# Macromolecules

# Using Thiol–Gold Bond Formation To Bridge Surfaces with a Polymer Brush: SFA Experiments and MD Simulations

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**Supporting Information** 

**ABSTRACT:** Complementary interactions between functionalized surfaces are challenging to quantify, as both kinetics and thermodynamics are important. Optimal reaction parameters are key to the efficient formation of hierarchical nanostructures. Here, we report both surface forces apparatus (SFA) studies and molecular dynamics (MD) simulations of the controlled binding of thiol functionalized polymer brushes to complementary gold surfaces. Polymer brush-brush, brush-mica, and brush-gold experiments were performed in toluene. These comparative studies reveal the subtle balance of nonspecific and specific contributions to the measured interactions. Importantly, the physical phenomena responsible for the measured force profile in the selective binding system, including the formation of thiol-gold bonds, the resulting adhesion between the surfaces, the work to separate the surfaces, and the anchor strength of the polymer brush can be



extracted. Corroborating MD simulations demonstrate that hysteresis in the approach and separation of these selectively bound surfaces is not the result of kinetic effects, but rather is due to the polydispersity of the brush itself and the resulting thiolated chain end distribution. We relate our findings to observations made in the formation of hierarchical particle aggregates.

## INTRODUCTION

The properties of polymer brushes at interfaces have been studied widely experimentally<sup>1–7</sup> and theoretically<sup>8–15</sup> in the context of colloidal stabilization, flocculation, wetting phenomena, and lubrication. The use of polymer brushes to bridge selective surfaces has been realized through noncovalent functionalization, such as ligand—receptor bonds (e.g., streptavidin—biotin) and antibody—antigen, or via chemical specificity, i.e., carboxyl—amino group, thiol—gold, or complementary DNA for biotechnological<sup>16–24</sup> and nanotechnological applications.<sup>25–30</sup> In this work, we study selective binding of a thiol-functionalized polymer brush to a gold substrate, where the thiol—gold binding energy is estimated to be 50 to 75  $k_{\rm B}$ T.

The high strength of the thiol—gold bond is intriguing from the standpoint of tailoring adhesion between selectively bound surfaces, for instance, gold nanoparticles and thiol-functionalized polymer brushes, as there must be a balance between the ease of formation of the thiol—gold bond and the binding strength of the brush end to the gold nanoparticles. Moreover, the molecular parameters of the brush, such as the chain length, polydispersity, and grafting density, play a crucial role in the interaction energy between surfaces. Thus, tuning the interactions between complementary surfaces should be possible through judicious selection of the binding pair and design of the polymer brush properties.

Using thiolated PEG–PS diblock copolymer chains, we quantified binding and adhesion forces between different molecular weight PEG–PS–thiol brushes, grafted to mica, to a selectively binding gold surface in toluene. Toluene is considered a good solvent for PS but a poor solvent for PEG, resulting in the polymer brush being anchored to the silica particles or mica by the PEG block.<sup>31–33</sup> For comparison, we measured the force profiles of the same PEG–PS–thiol brushes interacting with themselves (brush–brush system) and PEG–PS–thiol brushes interacting with mica (brush–mica), both nonbinding surfaces. Significantly, adhesion was observed only when the PEG–PS–thiol brush interacted with a gold surface. From the measured adhesion, we extracted the adhesion energy, and work to pull-off the PEG anchor block upon surface

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Figure 1. (A-C) Schematic drawings of the three different sample configurations consisting of thiolated (SH) polymer brushes prepared in this work: polymer brush–polymer brush(brush–brush), polymer brush–mica (brush–mica), and polymer brush–gold (brush–gold). The force profiles for the nonselective surface experiments (A and B), where chemical cross-bridging is not possible between the surfaces, are presented in Figure 2

separation. In addition, we utilized molecular dynamics (MD) simulations, with equivalent molecular parameters as in our experiments, to reveal the structure of the polymer brush and enable a detailed understanding of the interaction forces measured experimentally. These investigations provide insight into the origin of the hysteresis upon approach and separation of the PEG–PS–thiol brush and gold surfaces observed experimentally.

#### RESULTS AND DISCUSSION

Forces between Polymer-Coated Surfaces. Brush-Brush, Brush-Mica, and Non-Functionalized Brush-Gold Experiments: Absence of Adhesion. SFA measurements of the interaction forces between two cylindrically curved surfaces may be easily converted to other geometries, such as a flat surface interacting with a flat surface, a sphere interacting with a flat surface, or two spheres, using the Derjaguin approximation.<sup>34</sup> Hence, SFA measurements may be readily adapted to understand the interactions between functionalized nanoparticles and within supra-aggregates, such as depicted in the Supporting Information, Figure S1. In Figure 1, we present schematics of the sample configurations that were prepared and measured with the SFA. Figure 2 shows the measured force profiles in toluene for the two noncomplementary configurations (Figure 1, parts A and B), where no selective binding can occur. In both the brush-brush or brush-mica cases, no bonds can form between the surfaces and the interaction force profiles are purely repulsive (Figure 2). Figure 2A demonstrates the greater extension of the brush ( $\sim 2$  times) when the PS block is increased from 37k to 87k. Conversely, when one of the polymer-coated surfaces is replaced with a bare mica surface, the thickness of the compressed polymer material is reduced by approximately 50%, (Figure 2, parts B and C). To ensure that nonspecific binding was not occurring between either the PS or PEG block and the gold, we measured the force profile of the nonthiolated polymer, PEG6.5k-PS37k, with a gold surface. We found that it overlaid the force profile measured between a thiolated polymer of the same PS block length (PEG5k-PS37k-SH) and a bare mica surface (Figure 3). Hence, when a selective, i.e., complementary binding, surface is not available, the interaction is purely repulsive with no adhesion from nonspecific interactions, such as adhesion due to PS adsorption onto bare mica or PS or PEG blocks adsorbing onto gold. Furthermore, polymer desorption or free polymer does not appear to be an issue, as the data of Figures 2 and 3 represent many approach and separation cycles from two or more separate experiments. The high reproducibility

indicates there is no obvious change in the polymer brush grafting density over the course of the experiments.

Functionalized Brush-Gold Experiments. Next, the interactions of PEG-PS-thiol brush covered surfaces with a selective gold surface were studied, as depicted in the schematic in Figure 1C. In this case, chemical cross-bridges can form between the thiolated brush and opposing gold surface. Considering an energy of approximately  $50k_BT^{35-38}$  for the thiol-gold bond, one may have expected an adhesive jump into contact upon surface approach. However, for both molecular weight polymers investigated (PEG5k-PS37k-SH and PEG5k-PS87k-SH), no jumps due to attraction were observed on approach (Figure 4A and Supporting Information Figure S2). Given that thiol-gold bonds should form upon approach, it is tempting to suggest that an absence of a jump into contact is the result of nonequilibrium conditions. However, we anticipate that the reorientation of the thiolated end groups is fast compared to the total relaxation of the brush. While the entire brush should relax via an arm retraction mechanism, the reorganization of the thiolated end groups is much faster, as it is governed by Zimm dynamics. As an order of magnitude calculation, we determined the viscoelastic relaxation time (Zimm time),  $\tau_z$ , of a single PS37k-SH chain to be 4.0  $\mu$ s.<sup>39</sup> From this, we obtain that the relaxation rate of the polymer brush is roughly 8 orders of magnitude larger than the average rate of approach. Given the repeatability of the results achieved in Figures 2 and 3, we can assume that the brush is in equilibrium at each measurement point of the entire experiment. At very large compressions, it should be noted that even the reorientation of the thiolated ends is governed by arm retraction. Therefore, metastable states occurring at small distances, i.e., high compressions, may have an influence on our results. At large distances, configurations of extremely extended chains that enable bond formation can occur with a finite probability. From that point of view, our approach profile is related to metastable states. However, significant chain fluctuations above the brush height are extremely unlikely and short-lived, as there is a significant energetic barrier. As we will show later, these assumptions are supported by our MD simulations.

Another explanation for the lack of jump may be related to a barrier to thiol–gold bonding. On the basis of various experimental techniques, such as EELS, XPS and ESCA,<sup>40,41</sup> and computer simulations, e.g., ab initio simulations and Density Functional Theory,<sup>35–38,42–45</sup> the thiol–gold binding energy is approximately 50–75  $k_{\rm B}T$ , about half a single carbon–carbon bond. Additionally, work by Jung and Campbell found that there is an approximately 20  $k_{\rm B}T$  energy barrier



Figure 2. (A–C) Measured force profiles between different molecular weight PEG–PS–thiol copolymer brushes in the brush–brush and brush–mica surface configurations. All data were obtained in toluene, where the PEG block is in poor solvent and therefore anchors the brush to the mica surface. The different symbols reflect separate approach and separation cycles of the surfaces, as well as experimental repetitions, and varying polymer concentrations. Note that the force profiles are always repulsive and that there is a high reproducibility. This is expected for a stable polymer brush system and suggests that there is no significant influence of polymer desorption (i.e., free polymer) or degradation that would affect the force profiles.

to thiol-gold binding.<sup>46</sup> Since our SFA experiments cannot determine if this is the reason for the absence of a jump into contact, we performed MD simulations to fully elucidate the interactions, as discussed in the next section.

Upon surface separation, a significant adhesive force (normalized by the radius of curvature of the surfaces) was measured, yielding an adhesive minimum of approximately -3.3 mN/m (Figure 4A). This minimum was followed by a regime exhibiting a two-step process. First, there was a "transition" region between ~500 and ~900 Å, where the



**Figure 3.** Identical force profiles are measured between a thiolfunctionalized polymer brush (PEG5k–PS37k–SH) and a nonselective wall (mica, open square data points) when compared to a nonfunctionalized polymer brush (PEG6.5k–PS37k) and a selective surface (gold, closed circle data points). This absence of hysteresis or shift in the force profiles indicates that nonspecific interactions, from either the PEG or PS block attaching to the gold surface, does not exist.

force was approximately constant. As we will show later using MD simulations, the constant force during surface separation is due to stretching of the polystyrene blocks to their near maximum extensions. The second step was a jump out, during which there was a "pause" in the separation of the surfaces at a distance of approximately 1200 Å for roughly 2 s. During this step, chains are both continuing to stretch and PEG block desorption is occurring. The "pause" in the jump out is most likely the result of a mechanical balance between the double cantilever spring and those chains still bridging the surfaces. As the PEG anchor block is the weakest adhesion point in the system, this is a transient mechanical balance which quickly decays. Then, the surfaces finally separated completely to approximately 2000 Å, where presumably all PEG anchor blocks of the chains bound to the gold surface desorbed from the mica surface.

Consistent with this desorption behavior, on subsequent approaches and separations of the surfaces, no adhesive minima were observed (open circle data points of Figure 4A). Moreover, the force versus distance behavior for subsequent approaches was consistent with the interaction between two lower grafting density polymer brushes. This indicates that PS chains bound from the first approach were removed during separation and now hinder subsequent binding events.

Like PEG5k–PS37k–SH, the PEG5k–PS87k–SH system only exhibited adhesion during the separation of the surfaces. A similar adhesive minimum in the force of approximately -2.6mN/m was observed as the surfaces were separated (See Supporting Information, Figure S2). Again, a two-step jump process was found with the longer polymer chain. However, the "pause" (wait time) at the intermediate step was significantly longer. In addition, during the second approach and separation, adhesion was still present, although greatly reduced from -2.6mN/m, during the first separation, to about -0.5 mN/m.

The work of adhesion can be extracted from the measured force profiles by fitting to a polynomial and integrating this function. A polynomial is chosen for ease of computation. Hence, from the adhesive portion of the force profile for



**Figure 4.** (A) Surface forces measured for the first and second cycle of a PEG5k–PS37k–SH polymer brush interacting with a gold substrate. The first cycle consists of an approach (filled circles) and a separation (filled squares) of the surfaces. Note the hysteresis in cycle 1 and the presence of only repulsion in cycle 2. (B) The comparison of the repulsive portion (F/R > 0) of the interaction forces for polymer–gold (red filled squares) versus polymer–mica (black open squares) for cycles 1 and 2. As can be seen, the repulsion of the polymer–gold system is reduced and shifted closer to zero with respect to the repulsion observed in the polymer–mica system. The lines are the power law fits for each case,  $C_0D^{\alpha}$ . See text for more details.

Table	1.	Ph	vsical	Pro	perties	of	the	Poly	vmers	under	Investigati	ion <sup>a</sup>
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polymer	polydispersity $(M_{ m w}/M_{ m n})$	Ν	$(\text{\AA}^{R_{\mathrm{F}}})^{b}$	$({ m \AA}^{R_g})^c$	$l = aN \\ (Å)^d$	$\stackrel{h_0}{({ m \AA})}$	$\stackrel{ au_z}{(\mu \mathrm{s})}$	$\sigma_{ m est} {{ m chains}/\over { m nm}^2}$	$\sigma_{ m QCM,SiO_2}$ chains/ $ m nm^2$	$\sigma_{\rm QCM,Au} \ {\rm chains} / \\ {\rm nm}^2$
PEG5k-PS37k-SH	1.23	355	151	21	959	240	4.0	0.039	$0.195 \pm 0.0000$	$0.129 \pm 0.005$
PEG5k-PS87k-SH	1.34	835	248	32	2255	390	17.0	0.013	$0.013 \pm 0.001$	$0.012 \pm 0.003$
PEG6.5k-PS37k	1.06	355	151	21	959	240	4.0	N/A	N/A	N/A
PEG5k	1.05	114	25	15	399	N/A	15.4	N/A	N/A	N/A

<sup>*a*</sup>The values of  $R_{\rm F}$ ,  $R_{\rm g}$ , l,  $h_0$ , and  $\tau_z$  reported for the copolymers correspond to the polystyrene block in toluene. For PEG5k–PS37k–SH and PEG5k–PS87k–SH, the estimated grafting densities,  $\sigma_{\rm estv}$  were determined as described in the text and the measured grafting densities were obtained with QCM-D on both quartz,  $\sigma_{\rm QCM,SiO_2}$ , and gold,  $\sigma_{\rm QCM,Auv}$  covered crystals. For the SFA experiments, which correspond to the QCM-D experiments here, the polymer concentrations were 0.1 mg/mL for PEG5k–PS37k–SH and 0.2 mg/mL for PEG5k–PS87k–SH. <sup>b</sup>The Flory radius,  $R_{\rm F}$ , was determined by using the following expression for polystyrene in toluene:<sup>53,54</sup>  $R_{\rm F} = 0.3 M_{\rm w}^{0.585}$  and for PEG:  $R_{\rm F} = 0.41 a N^{0.6}$ . <sup>c</sup>The radius of gyration,  $R_{\rm g}$ , and the maximal extension, l, were determined using a monomer length of a = 2.7 Å for polystyrene and a = 3.5 Å for poly(ethylene glycol).<sup>12</sup> d'Here, the reported Zimm time,  $\tau_{zv}$  is the time required for the chain to relax over a distance, d, at 25 °C. For PEG, the solvent is water and d is given by the maximal extension, l. For PS, the solvent is toluene and d is  $h_{0v}$  the unperturbed brush height.

PEG5k-PS37k-SH (Figure 4A), the surfaces separate from a distance of 1200 Å, at the pause, to 2000 Å. The data over this region give an adhesive work of  $1.8 \times 10^{-12}$  J. This can be compared to the work to pull off thiol-PS-PEG chains bound to the gold substrate. As the weakest link is the adsorbed PEG anchor, we can determine the number of gold-thiol bonds formed from the work to separate the surfaces. In order to approximate the number of chains bound, we need to have an estimate of the PEG block sticking energy. The zwitterionic group of the PS-X system used by Taunton et al. is estimated to have a sticking energy to mica of  $6-8 k_{\rm B}T$  per chain.<sup>31</sup> It is argued that the repulsive energy per molecule due to being attached to the surface is just balanced by the sticking energy for the PS-X system. By plotting the molecular weight of the PS block on a double log plot, Taunton et al. demonstrate an approximately linear relationship of s with molecular weight. Using this same logic, we plotted the values of s for the two PEGx-PSy-SH systems with the data from Taunton et al. and determined that the PEGx-PSy-SH systems approximately lie along the same line (data not shown). Hence, we estimate the sticking energy of the PEG block as 6 to 8  $k_{\rm B}$ T per chain as well.

Using 6  $k_{\rm B}$ T per chain sticking energy for the PEG block to mica, the total adhesive work measured yields  $7 \times 10^7$  polymer chains in the contact area bound to the gold surface by a thiol group, i.e., the number of thiol–gold bonds. From the Langbein approximation, we determine that the contact area is  $1.5 \times 10^{-9}$ m<sup>2</sup> and converting the  $7 \times 10^7$  chains to mass we obtain a grafting density estimation of 3.3 mg/m<sup>2</sup> or 0.039 chains/nm<sup>2</sup>. According to Titmuss and co-workers, after 3–14 h of incubation with a PS(67k)–X system, they obtained 0.042 chains/nm<sup>2</sup> onto mica, where X is a zwitterionic group.<sup>47</sup> In addition, Taunton et al. report a grafting density of  $3.0 \pm 0.5$ mg/m<sup>2</sup> for their PS–X(140k) system. Hence this estimation of the grafting density for PEG5k–PS37k–SH appears to be reasonable.

Using the same approach for the larger molecular weight PEG5k–PS87k–SH, where the surfaces separate from a distance of 2,380 Å to a distance of 3,300 Å, yields an adhesive work of  $1.7 \times 10^{-12}$  J, similar to the value calculated for the PEG5k–PS37k–SH polymer. Again, taking the PEG sticking energy to be 6  $k_{\rm B}$ T per chain, we calculate there to be  $7 \times 10^7$  chains. Applying the Langbein approximation, the contact area is  $3.8 \times 10^{-9}$  m<sup>2</sup>, almost double that of the contact area for PEG5k–PS37k–SH. The grafting density is 0.013 chains/nm<sup>2</sup>

(2.1 mg/m<sup>2</sup>), about 2/3 of the PEG5k–PS37k–SH grafting density. In a similar system of PEG4k–PS80k polymer, Field and co-workers measured 2.9  $\pm$  0.5 mg/m<sup>2</sup> via neutron reflectivity.<sup>32</sup> Again, our estimated grafting density for PEG5k–PS87k–SH appears in line with previously reported experimental values for similarly sized PEG–PS copolymers.<sup>48</sup>

In parallel, we performed quartz crystal microbalance with dissipation monitoring (QCM-D) measurements of the polymer systems on quartz and gold substrates in toluene at the same concentrations as in the SFA experiments. Table 1 (See Experimental Section) contains a summary of QCM-D data for the PEG5k–PS87k–SH and PEG5k–PS37k–SH polymers. On quartz, the surface concentrations are  $2.1 \pm 0.1$  mg/m<sup>-2</sup> and  $13.6 \pm 0.0$  mg/m<sup>-2</sup> for PEG5k–PS87k–SH and PEG5k–PS37k–SH and PEG5k–PS37k–SH, respectively. The surface concentrations on gold substrates in toluene are  $1.9 \pm 0.4$  mg/m<sup>-2</sup> and  $9.0 \pm 0.4$  mg/m<sup>-2</sup> for the PEG5k–PS87k–SH and the PEG5k–PS37k–SH polymer, respectively. The measured grafting densities on quartz match well to the estimates from the SFA experiments for the PEG5k–PS87k–SH system but are significantly different from the PEG5k–PS37k–SH.

Although no jumps into contact were observed with either PEG5k–PS37k–SH or PEG5k–PS87k–SH and gold surfaces, there is an appreciable attractive component to the interaction profile due to selective bond formation between the thiol end groups and the gold surface. This is evident from the reduction in the repulsive force relative to the polymer–mica case (Figure 4B). Assuming that the repulsive, steric interactions and attractive, bridging interactions are additive, the attractive component in the force profile is due solely to thiol–gold binding and subsequent cross-bridge formation. Thus, the attractive interaction during the approach can be obtained by subtracting the polymer–mica experiment from the force profile obtained in the gold case.

We can quantify the effective adhesion, in terms of the work per chain, that results from gold—thiol binding by assuming the interaction occurs at equilibrium. Under these conditions, it is reasonable to assume equilibrium at every distance measurement. To model this, we consider the mechanical equilibrium of a plate with an adsorbed polymer brush that forms bridges with a second plate under an applied external pressure,  $f(D)^{10}$ 

$$f(D) = \Pi(D) - \sigma_{\rm b}(D)\tau_{\rm b}(D) \tag{1}$$

where  $\Pi(D)$  is the osmotic pressure of the brush as a function of surface separation,  $\sigma_{\rm b}(D)$  is the number of bridges per unit area as a function of surface separation, and  $\tau_{\rm h}(D)$  is the tension of a bridged chain as a function of surface separation. Applying eq 1 to the polymer-mica case  $[\sigma_b(D)\tau_b(D) = 0$  as no cross bridging is possible], we see that f(D) becomes solely the osmotic pressure of the single brush,  $f_{b-m}(D) = \Pi(D)$ . A similar expression for the polymer-gold case is  $f_{b-g}(D) = \Pi(D)$  –  $f_{adh}(D)$ , where  $f_{adh}(D) = \sigma_{b,gold}(D)\tau_{b,gold}(D)$ , the adhesive component due to the ends of the polymer chains binding to the gold surface. The difference between the polymer-mica and polymer-gold profiles gives  $f_{adb}(D)$ . For comparison of these expressions to SFA experiments, one needs to apply the Derjaguin approximation, where  $(F/R)_{SFA} = 2\pi E(D) = 2\pi \int$ f(D). Hence, the adhesion energy per unit area,  $\Delta_{adh}$ , is the difference between the force profiles for the polymer-mica and polymer-gold cases, respectively, and yields

$$\Delta_{adh} = \Delta \left(\frac{F}{R}\right)_{SFA}$$
  
=  $2\pi \int f_{b-g}(D) dD - 2\pi \int f_{b-m}(D) dD$   
=  $-2\pi \int f_{adh}(D) dD$  (2)

To model the interactions between the surfaces, we use a power law expression, as this is a facile method to describe a purely repulsive system.<sup>49</sup> As stated above, the effect of the adhesive gold component merely is subtracted from the osmotic pressure,  $\Pi(D)$ , and therefore may be modeled, as well, by the power law expression, such that the general form for either a brush-mica or brush-gold net interaction is:  $\int \Pi(D) dD = C_0 D^{\alpha}$ , where  $C_0$  and  $\alpha$  are fitting parameters. To determine an empirical expression for this net attractive force,  $\Delta_{adh}$ , we subtracted the fit power law for the brush-mica case from the brush-gold case to obtain

$$\Delta_{\rm adh} = C_{0,\rm bg} D^{\alpha_{\rm bg}} [1 - (C_0/C_{0,\rm bg}) D^{\alpha - \alpha_{\rm bg}}]$$
(3)

Hence, when the number of chains bound per unit area remains constant as a function of surface separation, i.e., all possible bridges are made, eq 3 is the expression for the tension energy per unit area on the bound chains as a function of distance,  $\Delta_{adh} = \int f_{adh}(D) dD = -\int \sigma_{b,gold}(D) \tau_{b,gold}(D) dD$ . The data points of Figure 5 were obtained by interpolation and



**Figure 5.** The difference between the complementary brush–gold system and the noncomplementary brush–mica system was determined using interpolation of the force profiles in Figure 4B. The interpolated data was subtracted to give  $\Delta(F/R)$  as a function of D, the filled and open symbols. The dashed line is  $\Delta_{adh}$  as given in eq 3 and obtained from the fits of Figure 4B.

subtraction of the force profiles in Figure 4B, where the polymer-mica case is subtracted from the polymer gold case. The resulting attractive force is due to the formation of selective bonds between the thiol functionalized brush and the gold surface. The dashed line is the change in adhesion energy calculated from eq 3, by fitting power laws to the force profiles of Figure 4B. Hence, it seems that subtraction of power law representations of the brush-gold and brush mica force profiles yields a reasonable estimate of the adhesive component.

In addition to the expression for the adhesion energy, we can determine easily the work of adhesion during the approach by integrating the power law fits to the SFA data and subtracting the two expressions. For the PEG5k–PS37k–SH polymer

system above, evaluating over the range from 30 to 300 Å gives  $2 \times 10^{-12}$  J. Hence, the total adhesive work difference between the polymer–mica and polymer–gold case is  $5 \times 10^8 k_{\rm B}$ T. From PEG desorption estimations,  $\sigma = 3.3 \text{ mg/m}^2$ , the estimated number of chains is  $7 \times 10^7$  and therefore an estimation of the adhesive energy per chain by this method yields  $7 k_{\rm B}$ T/chain, in excellent agreement with the assumed adsorption energy of 6 to 8  $k_{\rm B}$ T per PEG anchor block. Finally, based upon the molecular weight of the PEG block, the average binding energy per ethylene oxide monomer is approximately 0.06  $k_{\rm B}$ T.

Comparison of Adhesive Experiments to Simulations. Some aspects of the approach and separation behavior reported thus far are surprising. First, why did we not observe an adhesive jump during the approach? Given the large binding energy for a thiol-gold bond, one would expect a jump into contact once the surfaces approach a distance comparable to the unperturbed brush height.<sup>7,12</sup> As we have ruled out polymer desorption or free polymer as contributing to the observed behavior, could this be the result of an activation energy barrier for thiol-gold bond formation? Second, one may ask why a constant interaction energy was found over a distance of approximately 400 Å (the labeled "transition" region in Figure 4A); a similar behavior, although not exactly, was also observed with the higher molecular weight PEG5k-PS87k-SH polymer. Finally, from where does the mechanical instability at the end of the separation process come (the "pause" region in Figure 4A and Supporting Information, Figure S2)?

To clarify these points, we performed MD simulations, which allow us to monitor structural properties of the polymeric system in great detail. In previous work,<sup>50</sup> we have demonstrated that the cutoff Lennard-Jones potential, without the adhesive interaction, models the repulsive forces between nonfunctionalized polymer brushes and a neutral substrate very well. Figure 6 compares the measured interaction energy for the complementary brush–gold surfaces, in terms of energy per unit area and normalized distance, to the MD simulation of the system. Qualitatively, the simulation reproduces the hysteresis observed experimentally. Noting the details between simulation



Figure 6. Energy per unit area (in arbitrary units) as a function of normalized distance between the surfaces. Approach data from the SFA are black squares and separation are red circles. Approach data from the simulation are represented by the heavy (green) line and separation data by the lighter (black) line. By shifting the simulation data on the *y*-axis, it is possible to superimpose the minima of experiment and simulation. Also, it should be noted that the simulation cannot reproduce the "pause" observed in the experiment. The origin of the "pause" lies primarily in the mechanical properties of the SFA measuring system (see text for more details).

and experiment, we make two observations. The first is the onset of the repulsion in the experiment  $(D/h_0 \sim 1.4)$  versus the simulation (noted as "1" in Figure 6). There is some uncertainty in the distance measurement in the gold-polymer experiments that may partially account for this discrepancy. The distances were determined by fitting the contact positions of the mica-mica, brush-brush, and brush-gold systems using a peak-finding routine (for details, see Methods section). While the fitting was performed to reduce the sum of squared errors to a minimum, it is possible that deviations on the order of 30 Å exist in the real distance measurements. This does not alter the qualitative outcome, but may result in a shift relative to the numerical data. The second detail is the position of the adhesive minimum in the interaction energy per unit area, labeled "transition" in Figure 6. It is comparable to the experiment, after rescaling the distance with the unperturbed brush height,  $h_0$ . For the energy scale, we use arbitrary units to match the experimentally observed minimum with that of our simulations.

The qualitative agreement between simulation and experiment allows us to draw conclusions about the experimental observations based upon the structural properties extracted from the simulations. From the simulation configurations, it is clear that the polymer chains are both highly stretched and desorbing from the mica surface during the "transition" region (see Figure 7B). However, the behavior at large separations, specifically the jump with a "pause," indicating a mechanical instability in the SFA system, could not be observed in the simulations. The reason for this finding stems from an essential



**Figure 7.** Snapshots of the simulated system at different distances during separation. (A) corresponds to position 4, (B) corresponds to position 5, and (C) corresponds to position 6 of Figure 6. The thiol group is dark blue, the PEG block is yellow, and the polystyrene is red.

difference between the two methods. In the simulation, we controlled the surface separation and measured the force necessary to obtain a certain separation, while the SFA uses a double cantilever spring with which one of the surfaces is moved. The latter does not provide a controlled surface separation when the slope of the force curve is equal to or greater than the spring constant of the double cantilever spring. The desorption of a large part of the bridging chains leaves only a few bridges and leads to a sudden jump, where a large portion of the stretching energy stored in the SFA spring is suddenly released. The pause in the SFA system may be the result of longer chains from the polymer chain length distribution that are stretched to their maximum length, transiently providing enough pulling force to counterbalance some of the energy released from the initial part of the jump. This balance is highly unstable, lasting only a few seconds for the PS37k chains and about 4 times longer for the PS87k chains. The fact that the PS87k chains are approximately 2 times larger and have a higher polydispersity than the PS37k chains suggests that this is a plausible physical explanation for the existence of the pause. Obviously, this behavior could not be reproduced within the MD simulation, where we controlled the surface separation. Furthermore, since the polymer bonds in our numerical model are significantly stiffer than those in the experiment, the SFA measurements yield a larger adhesion plateau ("transition") than the simulations, where chains desorb from the surfaces earlier. However, apart from these marginal differences, we find a remarkably good agreement between experiment and simulation.

On the basis of this agreement, we can monitor the structural properties in the simulation to understand the findings from our physical experiments. We first focus on the question, why we did not observe an adhesive jump into contact, given the large binding energy for a thiol–gold bond. Figure 8 shows the monomer density distribution during the approach at different separations, corresponding to the numbers "1"–"3" in Figure 6. At a separation of  $D/h_0 \approx 1$  (position "1"), some of the thiol



**Figure 8.** Total monomer density profiles (solid lines), density distribution of the thiol end groups (dotted lines), and PEG end groups (dashed lines) for different surface separations (see Figure 6) during approach. Inset: The total monomer density distribution (solid lines) and distribution of the thiol end groups (dotted lines) are magnified to demonstrate the increase of the thiol end groups at the gold surface as the surfaces are brought closer together.

end groups have made contact with the gold surface (black dotted line). Once a thiol end group touches the gold surface, it binds and the thiol monomer density at the gold surface increases. Upon decreasing the separation (positions "2" and "3"), more and more thiol-gold bonds have formed and the monomer number density of the thiol ends increases, as shown in the inset of Figure 8. However, there is also a significant amount of "repulsive" monomers close to the gold substrate (solid lines), such that the net interaction between the surfaces remains repulsive because there are many more monomers of the backbone (PS) than thiol end groups. For example, from the inset of Figure 8, we see that the areas under the thiol density distributions are much smaller than the areas under the corresponding total monomer density distributions. This is a consequence of the fact that the end groups, in contrast to the primitive model of Alexander and DeGennes, are not located at the outer fringe of the brush profile. In fact, the thiol groups are hiding somewhere inside the brush. This would already be the case for monodisperse brushes, if one considers the end monomer distribution of a parabolic Milner-Witten-Cates brush.<sup>51</sup> We have measured this distribution for a free  $(D \gg$  $h_0$ ), monodisperse brush with a chain length equal to our average chain length (N = 60) and the same grafting density (see inset of Figure 9). The second curve in this inset shows the



**Figure 9.** Total monomer density profiles (solid lines), density distribution of the thiol end groups (dotted line with shade region), and PEG end groups (dashed lines) for different surface distances (see Figure 6) during separation. Inset: Chain end monomer distribution of a free brush  $(D \gg h_0)$  for our polydisperse brush (dashed line).  $z/h_0$  is the reduced distance from the wall within the brush, where z is the distance in the brush and  $h_0$  is the unperturbed monodisperse brush height. For comparison, we show also the end monomer distribution of a monodisperse brush.

end monomer distribution for our polydisperse brush, PDI = 1.23. Our result indicates that polydispersity greatly enhances the effect; i.e., the end thiol groups are located even in deeper layers of the brush rather than at the edge of the brush. This reduces the number of thiolated chain ends available for binding. Thus, the surfaces do not jump to contact during the approach due to the more dominant, repulsive interaction between the gold surface and the chain backbones.

Figure 9 depicts the monomer density profiles during the separation of the surfaces at different distances (corresponding to positions "4"-"6" of Figure 6). We observe an almost

homogeneous density distribution when the interaction energy is approximately zero (position "4"). Still, not all the thiol groups are sticking to the gold surface. Upon further separation, the backbones of the chains are pulled away from the gold surface. This provides space for the thiolated end groups and then all possible thiol-gold bonds are formed. When the interaction energy has reached the minimum (position "5"), some chains are strongly stretched, yielding an extremely extended monomer distribution, exceeding the unperturbed brush height by a factor of slightly more than 2. After the jump and completed desorption of the PEG monomers (position "6"), the monomer density distribution is that of the unperturbed, polydisperse brush. This behavior is confirmed by the snap-shots (Figure 7) taken from our simulation at the separations given at positions "4," "5" and "6" of Figure 6. Furthermore, we note that the density profile of the unperturbed brush ("6") decreases linearly with the distance from the surface. Such a behavior has been predicted by Milner, Witten, and Cates<sup>51</sup> for a polydisperse brush with uniform molecular weight distribution.

As already mentioned, metastable states have to be expected in the limit of very strong compressions. It is obvious that for an infinite waiting time all thiolated end groups should bind to the gold surface. Neither our experiments nor our simulations appear to explore these large time scales. However, even if we could wait until all thiol–gold bonds are formed, this would not influence the observed hysteresis. Without the simulation results and discounting kinetic effects, one may conclude that the presence of hysteresis in the experiment is the result of a barrier to thiol–gold binding.<sup>46</sup> However, the SFA findings are reproduced by the presented simulations, where no barrier to binding has been incorporated.

Our findings have consequences for the observations made of the gold nanoparticle– $SiO_2$  microparticle systems (Supporting Information Figure S1). The interaction of a gold nanoparticle with a much larger, polymer brush-covered  $SiO_2$  microparticle may be modeled as a sphere interacting with a flat surface, easily analogous to the geometry of the SFA surfaces. We propose that the reason for so few gold nanoparticles binding to the microparticles is the same effect—mainly that the thiolated chain ends are not easily available for the gold particles approaching the surface. In fact, it should be noted that this effect will influence any particle–particle interactions mediated by functionalized polymer brushes, as experimental polymer systems always contain polydispersity.

The last question remaining is related to the observation of a constant interaction potential, which occurs over a distance of  $D/h_0 \approx 2$  to 3 in the simulation and the experiment (see Figure 6). As we have learned from our simulations, the adhesion energy increases upon surface separation until the first (i.e., the shortest) chains start to desorb. Once the first chains desorb, the surface separation increases without a visible change of the interaction potential. Obviously, less attraction would be expected when less chains are bridging the substrates. On the other hand, with increasing separation, slightly longer chains become fully stretched and compensate for the loss of adhesion due to the desorption of the shorter chains. This continues, until finally even the longest chains desorb and no chains are left for compensation, thus yielding the configuration shown in Figure 7C.

### **SUMMARY**

In this work, we present the interaction force profiles of several molecular weight PEG–PS–thiol block copolymer brushes in toluene with the following configurations: polymer brush-brush, polymer brush and mica, and polymer brush and gold surface. We observed hysteresis in the force profiles between a surface bearing thiol functionalized copolymers and a gold surface only. We compared our measured force profiles with both computer simulations and adhesive theory. From the force profiles, we have made estimations of the change in energy due to thiol–gold bond formation and determined an empirical expression to describe the change in energy due to adhesion as a function of surface separation. Finally, we have estimated the work of adhesion of the PEG block due to desorption of the chans from the mica surfaces during separation.

Using the results of our MD simulations, which coincide qualitatively with the experimental data to a great extent, we have demonstrated that a jump into contact is not observed due to the repulsive backbones of the grafted chains, i.e., steric hindrance. The backbones of the chains make contact with the gold surface before all the thiol-gold bonds are able to form. Only during the separation process, when the repulsive backbones stretch and finally create space at the gold surface, are all the thiol-gold bonds formed. These bonds result in a large adhesion between the surfaces and thus, a strong bridging that is maintained over distances greater than twice the unperturbed brush height. While chain polydispersity might not explain the absence of a jump into contact completely, it does play a vital role in determining the interaction energy profile. MD simulations confirm that polydispersity alters the thiol end group distribution in the brush, resulting in fewer thiol moieties available for binding to the gold surface upon approach. In contrast to the expectation for monodisperse brushes, we obtain a linear monomer density profile for our polydisperse brush.

#### EXPERIMENTAL SECTION

**Polymer Materials.** *Polymerization.* End functionalized diblock coplymer molecules were synthesized with a constant PEG block of 5,000 g·mole<sup>-1</sup> and varied molecular weight PS block containing a functional thiol (SH) moiety attached to the terminus of the PS block. Two specific copolymers were used in this work, PEG5k–PS37k–SH and PEG5k–PS37k–SH. A summary of the synthesis and characterization is presented here and has been detailed elsewhere.<sup>52</sup>

Scheme A of Scheme 1 shows the synthetic route used to produce the PEG macroinitiator (PEG-RAFT) for production of functionalized PEGx-PSy-SH copolymers. Phenyl magnesium chloride was treated with carbon disulfide to produce a thiocarbonyl-thioacetate nucleophile, which was then added to PEG1 to prepare the  $\alpha$ methoxy- $\omega$ -S-thiobenzoyl-2-thiopropionate PEG (PEG-RAFT). Scheme B in the same scheme displays the synthetic route employed to prepare various molecular weights of PEGx-PSy-SH copolymers using standard RAFT techniques and utilizing the PEG macroinitiator (PEG-RAFT) of Scheme A. The intermediate block copolymer (PEGx-PSy-RAFT) was treated with NaBH<sub>4</sub> to yield the final product, PEGx-PSy-SH. TLC staining confirmed reduction of the thiobenzoyl-2-thiopropionate. Gel permeation chromatography (GPC) analysis did not display a shift in molecular weight, indicating the preservation of the ester functionality. Figure 10 displays GPC traces for the macroinitiator (PEG-RAFT), intermediate (PEGx-PSy-RAFT), and final products (PEGx-PSy-SH) for each thiolated polymer.

Polymer Solution Preparation. Table 1 is a compilation of the physical properties of the polymer systems used in the present work. A

Scheme 1. Synthetic Schemes of the PEG Macroinitiator (PEG-RAFT) Used in RAFT Polymerization (A) and the Polymerization of the Macroinitiator To Give the Resulting PEGx-PSy-SH Copolymers for This Study (B)

Scheme A. Synthetic Route of PEG-macroinitiator for RAFT Polymerization.



Conditions: A) Et<sub>3</sub>N, Toluene, 2-bromopropionyl bromide, 24h, RT; B) THF, RT, 5h; C) CS<sub>2</sub>, THF, -78°C for 15 min followed by RT for 1h



comparison is made to a nonfunctionalized PEG6.5k–PS37k obtained from Polymer Source, Inc. (Montreal, Canada).

The diblock copolymers were dissolved in toluene at concentrations from 0.02 to 8.0 mg·mL<sup>-1</sup>. Samples were sonicated and subsequently allowed to solvate for at least 8 h to ensure full dissolution of the polymer. After dissolution, polymer solutions were filtered with 0.1 or 0.2  $\mu$ m Anotop syringe filters (Whatman) prior to use.

#### METHODS

**Surface Forces Apparatus (SFA).** The Surface forces apparatus (SFA) has been described previously and used extensively to measure the interactions between various surfaces.<sup>34,55,56</sup> Here, we describe the specific apparatus properties for our experiments.

The sample surfaces were glued down to cylindrically curved supports using a 1:1 molar ratio of dextrose-*D*-galactose sugar mixture. The gold and silver surfaces were produced via thermal evaporation of pure, 99.999%, gold or silver onto freshly cleaved mica substrates. After preparation, the surfaces were immediately mounted into a Mark II SFA chamber.

At the beginning of each experiment, two bare mica surfaces were brought into contact in air to ensure that the surfaces were clean. The zero contact position was measured to determine the mica thickness. Afterward, the surfaces were separated ~1 mm and droplets of polymer solution (concentrations ranging from 0.1 to 1.0 mg·mL<sup>-</sup> were introduced between them, such that a defined volume of polymer solution was retained between the surfaces and thus ensuring saturation of the surfaces with polymer. The surfaces were then allowed to incubate with the polymer solution between them for a minimum of 8 h before the experiment was continued. Earlier studies have established that the PEG portion of the diblock adsorbs and anchors the PS portion of the chain to the mica surface in the selective solvent toluene.<sup>31–33,50</sup> After incubation, the SFA chamber was filled with spectral grade toluene and force profiles were obtained. First, the force profiles for the brush-brush configuration were measured. Next, the top surface was replaced by a clean sheet of mica of the same thickness and the force profiles for a single brush interacting with a nonselective surface, mica, were measured (brush-mica). Finally, for some experiments, the top surface was replaced a second time with a gold-coated mica surface and the force profiles for a single brush interacting with a selective surface, gold, were measured (brush-gold). See Figure 1 for schematic representations of the sample configurations described.

The top surface was fixed and the lower surface was mounted onto a double cantilever spring of spring constant  $\approx 460 \text{ N}\cdot\text{m}^{-1}$ . Surface separations were determined to an accuracy of  $\pm 1$  Å and intersurface forces were determined to an accuracy of  $\pm 4\%$ .<sup>20</sup> The average time for one approach and separation cycle was approximately 1 h. Experiments were performed with the surface separation controlled both manually and automatically by our own in-house software.<sup>20</sup> In the case of automated control, FECO images were acquired using a 2048 pixel × 512 pixel CCD detector (Princeton Instruments) with a resolution of  $\pm 0.25$  Å in wavelength and  $\pm 1 \ \mu$ m lateral distance across the sample surface. FECO peak wavelengths were identified to  $\pm 0.1$  Å as previously described.<sup>20</sup>

In the case of force profiles obtained using gold-coated mica, the thickness of the gold-coated mica was determined by performing peak-finding routines. The routines used both the contact data for the mica-mica and polymer-polymer surfaces measured during the experiments. First the mica thickness was determined using Mathematica 6.0 and a custom peak fitting routine developed in house (FECOFit). Next, the polymer thickness between the silvered mica surfaces was determined based upon the contact information before and after incubation with polymer solution. Finally, the determined mica and polymer thicknesses were used with the surface contact information from the gold-coated mica experiments to determine the gold-coated mica thickness. In each case, the thickness of the layer was determined with the sum of squared error typically less than a few angstroms. However, variations in the optical path when



**Figure 10.** GPC analysis of PEGx–PSy–SH diblock copolymers. Left are the PEG initiator (PEG-RAFT), PEG–PS-dithioester intermediate (PEG5k–PS37k–RAFT) and the final product, PEG5k–PS37k–SH. Right are the PEG initiator (PEG-RAFT), PEG–PS-dithioester intermediate (PEG5k–PS87k–RAFT) and the final product, PEG5k–PS87k–SH. In both cases, the PEG-RAFT was 5000 g-mol<sup>-1</sup>.

exchanging surfaces or changing contact positions can yield relative shifts of 5-10 Å.

$$U_{\rm LJ}(r_{ij}) = 4\varepsilon [(\sigma/r_{ij})^{12} - (\sigma/r_{ij})^6 - (\sigma/r_c)^{12} + (\sigma/r_c)^6]$$
(4)

The units of energy and length respectively are defined by  $\varepsilon$  and  $\sigma$ . The distance between monomer *i* and *j* is denoted by  $r_{ij}$  and  $r_c$  is the cutoff radius. We consider a purely repulsive potential by setting  $r_c = 2^{1/6}\sigma$  and shift  $U_{\rm LJ}$  to avoid a discontinuous force at the cutoff. For all interactions between monomers or surface atoms we use  $\varepsilon = 1$  (in LJ units). Chain connectivity is mimicked by finitely extensible, nonlinear, elastic springs, represented by the FENE potential<sup>57</sup>

$$U_{\text{FENE}}(r) = -\frac{1}{2}kr_0^2 \ln[1 - (r/r_0)^2](r < r_0)$$
(5)

where r is the distance between neighboring monomers in a chain and  $r_0$  is the maximum allowed bond length. As commonly done, we use k =  $30\epsilon/\sigma^2$  as the spring constant. The polymers are grafted onto a surface with one end. While the backbone of each chain interacts purely repulsively with itself, the other chains and the substrates, the interaction between the grafted chain end monomer and the (mica) substrate contains an attractive part. This is achieved by increasing the cutoff radius for this particular interaction to  $r_c^{\text{attr}} = 2.2^{1/6} \sigma$ , while the strength of interaction is set to  $e^{mica} = 30$ . The free chain ends, which mimic the thiolated end-groups of our experiments, interact with the opposing gold surface with  $e^{\text{gold}} = 50$ . For substrates, we use rigid, twodimensional hexagonal lattices with surface area  $A = L_x L_y = 84\sigma \times 73\sigma$ =  $6132\sigma^2$ , where  $L_x$  and  $L_y$  are the extensions of the substrate. The average chain length is N = 60 with a polydispersity index of 1.23 (Flory-Schulz distribution). The grafting density,  $\sigma_{g}$ , is chosen such that we obtain the same stretching factor,  $\sigma_{g} \tilde{R}_{F}^{2}$ , as for the experimental system with PEG5k-PS37k-SH. Taking the results of Kreer et al.<sup>58</sup> with the average chain length N = 60, we obtain  $R_{\rm F} \approx 5.9$ , which leads, with the data of Table 1, to approximately 300 grafted chains on the surface of area A.

We perform both approach and retraction of the surfaces on a time scale that is large, compared to the relaxation time of a polymer chain in the brush. In this way, we ensure a quasi-stationary process, where the confined liquid is in thermodynamic equilibrium at all times.

Newton's equations of motion are solved using the velocity–Verlet algorithm<sup>59</sup> with a time step of  $\Delta t = 2 \times 10^{-3} \tau_{LJ}$ , where  $\tau_{LJ}$  is the LJ time unit. The temperature is kept constant at  $T = 1.68\epsilon/k_B$  using a dissipative particle dynamics (DPD) thermostat (see Frenkel and Smit<sup>59</sup> and references therein). The thermostat adds to the conservative force a dissipative force,  $\mathbf{F}_{i}^{D}$ , and a random force,  $\mathbf{F}_{i}^{R}$ . These forces are applied in a pairwise form, such that the sum of thermostat forces acting on a particle pair is zero. With  $\gamma$  denoting the friction constant, the dissipative force reads

$$\mathbf{F}_{i}^{D} = -\gamma \sum_{j(\neq i)} \omega^{D}(r_{ij}) (\hat{\mathbf{r}}_{ij} \cdot \mathbf{v}_{ij}) \hat{\mathbf{r}}_{ij}$$
(6)

where  $\hat{\mathbf{r}}_{ij} = (\mathbf{r}_i - \mathbf{r}_j)/r_{ij}$  and  $\mathbf{v}_{ij} = \mathbf{v}_i - \mathbf{v}_j$  the relative velocity of particles *i* and *j*. We used the commonly employed weight function

$$\omega^{D}(r_{ij}) = \begin{pmatrix} (1 - r_{ij}/r_{c})^{2} & (r_{ij} < r_{c}), \\ 0 & (r_{ij} \ge r_{c}) \end{pmatrix}$$
(7)

with the same cutoff range  $r_{\rm c}$  as for the purely repulsive LJ interaction. The random force is given by

$$F_i^{\rm R} = \lambda \sum_{j(\neq i)} \omega^{\rm R}(r_{ij}) \theta_{ij} \hat{\mathbf{t}}_{ij}$$
(8)

where  $\theta_{ij}$  represents a random variable with zero mean, unit variance, and  $\theta_{ij} = \theta_{ij}$ . The weight function for the random force is  $\omega^{R}(r_{ij})$ . Friction and noise strength,  $\lambda$ , define the temperature via  $\lambda^2 = 2k_{\rm B}T\gamma$ . As in previous studies,<sup>15,60,61</sup> we have chosen  $\gamma = 5\tau_{\rm LJ}^{-1}$ .

To fulfill the fluctuation-dissipation theorem the weight functions for dissipative and random forces have to satisfy the relation

$$[\omega^{R}]^{2} = \omega^{D} \tag{9}$$

Our simulation model, without attraction to the gold surface and polydispersity, is well established and has been used in a variety of studies concerning the properties of polymer brushes.  $^{15,58,60-62}$ 

#### ASSOCIATED CONTENT

#### **G** Supporting Information

Application of polymer cross-linkers, functionalized brush-gold experiments, and methods. This material is available free of charge via the Internet at http://pubs.acs.org/.

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#### Notes

The authors declare no competing financial interest.

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