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A Nanotumbleweed: Breaking Away a Covalently Tethered Polymer Molecule by Noncovalent Interactions

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Abstract: A covalently tethered polymer molecule can spontaneously break away from the surface when polymer/surface interaction is sufficiently unfavorable. This is demonstrated in surface-initiated polymerization of a hydrophilic polymer, hyperbranched polyglycidol, from minority surface sites embedded in a hydrophobic self-assembled monolayer. As each hyperbranched polyglycidol molecule grows larger, it encounters more unfavorable interaction with the hydrophobic surface, and this leads to spontaneous bond rupture and desorption. This finding challenges the traditional view on noncovalent interaction of macromolecules with the local environment at interfaces and has broad implications for the understanding, design, synthesis, and applications of surface-tethered macromolecules.

Introduction

Covalently tethered macromolecules on surfaces are assumed to be stable in the absence of chemical attack. Breaking a covalent tether bond requires significant mechanical force, on the order of nanoNewtons (nN), as demonstrated in experiments using atomic force microscopy (AFM)[1,2] and optical tweezers.[3] Noncovalent adsorption of polymer molecules on solid surfaces is a strong function of polymer−solvent interaction; polymer molecules are thermodynamically favored to desorb from the surface in good solvents.[4,5] For surface-tethered (grafted) macromolecules, interactions of the macromolecule with the solvent, with the surface, and with each other are believed to determine their conformations, i.e., the swelling or extension of grafted polymer chains,[6−8] but not breaking the covalent anchoring bond. Here we demonstrate that a covalently tethered polymer molecule can spontaneously break away (desorb) from the surface when polymer/surface interaction is sufficiently unfavorable. We study surface-initiated polymerization of a hydrophilic polymer, hyperbranched polyglycidol (HPG), from minority surface sites embedded in a hydrophobic matrix. We demonstrate that as each HPG molecule grows larger, it encounters more unfavorable interaction with the hydrophobic surface and eventually leads to spontaneous covalent bond rupture and desorption, as driven by enthalpic gain from more favorable interaction with the solvent and entropic gain from more conformational freedom in the solution.

HPG molecules can be synthesized via a ring-opening, anionic polymerization reaction of glycidol from a variety of initiators capable of forming anions.[9,10] Initiation of HPG growth from surfaces has also been demonstrated on the hydrophilic silica surface with Si−OH groups as initiators, with film thickness increasing monotonically with growth time.[11] Here, we initiate HPG growth on −COOH sites embedded in a hydrophobic $-CH_3$ matrix using mixed alkanethiol self-assembled monolayers (SAMs) on Au. Formation of SAMs on Au from mixed solutions of thiols has been extensively studied in the past.[12−20] In general, the molar ratio of the two components in the mixed SAM is not linearly related to the composition in the mixed thiol solution. The adsorption of one component is usually favored over the other depending on their relative solubility. Kakiuchi and co-workers studied binary SAMs of HOOC-terminated and CH_3-terminated alkanethiols.[18−20] These authors showed that for thiols of similar lengths, 1-undecaethiol and 11-mercaptoundecanoic acid (MUA), the two components are completely miscible in the monolayer, whereas for those with very different lengths, hexadecanethiol and 3-mercaptopropionic acid, phase separation occurs in the SAM. We use mixed SAMs

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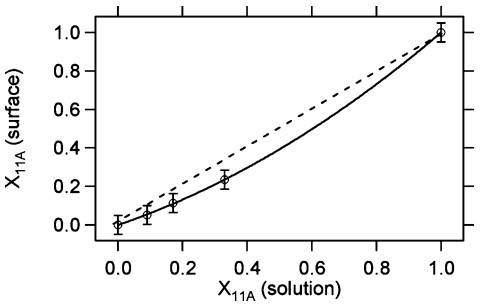

Figure 1. Mole fraction of mercaptoundecanoic (11A) in the mixed SAM with decanethiol (10C) vs the mole fraction of the acid in the solution. The surface mole fraction, X_{11A}(surface), was obtained from the normalized O_{1s} XPS peak area. X_{11A}(surface) = 1 for the pure 11A SAM. The dashed line is the linear relationship.

from binary mixtures of the following thiols, decanethiol, dodecanethiol, hexadecanethiol, 11-mercapto-1-undecanoic acid, and 16-mercapto-1-hexadecanoic acid, to control the surface hydrophobicity and the interaction energy between a surface-tethered HPG molecule and the two-dimensional matrix.

Experimental Section

We used ultraflat gold surfaces obtained from template stripping.[21] We prepared the mixed SAMs by immersion of clean Au surfaces in 1 mM (total thiol concentration) ethanol solutions of binary mixtures of the following thiols: decanethiol, dodecanethiol, hexadecanethiol, 11-mercapto-1-undecanoic acid, and 16-mercapto-1-hexadecanoic acid (90−99%, Aldrich). After incubation overnight and rinsing with ethanol, we removed weakly adsorbed HS−$(CH_2)_n$–COOH molecules using a deprotonation−reprotonation procedure.[22−24] We used X-ray photoelectron spectroscopy (XPS, Phi 540) to quantify the mole fractions in SAMs made from solution mixtures of mercaptoundecanoic acid, HS−$(CH_2)_{10}$COOH (abbreviated as 11A, where A = COOH), and decanethiol, HS−$(CH_2)_9CH_3$ (abbreviated as 10C; 10 is the total number of carbon atoms). The O_{1s} peak area (normalized to that of the SAM made from 100% 11A) was taken to be proportional to the surface mole fraction of the acid-terminated thiolate, X_{11A}(surface), as shown in Figure 1. The X_{11A}(surface) versus X_{11A}(solution) curve is not linear but is closer to the linear relationship than that reported by Kakiuchi et al.[20] We believe the difference is due to the removal of weakly adsorbed acid bilayer in the present study but not in that of Kakiuchi et al. On surface 11A/10C or 11A/12C, the two thiol molecules should be completely miscible in the SAM[20] and the mole fraction of the acid-terminated thiolate in each mixed SAM was X_{11A}(surface) $\sim$ 0.026 based on the calibration in Figure 1.

For HPG growth, we first deprotonated each Au/SAM surface by dipping it in $KOCH_3/CH_3OH$ (1:20 w/w) for 10 s, rinsing the surface with methanol, and then drying it under a N_2 stream. We then immersed the deprotonated surface in dry glycidol at 40 °C for HPG growth, as illustrated by the reaction scheme in Figure 2. After a fixed growth time, we remove the surface from glycidol, rinse it with methanol, and then dry it under a N_2 steam. We characterized the surface by AFM imaging (Digital Instruments) in the tapping mode under ambient conditions using a silicon tip (20 nm radius of curvature). For each growth time, we used three independent samples and carried out AFM measurements on three separate spots on each sample. Each reported data point for film thickness was an average of nine measurements, with the error bar (standard deviation) obtained from statistical analysis.

We used AFM images to determine the average volume per unit area (i.e., average thickness) of adsorbed HPG polymer molecules based on digital integration of each island (individual HPG molecule) with a threshold slightly above the very flat SAM background. This was feasible because (1) the substrate surface was flat (rms roughness $\leq$ 0.5 nm), (2) the dimensions of adsorbed HPG molecules were relatively large (10^{1-2} nm), and (3) the adsorbed HPG molecules were well separated from each other. As confirmation of the estimated thickness from AFM, we also measured film thickness by spectroscopic ellipsometry (Woollam M88). Here, each data point on film thickness was an average from three independent samples.

Results and Discussions

The AFM images in Figure 2 show surfaces following HPG growth for 5 min at 40 °C on SAMs of (a) decanethiol (10C), (b) mercaptoundecanoic acid (11A), and (c) a mixed SAM from a solution of [11A]/[10C] = 1:20, corresponding to X_{11A}(surface) = 0.026. HPG molecules do not grow on the hydrophobic $-CH_3$-terminated 10C SAM, but they do grow readily on the acid-terminated 11A SAM surface to form close-packed islands with the film thickness increasing with growth time (data not shown). As expected, the density of HPG molecules on the 2.6% 11A and 97.4% 10C mixed SAM surface is much lower than that on the 100% 11A surface. A zoom-in image (Figure 2d) of growth on the mixed SAM surface clearly reveals well-separated, individual HPG molecules with diameter and height ranging from a few nanometers to a few tens of nanometers.

We demonstrate the spontaneous desorption of HPG molecules from the systematic fluctuations in the size and coverage of HPG molecules as a function of growth time, as shown by tapping-mode AFM images in Figure 3 for HPG growth on a mixed SAM surface of 2.6% 11A and 97.4% 10C. This is most evident in the image for 7.5 min of growth time when both the size and the coverage of HPG molecules are significantly higher than those at either shorter or longer growth times. For a total growth time of 20 min, the amount of HPG molecules on the surface is negligible. This fluctuation is quantified in panel a of Figure 3, which shows average film thickness as a function of growth time from two independent measurements: AFM (open circles and solid line) and ellipsometry (open triangles and dashed line). In AFM, the average thickness is the total volume of HPG molecules in the unit surface area. Within experimental uncertainty, the two independent measurements are in excellent agreement. The amount of HPG does not increase monotonically with time; there are at least two peaks at 7.5 and 15 min. To establish the origin of this fluctuation, we present histogram analysis of the size (volume) of HPG molecules on the surfaces. Panel b in Figure 3 compares the histograms corresponding to the maximum (7.5 min) and a minimum (12.5 min) and a "shoulder" on the growth curve. There is a preferential enhancement at 7.5 min in the population of HPG molecules with sizes larger than $\sim$30 000 nm^3. In particular, molecules with sizes $\geq$100 000 nm^3, present on the surface with 7.5 min of growth time, are absent at either 3 or 12.5 min. Also shown in panel b of Figure 3 is the histogram for 20 min of growth; for this growth time, only a small number of HPG molecules with sizes $<$20 000 nm^3 are left on the surface. We conclude that HPG molecules growing to certain critical sizes prefer to desorb from the surface; the exact critical size in each case may vary depending on the local surface

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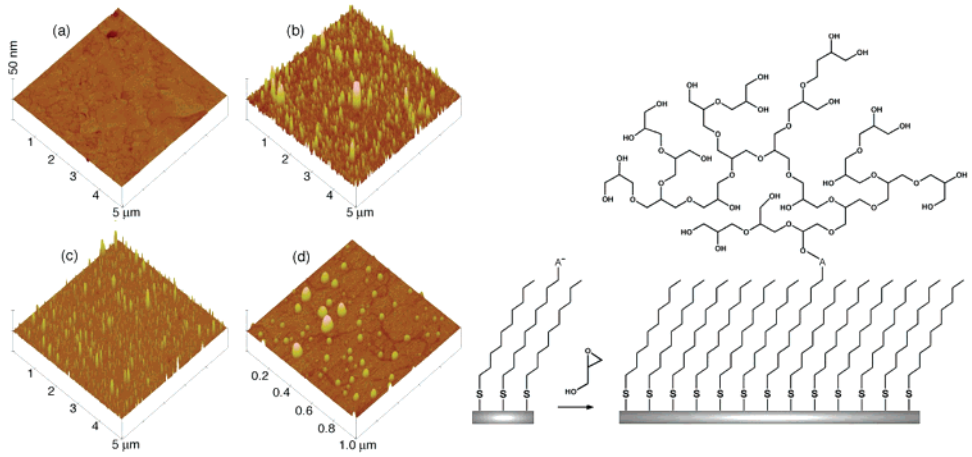

Figure 2. Tapping-mode AFM images of HPG molecules grown for 5 min at 40 °C on a SAM/Au surfaces obtained from (a) 100% decanethiol, HS−$(CH_2)_9CH_3$ (10C), (b) 100% mercaptoundecanoic acid, HS−$(CH_2)_{10}$COOH (11A), and (c) mixed thiols consisting of 2.6% mercaptoundecanoic acid and 97.4% decanethiol. The sizes of images (a−c) are 5 μm × 5 μm × 50 nm. Image d is a zoom-in (1 μm × 1 μm × 50 nm) of image c. The right side shows schematically the surface-initiated growth of HPG on a mixed SAM/Au surface. A^- represents a COO^- group for HPG initiation and growth.

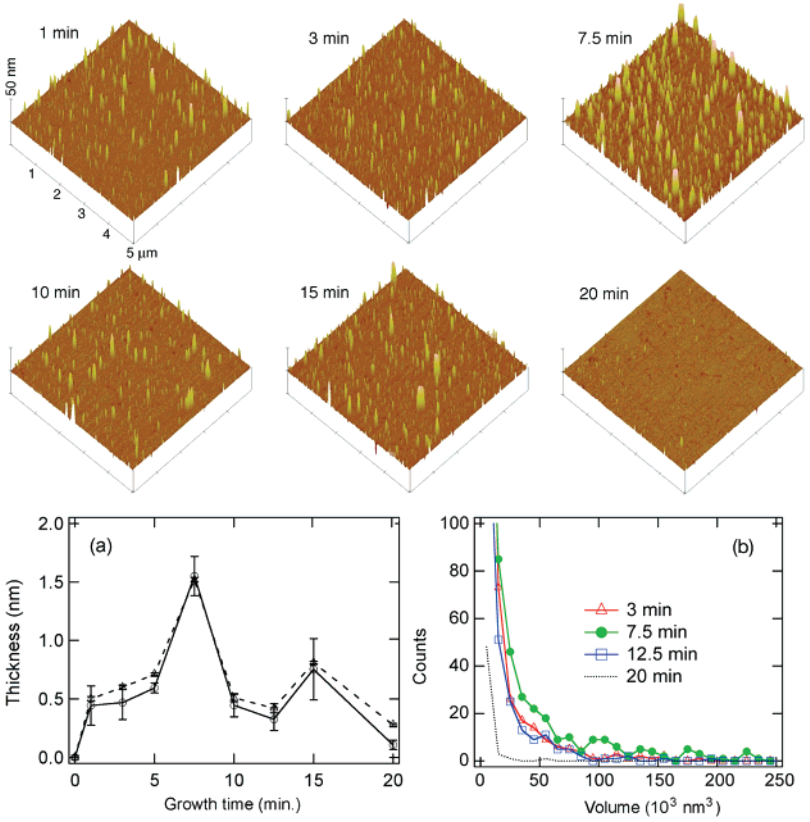

Figure 3. Tapping-mode AFM images (5 μm × 5 μm × 60 nm) taken for different growth times (1−20 min) at 40 °C of HPG on a SAM of 2.6% −S−$(CH_2)_{10}$COOH in a matrix of −S−$(CH_2)_9CH_3$. Note the *z*-scale is magnified to show individual HPG molecules. Panel a: amount of HPG (average thickness) as a function of growth time from AFM (circles and solid line) and ellipsometry (triangles and dashed line). Each data point from AFM was the average of nine independent measurements on three samples, with the standard deviation shown as error bars. Each data point from ellipsometry was averaged over three samples. Panel b: histogram analysis of the size (cubic nanometers) of HPG molecules on the surface for three growth times. The data sets were from individual images.

environment. These growth−desorption and regrowth−desorption cycles are responsible for the fluctuation in the population and size of HPG molecules. Note that these kinds of growth−desorption cycles do not continue indefinitely due to the gradual loss of anionic sites and the termination of polymerization reactions.

A surface-tethered macromolecule interacts with the local environment through noncovalent interactions, including van der Waals, electrostatic, and hydrogen bonding. The latter is the dominant interaction between a hydrophilic HPG molecule and the hydrophilic solvent (glycidol). Consider a typical hydrogen bond energy of 2−10 kcal/mol and a typical covalent bond energy of ∼200 kcal/mol. As an HPG molecule initiates on COO^- sites and grows larger on the mixed SAM surface, it inevitably encounters more unfavorable interactions with the hydrophobic matrix. The formation of 20−100 new hydrogen bonds may compensate for the loss of one covalent bond, a condition which can be easily satisfied when the HPG molecule

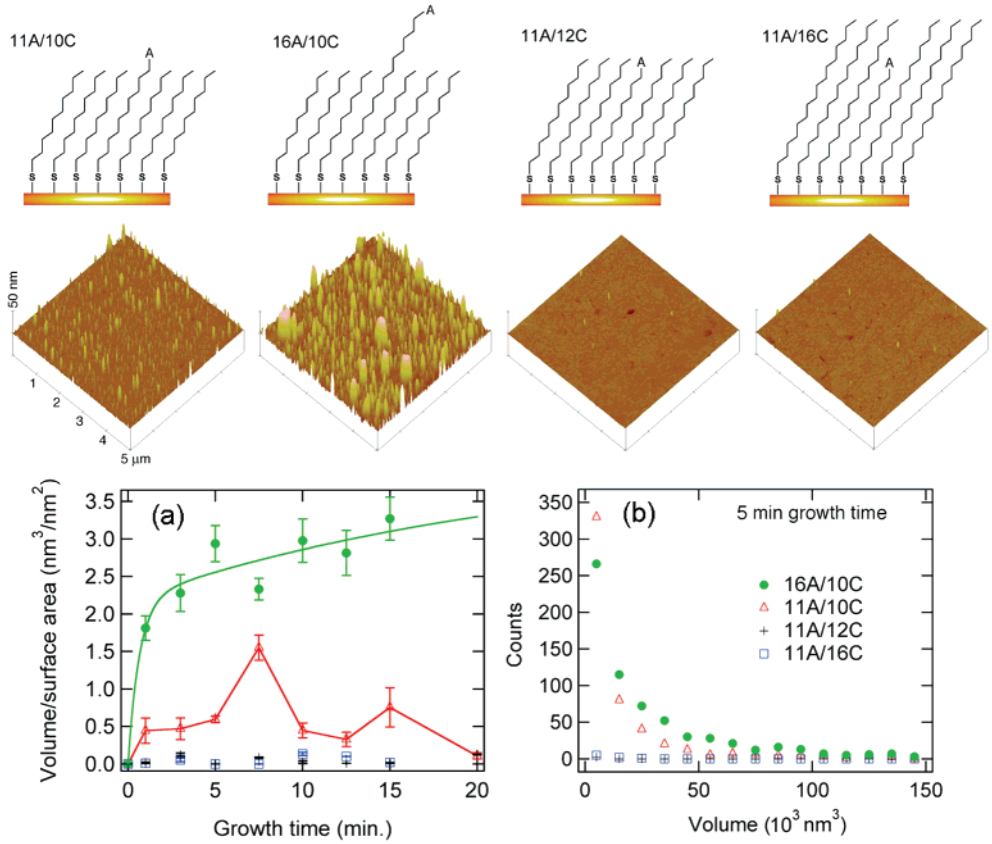

Figure 4. Top: schematic illustrations of the mixed SAM surfaces from solutions containing 5% COOH (A)-terminated alkanethiols and 95% CH_3-terminated alkanethiols. Middle: tapping-mode AFM images obtained after 5 min of growth of HPG on the four surfaces illustrated in the top panel. Panel a: amount of HPG (volume per unit surface area) as a function of growth time on four mixed SAM surfaces. Panel b: histogram analysis of the size (cubic nanometers) of HPG molecules on the four surfaces for 5 min of growth time. Symbols: 16A/10C (green circles), 11A/10C (red triangles), 11A/12C (black crosses), and 11A/16C (blue squares).

reaches a critical size. Breaking away from the surface also allows easier formation of new C−O bonds due to the continuing polymerization reaction and growth of each HPG molecule. In comparison to an end-tethered linear polymer which can adopt various conformations, the dentridic HPG molecule is much more rigid. As grown on the surface, an HPG molecule is conformationally restricted to half space and is under stress. Thus, breaking away from the surface is also expected to be favored entropically, because of the increased conformational freedom for an HPG molecule in the solution phase. This spontaneous bond-breaking event is in contrast to a recent demonstration involving the strong interaction between a surface and a macromolecule with long side chains that results in significant conformational deformation and the rupture of covalent bonds within the polymer backbone.[25] The HPG desorption mechanism bears resemblance to what has long been proposed in cell biology that ligand−receptor interaction may uproot a receptor protein from the cell membrane.[26]

To verify the proposed nanotumbleweed mechanism, we systematically vary the local chemical environment to control the interaction energy between a tethered HPG molecule and the surface. In particular, we vary the relative height of COOH initiation sites with respect to the surrounding CH_3 matrix in SAMs obtained from mixed thiol solutions with 1:20 acid-terminated to alkanethiol ratios, as illustrated at the top of Figure 4. On surface 11A/10C or 11A/12C, the two thiol molecules should be completely miscible in the SAM,[20] and the mole fraction of the acid-terminated thiolate in each mixed SAM should be $X_{11A}(\text{surface}) \sim 0.026$ based on the calibration in Figure 1. On surface 16A/10C or 11A/16C, the mole fraction of the acid-terminated thiolate in the mixed SAM is expected to be different from the calibration value, but this does not change the qualitative conclusions below. Here surface 11A/10 consists of COOH sites slightly (~2 Å) higher topographically than the CH_3 matrix. On surface 16A/10C, the COOH sites are more flexible and can extend ~8 Å away from the CH_3 matrix. On surface 11A/12C, the COOH sites are ~1−2 Å lower than the CH_3 matrix. On surface 11A/16C, the COOH sites are ~6−8 Å lower than the CH_3 matrix. AFM images in Figure 4 for 5 min of growth show that the sizes and amounts of HPG molecules on the 16A/10C surface are both substantially higher than those on the 11A/10C surface, whereas negligible growth is seen on either 11A/12C or 11A/16C. The differences are illustrated quantitatively by histogram analysis in the lower right panel of Figure 4. The lower left panel plots the average film thickness as a function of HPG growth time for the four surfaces. Whereas the average thickness fluctuates with growth time on the 11A/10C surface, it increases monotonically with growth time on the 16A/10C surface to reach a value of ~3 nm for ≥15 min. For comparison, there is negligible HPG growth on the 11A/12C or the 11A/16C surface.

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Although the above experiments establish the nanotumbleweed mechanism, we do not know which bond actually breaks. AFM experiments showed that the force needed to break a single thiolate molecule from the Au surface is 1.4−1.5 nN,[2,27] which is the same as that for the breaking of a single Au−Au bond.[28] The force needed to pull out a single thiolate from a SAM has not been measured, but we expect this to be >1.5 nN due to additional van der Waals interaction with surrounding molecules within the assembly. For comparison, breaking a single C−Si bond requires 2.0 nN.[2] Thus, we expect the force necessary to break a thiolate bond to be of similar magnitude to those for the breaking of a single C−C or C−O bond within the HPG backbone or at the SAM−HPG interface. Unfortunately, because the density of HPG molecules grown on the SAM surface is many orders of magnitude lower than that of thiolates, it is not possible to observe the loss of thiolates after HPG growth and desorption. As future tests of the proposed mechanism, one may intentionally incorporate weak points into the thiol molecules and correlate the size distribution for HPG desorption with the bond strength of the weak point. Another possibility is to use solvents with different solubility for HPG and correlate solubility with HPG desorption.

Conclusions

We demonstrate that a hydrophilic polymer, HPG, covalently tethered to minority surface sites embedded in a hydrophobic SAM can spontaneously desorb from the surface due to unfavorable interaction with the local surface chemical environment. The finding presented here suggests that the traditional view[6−8] on the noncovalent interaction of surface-tethered macromolecules with the solvent and with the local surface environment is incomplete. In addition to conformational changes, such noncovalent interaction can lead to the breaking of covalent bonds. This mechanism has significant implications for the understanding, design, and synthesis of surface-tethered macromolecules, as well as their applications, such as biosensing,[29] colloidal stabilization,[30] lubrication/tribology,[4] and biocompatibility of solid materials.[31]

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