



Supporting Information

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## “Reversibly Cross-linked Surface Grafted Polymer Brushes”

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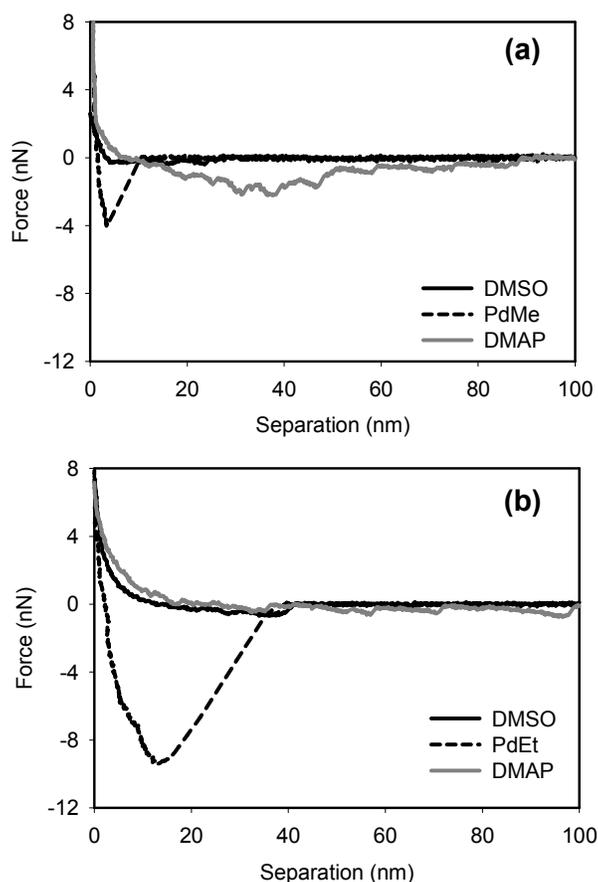
### **Experimental Section**

**Materials.** All compounds were used as received from Aldrich, except for 1,4,8,11-tetramethyl-1,4,8,11-tetraazacyclotetradecane (Me<sub>4</sub>Cyclam, Acros). Cross-linkers PdMe and PdEt<sup>1</sup> and  $\omega$ -mercaptoundecyl bromoisobutyrate<sup>2</sup> were synthesized as reported previously.

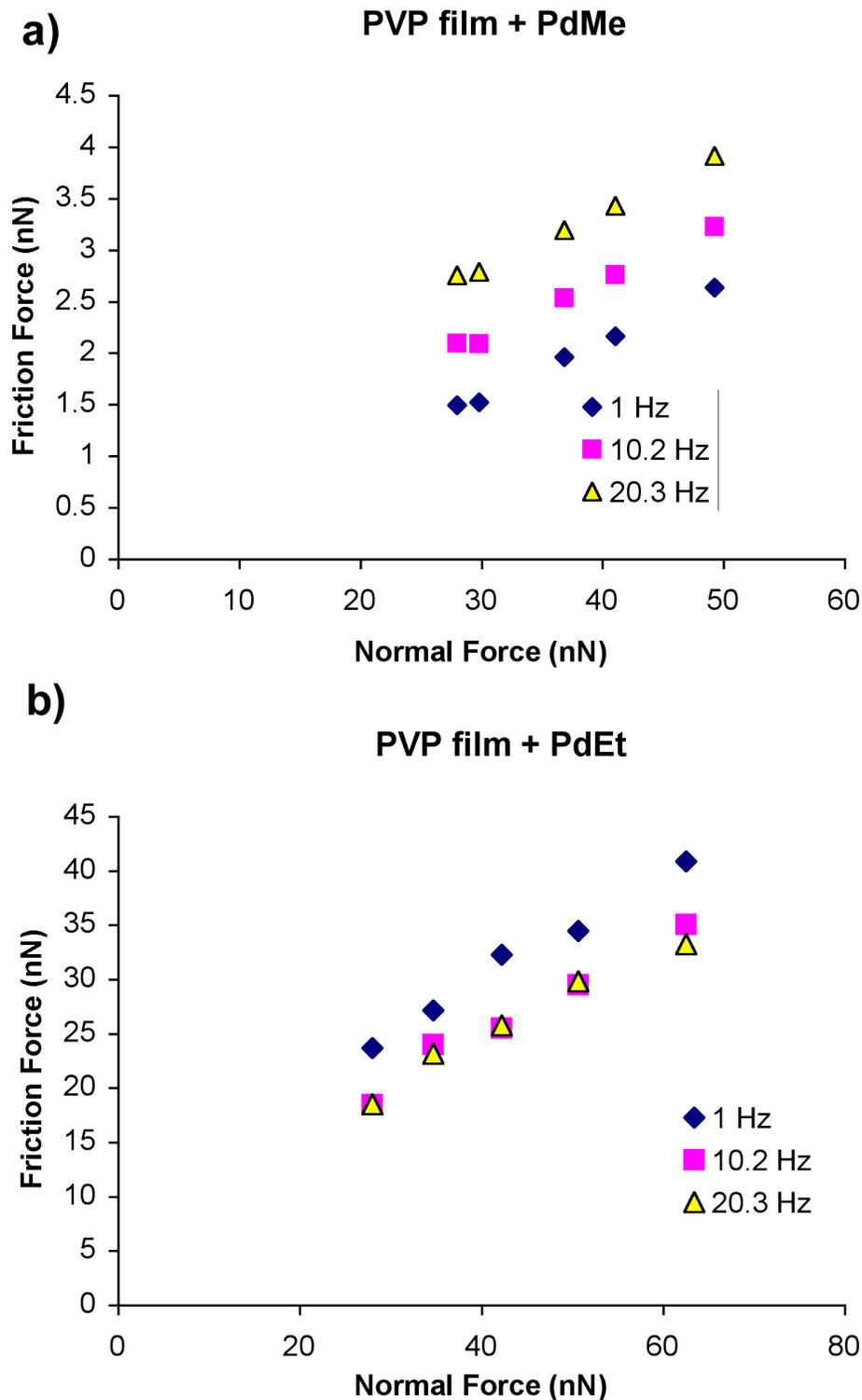
**Surface-Initiated Polymerization.** A self-assembled monolayer of the initiator on gold was obtained by immersing the substrate in a 1 mM ethanolic solution of the thiol initiator for 24 hrs. For the polymerization, all solutions and flasks were thoroughly flushed with dry nitrogen gas to remove oxygen prior to use. The polymerization solution was prepared by adding a solution of 4-vinylpyridine (4VP) monomer to an organometallic catalyst. The latter was formed in a nitrogen atmosphere by adding Cu<sup>I</sup>Cl (0.020 mmol) and Me<sub>4</sub>Cyclam (0.121 mmol) to 1 ml of MeOH as solvent. The mixture was then sonicated for 1-2 minutes to facilitate the formation of the Cu<sup>I</sup>Cl /Me<sub>4</sub>Cyclam complex. Next, 75 mmol of 4VP was dissolved in 38 ml mixture of 2-propanol/water (66:34, vol./vol.) and filtered into the catalyst-complex solution through a 0.45  $\mu$ m filter. The polymerization solution was then transferred into flasks containing the initiator substrates. Polymerization occurred for 120 min without stirring at room temperature under nitrogen. The substrate was then removed from the polymerization solution and immediately rinsed with copious amounts of 2-propanol to remove all traces of the polymerization solution, and subsequently dried under a stream of nitrogen.

**AFM.** All images and force measurements were performed using an atomic force microscope (AFM) (MultiMode with a low noise AFM head, Nanoscope III controller, Veeco, Santa Barbara, CA) at room temperature. The roughness and height of the PVP brush were measured as described previously<sup>3</sup>. Commercially available “V” shaped silicon nitride cantilevers (Veeco) were used in all experiments. The force constant of each cantilever was determined individually before the experiment from the power spectral density of the thermal noise fluctuations in solution<sup>4</sup>. The measured spring constant values for the cantilevers used in the experiments ranged between 390-700 pN/nm, in agreement with reported values using other methods, and as reported by the manufacturer. Gold-coated samples (2 x 1 cm<sup>2</sup>) were functionalized and polymerized as described above. Each sample was then cut into a two 1 x 1 cm<sup>2</sup> samples. One sample was used for the controls and measurements involving PdEt, and the second was used for the controls and measurements involving PdMe. All AFM measurements were done under identical conditions to ensure that both samples used in the two cross-linkers have very similar polymer brush characteristics such as height, and roughness. Prior to AFM measurements, each PVP sample was mounted on a metal disk and placed in the AFM. Usually a 40 µl aliquot of DMSO, cross-linker, or cross-linker + DMAP was placed on the top of the PVP brush and allowed to equilibrate for several hours. Normal force measurements (Figure S1) were performed on each PVP brush in each solution using a pulling rate of 580 nm/s, over a constant distance of 1000 nm with a resolution of 4096 points. Scanning electron microscopy images were taken on each cantilever to determine its dimensions.

Lateral forces were measured as a function of applied normal force at three different scan rates (Figure S2). The scan rate is expressed as the frequency of the repeating lateral scan across a constant scanning distance of 1  $\mu\text{m}$  in each direction. Lateral forces were calculated from the lateral deflection in the tip, averaged across the difference of consecutive trace and retrace scans. Lateral forces were calibrated according to protocols described elsewhere<sup>5</sup>.



**Figure S1.** Averaged retraction force curves measured between a silicon nitride cantilever and PVP brushes in (a) DMSO, after addition of PdMe ( $\sim 9$  mM in DMSO), and PdMe + 100 mM DMAP, and b) in DMSO, PdEt ( $\sim 9$  mM in DMSO), and PdEt + 100 mM DMAP. Each curve is an average of 10 individual measurements.



**Figure S2.** Dependence of lateral force on the normal force applied to a scanning AFM tip as a function of scan rate, expressed as the frequency of scanning for a constant 1  $\mu\text{m}$  scan length. (a) Surface-grafted PVP film cross-linked by PdMe; (b) surface-grafted PVP film cross-linked by PdEt. Note the difference in scale of the two data sets.

## References

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