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Polymer and Synthesis

Direct Polymerization of Polyacrylic Acid on Mica Substrates using ATRP – A Preliminary Study

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Summary: Unprecedented direct polymerization of sodium acrylate (NaA) on mica and silica substrates was undertaken using standard ATRP polymerization conditions at room temperature. The resulting thickness of the poly(sodium acrylate) (PNaA) grafted layer was determined using ellipsometry and AFM.

Polymers brushes covalently attached to surfaces provide the means to modify surface properties of substrates to develop responsive surfaces such as anti-fouling surfaces[1–3] selective permeation membranes[4,5] and self-biolubricating surfaces.[6,7] Polyelectrolytes (PE) brushes represent responsive layers because their degree of ionization can be reversibly varied via pH and ionic strength which results in conformational changes. Therefore, controlled conformational responses to variations in the surrounding environmental conditions result in tuneable interfacial surface properties.[8,9]

The most precise and reliable means for measuring surface interactions between brushes is the Surface Forces Apparatus (SFA). The transparency and atomically smooth surface of cleaved mica make it an ideal substrate for SFA measurements. Direct polymerization of polymer brushes from mica is desired because it affords the means to modulate molecular weight, which in turns influences the brush height and conformation. We recently demonstrated that poly-*tert*-butyl acrylate could be prepared on mica by controlled polymerization using ATRP.[10] Although poly-*tert*-butyl acrylate can be converted into polyacrylic acid by hydrolyzing the *tert*-butyl group[11], direct polymerization of acrylic acid involves fewer synthetic steps, and more particularly, the hydrolysis with strong acids is eliminated. This reduces the possibility of unwanted polymer cleavage from the substrate. Unfortunately, ATRP of acrylic acid is not possible as a result of reduced catalyst reactivity with the carboxylic acid.[12] Conversely, sodium acrylate (NaA) can be polymerized by ATRP.[13] Although NaA is possible to polymerize on silica substrates, its direct polymerization affording poly(-sodium acrylic acid) (PNaA) on mica has not been demonstrated. Successful polymerization of NaA on mica is important for investigating the changes in surface properties and surface forces induced by changes in ionic strength and pH. Herein, we present our preliminary results for the polymerization of NaA on mica as a proof of concept for direct synthesis of charged polymer brushes on mica in addition to demonstrating that absolute brush height measurements by AFM is possible.

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Results and Discussion

Polymerization of NaA was done using a previously reported ATRP initiator (**1**) that was immobilized on mica, as illustrated in Figure 1, with a controlled surface density

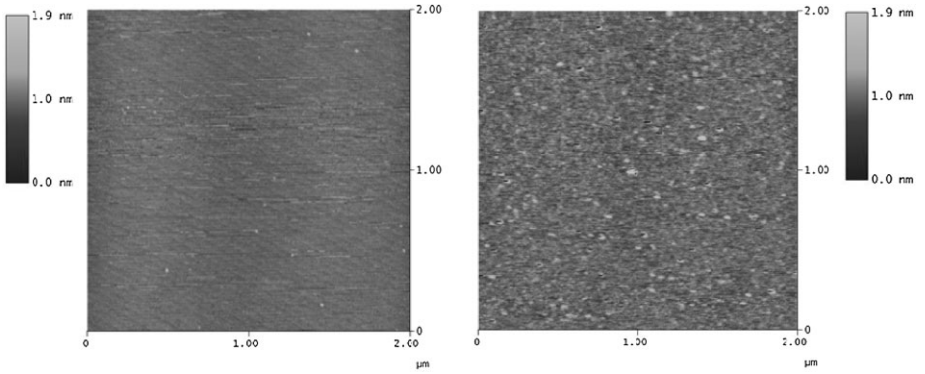
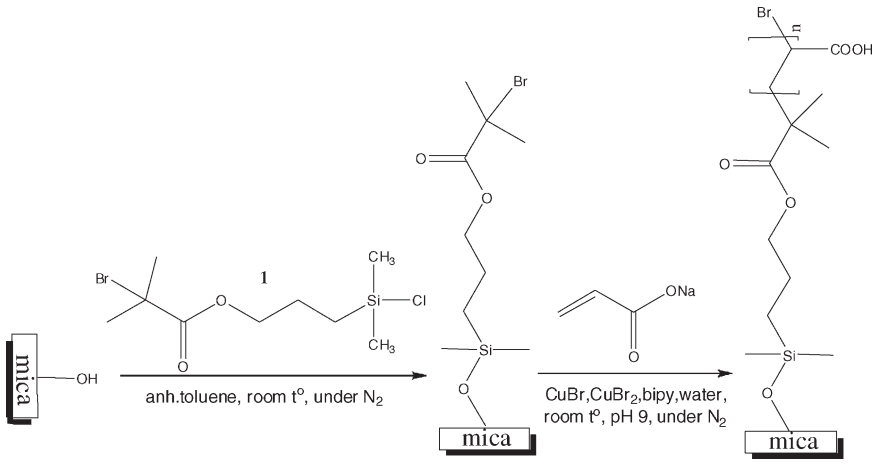


Figure 1.
AFM images of freshly cleaved mica and mica covered with initiator layer.

as previously reported.[14] Mica sheets were first cleaved. A mica strip was then laid across a portion of the freshly cleaved mica to form a mask. The exposed mica was subsequently activated by H_2O/argon plasma using a Plasma Prep II from SPI Supplies to create hydroxyl groups[15]. The initiator was chemically attached to these OH groups using self-adsorption from solution[14].

The polymerization of PNaA was done in the following manner: NaA was added to a fixed volume of water and then left to stir at room temperature until it was completely dissolved. The pH of the monomer solution was adjusted to that previously reported.[16] Bipyridine, CuBr and $CuBr_2$ were mixed in a round-bottomed flask and then deoxygenated under vacuum and backfilled with argon three times. The monomer solution was also deoxygenated under argon for 30 minutes after which it was transferred to the flask containing the copper-ligand mixture followed by stirring for 3 hours, until the solution was homogeneous. A clean initiator-functionalized mica substrate was placed in a flame-dried Schlenk flask under a stream of argon followed by deoxygenation under vacuum and then backfilled with argon three times. The above-described polymerization solution was transferred into the Schlenk flask at



Scheme 1.
Schematic of immobilization of **1** and direct polymerization of NaA on mica.

room temperature under a stream of argon followed by stirring. After 70 minutes, the surfaces were removed, rinsed with water, absolute ethanol, extracted and then washed three times for two hours with Milli Q, rinsed again with absolute ethanol and Milli Q water and then dried under nitrogen. A typical polymerization was done with the following: water (5 mL, 280 mmol), NaA (2.79 g, 30 mmol), bipy (155 mg, 0.99 mmol, CuBr (57 mg, 0.40 mmol), and $CuBr_2$ (18 mg, 0.08 mmol). AFM imaging and polymer film thickness measurements were carried out as previously reported.[10]

We initially investigated the smoothness of the immobilized **1** on mica. As seen in Figure 1, the root mean square (rms) value measured by AFM confirms that a homogeneous surface coverage on mica is possible. A smooth and homogenous initiator layer on the substrate is desired because the roughness of this layer can ultimately affect the polymer layer smoothness. A smooth initiator layer will ensure a smooth polymer layer (*vide infra*).

Direct ATRP of NaA on silica substrates was done as a control test and for comparing with NaA polymerized directly from mica. Comparisons of the resulting grafted polymer layers between mica and silica were done using an AFM step-height method. The surface topology, surface roughness and absolute thickness of the polymer layer were measured. The polymerization of NaA was done on mica with **1** in order to confirm that ATRP using this monomer was possible. The topology of the resulting polymer layer on mica compared to that of virgin mica is illustrated in Figure 2. From this figure, the smoothness of the polymer layer is evident. Moreover, the smooth polymer layer makes for easy determination of the absolute polymer thickness by comparing the step-height difference between the virgin mica and the polymer regions. The calculated thickness of the pNaA layer using the step-height method was 94.5 nm. The direct polymerization using NaA is advantageous because the polymerization can be done at room temperature. Moreover, by eliminating the hydrolysis step required with poly-*tert*-butyl acrylate,[11] for instance, there is no risk of degrafting the polymer from the substrate. Nonetheless, the step-height measurements confirm that directly polymerization at room temperature of NaA on mica is possible.

To confirm that the thickness of the polymer layer measured by step-height for mica was not an isolated phenomenon, we repeated the polymerization several times. Polymer layers on the order of 90 nm in thickness were consistently obtained and varied only as a function of polymerization time, consistent with controlled polymerization kinetics. The direct polymerization of NaA on a silica substrate was also investigated using similar polymerization conditions as with mica. The silicon wafer on which PNaA was obtained was investi-

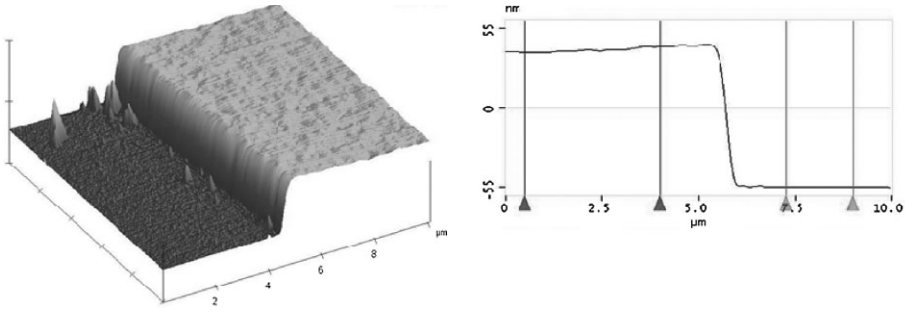
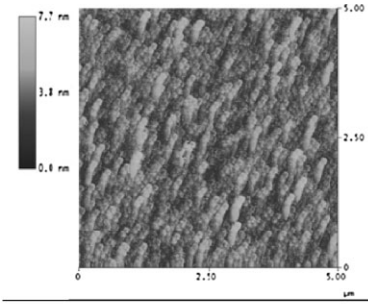


Figure 2.
AFM image showing the step-height difference between the polymer layer of PNaA and the pristine mica.



Roughness (5x5μm) obtained by AFM	0.1 nm
Thickness measured by ellipsometry	57.3 nm

Figure 3.
AFM topographical micrograph of PNaA polymerized on a silicon wafer.

gated by ellipsometry. The resulting polymer layer thickness was 57.3 nm (Figure 3, Table 1). Although comparable thickness were obtained for both PBA and PNaA (Table 1), the direct polymerization of the latter is advantageous because the polymerization is much faster and can be done at room temperature. Unwanted polymer degrafting possible by thermal cleavage is therefore minimized with the polymerization of NaA.

In conclusion, we demonstrated that NaA can be directly polymerized on activated mica using an ATRP initiator covalently linked to the substrate. The polymerization of NaA on mica resulted in thick PNaA films within 70 minutes of 95 nm in thickness. The absolute thickness of the polymer layer was measured by AFM using the step-height method. Under similar conditions, the ARTP polymerization of NaA on mica gave consistently thicker films than on silicon wafers. Direct polymerization of NaA on mica provides the means to prepare polymers with tailored degrees of polymerization and for eventual surface-properties studies using SFA.

Table 1.
Comparison of polymer layer thickness of PNaA polymerized via ATRP under similar polymerization conditions on mica and silica wafers.

Substrate	Film thickness, nm	Measurement Technique
Mica	94.5	AFM Step-height
Silicon wafer	57.3	Ellipsometry

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