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Glass Transition Temperature of Polymer Films That Slip

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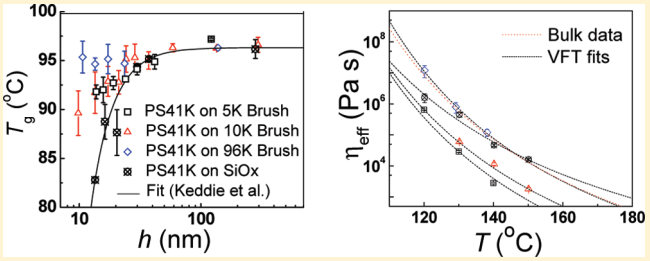
ABSTRACT: When a polymer is modified so that its glass transition temperature, T_g, is decreased (increased) from the inherent value, its dynamics is often supposed to be enhanced (suppressed). For polymer films, there is an ongoing debate about whether a change in T_g upon changing the film thickness is accompanied by a correlated change in the dynamics of the films. In this experiment, we measure the T_g of polystyrene films coated on different substrates on which the films dewet with different degrees of slippage and, therefore, different rates of dewetting. Our result shows that there is no correlation between the T_g and dewetting rate of the films.



INTRODUCTION

The origin of the thickness dependence of the glass transition temperature, T_g, observed in various polymer films[1−14] is one of the most challenging problems in contemporary polymer physics. An important related question is whether the change in T_g is accompanied by a change in the film's dynamics predictable by simple rationales.[15] Contrary to straightforward reasoning, ac dielectric spectroscopic measurements of Sharp et al.[16] and Serghei et al.[17] did not find any change in the dielectric relaxations of isotatic poly(methyl methacrylate) films coated on aluminum and polystyrene films coated on silicon, respectively, although the T_g of these films had been found to decrease with decreasing film thickness.[2,16] Dielectric relaxations are often attributed to small-scale local motions of the polymer main chain. Of practical interest is whether the change in the thin film T_g is correlated to larger-scale main-chain motions that determine the dewetting rate of the film should the film dewet. These include all free-standing polymer films and hence nanostructures in general[18] as well as a large number of supported films.

The purpose of this study is to measure the T_g of polymer films with different degrees of slippage at the polymer−substrate interface, as quantified by the slip length,[19] and examine if the T_g and slip length are correlated. A recent experiment[20] showed that the characteristic amplitude-growth time of surface capillary waves found in the films that slip can be 100 times shorter than if the film does not slip,[21] causing the slipping films to dewet much faster. According to previous results,[19,20,22,23] slippage takes place in entangled polymer films coated on a layer of end-grafted polymer brush with a shorter chain length. In this experiment, both the T_g and dewetting behaviors of thin films of PS with a number-average molecular weight, M_n, of 41 kg/mol deposited on an end-grafted PS brush with different M_n from 5 to 96 kg/mol are studied. The T_g of such film on brush systems have been studied before,[24,25] but no attempt has been made to correlate the dewetting dynamics and the T_g.

EXPERIMENTAL SECTION

Sample Preparation. The polymer films were prepared by spin-casting polystyrene (PS) with M_n = 41 kg/mol (purchased from Scientific Polymer Products, Ontario, NY) onto either Si (100) covered with an oxide layer (denoted by SiO_x-Si below) or PS brush with M_n = 5K, 10K, or 96K g/mol. The 10K and 96 K brushes were monocarboxy-terminated PS (purchased from Polymer Source Inc., Montreal, Canada), while the 5K brushes were monohydroxy-terminated PS (purchased from Scientific Polymer Products.) We use the "grafting to" method to make the brush layer. Specifically, the brush polymer was spin-cast onto a SiO_x-Si substrate and annealed in a 10^{-2} Torr vacuum at 180 °C for 24 h. The ungrafted brush chains were removed by thorough rinsing with toluene. The final thickness of the brush was measured by ellipsometry. Thin films of the 41K PS with thickness, h, between 10 and 300 nm were then spin-cast onto the brush layer from solutions of the polymer in toluene with concentrations between 0.3 and 4.5 wt %. Details of the polymers used and the brush films are listed in Table 1.

Measurement of T_g. A single-wavelength Stokes ellipsometer by Gaertner Scientific Corp. was used to measure the T_g of the films. Prior to the T_g measurement, the sample was annealed with annealing conditions (i.e., the annealing temperatures and times) chosen such that no holes could be found in the film by atomic force microscopy (AFM) after the measurement. For the films deposited on SiO_x-Si and the 10K and 96K brushes, the samples were annealed at 125 °C for 1 h and then placed on the ellipsometer at 140 °C for 10 min before the T_g measurement began, whereupon the sample temperature was decreased at a rate of 1 °C/min from 140 to 36 °C. A different annealing condition, however, was required for the films deposited on the 5K brush as they dewetted somewhat faster. These films were annealed at 126 °C for 30 min on the ellipsometer and measured upon cooling at the same rate of 1 °C/min to 36 °C. We estimate that the annealing times used in this

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Table 1. Sample Parameters of the Polymers Used

	M_n (kg/mol)	PDI	thickness (nm)	σ (chains per nm^2)[a]	$\sigma' \equiv \sigma N_B^{1/2}/(a\rho_0)$[b]	$\alpha = N_M/N_B$[c]
PS brush	96	1.07	$h_b = 14.5 \pm 0.5$	0.095	0.71	0.43
PS brush	10	1.07	$h_b = 5.0 \pm 0.4$	0.32	0.78	4.1
PS brush	5	1.10	$h_b = 4.2 \pm 0.2$	0.53	0.90	8.2
PS	41	1.07	$h = 10-300$	NA	NA	NA

[a] σ is the grafting density of the brush polymer on the SiO_x-Si substrate. [b] $\sigma' = \sigma N_B^{1/2}/(a\rho_0)$ is the normalized grafting density. Here, N_B is the degree of polymerization of the brush polymer; a and ρ_0^{-1} are the segmental length and volume, respectively. [c] α is the ratio of the degree of polymerization of the polymer film (M_n = 41K g/mol) to that of the brush polymer.

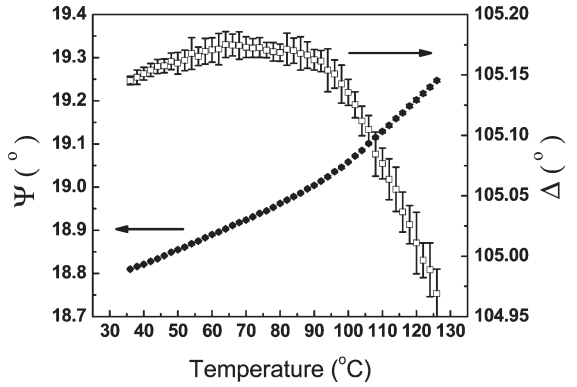

Figure 1. An example of ellipsometric angles Ψ and Δ plotted as a function of temperature. The data were taken from a 30 nm thick 41K PS coated on a 5K PS brush.

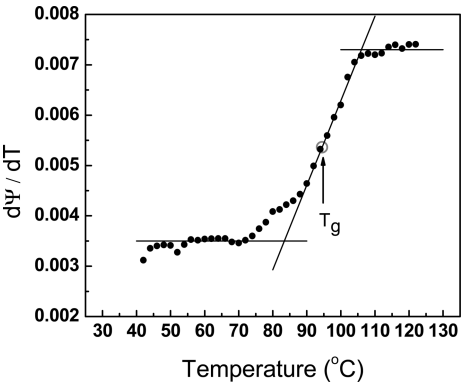

Figure 2. Illustration of how the T_g of a film was determined from the first derivative of an ellipsometric angle. The data were taken from a 30 nm thick 41K PS coated on a 5K PS brush.

experiment exceed the reptation times of the 41K PS, which are ~50 s at 140 °C, ~22 min at 126 °C, and ~28 min at 125 °C.[26,27]

The ellipsometric angles, Ψ and Δ, were monitored at a wavelength of 633 nm and incident angle of 70° at 2 °C temperature intervals. An average of 30 measurements taken over a period of 30 s at each measured temperature was used for statistical averaging. Figure 1 shows a typical set of Ψ and Δ data we obtained. For a small change δh in the film thickness, the changes, $\delta\Psi$ and $\delta\Delta$, in Ψ and Δ are proportional to δh,[28] allowing the T_g—namely the temperature at which the thermal expansion coefficient of the film changes discontinuously—to be determined directly from the raw data. As the data of Figure 1 show, the noise of one of the ellipsometric angles can be bigger than the other. The data with less noise were used to analyze the T_g. To better pinpoint the location of the T_g, the first derivative of Δ or Ψ, obtained by numerical differentiation over a temperature range of 8 °C, was plotted as a function of temperature, whereupon three distinct regions become discernible (Figure 2), corresponding to the glassy (low-T) and rubbery/liquid (high-T) regions separated by an intermediate transition region. The value of T_g was determined to be the center of the transition region, which was fitted to a linear function; the glassy and rubbery/liquid regions were fitted to a constant as Figure 2 illustrates.

Measurement of Dewetting Hole Growth Rate. An optical microscope was used to observe the dewetting of the films with h = 10−60 nm deposited on the 10K and 5K brushes in real time at an elevated temperature between 130 and 160 °C. Color images of the film at various dewetting times were recorded by a CCD camera mounted on the microscope and controlled by a computer. The images were then converted to grayscale and analyzed by taking a radial cross section of individual dewetting holes, from which the dewetting radius, $R(t)$, and rim width, $W(t)$, were measured as a function of time, t. In order to determine the slip length, b, the contact angle, θ_c, at the dewetting front was also needed (to be discussed below). We measured θ_c by quenching the dewetting film to room temperature and using AFM to capture the profile of several representative holes near the dewetting front.

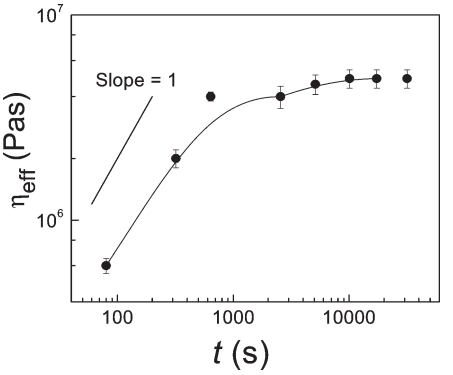

Figure 3. Effective viscosity plotted as a function of time for a 41K 10 nm thick PS film coated on a 96K PS brush upon annealing at 120 °C. The solid line passing through the data is a guide to the eye.

Viscosity Measurement. We used the method reported in refs 29 and 30 to measure the viscosity of films with h = 10 nm. A time series of images of the film surface were taken using tapping-mode AFM as the film was annealed at the measurement temperature, T. The surface height data were converted to a power spectral density (PSD), $A_q^2(t)$, by first multiplying it with a Welch function, performing a Fourier transformation, and then radially averaging the result to get the PSD. It has been shown that the time variation of the PSD is given by

$$A_q^2(t) = A_q^2(0)\exp(2\Gamma_q t) + \left[\frac{k_B T}{G''(h) + \gamma q^2}\right](1 - \exp(2\Gamma_q t)) \quad (1a)$$

where

$$\Gamma_q = -M[G''(h)q^2 + \gamma q^4] \quad (1b)$$

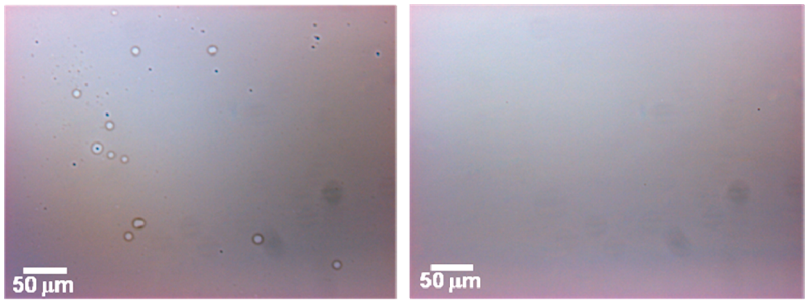

Figure 4. Comparison between the optical micrograph of a 41K 30 nm thick PS film coated on (a) a 10K PS brush and (b) a SiO_x-Si substrate after annealing at 150 °C for 4 h. Dewetting holes, appearing as light circular regions with a darker rim, have formed in (a) while no dewetting is observed in (b).

k_B is the Boltzmann constant, q is the wavevector, h is the film thickness, γ is the surface tension, M is the mobility, and $G(h)$ is the interfacial potential of the system. The effective viscosity, η_{eff}, of the film is defined by M and h to be $\eta_{eff} \equiv 3M/h^3$. Equation 1a can also be written as

$$A_q^2(t) = A_q^2(t - \Delta t)\exp(2\Gamma_q \Delta t) + \left[\frac{k_B T}{G''(h) + \gamma q^2}\right](1 - \exp(2\Gamma_q \Delta t)) \quad (1c)$$

where Δt is the time interval elapsed between the PSD data taken at time t and a time before. By fitting the PSD data to eq 1c, we can determine the value of η_{eff} at different annealing times, t. A representative set of data of η_{eff} vs t is shown in Figure 3. As seen, η_{eff} initially rises approximately linearly with time and then approaches a steady value after about 10 000 s (cf. the estimated reptation time of the polymer in that experiment was ~7600 s). The initial rise in η_{eff} was caused by the film being in the rubbery state, where the shear modulus, μ_0, of the film could produce an apparent effective viscosity that follows $\sim\mu_0 t$ in the PSD data.[31] Only in the terminal flow regime does η_{eff} accurately reflect the effective viscosity of the film. Therefore, we adopted the plateau value of η_{eff} for the measured value of η_{eff}.

A few words need to be said about the interfacial potential $G(h)$. In the systems we have previously studied,[29,30] $G(h)$ came solely from van der Waals interactions. With the addition of the polymer brush, entropic interactions between the polymers in the film and the polymers in the brush must also be taken into consideration. Here we assume that $G(h)$ is the sum of a van der Waals potential, $G_{vdW}(h_b + h)$[32] (where h_b is the thickness of the brush), and a melt-brush potential, $G_{MB}(h)$.[33,34] For $G_{MB}(h)$, we used the potentials published by Matsen and Gardiner,[33] obtained via self-consistent field theory calculations and found to depend on the normalized grafting density of the brush, σ', and the ratio of the degree of polymerization of the film to that of the brush, α. Matsen and Gardiner calculated the potentials using $\sigma' = 1$ and α = 1, 2, 4, and ∞. While the values of σ' employed in this experiment (= 0.71, 0.78, and 0.9; Table 1) are not too different from 1, some of the α values (= 0.43, 4.1, and 8.2; Table 1) are quite different from the ones used by Matsen and Gardiner. For each of our film−brush systems, we approximated $G_{MB}(h)$ by the Matsen and Gardiner potential corresponding to the value of α closest to our system. To account for the differences in α between the calculated potentials and our samples, a multiplication factor was included in $G_{MB}(h)$, which, together with η_{eff}, constituted the fitting parameters in our model. We found that the multiplication factors needed to fit the data were 5 and 1 for the films with α = 0.43 and 4.1, respectively. In the case where α = 8.2 (where $h_b + h$ = 13 nm is much bigger than the radius of gyration of the brush polymer), G_{MB} was found to be negligible compared to G_{vdW}.

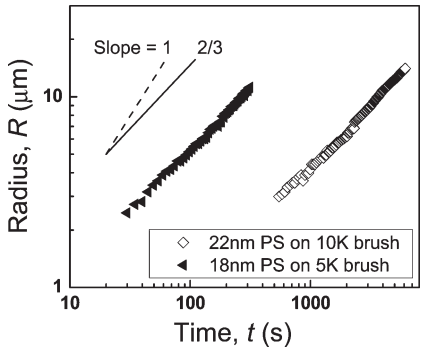

Figure 5. Radius vs annealing time of two holes, one found in a 22 nm thick film coated on a 10K PS brush (open diamonds) and one in a 18 nm thick film coated on a 5K PS brush (solid triangles) upon annealing at 160 °C.

RESULTS AND DISCUSSION

Figure 4 shows the optical micrographs of two h = 30 nm PS films, one deposited on a 10K brush and one on a SiO_x-Si substrate, after annealing at 150 °C for 4 h in vacuum. The dewetting rate is evidently faster in the former, which has already begun to dewet after annealing for 4 h, although the contact angle found for the film on a 10 K brush (= 8°) is smaller than that on SiO_x-Si (= 15°). To determine if the films slip on the brushes, we study the growth rate of the holes found in the films as they dewet. According to Redon et al.,[35] when there is no slip, $R(t) \sim t$, where R is the radius of the holes and t is the elapsed time since the birth of the holes. This linear dependence of $R(t)$ was observed by Masson et al. in entangled PS deposited on silicon.[36] But when there is slip,[19,23] $R(t) \sim t^{2/3}$. Figure 5 shows two representative $R(t)$ vs t data obtained from $h \sim 20$ nm films deposited on a 10K and 5K brush. The $t^{2/3}$ dependence is apparent in the data. According to Brochard-Wyart et al.,[19] the holes growth rate, $V \equiv dR/dT$ is governed by a balance between the unbalanced capillary force, $F \approx {}^1/_2\gamma\theta_c^2$ and the viscous force. In the limit where the slip length, b, is much bigger than h[37]

$$b = \frac{2\eta V(t) W(t)}{\gamma \theta_c^2} \quad (2)$$

with $W(t)$ being the width of the rim surrounding the hole at time t. By applying eq 2 to our data, we found that the calculated value of b was a constant, independent of t, h, and T, and equal to 200 ± 25 and 360 ± 35 nm for the films deposited on the 10K and 5K

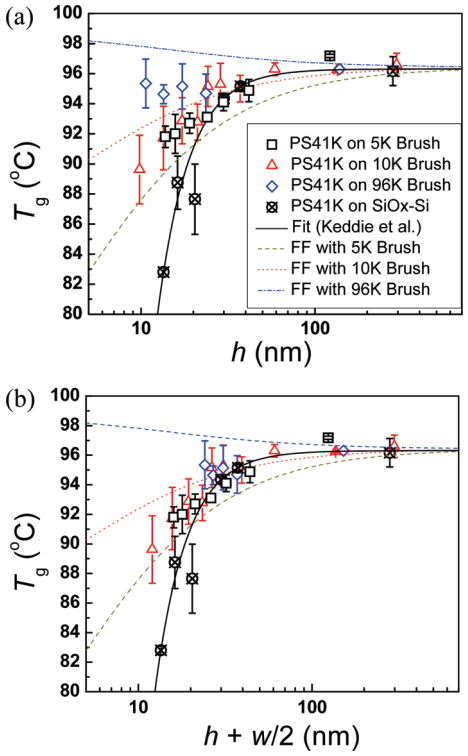

Figure 6. (a) T_g vs h of 41K PS films coated on various substrates (symbols). The solid line represents the best fit of the model by Keddie et al.[2] to the data of the films coated on SiO_x-Si. The dashed lines are the best fits to Fox and Flory's (FF) model.[7,38] (b) The same data in (a) but plotted as a function of $h + w/2$, where w is the interfacial width between the film and the substrate underneath.

brushes, respectively. This result shows that the degree of slip is the most severe on the 5K brushes, consistent with our observation that the films deposited on these brushes dewetted the fastest.

Next, we discuss the result shown in Figure 6a for the measured T_g of the films deposited on various substrates, plotted versus the film thickness, h. As seen, the T_g follows the order T_g(PS on 96K brush) > T_g(PS on 10K brush) ≈ T_g(PS on 5K brush) > T_g(PS on SiO_x-Si), which correlates well with the order of the contact angles, which are respectively 0° (this means that we never saw the films dewet in this experiment), 7.5 ± 0.5°, 10 ± 2°, and 15 ± 2°. For the films deposited on a brush, the film polymer actually penetrates the brush, with an extent that increases as the brush chain length gets longer with respect to that of the polymer. We calculated T_g assuming the extreme case where the film polymer and the brush polymer were thoroughly mixed by using the Fox and Flory (FF) equation.[7,38] The result, displayed in Figure 6a, shows clearly that the FF model cannot describe the data nor does it demonstrate a tendency for better agreement with the data as the chain length of the brush is increased.

As the film polymer penetrates the brush, the effective spatial extent of the film is bigger than its bare thickness, h. Therefore, it is not obvious how the film thickness should be counted here. We examine the significance of this effect on the thickness dependence of T_g by replotting the T_g data as a function of the sum of h and the penetration depth of the film into the brush, $w/2$, where w is the film−brush interfacial width.[33] To estimate the values of w, we linearly interpolate the values reported by Matsen and Gardiner.[33] The result is shown in Figure 6b. As seen, the order of the T_g remains the same as that found before.

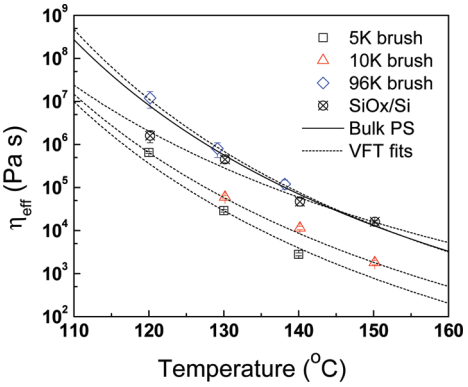

Figure 7. Plots of effective viscosity vs temperature for 10 nm thick 41K PS films coated on various substrates (symbols). The dashed lines are the best fits to the VFT relation. The solid line represents the viscosity of the 41K bulk PS.

Table 2. Comparison between the VFT Fitted Parameters of the M_n = 41K PS Bulk Material and 10 nm Thick Films Supported by a PS Brush or SiO_x/Si Substrate

sample	T_K (K)	η_∞ (Pa s)	A (K)[a]
film on 96K brush	322 ± 2	0.0015 ± 0.0007	1620
film on 10K brush	316 ± 2	0.0005 ± 0.0002	1620
film on 5K brush	318 ± 3	0.00016 ± 0.000 06	1620
film on SiO_x/Si	307 ± 2	0.014 ± 0.004	1620
bulk[b]	320	0.002	1620

[a] A was fixed to the bulk value in all the fits. [b] Published data.[27]

Figure 7 shows a plot of η_{eff} vs T of h = 10 nm films deposited on the same substrates studied above. The dashed lines represent the best fits to the Vogel−Fulcher−Tammann (VFT) relation, namely $\eta_{eff} = \eta_\infty \exp[A/(T - T_K)]$, with the fitted values of the parameters given in Table 2. On comparing the data of different films, we find that the degree of slip in the films is reflected more by η_{eff} than by T_g. In particular, η_{eff} is found to be similar between the films cast on SiO_x-Si and the 96K brush, but it gets smaller with decreasing chain length of the brush for the films cast on the 5K and 10K brushes. It is interesting to note that the η_{eff} of the films (M_n = 41K g/mol) cast on the 96K brush is almost the same as the viscosity of the 41K PS (bulk or films coated on SiO_x-Si; Figure 7) despite the facts that the film penetrates to a large extent into the 96K brush and that the molecular weight, and hence the viscosity, of the 96K brush is higher than that of the film. This result shows that the flow mobility of the films[30] is governed by the top, free film only while the brush film makes no contribution.

CONCLUSION

In summary, we have studied the T_g and dewetting properties, including the slip length and effective viscosity of 41K PS films cast on SiO_x-Si and PS brushes with M_n = 5K, 10K, and 96K g/mol. We find that there is no correlation between the T_g and the dewetting properties studied. In particular, the T_g follows the order: T_g(PS on 96K brush) ≈ T_g(bulk) > T_g(PS on 10K brush) ≈ T_g(PS on 5K brush) > T_g(PS on SiO_x-Si) while the effective viscosity follows a different one: η_{eff}(PS on SiO_x-Si) ≈ η_{eff}(PS on

96K brush) > η_{eff}(PS on 10K brush) > η_{eff}(PS on 5K brush). The latter is consistent with the order found of the slip length, namely 0 nm for SiO_x-Si and the 96K brush, 200 nm for the 10K brush, and 360 nm for the 5K brush. On the other hand, the T_g correlates well with the interfacial energy between the film and the substrate, with T_g decreasing with increasing interfacial energy as noted before.[24,25,39,40] Conventionally, T_g can be used to predict the relative fluidity of a polymer at a given temperature, namely by judging how far the temperature is above the T_g. Our result shows that T_g alone is not adequate for predicting the relative fluidity of a polymer film or nanostructure, where the T_g is modified by size reduction or change of an interface.

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