

Visualization of Mechanochemically-Assisted Degrafting of Surface-Tethered Poly(Acrylic Acid) Brushes

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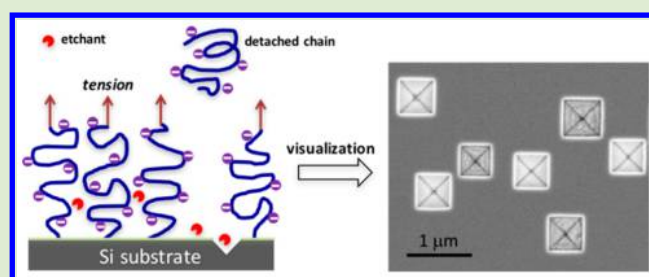
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Supporting Information

ABSTRACT: We report visualization of mechanochemically assisted degrafting of surface-tethered poly(acrylic acid) (PAA) brushes in a basic aqueous buffer at nanometer to micrometer length scale by monitoring changes in local etching of silicon substrates. PAA brushes were prepared by surface-initiated atom transfer radical polymerization and incubated in 0.1 M ethanolamine buffer (pH 9.0) with 0.5 M NaCl. Morphological changes of the underlying substrates were monitored by scanning electron microscopy and atomic force microscopy. The appearance of regular-shaped pits indicated etching of the substrate, and both their number and size grew with increasing

incubation time. We compared the etching behaviors for PAA, poly(methyl methacrylate) (PMMA), and poly(poly(ethylene glycol) methacrylate) (PPEGMA) brushes grafted on silicon substrates. After incubation for 7 days, the substrate of PMMA brush remained intact. In PAA brush systems, we detected the formation of a few large pits whose size grew in time. Many pits showed up on the substrate of PPEGMA brush but with substantially smaller size compared to PAA. Our findings suggest that hydrophobicity and stability of the grafted polymers play an important role in the morphological changes of the underlying silicon substrates under given incubation conditions.



Long-term stability of surface-grafted polymer brushes is important for many of their applications, for example, tuning surface properties, antifouling coatings, enabling cell culture, and so on.^{1–3} The longevity of systems featuring polymers grafted chemically to the underlying surface had not been regularly scrutinized. Recent reports pointed out that the stability of polymer brushes may get compromised under certain conditions (e.g., pH and ionic strength), resulting in degrafting and removal of polymer chains from the substrates.^{4,5} Examples include degrafting of poly(poly(ethylene glycol) methacrylate) (PPEGMA) brushes in cell culture media,^{6,7} surface-tethered hyperbranched polyglycidol during polymerization of glycidol,⁸ polyacrylamide brushes in methanol with a strong base,⁹ and polyelectrolyte (i.e., charged polymer) brushes in buffer solutions.^{10–19} The instability occurs more often in polyelectrolyte brushes than neutral polymer brushes. This is because in polyelectrolyte brushes additional tension can be generated along the grafted chain backbones resulting from strong swelling due to electrostatic repulsion and osmotic stress, which may make the weak bonds at the bottom-most portion of the grafted chains close to the substrate, where the tension is ultimately focused,²⁰ mechanochemically activated for cleavage or hydrolysis.

Previous studies exploring the instability of surface-grafted polyelectrolyte brushes focused primarily on thickness changes

of the brush, while little attention was paid to the morphological alternations in the brush layer or the substrate. In this Letter, we report visualization of local etching of silicon substrate that reflects mechanochemically assisted degrafting of surface-grafted poly(acrylic acid) (PAA) brushes in basic buffer solutions at nanometer to micrometer length scale.

Silicon wafers commonly used as substrates for polymer brushes prepared by “grafting from” method feature a thin layer (ca. 1.5 nm) of silica (SiO_x) to which the surface initiator layer is anchored and polymer grafts are grown from. Silicon substrates can be etched in basic solutions and silica can be used as masking layer for silicon etching for certain applications; however, silica can be dissolved slowly in common buffers and even in relatively inert solutions with neutral pH.²¹ We reported previously that PAA brushes are unstable in ethanolamine buffer (pH 9.0) accompanied by detachment of PAA chains, which could lead to the formation of local cavities (or channels) in the densely grafted PAA brush layer.¹⁹ Therefore, we hypothesize that effective etchants may penetrate through the brush layer at the cavities faster than elsewhere, leading to local etching of the underlying silicon substrate

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(including the top silica layer), as shown in Figure 1. The etched substrate could also offer visual evidence for detecting mechanochemically assisted degrafting of PAA chains.

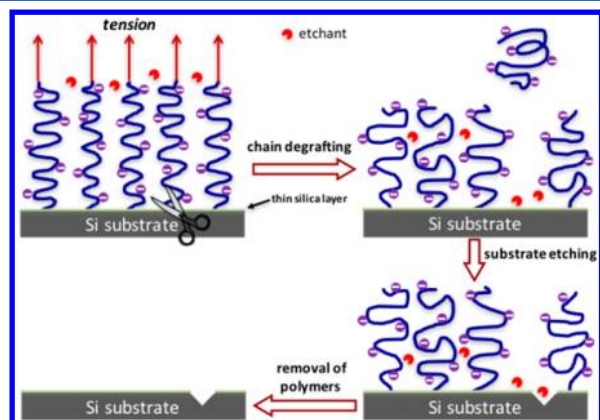


Figure 1. Swelling-induced tension due to osmotic stress and electrostatic repulsion results in local degrafting of PAA chains from silicon substrate in basic buffers. This enables penetration of etchants through the brush layer to the substrate surface and subsequent etching of the underlying silicon substrate.

To prove our hypothesis, we prepared PAA brushes grafted from Si [100] substrate by surface-initiated atom transfer radical polymerization (SI-ATRP) with initial thickness of 73 nm and grafting density of ~ 0.5 chains/nm²,²² and incubated them in 0.1 M ethanolamine buffer (pH 9.0) with 0.5 M NaCl at room temperature. To monitor morphological changes of both the PAA brushes and the underlying substrates during incubation, we removed the grafted PAA chains using piranha solution and imaged the substrates with scanning electron microscopy (SEM) as well as atomic force microscopy (AFM). As shown in Figure 2, at early stages (e.g., after 1 day of incubation in the buffer solution) the PAA brush surface was smooth and the substrate remained intact. Small cavities (indicated by red arrows) started to show up in the brush layer

and pits on the substrate after incubation for 4 days, indicating the degrafting of local chains and the beginning of silicon substrate etching. After 7 days of incubation, the PAA brush layer was covered with well-defined shapes featuring square pits that were etched into the silicon substrate. Figure 2 also demonstrates that both the number and the size of the pits grew with increasing incubation time. We attempted to track the thickness change of the PAA brushes by ellipsometry, but we were only able to measure the thickness changes at short incubation times (up to 16 h, as shown in Figure S1 in Supporting Information). We could detect clearly the typical trend of PAA brush thickness change in basic buffer solutions: it increased initially due to PAA brush swelling and decreased afterward due to mechanochemically assisted degrafting from the substrate. At long incubation times, the brushes became filled with salts that were difficult to be washed off, and the brush surfaces became very rough as the etching proceeded, which made it impossible to measure their thicknesses accurately.

Since the pits were etched into the silicon substrates, we speculated that their 3D structure should be related to the orientation of silicon crystal planes. For Si [100] substrates, the etched pits feature inverted square pyramid-shaped due to different etching rates of different crystal planes. To reveal the structure of the pits, we took high-resolution images of the pits by AFM (Figure S2 in Supporting Information) and SEM after removing the remaining PAA brushes. As shown in Figure 3,

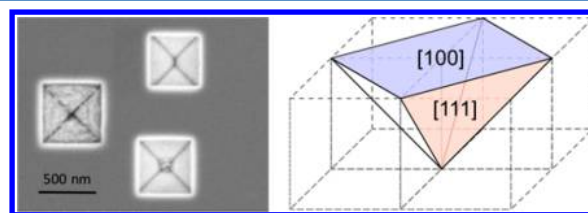


Figure 3. High-resolution SEM micrograph (left) and schematic (right) of the etched pits on Si [100] substrate. Scale bar = 500 nm.

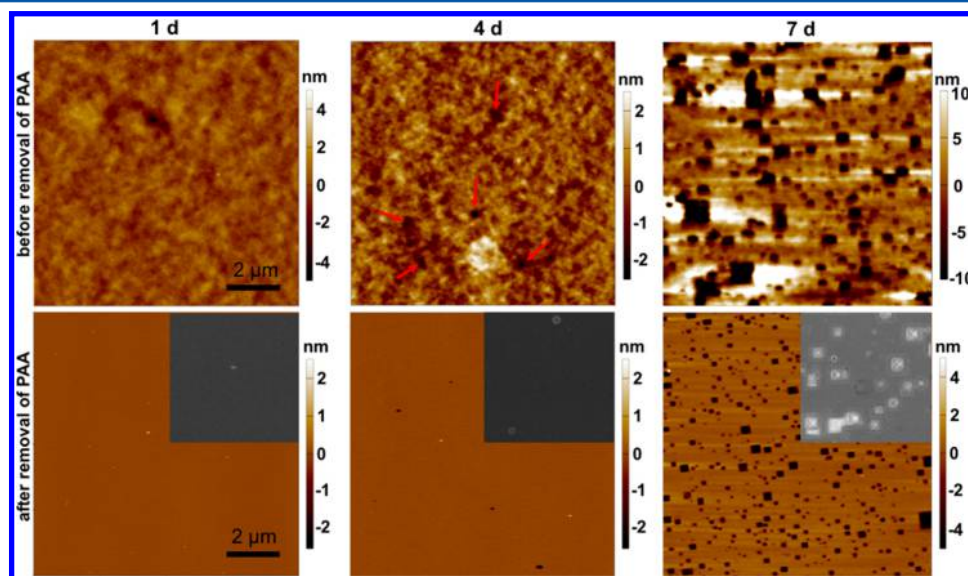


Figure 2. PAA brushes after incubation in 0.1 M ethanolamine buffer (pH 9.0) with 0.5 M NaCl for various days. The AFM images were taken before and after removal of grafted PAA chains using piranha solution. Scale bar = 2 μ m. Insets: corresponding SEM micrographs with size of 5 μ m \times 5 μ m.

the etched pits have four side-walls (defined by the [111] planes that have an angle of 54.7° with the [100] plane)^{23,24} either merging at one point or not, indicating that they are inverted square pyramids or truncated inverted square pyramids, which agrees with our speculation. In the case of Si [111] substrates, most of the etched structures displayed well-defined shapes with hexagonal pits (Figure S3 in Supporting Information). This provides substantial evidence for our earlier hypothesis that the protrusions seen inside the substrates are due to the penetration of the etchant, which is facilitated by polymer degrafting that creates accessible areas on the substrate that will be etched away.

To assess whether the observed etching behavior is correlated with degrafting of the PAA chains, we prepared stable hydrophobic poly(methyl methacrylate) (PMMA) and hydrophilic poly(poly(ethylene glycol) methacrylate) (PPEGMA) brushes grafted on Si [100] substrates by SI-ATRP and incubated them in 0.1 M ethanolamine buffers (pH 9.0) with 0.5 M NaCl for 7 days at room temperature. We also exposed bare Si [100] substrates without any grafts to the same etchants and used them as a control. PPEGMA brush may be unstable under certain conditions,^{6,7} but it is much more stable than PAA brush under the same conditions of our experiment (Figure S4 in Supporting Information). Figure 4 shows SEM

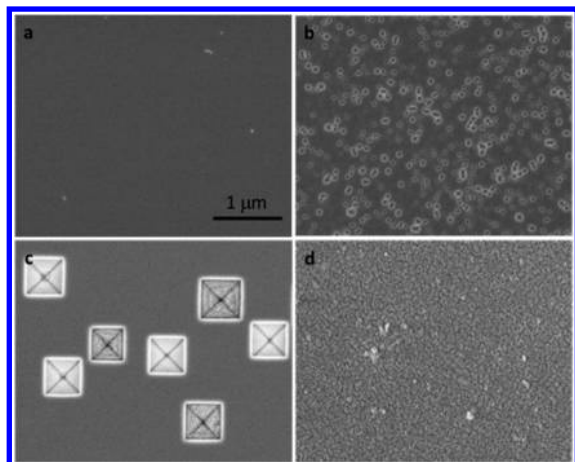


Figure 4. Various polymer brushes grafted on Si [100] substrates were incubated in 0.1 M ethanolamine buffers (pH 9.0) with 0.5 M NaCl for 7 days. SEM images of the substrates were taken after removal of polymer grafts by piranha solution: (a) PMMA brush with initial thickness of 60 nm; (b) PPEGMA brush with initial thickness of 34 nm; (c) PAA brush with initial thickness of 73 nm; (d) bare Si substrate without any grafts as a control. Scale bar = 1 μm .

micrographs of the substrates after removal of polymer grafts by piranha solution. The Si substrate of PMMA brush remained flat and smooth after incubation (Figure 4a). Comparing Figure 4b and c, many etched pits with substantially smaller sizes (~ 10 nm) showed up on the substrate of PPEGMA brush than on the PAA brush substrate. As shown in Figure 4d, the bare Si substrate was etched “homogeneously”, and its surface features an “orange peel” morphology, which is typically seen in homogeneous etching.

We propose a mechanism illustrated in Figure 5 to interpret the experimental observations and results. Hydrophobicity of the surface-tethered polymer brush plays an important role. For stable and hydrophobic PMMA brush, the grafted chains collapse in aqueous media (e.g., the buffer used for incubation

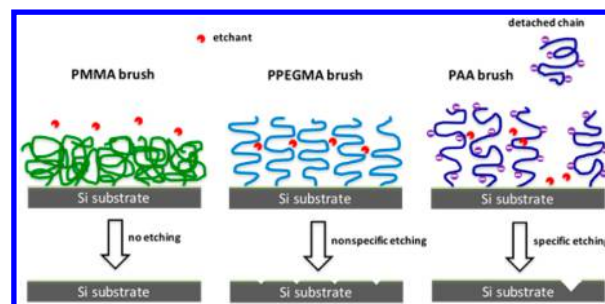


Figure 5. Schematic illustration of the etching behaviors for PMMA, PPEGMA, and PAA brushes grafted on silicon substrates.

in this work) and form a dense shielding layer that prevents the etchants from penetrating through itself and etching the underlying silicon substrate. Stable hydrophilic PPEGMA brush swells in the aqueous buffer solution; the etchants may penetrate the polymer layer slowly to reach the substrate surface and then start etching. Multiple structural defects in surface-grafted polymer brush are present,^{25,26} and etching is likely more pronounced at the defect sites, resulting in the formation of many small etched pits. Instability of surface-tethered polymer brush may promote the etching of the underlying silicon substrate. In aqueous incubation buffer of pH 9.0, the densely grafted PAA chains become charged, resulting in additional tension along the swollen and stressed chains, which leads to mechanochemical degrafting of PAA chains. This process creates channels at the local degrafting areas, which enables etchants to reach the substrate surface fast with relatively high concentrations, causing etching at the degrafted areas and the subsequent formation of isolated large pits. Note that, once the PAA chains are degrafted locally from the substrate, the tension in the surrounding chains that remain tethered will be partially released due to reduced crowdedness. This process slows down (or even inhibits) further mechanochemically assisted degrafting of the surrounding remaining chains. As shown in Figure 2, the size of the etched pits grows with time, which suggests that these surrounding remaining chains are likely removed together with the attached substrate material, which is etched away as the etching process takes place. Etching of the substrate could thus promote further degrafting of PAA chains. Without any polymer grafts, the surface of bare silicon substrate is completely exposed to the buffer solution, and it is homogeneously etched, resulting in the “orange peel” like morphology.

To summarize, we have studied the morphological changes of both PAA brush surface and the underlying silicon [100] substrate during incubation in basic buffer solutions. We have shown that the substrate was etched slowly with time, leading to the formation of inverted square pyramid-shaped pits. Both the number and the size of the pits grew with increasing incubation time. This particular shape of the etched pits is related to the orientation of silicon crystal planes. We also compared the etching behaviors for PAA, PMMA, and PPEGMA brushes grafted on silicon substrates during incubation process. The results suggest that the morphological change of the polymer brush substrate is correlated with hydrophobicity and stability of the grafted polymers. For stable and hydrophobic PMMA brush, densely grafted PMMA chains collapsed in the aqueous buffer and formed a thick shielding layer protecting the underlying substrate from etching. For stable and hydrophilic PPEGMA brush, etchants could

penetrate through the swollen polymer layer (especially at defect sites in the layer) and reach the substrate surface slowly, resulting in the formation of a number of small-sized etched pits on the substrate. For hydrophilic PAA brush, the PAA chains were mechanochemically unstable due to osmotic stress and electrostatic repulsion accompanied by detachment of local chains, which created channels or cavities in the dense polymer layer. Therefore, the etchants were able to arrive at the substrate surface through these channels fast with high local concentrations, leading to specific etching at degrafting sites with large regular-shaped pits that could be visual evidence for mechanochemically assisted degrafting. Degrafting behavior of the tethered polymer brushes as reflected by etching of the underlying Si substrates could also be applied to other brush-substrate systems.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: [10.1021/acsmacrolett.8b00241](https://doi.org/10.1021/acsmacrolett.8b00241).

Materials and methods, synthesis and characterization, and supporting figures (PDF).

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Notes

The authors declare no competing financial interest.

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