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Shear Modulus of a Polymer Brush

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ABSTRACT: Eighteen years ago, Fredrickson et al. [*Macromolecules* **1992**, *25*, 2882−2889] predicted that a molten polymer brush possesses a shear modulus that would cause its surface structure to deviate from a liquid. Their prediction, though broadly used, has been largely unchecked. Here, we present experimental data on polystyrene brushes that validate Fredrickson et al.'s prediction. We also present data obtained by following the time evolution of the surface structure of an entangled brush, which shows that the equilibrium shear modulus is established prior to the onset of the terminal flow regime. This suggests that the dynamics of entangled polymer brush is not governed by chain reptation motions, contrary to a previous presumption.

Introduction

A large volume of literature accumulated over the past two decades demonstrates that polymers confined in thin films with thickness on the order of the unperturbed gyration radius, R_g, of the polymer can be in a different state of matter than that of the material in bulk.[1−5] A remarkable observation reported recently found that entangled polystyrene (PS) homopolymers cast on silicon with thickness, *h*, from $1R_g$ to $2R_g$ exhibited "non-liquid-like" behaviors (i.e., behaviors that are not expected of simple liquids) even though the films had been annealed extensively at temperatures well above the glass transition temperature and hence should be in the terminal flow regime.[6−9] These observations have been suggested to arise from strong pinning of the polymer chains to the substrate surface since that would render the films a Guiselin brush.[10,11] (A Guiselin brush is a polymer brush formed by a homopolymer film resting at equilibrium on a substrate surface, but where the chain segments touch the substrate surface, they form a bond with the surface.) According to the theory of Fredrickson et al.,[12] a polymer brush in the molten state possesses a shear modulus, so it should exhibit non-liquid-like behaviors. In a recent experiment,[13] we found that PS homopolymer indeed formed an irreversibly adsorbed monolayer on silicon after extensive annealing, making the Guiselin brush hypothesis plausible. On the other hand, not all results support the Guiselin brush hypothesis. For example, a recent study of ours showed[9,14] that the same non-liquid-like behaviors could be found in polymer *liquid* films if the films were not fully equilibrated. In addition, there is a factor of ∼5 to ∼10^5 disagreement between the observed shear modulus of the reportedly "non-liquid-like" films (please see the data displayed in Figure 3 of ref 7 and Figure 1 of ref 8) and that predicted by Fredrickson et al.'s brush model.[12] On the other hand, the brush model[12] had been developed only for *monodisperse* brush films that are sufficiently dense that the brush chains are stretched away from the substrate surface. In this experiment, we measure the surface spectrum (or power spectral density, PSD) of monodisperse PS brush films with various molecular weights (from 2 to 670 kg/mol) as well as a polydisperse brush film that mimics the Guiselin brush.[10,11] Our result shows that Fredrickson et al.'s brush model applies well to the monodisperse brushes, but not the Guiselin-like brush. Finally, we examine the equilibration process of an entangled, monodisperse polymer brush and find that it takes place notably faster than it does in a homopolymer film with comparable molecular weight. We discuss the implication of this result to the unusual dynamical behavior of polymer brushes observed by Foster et al. using X-ray Photon Correlation Spectroscopy (XPCS).[15]

Experimental Section

Silicon (100), diced into 1 × 1 cm^2 pieces, were used as substrates. To clean the substrates, we submerged them in a piranha solution (i.e., H_2SO_4:H_2O_2 in 7:3 ratio by volume) that was preheated to 90 °C for 20 min. Thereafter, we rinsed them in excessive deionized water and dried them with 99.99% nitrogen. The process of rinsing and drying was repeated more than 10 times to remove any trace amount of acid from the substrate surface. This cleaning protocol removed the organic contaminants and left the substrate surface covered with Si−OH groups.[5] The substrates were then exposed to oxygen plasma for 30 min to produce a uniform oxide layer.

The brush polymers are monocarboxy-terminated PS (α-PS-COOH, purchased from Polymer Source Inc., Montreal, Canada) with number-average molecular weight, M_n = 2−670 kg/mol, and polydispersity index, $M_w/M_n \leq 1.07$ (except for the 2 kg/mol brush, which has M_w/M_n = 1.2). We used 3-aminopropyltrimethoxysilane (APTMS, purchased from Gelest Inc., Morrisville, PA) as a tethering promoter of the brush chains. Because APTMS is hydrophilic, it also helps prevent adsorption of the hydrophobic PS chains to the substrate surface. To coat the APTMS on silicon, we immerse the cleaned silicon substrates into a 0.2 vol % solution of APTMS in toluene for 20 s in an anhydrous and anaerobic atmosphere, achieved by maintaining a slight positive pressure of 99.99% nitrogen in a glovebag. Afterward, the substrates were rinsed thoroughly by a copious amount of toluene followed by ultrasonication in toluene for 30 min to remove any physiosorbed APTMS molecules. Then they were thoroughly rinsed in deionized water and dried by 99.99% nitrogen before stored in a dust-free enclosure filled with 99.99% nitrogen and ready for use. We have checked by tapping-mode atomic force microscopy (AFM) that the surface of the APTMS films was uniform, showing no sign of defect, and had a small root-mean-square roughness of ∼0.2 nm. The thickness of the APTMS film had been determined by both ellipsometry and tapping-mode AFM measuring the cross-sectional profile of a

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scratched film. Both methods give the same thickness value of ca. 7.0 ± 0.6 Å (data not shown), which is approximately equal to the reported length of an APTMS molecule,[16] indicating that the APTMS film is consisted of a monolayer of APTMS.

We employed the "graft to" method to append the brush polymer onto the substrates. Thin films of the brush polymer with thicknesses greater than $4R_g$ were spun-cast onto the APTMS-treated substrates. To facilitate the reaction between the carboxylic end group of the brush chains and the amino group of the APTMS monolayer, we annealed the spun-cast films at 180 °C for 24 h under a 10^{-3} Torr vacuum. The untethered brush chains were removed by thorough rinsing in toluene followed by immersion in a beaker of 100 mL toluene for 10 min. The thickness of the resulting brush film, h, was determined by ellipsometry. To bring the polymer brushes to equilibrium, we annealed them at 150 °C for a minimum of 24 h whereupon further annealing did not produce any noticeable change in the PSD. To measure the PSD, we captured topographic images of the films by tapping-mode AFM. Then we multiplied the data with a Welch function before Fourier-transforming and subsequently radial averaging them, which result in the PSD. Details of the data processing procedure can be found in refs 5 and 9.

Theory

For a uniform elastic film with zero-frequency shear modulus, μ_0, the equilibrium PSD is given by[12]

$$A_q^{\,2} = \frac{k_B T}{\gamma q^2 - \dfrac{A_{\mathrm{eff}}}{2\pi h^4} + \dfrac{3\mu_0}{h^3 q^2}} \qquad (1)$$

where k_B is the Boltzmann constant, q is the wavevector, T is the absolute temperature, γ is the surface tension, and A_{eff} is the effective Hamaker constant of the film.[17] In obtaining eq 1, the approximation $qh \ll 1$ has been used, which is valid in most experiments. Equation 1 differs from the result of the classical capillary waves theory (which applies to liquid films) by the presence of the $3\mu_0/(h^3q^2)$ term. It accounts for the mechanical energy required to elastically deform the film to produce a sinusoidal surface profile with wavelength $2\pi/q$ and amplitude consistent with the equipartition law.

According to Fredrickson et al.'s brush model,[12] a molten, monodisperse polymer brush possesses a finite zero-frequency shear modulus given by

$$\mu_0 = \frac{3k_B T \nu \sigma^2}{b^2} \qquad (2)$$

where ν is the monomer volume, σ is the grafting density (i.e., the number of brush chains per unit area), and b is the statistical segment length of the brush chains. By using $\sigma = h/(\nu N)$, where N is the degree of polymerization of the brush, eq 2 can be rewritten as

$$\mu_0 = \frac{3k_B T}{b^2 \nu}\left(\frac{h}{N}\right)^2 \qquad (3)$$

Equation 3 shows that μ_0 can be adjusted by adjusting h/N. Given that $h \sim N^{1/2}b$,[18,19] eq 3 suggests that μ_0 is $\sim 1/N$ and can be conveniently tuned by adjusting the molecular weight of the brush. In this experiment, the number-average molecular weight, M_n, of the brush polymer ranges from 2 to 670 kg/mol. Correspondingly, the value of μ_0 is expected to span more than 2 orders of magnitude in range. For the brush chains to be stretched, the brush height must be at least $1R_g$ or the grafting density σ must exceed about $1/(b^2N^{1/2})$.[12] We find that by making the starting thickness of the brush films greater than $4R_g$ during spin-coating, its final thickness after grafting and rinsing is between $1.3R_g$ and $2.5R_g$. Table 1 shows the sample parameters of the monodisperse PS brushes used in this experiment, including the molecular weight, thickness, grafting density, and the value of $1/(b^2N^{1/2})$. In computing the grafting density, σ, we have assumed ν = 0.167 nm^3 (obtained by using 1.03 g/cm^3 for the mass density of PS at 150 °C[20,21]) and the segmental length, b = 0.7 nm.[22]

Table 1. Parameters of the Monodisperse Polystyrene Brushes Used in This Experiment To Verify Fredrickson et al.'s Brush Model[12]

M_n (g/mL)	h (nm)	grafting density (chains per nm^2)	$1/(N^{1/2}b^2)$
2 000	2	0.62	0.49
10 000	6	0.37	0.22
48 000	14.7	0.19	0.1
48 000	7.7	0.1	
96 000	14.6	0.094	0.07
96 000	13.7	0.089	
670 000	45.8	0.042	0.027
670 000	45	0.042	

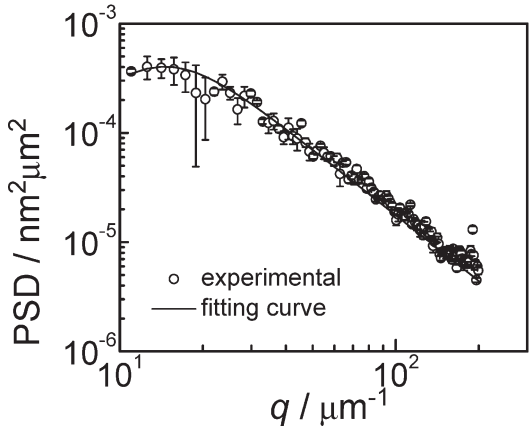

Figure 1. A log−log plot of the power spectral density, PSD, of a M_n = 96 kg/mol and h = 14.6 nm polystyrene brush film. The open circles depict the experimental data. The solid line depicts the best fit to eq 1.

Results and Discussion

Figure 1 shows the PSD of a PS brush film with M_n = 96 kg/mol and h = 14.6 nm after equilibration at 150 °C. We fit this data to eq 1 by treating μ_0 and γ as the only fitting parameters while the other parameters were held fixed to either the experimental values (i.e., T = 150 °C and h = 14.6 nm) or published values ($k_B = 1.38 \times 10^{-23}$ J/K and $A_{\mathrm{eff}} = 5 \times 10^{-21}$ J[17]). The best fit to the data is shown by the solid line in the same plot. As seen, the model describes the data quite well, with the best fitted value of μ_0 being 55 kPa, which compares very well with the value of 54 kPa predicted by eq 3.

We repeated the measurement on films with other molecular weights. Figure 2 shows a plot of the result as μ_0 versus $(h/N)^2$. The solid circles depict the experimental data, and the solid line depicts the values calculated by using eq 3, with no adjustable parameters. As one can see, the experimental data agree with the theoretical prediction very well, providing strong support to the brush model.

To examine whether the brush model is suitable for use to analyze the shear modulus of a Guiselin brush, we construct a composite brush mimicking the Guiselin brush. Specifically, it consists of a mixture of dicarboxy-terminated PS (α,ω-PS-(COOH)$_2$) (that constitute the loops) and monocarboxy-terminated PS (α-PS-COOH) (that constitute the tails) in a distribution resembling that proposed by Shull.[11] Details of the distribution of our brush and that proposed by Shull are shown in Table 2. As seen, the molecular weights of the three "tail"

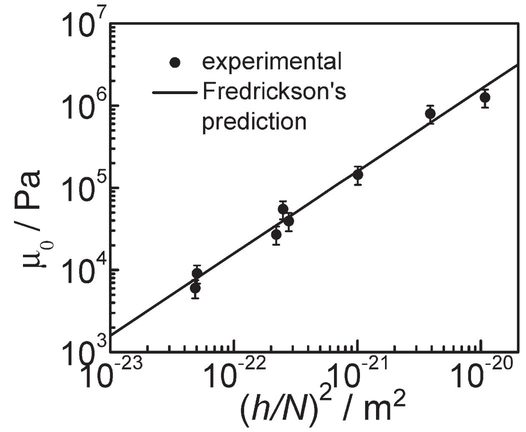

Figure 2. Equilibrium shear modulus μ_0 as a function of $(h/N)^2$. The solid circles are the experimental value of μ_0 obtained by fitting the PSD of the films to eq 1. The solid line depicts the calculated μ_0 by using Fredrickson et al.'s prediction (eq 3).

Table 2. Distribution of the Tails (α-PS-COOH) and Loops (α,ω-PS-(COOH)$_2$) We Used To Make the PS Guiselin-like Brush According to Shull's Design[11]

	design by Shull		our brush	
	M_n (kg/mol)	vol %	M_n (kg/mol)	vol %
tail (1)	3.3	14	3.0	14
tail (2)	5.0	20	4.7	20
tail (3)	6.7	30	6.0	30
loop (1)	1.1	13	0.8	36
loop (2)	1.7	14		
loop (3)	2.4	9		

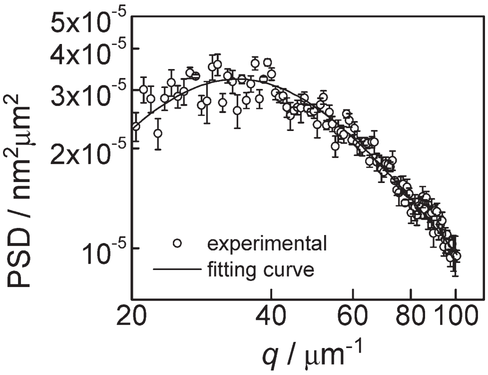

Figure 3. A log−log plot of the power spectral density, PSD, of the Guiselin-like brush. The open circles represent the experimental data. The solid line is the best fit to eq 1.

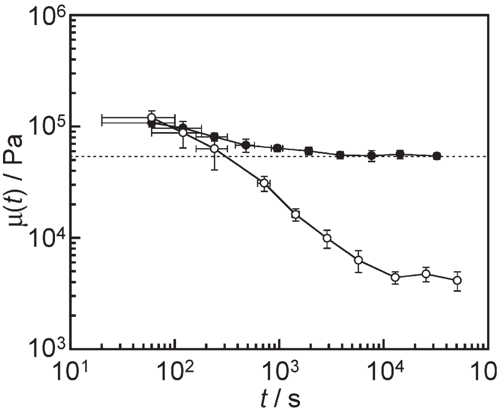

Figure 4. Plots of shear modulus versus annealing time of a PS brush (solid circles) and a PS homopolymer film (open circles) with M_n = 96 and 97 kg/mol, respectively. The dotted line is a guide to the eye showing the asymptotic shear modulus of the brush film. The value predicted by Fredrickson et al.'s model is ~70 kPa.

polymers (α-PS(COOH)) agree within 10% with the values in Shull's design,[11] but for the "loop" polymers (α,ω-PS-(COOH)$_2$), only one out of three loop polymers is used here. These discrepancies may be the reason why the final height of the composite brush was only 2.3 nm or 0.85R_g of the mimicked free polymer. Given these caveats, we discuss the result obtained from the composite brush. Similar to the monodisperse brushes, the PSD of the composite brush fits well to eq 1 (see Figure 3). However, the value found for the shear modulus (= 290 Pa) is only ~1/420 times that predicted by the brush model. On the other hand, this value is close to those measured by diffuse X-ray scattering of (untethered) PS homopolymer films. On the basis of this result, we judge that the brush model is unsuitable for use in analyzing the properties of a Guiselin brush.

Frederickson et al.[12] had cautioned that the equilibrium shear modulus might not be observed in experiment if the polymer brush had a large molecular weight. It is because the relaxation time of entangled polymers could grow exponentially or even faster with the molecular weight.[23] In a recent experiment, Foster et al.[15] found by XPCS that the relaxation times of the surface fluctuations of densely grafted PS brushes at 130 °C were so large as to lie outside the experimental window of the XPCS apparatus, i.e., greater than ca. 10 000 s for all values of q investigated. The fact that our data in Figure 2 show good agreement with Frederickson et al.'s prediction[12] up to M_n = 670 kg/mol suggests that the relaxation time of the high molecular brushes may not be as long as Fredrickson et al. had envisaged.[12] We examine how a monodisperse polymer brush with M_n = 96 kg/mol and h = 10.6 nm equilibrates. To allow the equilibration to take place at a convenient time of about 1 h, we use an annealing temperature of 110 °C. For comparison, we also measure the evolution of a PS homopolymer film with M_n = 97 kg/mol and h = 17.6 nm under the same annealing condition. The results are displayed in Figure 4 as the time-dependent shear modulus, $\mu(t)$, versus annealing time, t. As one can see, the data of the homopolymer film (open circles) decreases continuously with time and reaches a plateau value of ~3.5 kPa after ~10^4 s. This is in good quantitative agreement with an earlier result obtained from a homopolymer film under similar experimental conditions.[9] With sufficient annealing, the plateau region eventually terminates and is replaced by a regime, where $\mu(t) \sim 1/t$, that can be shown to be attributable to the terminal flow regime.[5,24] On the other hand, the evolution of the brush film (solid circles) took a distinctly different path. Specifically, the time-dependent shear modulus has dropped nearly to the steady value of ~55 kPa after 700 s; once the shear modulus leveled off, no further change was seen over a period of ca. 25 000 s. Since the steady value of ~55 kPa is close to the equilibrium value of ~70 kPa predicted by eq 3, we interpret the observed steady state to be the equilibrium state of the brush. This would imply that the brush film had reached equilibrium without entering the molten state or terminal flow regime. Conventionally, the rubbery plateau shear modulus of an entangled polymer is governed by the density of entanglement in the polymer. Our result thus shows that the elastic energy associated with mechanical stretching of the brush chains must exceed that required to deform the entanglement network of the film in the rubbery state. As a result, the entropic elasticity that brings about the solid character expected of the brush in the molten state is operational already in the rubbery state. If our interpretation is correct, a dense, monodisperse polymer brush is always in a viscoelastic state. To understand its dynamical properties, one must consider the brush film to be viscoelastic;

attempts based on chain reptation motions alone would not be enough.

Conclusion

In conclusion, we have carried out three measurements to verify Fredrickson et al.'s brush model and to understand several experimental observations. First, we measured the equilibrium shear modulus of PS brushes with a wide range of molecular weights from 2 to 670 kg/mol by analyzing the power spectral density of the brush films. The result demonstrated excellent agreement with Fredrickson et al.'s model and so provided strong endorsement to the model. Then we constructed a Guiesline-like brush by mimicking the design of Shull and found that the shear modulus of this brush was smaller than that predicted by the brush model by more than 2 orders of magnitude. This shows that Fredrickson et al.'s model is unsuitable to be used to predict the shear modulus of a Guiselin brush. Finally, we examined the equilibration of an entangled polymer brush by measuring the time-dependent shear modulus of a PS brush film with M_n = 96 kg/mol and comparing it with that of a PS homopolymer film with similar molecular weight. We observed that the equilibrium shear modulus of the brush was established prior to the onset of the rubbery plateau of the homopolymer film. This illustrates that the elastic energy associated with mechanical stretching of the brush chains always exceeds that required to deform the entanglement network of the film in the rubbery state. Therefore, the physical properties of a polymer brush cannot be directly inferred from those of homopolymer counterpart as previously contemplated.

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