Neutral and Charged Brushes Covalently Grafted from OH-Functionalized Mica Surfaces using Surface-Initiated ATRP – Swelling Investigation by AFM

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Poly(acrylic acid) (PAA) and poly(*tert*-butyl acrylate) (PBA) brushes of various grafting densities were prepared via surface-initiated polymerization of *tert*-butyl acrylate on mica. PAA was prepared by hydrolyzing the PBA brushes. The swelling behavior of PBA and PAA brushes was studied as a function of grafting density by AFM. The swelling of the polymer layer was found to be higher for PAA in water than for the PBA sample swollen with DFM.

Introduction

Stimulus-responsive brushes such as polyelectrolyte (PE) brushes are of particular interest for their capacity to control interfacial properties of surfaces.[1,2] Among many potential applications of PE brushes are; anti-fouling surfaces,[3–5] selective liquid membranes,[6,7] and biolubricants.[8,9] PE brushes are particularly interesting because their degree of dissociation can be adjusted contingent on pH, ionic strength of the medium, solvent, and counter ions. Changes in the brush charges bring about conformational changes with some representative conformations possible being depicted in Figure 1. The conformation of PE brushes is therefore responsive to variations in their surrounding environment providing the means to tune the surface properties of a film.

Another means by which to modify the brush conformation is by varying the density of the initiator that is immobilized on the substrate. We previously demonstrated that the density of an ATRP initiator (**1**) covalently linked to a mica substrate could be controlled by reaction time and concentration.[10,11] This study was done using mica because it is the best surface for examining surface forces via a Surface Forces Apparatus (SFA). We additionally demonstrated unprecedented ATRP polymerization of *tert*-butyl acrylate with **1** covalently linked to the mica, and the resulting PBA brush thickness was characterized by AFM. Such film thickness studies are of importance because they provide insight into the polymer morphologies possible by adjusting the density and molecular weight of PBA.

PBA is an interesting polymer because it can be hydrolyzed to afford PAA. This polyelectrolyte and its derivatives are the most commonly used weak polyacid for studying the swelling behavior of weak PE brushes. The brush swelling can be examined by measuring variations in brush height using techniques such as AFM,[12–14] ellipsometry,[15–17] and SFA.[18,19]

Although mica and the polymer grafted on it cannot be characterized with standard spectroscopic techniques such as ellipsometry and reflectometry, we found that the absolute thickness of the polymer layer could be determined using a step-height method by AFM.[10] Our interest in polymers covalently bound to mica prompted us to investigate the swelling behavior of a

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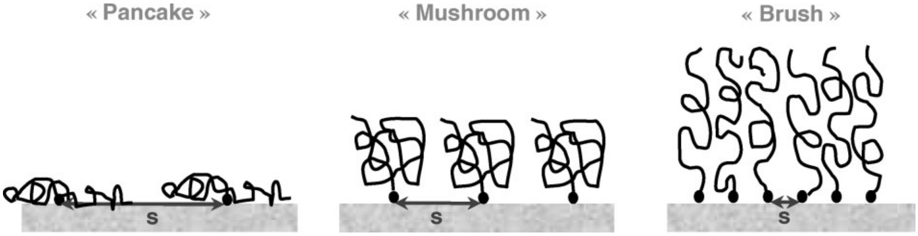

Figure 1.
Various polymer brush conformations possible.

neutral and polyelectrolyte polymer in different solvents. Such a study is important for understanding the changes in brush height as a function of solvent and to better characterize the polymer layer prior to surface forces measurements using the ultrasensitive SFA technique. Herein, we present results obtained by an AFM step-height method measuring the film thickness of PBA and PAA on mica as a function of grafting density.

The required PBA layer for this study was obtained by ATRP and was characterized by the step-height method using AFM shown in Figure 2. The difference between the virgin mica and the polymer thickness is evident from this image. The thickness of the polymer layer was found to increase with the polymerization time. Variations in the film thickness also occurred with changes in the density of **1** immobilized to the surface for a given polymerization time.

Since DMF is a good solvent for PBA, it was chosen to swell the polymer layer resulting in increased height differences between the virgin substrate and the polymer. DMF is also advantageous for liquid AFM measurements because it is not volatile. Volatile solvents are detrimental for AFM measurements because their vapors disrupt the laser beam resulting in inaccurate measurements. As seen in Table 1 and Figure 3 for a grafting density of 0.33 chains/nm^2, the polymer layer swells from 25 nm in the dry state to 33 nm with DFM. The increase in the layer thickness between the states is a result of the good solvent character of DMF, and as such, it is capable of penetrating into the brushes to minimize interchain interactions. The results confirm that the brush height can be influenced by solvent and that the absolute brush height can be measured by AFM.

PEs such as PAA contain ionizable groups that can carry charges. These charges within the polymer brushes can be modified by pH. Subsequently, the inter-brush electrostatic charges can be varied

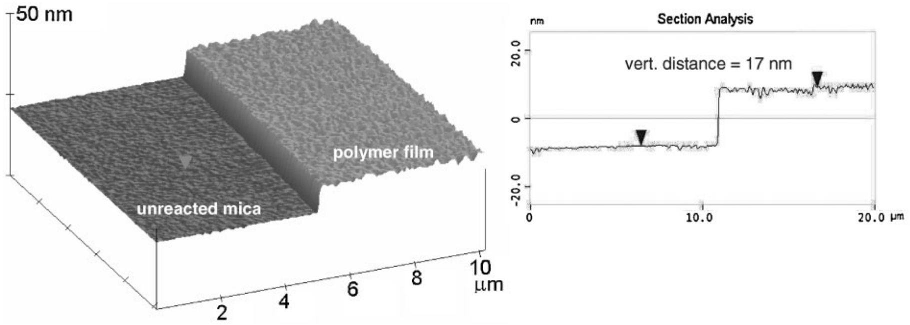

Figure 2.
AFM 3D image and cross-section image showing the step-height difference between the virgin mica and the polymer layer.

Table 1.
Film swelling behaviour of PBA in DMF and PAA in salt-free solution at pH 9.

Grafting density (number of chains/nm^2)	PBA			PAA		
	h (± 2 nm) in air	h (± 5 nm) in DMF	Q	h (± 2 nm) in air	h (± 5 nm) in salt-free solution pH 9	Q
0.04	2	0.6	0.3	2.4	16.4	6.8
0.07	6	31	5.2	2.4	20.0	8.0
0.33	25	33	1.3	10.4	87	8.3
0.4	33	36	1.1	17	143	8.4

resulting in changes in the polymer brush height. This phenomenon was examined using PAA obtained by hydrolyzing PBA immobilized on mica. After removing the protective *tert*-butyl group by hydrolysis (Figure 4), the thickness of the dry and swollen layers at pH 9 without added salt was measured. The swelling ratio (Q), defined as the ratio between the swollen and the dry thickness, was additionally determined. The decrease of approximately 50% in dry film thickness upon converting PBA to PAA is expected because of a decrease in molecular density resulting from the loss of the bulky *tert*-butyl groups. The advantage of comparing the brush heights between PAA and PBA for identical samples is that fluctuations in film thicknesses as a result of varying degree of polymerization occurring with different samples is none existent. As seen in Table 1 and Figure 3, the swelling of the PAA film is significantly greater than that of PBA in DFM regardless of the grafting density. The difference in swellen ratio between PBA and PAA is a result of conformational change from a flexible to a stretched brush conformation because of electrostatic interactions and the absence of affinity of PAA with the surface. These data confirm not only that inter-chain electrostatics cause the PAA brushes to elongate relative to their neutral form, but that the AFM step-height method is a viable means for measuring absolute film thickness.

In conclusion, our results demonstrate that the AFM step-height technique is a viable method for measuring absolute thickness of polymer layers on mica. This technique is therefore suitable for measuring morphological changes induced by variations in ionic strength and pH detectable by changes in the polymer thickness. This is supported by the larger swelling of the PAA film in water relative to the PBA layer in DMF.

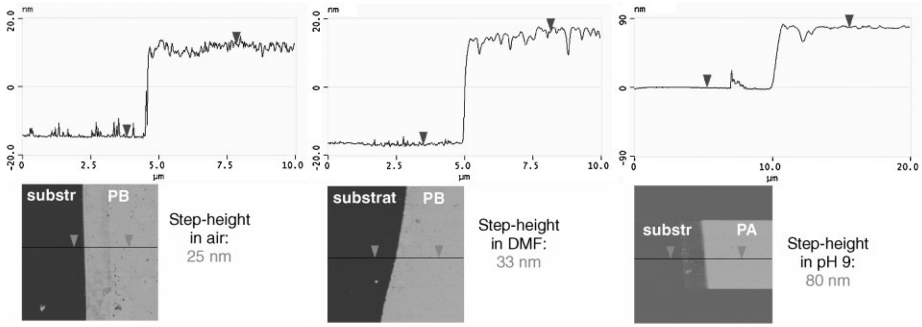

Figure 3.
AFM Cross-section analysis showing the PBA film thickness in air and in DMF and the PAA film thickness in pH 9 aqueous solution.

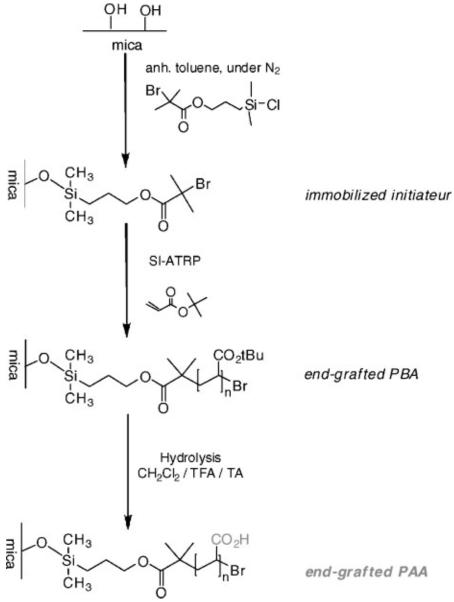

Figure 4.
Adsorption reaction of the ATRP initiator on activated mica followed by surface-initiated ATRP of *tert*-butyl acrylate and hydrolysis of PBA to form PAA.

Experimental Part

Initiation **1**, grafting to activated mica, and the polymerization of PBA using ATRP were done according to previous reports.[10,11] Prior to plasma activation and immobilization of **1**, a sheet of freshly cleaved mica was placed across the mica. The mica protective layer was removed postpolymerization to afford a distinct zone for measuring the absolute step-height difference between the atomically smooth unreacted mica surface and the polymer film. Measurements were done using the AFM set-up previously described.[10,11] The PBA films were measured both dry and in DMF using a home-built solvent cell. Converting PBA into PAA was done by submerging the mica samples in a 10:1 (v/v) mixture of dichloromethane:TFA overnight followed by rinsing with ethanol followed by milliQ water.

Acknowledgements: The authors acknowledge financial support from the Natural Sciences and Engineering Research Council Canada and le Fonds de Recherche sur la Nature et les Technologies. B.L. thanks the Université de Montréal for a graduate scholarship. Prof. Prud'homme and Ms. M. François are also acknowledged for granting access to their AFM and for preliminary work, respectively.

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