas, herein we propose an approach to tune the η_{eff} of polymer films by modifying the chemical groups in the polymer and those on the substrate surface whereby the polymer-substrate interaction is adjustable. Polystyrene (PS) supported by oxide-coated silicon is used as the model system. Chemical modification of the polymer is attained by ultraviolet ozone (UVO) treatment of the films for an exposure time of 1.0 s;^{20, 21} that to the substrate surface is attained by submerging the substrates in an aqueous hydrogen fluoride solution (HF) followed by drying in N_2 or submersion in a piranha solution and then

deionized water (DIW) before drying or both. Our data showed that enhancement or reduction of the η_{eff} confinement effect by different degrees can be achieved in a predictable manner, confirming the proposed approach.

I. EXPERIMENTAL SECTION

Substrate Preparation. Single-crystal (100) silicon wafers covered by a 100 ± 5 nm thick thermal oxide or those covered by a native oxide layer (Si-TECH Inc., Topsfield, MA) were used as substrates. The wafers were cut in to $1 \text{ cm} \times 1 \text{ cm}$ slides before submersion in a freshly prepared piranha solution at 130°C for 20 min to remove dust and organic contamination. If a hydrophilic surface was desired, silicon wafers with a 100 nm oxide layer were used, and rinsed in DIW after piranha submersion. This leaves the substrate surface with excessive silanol (Si-OH) groups³⁶ and a water contact angle (CA) of 0° . We refer to these substrates as SiOH below. If more hydrophobic substrate surfaces were desired, wafers with a native oxide layer were employed, and submerged in a 0.05% hydrofluoric acid (HF) aqueous solution (Fisher Scientific Co.) after the above piranha cleaning procedure. As Figure 1 shows, CA increases with HF etching time, t_{HF} for $t_{\text{HF}} > \sim 4$ min then saturates to $\sim 77^\circ$ after $t_{\text{HF}} \sim 14$ min. To further adjust the condition of the substrate surface, we took the HF-etched substrates that had attained the saturated CA, then either dried them directly with N_2 gas (resulting in substrates referred to as SiH below) or submerged them again in a piranha solution followed by DIW rinsing before N_2 drying. The latter procedure was found to return CA to 0° , showing that the ultimate substrate surface groups were predominantly Si-OH. Because the preparation procedure of these substrates is intermediate between that of the SiOH and SiH substrates, we label them as SiHOH. To examine the surface chemistry of different substrates, we employed X-ray Photoelectron Spectroscopy (XPS). The result, displayed in Table 1, shows that

Figure 1. Water contact angle of our HF-etched substrates against HF etching time, t_{HF} .

the relative atomic concentration of oxygen decreases in the order $\text{SiOH} > \text{SiHOH} > \text{SiH}$, as expected. Analogously, high-resolution XPS Si-2p spectra of these substrates (Figure 2) show that the peak height of SiO_2 to that of Si decreases in the same order. These results suggest strongly that the surface chemistry of SiHOH is intermediate between that of SiOH and SiH. A few words should be said about the relatively high concentration of atomic carbon found on the surface of SiH than on the other substrates (Table 1). This is unexpected because we had taken strict steps to avoid any possible chance of organic contaminants in preparing the SiH surfaces. Specifically, we

Table 1. Relative atomic concentrations of O-1s, C-1s, Si-2p and F-1s on different silicon surfaces.

	SiOH	SiHOH	SiH
O-1s	58.4%	48.2%	17.4%
C-1s	6.4%	5.5%	21.7%
Si-2p	31.6%	43.8%	52.5%
F-1s	3.4%	2.5%	6.3%

Figure 2. High-resolution XPS Si-2p scans of our substrates after normalization by the total area under the SiO₂ and Si peaks.

had carefully cleaned the substrates, solvent containers and tools with piranha solution before HF treatment. We believe that the relatively high level of carbon found may be due to high reactivity of SiH surfaces to air-borne organics, which are probably present in the fume hood where HF treatment was performed.

Polymer Film Preparation. Polystyrene (PS) with a weight-average molecular weight, M_w , of 451 kg/mol and polydispersity index, PDI, of 1.06 were purchased from Scientific Polymer Products (Ontario, NY). Below we label our polymer as PS451k. Thin films of PS451k were prepared by spin-coating its solutions in toluene onto cleaned substrate surfaces.²⁰ Film thicknesses were determined by ellipsometry using a single-wavelength (633 nm) Stokes ellipsometer by Gaertner Scientific Corp. (Skokie, IL). Unless otherwise stated, the films were used without thermal annealing. For η_{eff} measurements (to be detailed below), we have found that any out-of-equilibrium properties of the films arising from the spin-coating process do not produce noticeable influence on the result.³⁷ One probable reason is that η_{eff} is determined after the

viscoelastic time where some of the out-of-equilibrium properties such as residual stress and residual solvent have diminished to negligible level.

Ultraviolet Ozone (UVO) Treatment. Ultraviolet ozone treatment of the films were performed in a commercial UVO cleaner (ProcleanerTM Plus, BioForce Nanosciences Inc., Ames, IA) that is equipped with a mercury grid lamp with emission wavelengths of 185 to 450 nm. Before treatment, the UVO cleaner was allowed to warm up for 30 min. The nominal output of the UVO lamp was 19.39 mW/cm² at a distance of 11.1 mm. The distance between the sample and grid lamp was maintained at 7.4 mm during treatment and the exposure time was kept at 1.0 s. We have checked that this treatment procedure generated reproducible changes to the η_{eff} of the films as illustrated in the accompanying Supporting Information. Moreover, η_{eff} increased unequivocally when the UVO exposure time was increased to 3.0 s in steps of 0.5 to 1.5 s (Supporting Information). These validate our use of 1.0-s UVO treatment time to modify the η_{eff} of the films.

X-ray Photoelectron Spectroscopy (XPS). Surface elemental composition analyses were performed on XPS spectra acquired from the substrates and polymer films of this experiment. For studies of polymer films, we used film thickness, h_0 , of ~110 nm whereat the impact of the substrate surface on the XPS signal was negligible, as confirmed by absence of Si in the signal received (data not shown). Spectra taken at take-off angles (defined as the angle between the analyzer and sample surface), θ , of 25° and/or 90° were recorded on an Axis Ultra DLD multi-technique system equipped with a mono-chromated AlK α radiation operated at 75 or 150 W. Charge neutralization was accomplished by using a low-energy flood gun operating with a filament current of 1.7 A, a charge balance of 3.1 V and a filament bias of 0.5 V. All spectra were acquired in hybrid mode, using both the electrostatic and magnetic lenses. Elemental surface compositions (atomic %) were calculated from peak areas obtained from the high-resolution spectra after

subtraction of a linear background, and using the relative sensitivity factors provided by the instrument manufacturer. Surface chemical information was obtained by analyzing the chemical shifts of the carbon-1s C-C/C-H peak taken to be centered at 285.0 eV. Peak fit and area calculation were carried out by using the CasaXPS software.

Water Contact Angle Measurement. To assess the surface condition of a specimen, water contact angle (CA) was measured by using a Kruss DSA 100 contact angle goninometer under ambient conditions. Measurements were obtained by placing droplets of purified water (5 μ L in volume) at five different locations of the specimen surface and using the average of five measurements as CA and the standard deviation as error. The specimens studied include SiOH, SiH and SiHOH and PS451k films with $h_0 = 5$ and 20 nm supported by SiOH before and after UVO treatment, with and without thermal annealing.

Effective Viscosity (η_{eff}) Measurement. A common measure for the transport property of polymer films is mobility, M_{tot} , or equivalently, effective viscosity, η_{eff} .¹⁵ In this experiment, M_{tot} or η_{eff} is determined by using a method developed by our group in the past decade.^{15, 38, 39} In brief, a sequence of topographical images of the specimen film were captured at different annealing times by tapping-mode atomic force microscopy (AFM). The data were then multiplied by a Welch function, Fourier-transformed and radial-averaged to produce the power spectral density (PSD).^{40,}
⁴¹ Thermal annealing was conducted in a nitrogen atmosphere to protect the films against thermal degradation. We limited the annealing time, t , to be within the initial stage where no holes were detectable by AFM. It has been demonstrated that t -dependent PSDs of entangled, viscoelastic polymer films can be described by:³⁸

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

$$\text{where } A_{q,0}^2 = A_q^2(0) \left[\frac{3\mu_0 / (h_0^3 q^2)}{\gamma q^2 + 3\mu_0 / (h_0^3 q^2)} \right]^2 + \frac{k_B T}{\gamma q^2 + 3\mu_0 / (h_0^3 q^2)} \quad (1b)$$

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

In equations (1a)-(1c), q is the wave vector, k_B is the Boltzmann constant, T is temperature in degrees Kelvin, Γ'_q is relaxation rate of the surface capillary wave mode with wave vector q , γ_s is surface tension, μ_0 is rubbery shear modulus, and $G(h_0) = -A/(12\pi h_0^2)$ is interfacial potential of the film, and A is the Hamaker constant.⁴² Equations (1a)-(1c) predict that there is a characteristic (viscoelastic) time, τ , below which the film surface evolves like that of elastic solid with a shear modulus of μ_0 . But for $t \gg \tau$, the film surface evolves like that of viscous liquid with viscosity, $\eta_{\text{eff}} \equiv h_0^3/(3M_{\text{tot}})$. The value of τ is given by η_{eff}/μ_0 . Figure 3 displays a representative sequence of PSDs obtained in this experiment. The solid lines denote the best fit to equations 1(a)-1(c) by following the steps described in Ref.¹⁹. As one sees, the experimental PSDs agree with the fit lines well.

Physically, M_{tot} is the steady-state in-plane, unit-width current produced in the film when a unit-pressure gradient is applied across it. Mathematically, $M_{\text{tot}} \equiv [-\int_0^{h_0} v(z) dz / h_0] / |\nabla P|$, where z is the coordinate perpendicular to the film plane, $v(z)$ is velocity profile of the thin film fluid, ∇P is in-plane pressure gradient applied across the film.³⁸

Figure 3. Illustration of the experimental PSDs and model used to determine η_{eff} . The open circles denote the PSDs of a 20 nm thick PS451k film supported by SiOH upon annealing at 172 °C for various times given in the figure legend. The solid lines are the best fit to equations 1(a)-1(c) assuming that $\eta_{\text{eff}} = 5.0 \times 10^5 \text{ Pa}\cdot\text{s}$ and $\mu_0 = 800 \text{ Pa}$. The dashed line denotes the equilibrium PSD of the film.

II. RESULTS AND DISCUSSIONS

Figure 4 displays the main result of this study. In this figure, the data are plotted as η_{eff} versus h_0 for pristine (open symbols) and UVO-treated films (solid symbols) supported by different substrates of SiOH (squares), SiHOH (triangles) and SiH (circles). For pristine films, η_{eff} decreases with decreasing h_0 for all substrates. However, the degree of η_{eff} depression is different for different substrates, following the order $\text{SiH} < \text{SiHOH} < \text{SiOH}$. This order is consistent with our previous result¹⁷ and coincides with the order of substrate hydrophobicity implied by the results of Table 1 and Figure 2. Because PS is hydrophobic, we interpret the order of η_{eff} depression to be caused by increasing polymer-substrate interactions with increasing substrate Si-H groups.

Next, we discuss the data of UVO-treated films (solid symbols) in Figure 4. As one sees, η_{eff} of all these films converge to the same saturated, thick-film ($h_0 > 50$ nm) value of $(4 \pm 1.4) \times 10^6$ Pa·s. This value is comparable to the published bulk viscosity of PS451k, namely 1.9×10^6 Pa·s at $T = 172$ °C⁴³. As h_0 decreases below about 20 nm, close to the radius of gyration of the polymer, R_g (≈ 18 nm⁴⁴), η_{eff} increases with decreasing h_0 . However, the degree of η_{eff} increase is different for different substrates, and follows the order SiH < SiHOH < SiOH.

Figure 4. Effective viscosity versus film thickness, h_0 , of pristine and UVO-treated PS451k films supported by different substrates as marked in the figure legend. The measurement temperature was 172 °C. The solid lines are fits to the three-layer model (Equations (2a) and (2b)). The data of pristine films on SiOH are reproduced from Ref.¹⁷.

In an earlier experiment, a different polymer film system, namely unentangled poly(methyl methacrylate) (PMMA) on SiOH was also found to exhibit increasing η_{eff} with decreasing h_0 .¹⁶ In that study, the η_{eff} increase was attributed to the formation of specific bonds between the oxygen-carrying groups of PMMA and Si-OH groups of the substrate surface.¹⁶ Here, we explore whether a similar substrate effect may operate in the UVO-treated films. It has been reported that

exposure to UVO causes production of oxygenated species in PS.^{45, 46} To examine this effect systematically, we performed XPS chemical analyses of PS451k films exposed to UVO for different times, t_{UVO} , up to 20 s. Figure 5 shows the atomic concentration of oxygen found plotted as a function of t_{UVO} . As one sees, the oxygen content of the sample increases progressively with t_{UVO} . To elaborate how the added oxygen modifies the polymer chemically, we examine the high-resolution XPS carbon-1s spectra of the samples. To illustrate our result, we display the spectrum of the $t_{\text{UVO}} = 20$ s sample in Figure 6. There, we distinguished three oxygen-carrying C-1s peaks

Figure 5. Atomic concentration of oxygen from XPS survey scans plotted against UVO exposure time, t_{UVO} . The XPS take-off angle, θ , was 25°.

corresponding to O–C=O, C=O, and C–OR besides the CH–C–C and aromatic π - π^* peaks. Table 2 displays the fit values of the C-1s peak area fraction of each of the oxygenated groups and the π - π^* peak. From these data, it is apparent that the oxygenated groups are formed in expense of the C=C bonds in the aromatic phenyl rings. More importantly, the finding that oxygenated groups are present in the PS polymer after treatment by UVO supports the idea that there are likely

Figure 6. Peak-fit high-resolution XPS C-1s spectra of a UVO 20s-treated PS film.

Table 2. Functional group distribution, expressed in C-1s peak area (%), of PS films treated with various UVO exposure times, t_{UVO} .

t_{UVO} (s)	0.0	1.0s	5.0s	10.0s	20.0s
C-OR	0.0	0.6	0.6	2.9	5.9
C=O	0.0	0.0	0.1	1.1	2.2
O-C=O	0.0	0.0	0.0	0.8	5.0
$\pi-\pi^*$	7.3	6.9	6.4	6.0	5.4

to be specific bonds between the UVO-treated PS polymer and silanol groups on the substrate surface. From the XPS measurements of the substrates, one anticipates that the concentration of silanol groups decreases in the order $\text{SiOH} > \text{SiHOH} > \text{SiH}$. This order corroborates with the order of η_{eff} enhancement displayed by the UVO-treated thin films in Figure 4, supporting the η_{eff} enhancement to be caused by interactions between the polymer and substrate surface. It is

noteworthy that η_{eff} of the UVO-treated PS films on SiH is enhanced with respect to that of the pristine films even though the interactions between SiH and UVO-treated PS are expected to be small. We believe the reason is that SiOH may not be completely absent from the surface of SiH. This idea is supported by the data of Table 1 and Figure 2, showing that the atomic concentration of oxygen and relative amount of SiO₂ on SiH are not zero. Probably, oxidation of SiH took place immediately after HF etching under ambient conditions.

If specific bonds are formed between the oxygenated groups on the chains and silanol groups on the substrate surface, the concentration of oxygen near the free surface of the films may decrease with annealing time as the oxygenated groups get consumed to form the bonds. To examine this picture, we measured water contact angle (CA) of UVO 1s-treated films with $h_0 = 5$ nm ($< R_g$) and 20 nm ($> R_g$) before and after annealing at 172 °C for times exceeding the viscoelastic time, τ , of the films. The result is shown in Table 3. It reveals that after UVO treatment but before thermal annealing, CA is smaller than that of pristine PS films. This is expected because introduction of oxygenated groups should make the polymer more hydrophilic. After thermal annealing, CA returns to the CA found of pristine PS, supporting the proposal that surface oxygenated groups may be depleted due to substrate specific bond formation. Nevertheless, one observes that the same finding can also result from intra-chain segregation of the oxidized chain segments from the free surface (which lowers surface energy) without migration of the surface chains to the substrate surface. Migration of the oxidized surface chains may cease to occur if the enthalpic barrier for them to diffuse across the more hydrophobic chains below is too large.

Table 3. Water contact angles (CA) of pristine and UVO 1s-treated films with $h_0 = 5$ and 20 nm with and without thermal annealing after UVO treatment. ^{a)}

Sample	Pristine	UVO1s	UVO1s, annealed
PS451k, 5nm	89.3 ± 0.9	86.3 ± 0.7	88.8 ± 0.5
PS451k, 20nm	89.3 ± 0.7	85.9 ± 0.4	89.2 ± 0.5

^{a)} The annealing temperature was 172°C and annealing times of 4.5 h and 1 h for the $h_0 = 5$ and 20 nm film, respectively, which are longer than the viscoelastic time, τ , of the films.

To clarify if the surface chains of the UVO-treated films actually diffuse away from the free surface (crudely referred to as the region within R_g of the free surface) upon annealing, we perform angle-resolved XPS on UVO 1s-treated PS451k and PS13k films with $h_0 = 110$ nm ($> 4R_g$) before and after thermal annealing at 172 °C for 15 min ($> \tau \approx 400$ s). The choice of PS13k in this study is due to considerations of the XPS effective sampling depth, d , in PS as follows. Assuming that the distance over which photoelectrons can travel in a material before notable dissipation is 3λ , where λ is the attenuation length, $d = 3\lambda \sin\theta$.⁴⁷ By adopting $\lambda = 2.2$ nm for C-1s electrons with a kinetic energy of ~ 1200 eV in polymer,⁴⁸ one estimates d to be 6.6 nm and 2.8 nm at $\theta = 90^\circ$ and 25° , respectively. For PS13k, $2.8 < R_g \approx 3.1$ nm⁴⁴ < 6.6 nm. Then if the oxidized surface chains diffuse by distances larger than one R_g (two R_g 's) and oxidation does not take place in the whole film, the XPS oxygen 1s signal of annealed UVO-treated PS13k obtained at $\theta = 25^\circ$ (90°) should be the same as that of pristine PS13k. However, if the oxidized chains remain at the top of the film after annealing, the oxygen 1s signal of annealed UVO-treated PS13k obtained at

$\theta = 25^\circ$ should remain the same as that before annealing, i.e., higher than that of pristine PS13k. The results are summarized in Table 4. To remove any confusions that may arise from unaccountable oxygen 1s signal of the pristine polymer that can be caused by contaminants (denoted by ϕ_{Pristine}), we consider the oxygen 1s signal after subtraction by ϕ_{Pristine} , which are displayed in column 3 and 4 of Table 4 for the UVO-treated films before and after thermal

Table 4. Concentration of oxygen (in atomic %), ϕ , based on XPS spectra of pristine and UVO 1s-treated PS451k and PS13k films ^{a)} before and after thermal annealing.

Oxygen 1s	ϕ_{Pristine} (%)	$\phi - \phi_{\text{Pristine}}$ (%)	
	Pristine	UVO1s	UVO1s, annealed ^{b)}
PS451k ($\theta = 90^\circ$)	0.13	0.48	-0.02
PS451k ($\theta = 25^\circ$)	0.11	0.42	0.01
PS13k ($\theta = 90^\circ$)	0.47	0.30	-0.08
PS13k ($\theta = 25^\circ$)	0.38	0.43	0.07

^{a)} The film thickness is 110 nm, $> 4R_g$.

^{b)} Thermal annealing was performed at 172 °C for 15 min.

annealing, respectively. For PS451k, the surface concentration of oxygen of the UVO-treated films as determined at $\theta = 25^\circ$ returns to the level of pristine PS451k after annealing. This finding is consistent with the water contact angle result displayed in Table 3, strengthening the XPS result. For PS13k, the concentration of oxygen of the UVO-treated films determined at both $\theta = 25^\circ$ and

90° return to the pristine film level after annealing. This shows clearly that the oxidized surface chains diffused by distances larger than $2R_g$ on annealing.

The results of Tables 2 and 3 portray a picture of the UVO-treated films with a higher concentration of oxygenated groups on the substrate surface than that near the free surface.

Correspondingly, the polymer mobility should decrease toward the substrate surface. We propose a three-layer model with a conforming mobility gradient to model the η_{eff} of the UVO-treated films (Figure 4). In this model, the films are assumed to consist of a bulk-like layer (where the viscosity equals bulk viscosity, η_{bulk}) situated between a surface mobile layer (with thickness h_t and mobility M_t) on top and an immobile layer at the bottom (with thickness h_b and zero mobility).¹⁶ By further assuming the no-slip boundary condition on the substrate surface, mobility of the film can be written as:¹⁶

$$M_{\text{tot}} = \left[\frac{(h_0 - h_b)^3}{3\eta_{\text{bulk}}} - \frac{h_t^3}{3\eta_{\text{bulk}}} \right] + M_t, \quad (2a)$$

$$\text{where} \quad M_t = \frac{M_t(\infty)}{1 + \exp[-(h_0 - l_t) / \Delta l_t]}. \quad (2b)$$

Here, $M_t(\infty)$ is the maximum value of M_t attained when h_0 is large ($\gg l_t + \Delta l_t$), l_t is the thickness whereat $M_t/M_t(\infty) = 0.5$, $3\Delta l_t$ is approximately the half-width about l_t whereat $M_t/M_t(\infty)$ transitions from ~ 1 to ~ 0 with decreasing h_0 . Such a depression in M_t with decreasing h_0 is attributed to the attractive interaction between the UVO-treated polymer and substrate surface. We had previously used this model to describe the η_{eff} versus h_0 data of PMMA on SiOH with good consistency.¹⁶ In this experiment, we also find that the model is able to describe the data well as evident from the good agreement between our model (solid lines) and experimental data in Figure 4. (We had not

fit the model to pristine films because previous experiment had found slippage in highly entangled pristine PS films such as PS451k supported by SiOH ¹⁷.) The corresponding fit parameters are displayed in Table 5. One observes that among the different fit parameters, Δl_t is the only one that varies beyond uncertainty with substrate type. Based on this finding and the finding that Δl_t decreases with the concentration of Si-OH on the substrate surface, one may reason that mobility gradient in the film gets steeper with concentration of the substrate Si-OH. Moreover, it is the main reason for the observed variation in η_{eff} enhancement of the UVO-treated films.

Table 5. Summary of the three-layer model fit results for UVO 1s-treated PS451k films on various substrates.

	h_d	l_t	Δl_t	$M_t(\infty)$	$\eta_t/\eta_{\text{bulk}}^{\text{a)}$
	(nm)	(nm)	(nm)	(nm ³ ·Pa ⁻¹ ·s ⁻¹)	
SiOH	0 to 3.6	14.0±1.0	0.97±0.13	(5.4±1.6)×10 ⁻⁴	1.1
SiHOH	0 to 3.6	13.0±1.0	1.16±0.15	(5.0±1.5)×10 ⁻⁴	1.2
SiH	0 to 3.6	12.0±1.5	1.48±0.18	(6.5±2.0)×10 ⁻⁴	0.9

^{a)} The values of h_t was obtained by assuming the surface layer thickness h_t to be R_g and the relation, $\eta_t = h_t^3/3M_t(\infty)$.

It may not be immediately apparent why the parameter l_t , which also governs diminishment of M_t with h_0 reduction as Δl_t does, is relatively independent of the substrate OH groups. Here, we discuss a picture that may explain this. As discussed before, specific bonds are formed between the oxidized PS chains and substrate OH groups. We anticipate these bonds to cause the bonded

chains to lose mobility. In turn, the chains that entangle with the bonded chains may also suffer mobility deterioration. Specifically, the more specific bonds are formed the more small “loops” there would be on the substrate surface, which are expected to be effective in suppressing the mobility of the entangled chains by virtue of the smaller effective tube size (of the reptation model). Such a picture may explain the decrease in Δl_t with substrate OH groups. Separately, the region over which the bonded chains may influence the mobility of other chains should be within the vertical dimension of the bonded chains, which should be $\sim R_g$ from the substrate surface, independent of number of substrate bonds formed. This is in keeping with the observation that l_t is approximately independent of the substrate type and smaller than R_g .

Previously, Zhang et al.⁴⁹ reported that T_g of PS on oxide coated silicon (PS-SiOx) decreases with the thickness of SiOx, d_{SiOx} . Zhang et al. attributed the observed T_g - d_{SiOx} dependence to variations of the interfacial potential, $G(h_0)$, with d_{SiOx} . In this experiment, we found that η_{eff} of pristine PS decreases with d_{SiOx} . Since both decreased η_{eff} and decreased T_g imply enhanced dynamics, we explore whether our result may be connected with variations in $G(h_0)$. In modeling the PSD data of the films with $h_0 = 5$ nm, we allowed the Hamaker constant, A , and hence $G(h_0)$ ($\equiv -A/12\pi h_0^2$) to vary. (We did not vary A for the thicker films because the fit was independent of A for these films.) Comparison between the fit and theoretical values of A ⁴² for PS-SiOx with different d_{SiOx} (Table S1) suggests that $0 < d_{\text{SiOx}} < 2$ nm for SiHOH and SiH. This finding is consistent with independent measurement by ellipsometry that $d_{\text{SiOx}} < 0.1$ nm for the two kinds of substrates. In spite of the closeness in the fit values of A , η_{eff} of UVO-treated PS films on these substrates differ by 10 times (Figure 4). This shows that variations in the η_{eff} confinement effect of these films are unlikely to be caused by variations in the interfacial potential.

As noted above, η_{eff} of UVO-treated and pristine films converge at large h_0 , showing that viscosity of the polymer is unaffected by the UVO treatment. This is in keeping with the short treatment time (i.e., 1.0 s) and low concentration of oxygenated groups found in the treated films (Figure 5 and Table 2). By using the fit values of $M_t(\infty)$ in Table 5 and assumption that the surface layer thickness, h_t equals to R_g , we estimated the surface viscosity, η_t , and report them in the last column of Table 5 after normalization by η_{bulk} . (The assumption, $h_t = R_g$, is rationalized by the consideration that mobility concerns translational motions of polymer chains and so the thickness of the surface layer should be at least one R_g .) The result shows that $\eta_t \approx \eta_{\text{bulk}}$ for all the films. We attribute the bulk-like mobility of the surface chains to their entanglement with the inner chains that are bulklike, which may impose viscous drag on the surface chains to enforce the same, bulklike mobility. The facts that both the surface mobility and bulk viscosity of the polymer remain unchanged after the present UVO treatment further supports the proposition that modifications to the observed η_{eff} confinement effect are mainly caused by modulations of the polymer-substrate interactions.

III. CONCLUSION

We have demonstrated that the effective viscosity confinement effect of polymer films can be controlled by using selective chemical modification of the polymer chains and/or substrate surface. The system used for demonstration was PS supported by oxide-coated silicon. Chemical modification of the polymer was achieved by exposing it to UVO for 1.0 s in a commercial UVO cleaner. Chemical modification of the substrate surface was achieved by varying the procedure used to clean the substrates. Based on the results obtained by water contact angle measurements,

XPS surface elemental analyses and layer model analyses, we conclude that the control demonstrated on the effective viscosity confinement effect was achieved by adjustments of the polymer-substrate interactions.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publication website at DOI: It contains data that demonstrates consistency of our UVO treatment method for control of η_{eff} of the sample films, the XPS data of Tables 2 and 4, T_g of the pristine and UVO-treated films on SiOH and Hamaker constants of our $h_0 = 5$ nm films.

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For Table of Contents use only

Tuning the Effective Viscosity of Nanometer Polymer Films by Chemical Modification

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SUPPORTING INFORMATION

Tuning the Effective Viscosity of Polymer Films by Chemical Modifications

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

We have measured η_{eff} of two sets of sample films treated by using our UVO treatment method and found that the η_{eff} values were reproducible within measurement uncertainty. In particular, 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 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.

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Figure S1. η_{eff} versus 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 slippage¹. (Reproduced from the Supporting Information of Ref. ²)

II. X-ray Photoelectron Spectroscopy data of Tables 2 and 4

Figure S2 displays the original XPS spectra used to produce the data of Table 2. Each spectrum had been normalized by the total area under the spectral peaks.

Figure S3 displays the XPS data used to produce the data of Table 4. Each spectrum had been normalized by the total area under the corresponding spectral peaks and adjusted using the relative sensitivity factors (RSF) of 0.78 for O-1s and 0.278 for C-1s provided by the XPS instrument.

Figure S2. Normalized high-resolution C-1s XPS spectra of PS451k films with different UVO exposure times after subtraction by a linear background.

Figure S3. Normalized high-resolution C-1s and O-1s XPS spectra of (a) PS451k and (b) PS13k films after subtraction by a linear background. Peak areas are rescaled by using the RSFs used to compute the atomic concentration.

III. Glass transition temperature, T_g , of pristine and UVO-1s treated PS451k films supported by SiOH

Figure S4 displays T_g (measured by ellipsometry³) versus thickness of pristine and UVO-1s treated PS451k films supported by the SiOH substrates. The result shows that the T_g versus film thickness of these films are the same. We believe that it is due to the low concentration of chemical groups introduced by our brief (one-second) UVO treatment and the weaker effect expected of interfacial specific bonds (especially at low density) on T_g than η_{eff} .

Figure S4. T_g versus film thickness of PS451k pristine and UVO1s-treated films supported by SiOH. The data of Keddie et al.⁴ for pristine PS-SiOH (solid line) is also included for comparison.

IV. Hamaker constants of our $h_0 = 5$ nm films

The table below shows the best fit values of the Hamaker constants, A_{exp} , to the data of the $h_0 = 5$ nm UVO-1s PS451k films on different substrates. The theoretical Hamaker constant, A_{theory} , of PS-SiOx with different SiOx thicknesses, d_{SiOx} are shown side-by-side for comparison.

Table S1. Experimental and theoretical Hamaker constants of the $h_0 = 5\text{nm}$ UVO-1s PS451k films on different substrates

	$A_{\text{expt}} (10^{-20} \text{ J})$	$A_{\text{theory}} (10^{-20} \text{ J})^{\text{a)}}$
SiOH	2.75	0.734 ($d_{\text{SiOx}} = 106 \text{ nm}$)
SiHOH	-4.30	-5.75, 1.27 ($d_{\text{SiOx}} = 0, 2 \text{ nm}$, resp.)
SiH	-3.50	-5.75, 1.27 ($d_{\text{SiOx}} = 0, 2 \text{ nm}$, resp.)

a) Data taken from our previous publication.⁵

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