Communication

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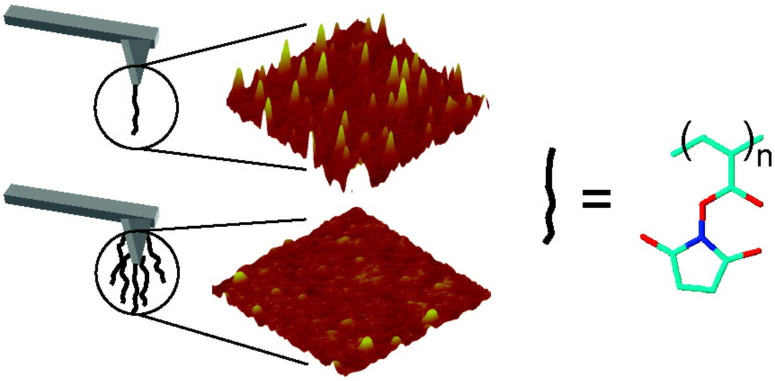

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One-Step Polymer Grafting from Silicon Nitride SPM Probes: From Isolated Chains to Brush Regime

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The design of high-quality long-term stable organic coatings on SPM probes is important both for demanding applications in force spectroscopy[1] and for the development of cantilever-based sensors.[2] Silicon nitride (Si_3N_x) is reputed to be a chemically inert material, and its surface modification remains problematic.[3] To our knowledge, the direct attachment of a polymer onto Si_3N_x substrates or SPM probes has never been reported. Gold-coated probes are widely used for immobilizing polymers, but the gold coating increases the tip diameter, which is a severe drawback for simultaneous topography and recognition imaging.[1] For single molecule recognition applications, one or very few polymeric linkers need to be tightly tethered to the tip apex.[1] As for sensor applications, the tight attachment of polymers in the brush regime has great potential for the development of highly sensitive sensors and efficient actuators.[4]

We recently showed that a polymer end-grafted from SPM probes could be used for single molecule mechanochemistry,[5] but details on the synthesis and characteristics of the polymer could not be given in that report focused on the application. Here we give a detailed account of the functionalization of Si_3N_x tips by a reactive polymer. We show that the synthesis conditions can be adjusted to obtain probes holding all of the requirements either for single molecule force spectroscopy (isolated chain regime) or for sensor capacities and stimuli-responsive behavior (brush regime).

The grafting is based on an electro-initiated polymerization. This very simple one-step "grafting-from" process results in the direct chemisorption of polymer chains onto the surface. We refer the reader to ref 6 for a review of the basic principle and mechanism of the electrografting process. Briefly, the substrate to be grafted is simply dipped into the monomer solution and is polarized in the cathodic range until the so-called "grafting peak" is observed, using a classical three-electrode setup. It is an electro-initiated process that requires the presence of a few charges only for the grafting step.[6] The chain propagation that follows is a chemical process that does not need current to be sustained (as opposed to the more widely used anodic electro-polymerization). The polymer selected for grafting is poly-*N*-succinimidylacrylate (PNSA). The choice is based on the high room temperature reactivity of the activated esters along the backbone, paving the way for further easy coupling reaction with nucleophilic compounds, both in water and in organic solvents.[7]

The monomer (0.05 or 1 M) was dissolved in dry *N*,*N*-dimethylformamide (DMF, a good solvent for PNSA) containing tetraethylammonium perchlorate as conducting salt. We expected to obtain longer chains for a higher monomer concentration, with the rate of chain propagation increasing with the monomer concentration. The cantilever was dipped into this solution and was used as a cathode and selectively polarized on the tip side. Two or three sweeps between the initial potential and the potential at the top of the grafting peak, at 2.1 V, were realized. It is worth mentioning here that the electrical resistivity of Si_3N_x strongly depends on its stoichiometry. Si_3N_4 is known to be an insulating material, but if the stoichiometry deviates from Si_3N_4, conduction can appear.[8] Accordingly, it has been shown in the literature that the surface of Si_3N_x cantilevers strongly deviates from the nominal Si_3N_4 stoichiometry.[9] The voltammograms (see Supporting Information) show a characteristic grafting peak,[7] which means that the current is sufficient for the grafting to be successful. Indeed, only one single electron is sufficient to initiate one polymer chain.[6] The lower current intensity in successive sweeps demonstrates the surface passivation. The grafting density increases in each sweep, with new chains being initiated from still vacant surface sites.

After the electrografting process, the probes were rinsed several times with dry DMF and acetonitrile. Macroscopic Si_3N_x substrates (obtained by CVD) were electrografted using the same conditions. Figure 1 shows AFM topography images obtained on those substrates. Typical structures of an end-grafted polymer are observed. The images suggest that an isolated mushrooms regime, with a distance of about 80 nm between the islands (see Supporting Information), is obtained using a 0.05 M concentration and two sweeps, whereas a brush regime is obtained with a 1 M concentration and three sweeps (the chains overlap and form a continuous phase).

The presence of the polymer on the SPM tips was evidenced by force spectroscopy. Approach−retraction curves were recorded in DMF between the modified probes and a bare silicon substrate. Figure 2a shows the repulsive forces observed during the approach step. This repulsion is typical of an end-grafted polymer under compression in a good solvent.[10] For a monomer concentration of 0.05 M and two sweeps (left panel), the shape of the approach profile is characteristic of an isolated chain regime. The profile does not follow a single exponentially decaying function characteristic of the compression of moderately dense brushes.[11] "Escape transitions", characteristic of the compression of isolated chains,[12] can be distinguished (arrows in left panel). It means that the chains have enough space to escape from the tip−surface region of compression, which is the typical behavior for a very low grafting density.[12] The onset of repulsive forces, at about 20 nm, is close to the Flory radius, R_F, of the polymer coil ($R_F \approx lN^{3/5} = 21$ nm, the degree of polymerization, N, being estimated at 320; see below). The distance between the grafting points is thus higher than the diameter of the coil, that is, higher than 42 nm. No more than one chain is therefore grafted at the tip apex. For a monomer concentration of 1 M and three sweeps (right panel), monotonically

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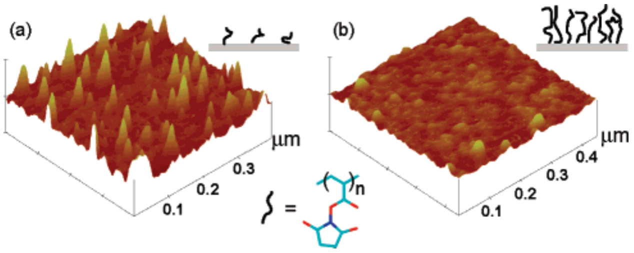

Figure 1. AFM topography images of PNSA brushes on Si_3N_x substrates obtained using the same conditions as those used to modify the SPM probes: (a) two sweeps, 0.05 M monomer solution; (b) three sweeps, 1 M monomer solution (intermittent contact mode in air, max z scale = 5 nm).

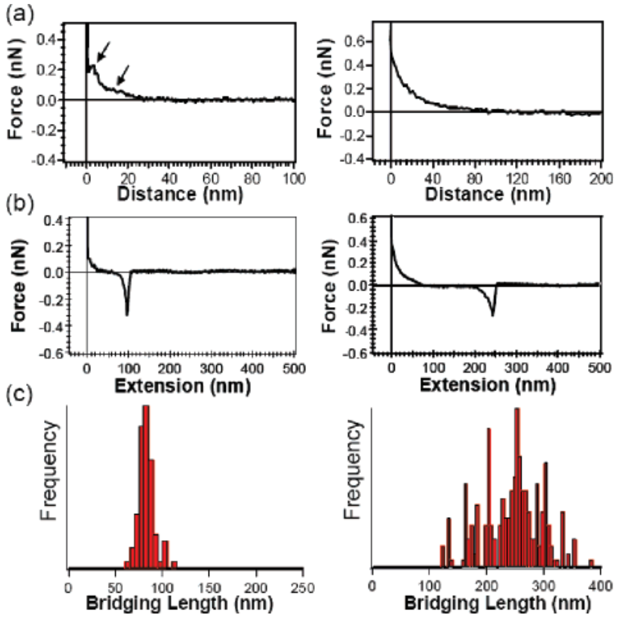

Figure 2. (a) Approach profiles obtained in DMF between a PNSA-modified tip and a bare Si substrate. (b) Bridging interaction obtained in DMF on a NH_2-modified Si substrate and (c) histograms (obtained from three different tips) of the bridging lengths. Left panels: PNSA tip obtained by electrografting from a 0.05 M monomer concentration and two sweeps. Right panels: 1 M monomer concentration and three sweeps.

repulsive forces are observed in the approach curve. They follow an Alexander–de Gennes profile (see the fitting curve in Supporting Information), which means that we are in a moderately dense brush regime.[11] The onset of the repulsive forces (80 nm) corresponds to the thickness of the swollen brush.

For most curves, the retraction profile was similar to the approach one, indicating that no polymer–substrate interaction occurred. To increase the probability of bridging, we investigated the interaction with a NH_2 surface for which it has strong affinity (see ref 5 for a detailed investigation on the nature of this interaction). In about 15% of the retraction curves, bridging interactions were detected (Figure 2b). For the 0.05 M monomer concentration and two sweeps, the very narrow distribution of the bridging lengths, centered on 80 nm, suggests that only one chain is accessible at the tip apex. An average length of 80 nm corresponds to a degree of polymerization of about 320 (=80/0.25, 0.25 nm being the length of one monomer; see ref 13 and Supporting Information for details on the accuracy of this method to estimate the molecular weight of polymers). As a comparison, the histogram of the bridging lengths obtained for the 1 M concentration and three sweeps shows a much broader distribution of lengths, indicating that several chains can be probed in the contact area. The average value is centered on 250 nm. It corresponds to a degree of polymerization of about 1000. The thickness (80 nm) is thus higher than the Flory radius of the coil ($R_F \approx lN^{3/5} = 44$ nm), which means that the chains are significantly stretched out, indicative of a brush regime. Curve fitting by an Alexander–de Gennes profile (see Supporting Information) shows that the distance between the grafting points is about 21 nm, which means that the chains significantly overlap, confirming the brush regime.

In conclusion, we have shown that a reactive polymer can be directly grafted from commercial silicon nitride SPM tips, without any intermediate layer. The conditions can be chosen to achieve an isolated mushroom regime, with only one single chain accessible at the tip apex, or a brush regime. Those modified tips can be used for biomolecular recognition force spectroscopy since the activated esters along the grafted polymer can be post-functionalized by amino derivatives and thus by proteins or other biological compounds.[14]

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Supporting Information Available: Experimental details, curve fitting, and grafting density estimation. This material is available free of charge via the Internet at http://pubs.acs.org.

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