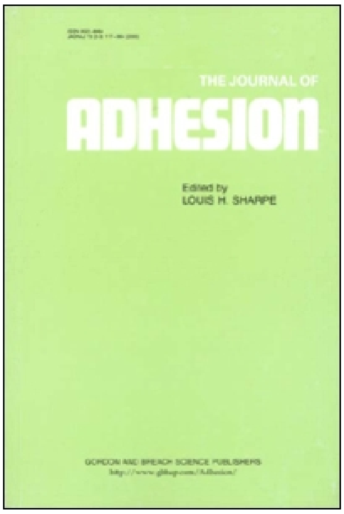

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Single-Molecule AFM Study of Polystyrene Grafted at Gold Surfaces

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Single-molecule studies under poor solvent conditions show that atomic force microscopy (AFM) measurements of contour lengths of polystyrene 12K and 17K relate well to gel permeation chromatography (GPC) data when grafting concentrations are low (not greater than 0.7 mM). Contact angles and ellipsometry have been used to characterize the surfaces and indicate low grafting densities at this grafting concentration. Persistence lengths (p) of different length polystyrene chains, when fitted to a WLC (worm-like chain) model, show values of $\mathrm{p} = 0.23\,nm \pm 0.10\,nm$ *and* $\mathrm{p} = 0.25\,nm \pm 0.13\,nm$*, for 12 K and 17 K polystyrene, respectively, when the persistence lengths are fitted to log-normal distributions. These values are close to the expected theoretical value of 0.23 nm and*

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further confirm that mostly single molecules were studied on these polystyrene surfaces. Higher grafting concentrations ($\geq$1 mM) resulted in pulling multiple molecules.

Keywords: AFM; Atomic force microscopy; GPC; Polydispersity; Polystyrene; Single molecule

INTRODUCTION

New methods of characterizing polydispersity at surfaces are of both practical and fundamental interest for developing technologies in engineering, adhesion, lubrication, friction, biology, and medicine [1–5]. For example, chain lengths control bioadhesion inhibition by polyethyleneglycol [2]. Depletion forces that control particle binding to surfaces are expected to depend on the polymer solution's molecular weight [4].

Scanning force microscopy of single molecules provides a method to measure chain lengths at surfaces. An earlier study of polydimethylsiloxane (PDMS) grafted at a silicon surface showed a close correlation of AFM-measured contour-length distribution with gel permeation chromatography (GPC) data, despite the fact that the experiments involved nonspecific binding of the AFM tip to the polymer grafted at the surface [6]. It was also observed that because of the high polydispersity of the PDMS studied and limited available reactive sites at the surface, the entropy of mixing, ΔS_{mix}, played an important role in determining the contour lengths of molecules grafted at the surface [6].

The study reported here further investigates the ability of the single-molecule AFM technique to detect contour-length distributions of polystyrene chains grafted to surfaces and uses GPC polydispersity measurements for comparison. Two relatively monodisperse polystyrene polymers (of lower polydispersity indices, PI), (Mw = 12300, Mn = 12000, PI = 1.03 [1.1]) and (Mw = 17800, Mn = 17000, PI = 1.03 [1.2]), were selected for the study. The synthetic path that has been followed in making these polystyrene films/monolayers is through self-assembled monolayers (SAMs) that were prepared from polystyrene disulfides covalently attached to gold surfaces [5, 7–10]; an amino-terminated polystyrene is reacted with an aldehyde and disulfide-containing compound. The molecular weights selected for the study are less than the bulk entanglement molecular weight (M_e) of polystyrene, 19100 g/mol [11, 12]. The AFM data of the grafted polystyrene correlate well with GPC data. The study also shows that grafting concentrations influenced whether single molecules could be studied.

EXPERIMENTAL METHODS

Materials

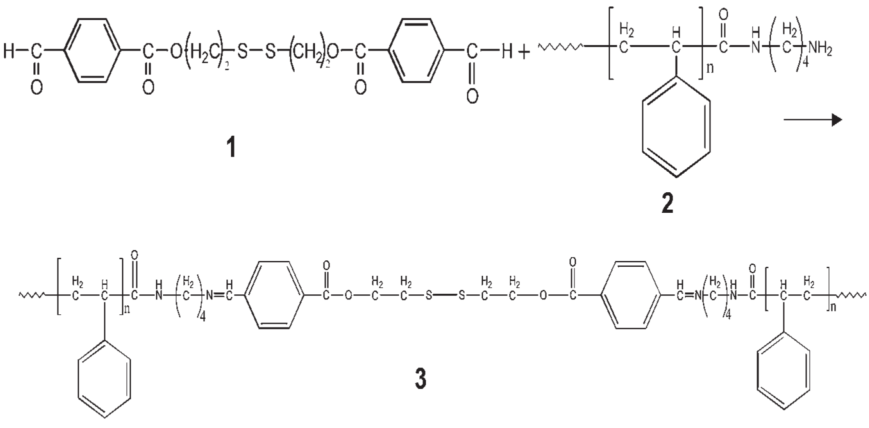
Amino-terminated polystyrenes of Mn 12000, Mw 12300, PI 1.02, and Mw 17300, Mw 17820, and PI 1.03 were used as purchased (Polymersource, Inc., Montreal, Canada). The disulfide-containing aldehyde shown in Scheme 1 was prepared by Liu *et al.*'s method [13]; CH_2Cl_2 and THF (Spectropure, Inc., Tempe, AZ, USA) were used after dehydration with sodium benzophenone.

Methods [14]

Equimolar amounts of an amino-terminated polystyrene (see Scheme 1) and a sulfur-containing aldehyde were dissolved in anhydrous CH_2Cl_2 and reacted at 40–50°C for 6 h while nitrogen gas was allowed to flow over the reaction. Then, the heterogeneous mix was stirred overnight in CH_2Cl_2 with nitrogen flowing but without added heat. The solvent was evaporated, and the solid material was then dried under vacuum for ~2–4 h, yielding a crystalline white solid. Warm ethanol was added to wash away the unreacted sulfur-containing aldehyde (1, Scheme 1), and then the filtered residue was allowed to dry.

Preparation of Gold Surfaces [15]

Glass disks were washed in detergent, and then rinsed repeatedly using water, followed by deionized water. The disks were then soaked



SCHEME 1 Disulfide-containing aldehyde (1) and an amino-terminated polystyrene (2) are combined to form disulfide-containing polystyrene (3).

in ethyl alcohol for ~10 min and dried using nitrogen gas. Using vaccum deposition (Ladd Vacuum Evaporator, Ladd Research, Walliston, VT, USA), nickel (~12 mg/cm^2) was first deposited onto the glass surface followed by gold (~90 mg/cm^2). Nickel is used to make sure that the gold adheres well to the surface [15]. The gold surfaces were stored in ethanol to prevent contamination, as has been discussed by Ulman [5]. Rinsing the gold disks for approximately 5 min in piranha solution (30:70 H_2O_2:H_2SO_4) is another method used to clean Au surfaces. Longer cleaning times with piranha solution will roughen the surface or peel off the gold layer [5].

Grafting Prepared Disulfide-Containing Polystyrene of Molecular Weights 12300 and 17820 onto a Gold Surface [5, 7–9]

Dry gold substrates were immersed in dissolved disulfide polystyrene polymers (3, Scheme 1) using dry THF or CH_2Cl_2. The gold surfaces were allowed to react for approximately 12 h [5, 7– 9]. The initial grafting concentrations were in the mM range, following Allara *et al*. [7, 8] who showed that concentrations in the range 0.01–0.001 M of disulfides effectively form monolayers in an appropriate high-purity solvent at ambient temperature [8–10]. Grafting concentrations of 0.7 mM and greater for polystyrenes were used. Literature [8, 10] shows that there is a strong preference for the disulfide group to attach to the gold surface relative to other polar or nonpolar organic functional groups.

Cleaning of Grafted Gold Substrates before AFM Experiments [16]

Surfaces were rinsed and sonicated for about 30 s in dry THF or CH_2Cl_2 about five times. Longer sonication times may peel the gold layer. Then, the surfaces were washed in a solution of dodecyl sulfate (Boehringer, Mannheim, Germany). The surfaces were then rinsed in deionized water several times (Chidsey *et al*. [16]) and dried using nitrogen for a few minutes before the AFM experiments.

Contact-Angle Measurements

Contact-angle measurements of the Au and Au–polystyrene surfaces with ultrapure water were obtained using an apparatus (Advanced Surface Technologies, Inc., Bellerica, MA, USA) equipped with a video camera. With this apparatus, advancing contact angles can be measured with $\pm 3^\circ$ accuracy.

Ellipsometry [17–19]

A single wavelength null ellipsometer (Model L117, Gaertner Scientific Corporation), was used to measure the thickness of polystyrene (Mw = 12300 and Mw = 17820) monolayers (0.7 mM deposition). The measurements were done at a 70° angle of incidence with an He-Ne laser (632.8 nm) as a light source. The measurements were done on bare gold surfaces and polystyrene-grafted surfaces. After approximately 12 h of grafting, the surfaces were stored in deionized water for another 12 h before taking the reading.

AFM Methods

AFM experiments were performed using Digital Instruments Multimode or Dimension 3100 equipped with controller and fluid cells (Digital Instruments, Santa Barbara, CA, USA). For the experiments, CSC12 Ultrasharp contact silicon cantilevers were purchased from K-TEK International, Inc., Portland, OR, USA. Cantilever-tip curvature radius reported by the manufacturer was ~10 nm or <10 nm. These experiments were carried out by the cantilever with a spring constant of 0.07 N/m as reported by the manufacturer. This value is expected to have 25% uncertainty. The tips were cleaned using argon plasma for 2 min. High-power argon plasma resulted in consistently high adhesion forces, which indicated the silicon tip had dulled. Cleaned AFM tips were used immediately. Experiments were performed in a 25- mM NaCl solution to reduce capillary forces between the AFM tip and the surface [17]. Solutions were prepared to have a nominally neutral pH but were not buffered. The contour and persistence lengths and force interactions of the polymer chains were obtained using models described in subsequent sections.

RESULTS AND DISCUSSION

Characterization of the Surface Grafted with Monolayers

Contact-Angle Results and Ellipsometry Results

Contact angles and thicknesses obtained using ellipsometry are shown in Table 1. Blank gold surfaces were found to have water contact angles of approximately 75°. The contact angle depends on the surface cleaning method. This contact angle indicates that the gold surfaces were not perfectly cleaned before grafting. High angles are often observed; see *Sensors* **3**, 61–68 (2003) and *Biochemical and Biophysical Research Communications* **279**, 265–269 (2000). The

TABLE 1 Advancing Contact Angles of Polystyrene 12 K and 17 K and Ellipsometry Results

Sample	Contact angle (advancing)	Thickness (nm) based on elipsometry
Blank gold	75°	~0
Polystyrene 12 K (0.7 mM)	83°	~0.6 nm (~Rg = 0.56 nm)
Polystyrene 12 K (1.2 mM)	89°	
Polystyrene 17 K (0.7 mM)	84°	~0.6 nm (~Rg = 0.67 nm)
Polystyrene 17 K (1.4 mM)	90°	

advancing contact angles of polystyrene surfaces were found to be 83–90°. Higher grafting concentrations (1.2-mM and 1.4-mM surfaces) exhibited higher contact angles (~90°) and lower grafting concentration showed lower contact angles (~83°) as expected [3, 5]. The polystyrene polymers have a CH_3 group at the end and, if the polymer chains were closely packed, the contact angle would be expected to be greater than 90° [5]. The lower contact angles may indicate lower molecular densities or disordered monolayers [5].

The ellipsometry technique has been discussed elsewhere [18–20]. These results were obtained using a model of a single film, air–polystyrene and 1-2 polystyrene–gold interfaces. The refractive indices of ambient air, the monolayer, and the gold substrate were estimated as 1, 1.59 [12], and $0.166 - i \times 3.15$ or $0.166 - i \times 3.21$ [20], respectively. The thicknesses of both films of polystyrene of Mw = 12300 and Mw = 17820 were approximately 0.6 nm, close to the estimated value of unperturbed radius of gyration, Rg, where

$$Rg = \frac{l\sqrt{M/M_0}}{\sqrt{6}}. \tag{1}$$

Here, the molecular weights, M (12300 and 17820), the monomer weight, M_0 (104), and the effective segment length, l (1.254 Å) [21] were used, yielding Rg is ~0.56 nm and ~0.67 nm for the lower and higher molecular weights, respectively [2, 3].

Samples to be studied by ellipsometry were stored in deionized water for a day [19] before measurements. When readings were taken within a few minutes after grafting the polymer, results were erratic and not constant across the surface, a phenomenon that is not currently understood.

Estimation of Grafting Densities from Ellipsometry Results [22–24]

The surface coverage of polystyrene estimated using ellipsometry is 0.005 chains/nm^2 [22–24]. Low grafting densities are supported by the contact-angle measurements for polystyrene(0.7 mM) as shown in Table 1.

AFM Results

Model for Nonlinear Extension of the Chain

We utilized single-molecule AFM to determine the distribution of contour lengths (polydispersity) of polystyrene grafted at gold surfaces. The extension of a chain can cause non-Gaussian distributions of its end-to-end length. The forces required to generate such conformations can be calculated using an entropic WLC model as shown below.

$$WLC = F_{\text{chain}} = \frac{k_B T}{p}\left[\frac{1}{4(1 - r/L_{\text{contour}})^2} - \frac{1}{4} + \frac{r}{L_{\text{contour}}}\right]. \qquad (2)$$

The experimentally obtained data of nonlinear extension of the polymer chain is fitted to the WLC model. WLC or freely jointed chain (FJC) models have been discussed extensively elsewhere [1, 25–28]. The fitting parameters in Equation (2) are p, the persistence length, and L_{contour}, the contour length; the known factors are the elastic restoring force of the polymer chain, F_{chain} (nN), and the chain end-to-end separation distance r (nm). The Boltzmann constant, k_B (J/K), and absolute temperature, T (298 K), are constants. When the WLC model is used, persistence lengths, p, are obtained. If the FJC model is used, the Kuhn length (bond length) and L_{contour} (the fully extended length of the chain, the contour length) are obtained.

The polystyrene force plot data in the lower grafting concentrations show mainly one nonlinear extension of a polymer chain but also multiple ruptures of the polymer chain or chains from the AFM tip are observed. Here a WLC slipping model is used. This model considers a polymer chain with two or more attachments at the AFM tip or at the surface as shown in Figure 1A and B.

The WLC model fits r_0 (with p_0, F_0) as shown in Figure 1A(i) for the first rupture observed in the force plot. The second rupture (point A) does not take place until the first one has occurred at point B- and, thus, another WLC fit is used for the parameters r_1 (with p_0, F_1) as shown in Figure 1A(ii), which is observed as a second rupture in the force plot. Therefore, this model considers one polymer chain with a

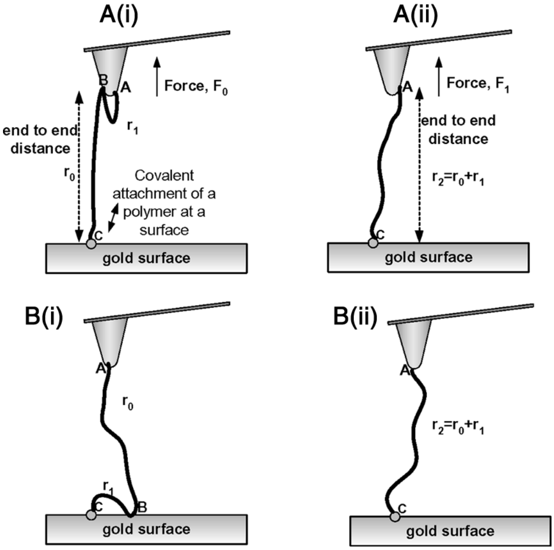


FIGURE 1 WLC model of a "slipping" polymer chain from a tip or a surface, a model used to fit data of multiple ruptures. The chain may be slipping at the tip or the surface as shown in A (i) and (ii) or at the surface B (i) and (ii). Slipping of a polymer chain 1(a) may be rupturing from the AFM tip at points B and then A. A polymer chain slips off the surface 2 at point B and then from the AFM tip at point A.

single persistence length, p_0, for WLC fits to both regions before ruptures. Therefore, an example of a WLC fits for a two-rupture profile, under the slipping model, is as follows:

$$F = \frac{k_BT}{p}\left(\begin{array}{ll} \dfrac{k_BT}{p}\left(\dfrac{1}{4[1-(r_0/L_0)]^2} - \dfrac{1}{4} + \dfrac{r_0}{L_0}\right), & \text{before first rupture} \\ \dfrac{k_BT}{p}\left(\dfrac{1}{4[1-(r_2/L_2)]^2} - \dfrac{1}{4} + \dfrac{r_2}{L_2}\right), & \text{after first rupture} \end{array}\right). \tag{3}$$

Here, the force dynamics are the slipping type (1) as shown in Figures 1A(i) and (ii), and r_0 and r_1 are first and second ruptures. The same value of persistence length, p, is used for each WLC fit. Similarly, this model can also represent a case shown in Figure 1B(i) and (ii) with the first rupture at the surface and the second one at the AFM tip. The

WLC model fits can be also be accomplished for multiple chains with different persistence lengths for each region between rupture events when p is not treated as a constant parameter; it can be allowed to change for the first and second rupture.

The low forces of rupture ($\sim$0.1 to 0.15 nN) are smaller than those required to break covalent bonds, and, hence, the final rupture is polymer-surface adhesion-bond breakage. Literature reports an Au-S anchor has rupture strength of 1.4 ± 0.3 nN [29] at similar loading rates.

Data Analysis

1) *How an automated program works*
   An automated program selects potential pulling events in all the force-plot data collected and uses WLC and FJC models to fit it.
2) *Selecting relevant data*
   The data selected by the automated program are further analyzed manually to ensure that the force plots contain a nonlinear force extension profile.
3) *Cause of noise or sine waves in the force plot data*
   Noisy force plots are caused mainly by vibrations felt by the AFM instrument during the experiment. Sine waves in the force plots are caused by the photodiode detector picking up laser reflections from the surface. These types of force plots are easily recognizable and the sine profiles are subtracted from the data sets.
4) *Guidelines for selecting the saved data*
   The rule is not to ignore any data representing pulling events because they should contribute to the statistical distributions, which represent further meaning. However, some of the force plot data with potential pulling events closely overlay the primary adhesion and are not useful because the WLC model will not usefully fit to three or fewer points.

Organizing Polystyrene Force Plot Data

Table 2 summarizes the polystyrene force plot data. A polystyrene sample (12 K and 0.7-mM grafting concentration) showed 224 clear pulling events in 18 μm^2, which makes an average of 12 pulling events per μm^2 and, thus, a probability of 0.011 (each μm^2 contains 1024 force plots). 17K (0.7-mM) polystyrene force plot data showed 248 pulling events in 15-μm^2, giving an average of 16 pulling events per μm^2 and a probability of 0.016. A higher concentration polystyrene sample (1.2 mM) exhibits a high number of pulling events ($\geq 25/\mu m^2$) with a

TABLE 2 Probability of Picking Up Polystyrene Chains/μm^2 and Distribution of Persistence Lengths

Polymer	Grafting concentration	Probability of picking up a polymer chain/μm^2	Persistence length fitted to a Gaussian	Relative occurrence of A:B (force plots as shown in Figure 2)
PS 12 K	0.7 mM	0.011	0.23 ± 0.10 nm	67%:33%
PS 12 K	1.2 mM	0.024		
PS 17 K	0.7 mM	0.016	0.25 ± 0.13 nm	80%:20%

Note: Also shown is the distribution of percentages of the data that fit well to the WLC model and those that do not (Figure 2).

probability of 0.024. Following this process of analysis, the polystyrene force plot data showed that 85–90% of the time the AFM tip is pulling single molecules. Ten to fifteen percent of the time it was not clear whether the pulling events were of single molecules because of poor fits by the WLC model. It could be that a part of this 10–15% fraction is due to contamination. Mass spectral analysis could assist in answering

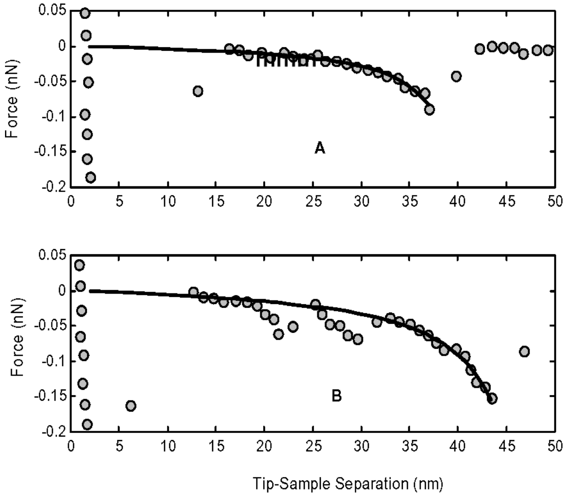


FIGURE 2 Force plots A and B show the ruptures of primary and secondary adhesion of a 17 K polystyrene sample: **A**) an example of a force plot where the WLC model (black solid line) fits well to the polymer-stretching data, $p = 0.26$ nm, $L_{Contour} = 36.9$ nm, err = 0.8 nm; **B**) an example where the data deviate from the WLC model (black solid line), $p = 0.184$ nm, $L_{Contour} = 44.5$ nm, err = 0.5 nm.

this question. Table 2 also shows the distribution of persistence lengths using the WLC model to fit the force plot data similar to that shown in Figure 2. Figure 2A shows a WLC model fit to a polystyrene data. The persistence length was estimated as 0.26 nm, which is close to a theoretically obtained value of 0.23 nm [1].

Table 2 indicates that a higher fraction of force plots for 12 K polystyrene deviated from the WLC fit (33%) compared with 17 K polystyrene. The only difference in the preparation was the organic solvent used to graft the sample. THF was used to prepare the 12 K polystyrene sample, and CH_2Cl_2 was used to prepare the 17 K polystyrene sample.

Figure 3 shows a force plot with multiple ruptures. These data were fit to a WLC slipping model, as discussed earlier. Figure 3A shows persistence lengths obtained from the multichain, multipersistence fit to be 0.31 nm, 0.36 nm, and 0.23 nm, which are close to those expected values of 0.23 nm mentioned earlier. Here, the grafting concentration was ~0.7 mM. Figure 3B also shows multiple ruptures but the

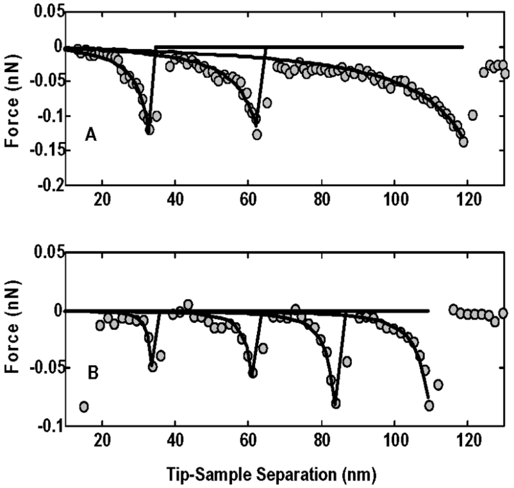


FIGURE 3 WLC "slipping" model fit (black solid line) to force plots with multiple ruptures: **A**) persistence lengths 0.312 nm, 0.36 nm, and 0.233 nm; contour lengths 34.1 nm, 64.1 nm, 122 nm. The persistence lengths indicate rupture of single molecule (0.7-mM, 17 K polystyrene sample). **B**) An example of a higher grafting concentration (1.2-mM, 12 K polystyrene sample); more multiple ruptures are observed. Persistence length for this WLC fit was 3.47 nm; this unusual example presumably indicates a surface species that is not a single chain and may even be chemically distinct. Contour lengths were 33.1 nm, 60.7 nm, 83.6 nm, and 109 nm.

persistence-length value from the same model are *circa* 3.5 nm; this value is anomalously high and may reflect interaction with an aggregated or even chemically distinct surface species. In this last case, the grafting concentration was $\sim$1.2 mM.

Statistical Distributions of Contour Lengths of Polystyrene using AFM Data vs. Calculated GPC

The expected chain contour length calculated from bond angles (109°), bond lengths (1.54 Å), and molecular weight of a polystyrene monomer (104) is 24 nm for a polystyrene sample of molecular weight 12300 and 41 nm for a molecular weight of 17820. Using GPC data of Mn (12000 and 17300) and the determined polydispersity indices (1.2 and 1.21), we convert the molecular weights using the following equation:

$$L_i = \frac{M_i \times 0.25\,\text{nm}}{104} \tag{4}$$

Here, 104 Daltons is the molecular weight of a polystyrene monomer, and 0.25 nm is the length of one monomer. The overlay of the GPC data of both molecular weights is shown in Figure 4. The GPC data correlate well to the AFM contour-length data in both molecular weights. Figure 4 also shows the contour lengths (polymer stretching divided by the extension ratio) and the polymer-stretching data of the 12 K and 17 K polystyrene. Figure 5 shows the distribution of fitted persistence lengths.

The vertical lines are peak positions calculated from log-normal fit to the data. 12 K and 17 K polystyrene show values of 28 nm and 40.9 nm. Table 3 shows the values obtained for Mn, Mw, and PI using AFM are close to the values determined using GPC.

Effect of Higher Grafting Concentrations

As the grafting concentration of polystyrene 12 K is approximately doubled from 0.7 mM to 1.2 mM, the observed probabilities of picking up the polystyrene chains increase from $\sim$12–15 chain-stretching events per micrometer to an average of 25 chain-stretching events per micrometer (Table 3). Figure 6 show contour lengths shifted to the right, which could be because this polymer was not monodisperse (PI $\approx$1.15). As shown in our earlier work [1], the entropy of mixing, ΔS_{mix}, can play a key role. More complicated force plots were occasionally obtained, such as the one shown in Figure 3B, with multiple pulling events that are not of single polystyrene molecules ($l_p = 3.47$ nm).

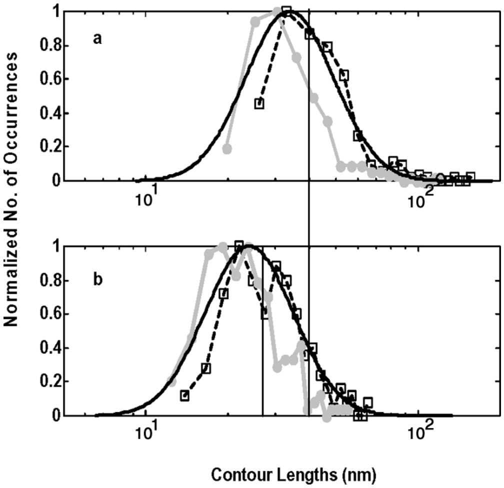


FIGURE 4 GPC data overlaid with AFM contour length data: **a**) 17 K polystyrene (0.7 mM) AFM contour-length data (squares); polymer-stretching data (gray solid line); GPC data 17 K, PI = 1.15 (black solid line). **b**) 12 K AFM contour-length data (0.7 mM) (squares), after dividing by the extension ratio; polymer stretching (gray line); GPC data of 12 K, PI = 1.15 (black solid line). Vertical lines show peak positions of contour lengths calculated from log-normal fit to the data. (It appears Gaussian on the log scale.) 12 K peak position is 28 nm and 17 K is 40.9 nm.

Calculation of Interfacial Tensions using Au and Si AFM Tips [28]

The work of adhesion of separating the AFM silicon tip (1) (in fact, an SiO_2 surface) from the polystyrene-grafted gold surface (2) in water as medium (3) is estimated using the following equation:

$$W_{132} = W_{12} + W_{33} - W_{13} - W_{23} \tag{5}$$

$$W_{132} = \gamma_{13} + \gamma_{23} - \gamma_{12}. \tag{6}$$

We can estimate γ_{13} and γ_{23} from Young's equation.
SiO_2–H_2O,

$$\gamma_{13} = \gamma_1 - \gamma_3 \cos\theta_{13} \tag{7}$$

polystyrene–H_2O,

$$\gamma_{23} = \gamma_2 - \gamma_3 \cos\theta_{23} \tag{8}$$

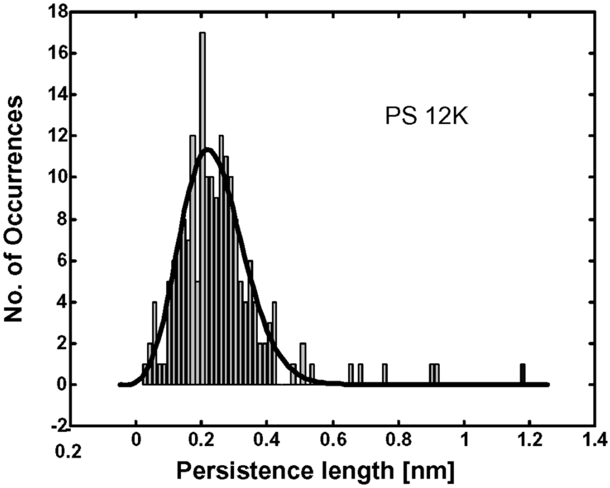


FIGURE 5 Distribution of persistence length for 12 K polystyrene measured by AFM. Center: 0.238 nm, sigma ≈ 0.098 nm.

and SiO_2–polystyrene,

$$\gamma_{12} \approx \gamma_1 + \gamma_2 - 2\sqrt{\gamma_1\gamma_2}. \tag{9}$$

Solving Equation (4) using Equations (5), (6), and (7), we obtain

$$W_{132} = 2\sqrt{\gamma_1\gamma_2} - \gamma_3(\cos\theta_{13} + \cos\theta_{23}). \tag{10}$$

The critical surface tension of wetting (γ_c) of a polystyrene was obtained using a Zisman plot such as shown in Figure 7 using NaCl solutions of known surface tensions.

Similar experiments were done on a silicon surface and a gold surface. The surface tension of polystyrene, γ_2, was 32.4 dyn/cm

TABLE 3 Comparison of the AFM Data (Polymer Stretching) with GPC Data

Compound	GPC data	AFM data
Polystyrene 12 K		
Mn	12000	10265
Mw	12300	11383
PI	1.03 (1.15, deter in lab)	1.11
Polystyrene 17 K		
Mn	17300	15234
Mw	17820	17717
PI	1.03 (1.15, deter in lab)	1.16

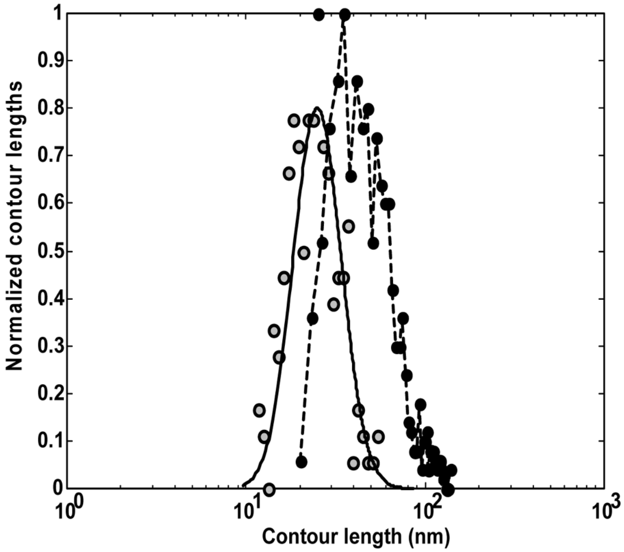


FIGURE 6 Increasing grafting concentration of 12 K polystyrene from 0.7 mM to 1.2 mM shifts the data to the right (gray line and black circles). GPC plot (black solid line) correlates well with 0.7-mM grafting concentration.

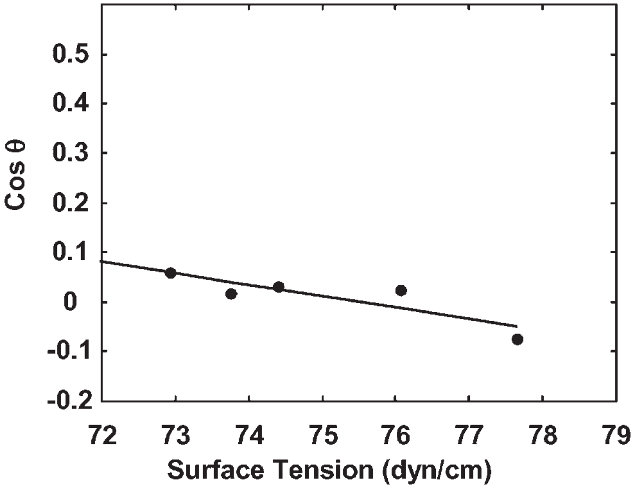


FIGURE 7 Zisman plot of polystyrene surface. The y axis is the cosine of the contact angles (θ) obtained using NaCl solutions with known surface tensions (γ). After linear regression of the cos θ and extrapolating to 1, the value of surface tension of wetting is 32.4 ± 3 dyn/cm. Literature [27, 30] reports a value of 33 dyn/cm for a polystyrene surface.

(literature value is 33 dyn/cm [21, 30], $\gamma_{\text{Au (1)}} = 45$ dyn/cm, $\gamma_{\text{SiO2 (1)}} = 67$ dyn/cm, $\gamma_{\text{water}} = 72$ dyn/cm [21]. Contact angles $\theta_{13(\text{Au–water})}$ and $\theta_{23(\text{polystyrene–water})}$ were 75° and 83°, respectively. The interfacial tension estimate using Equation (8) for the Au/polystyrene interface was found to be higher (52 dyn/cm) than for silicon/polystyrene (32.6 dyn/cm). Rupture forces of the polystyrene polymer chain using an Au AFM tip were found to be $\sim 0.15 \pm 0.05$ nN, also higher than for a SiO_2 AFM tip, 0.09 ± 0.04 nN, when force distributions were fit to a Gaussian distribution. These results further support our assertion that the chains grafted to the surface physisorb to the tip.

CONCLUSIONS

Both molecular weights of polystyrene studied were below the molecular weight of entanglement for polystyrene in bulk (19100 g/mol). The contour lengths measured correlated well with the GPC data. Persistence lengths obtained using a WLC model indicated that mostly single molecules were studied. Polymer-rupture forces using different AFM tip materials, Si and Au, in the same medium, H_2O, indicate higher interfacial tensions between the Au AFM tip and the polystyrene surface. The grafting densities were estimated using ellipsometry and found to be 0.005 chains/nm^2 for 0.6-nm-thick film, which is close to a recently reported [31] value for the mushroom conformation of 15 K polystyrene (0.009 chains/nm^2).

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