Macromolecules **1998,** *31,* 4297−4300

Direct Force Measurements at Polymer Brush Surfaces by Atomic Force Microscopy

Tommie W. Kelley, Phillip A. Schorr, Kristin D. Johnson, Matthew Tirrell,* and C. Daniel Frisbie*

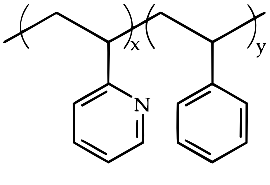
Department of Chemical Engineering and Materials Science, University of Minnesota,
421 Washington Avenue SE, Minneapolis, Minnesota 55455

Received October 27, 1997; Revised Manuscript Received February 12, 1998

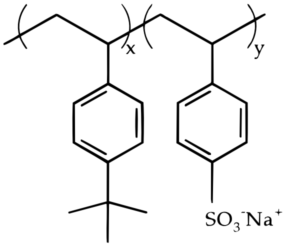
ABSTRACT: We present the results of two studies: (1) a comparison of force−distance ($F-D$) profiles obtained by atomic force microscopy (AFM) and the surface forces apparatus (SFA) for a poly(2-vinylpyridine)−polystyrene (PVP−PS) brush in good solvent; (2) a series of $F-D$ profiles for a poly(4-*tert*-butylstyrene)−sodium poly(styrene-4-sulfonate) (PtBS−NaPSS) brush as a function of aqueous NaCl concentration. The AFM force profiles of the neutral PVP−PS brush are less steep than the corresponding surface forces data in the regime of high brush compression, in agreement with a recent molecular simulation study that indicated the tip would splay polymer chains and penetrate the brush. We also observe a bimodal distribution of interaction distances for the AFM force profiles of the PVP−PS brush which we ascribe to the tip sampling regions of higher and lower chain density during consecutive force measurements. AFM $F-D$ profiles of the PtBS−NaPSS brush show a strong dependence of interaction distance on NaCl concentration, and a plot of interaction distance vs salt concentration shows predicted power law behavior. Images of both the PVP−PS and PtBS−NaPSS brushes show that the chain density is not uniform which gives rise to variations in the interaction distances measured by AFM. By facilitating measurements of local force profiles, AFM complements SFA measurements of interfacial forces and allows measurement of brush heterogeneity.

Introduction

The utility of atomic force microscopy (AFM) for direct force measurements at interfaces rests in its ability to probe forces over areas as small as 10 nm^2. This high spatial resolution capability makes AFM a complementary approach to the surface forces technique which has been used extensively to measure interfacial forces between proximal surfaces[1a] over areas on the order of 1 μm^2. We are exploring the utility of AFM for probing polymer brush surfaces and report here two recent results, first, a comparative study of force−distance ($F-D$) profiles obtained by both AFM and the surface forces apparatus (SFA) on a neutral polymer brush in a good solvent and, second, a series of AFM $F-D$ profiles at a polyelectrolyte brush in water as a function of NaCl concentration. For these studies, we have chosen neutral and polyelectrolyte brushes formed by selective solvent adsorption of poly(2-vinylpyridine)−polystyrene (PVP−PS) and poly(4-*tert*-butylstyrene)−sodium poly(styrene-4-sulfonate) (PtBS−NaPSS) diblocks, respectively, on mica. The neutral PVP−PS brushes have been studied extensively with SFA,[1] and SFA measurements on PtBS−NaPSS brushes are under way.[2]



PVP-PS



PtBS-NaPSS

A previous report by Overney et al.[3a] demonstrated that AFM $F-D$ profiles are sensitive to the effect of solvent on PVP−PS brush height in that they observed a longer-ranged repulsive force in a good solvent for PS than in a poor solvent. They also compared their $F-D$ profiles to self-consistent field theory for proximal brush surfaces and found that the theory predicted a steeper overall force profile than their measured AFM $F-D$ curves. A probable explanation was that the AFM tip penetrated the brush.[3,4] In a recent molecular simulation study, Murat and Grest considered explicitly the interaction of a sharp tip with a polymer brush and predicted that the AFM $F-D$ profiles at homogeneous polymer brush surfaces should be shallower in the region of high brush compression (small D) than profiles obtained with the SFA.[5] Their simulation showed that splaying of polymer chains during tip penetration resulted in a smaller buildup of monomer density underneath the tip than the buildup that occurred between large, flat compressing surfaces. The lower density underneath the sharp tip resulted in less steric crowding and therefore lower repulsive forces. Our comparative AFM and SFA study on a neutral PVP−PS brush reported here confirms the Murat and Grest prediction and the previous experimental work. However, our AFM measurements also reveal a bimodal variation in interaction distance (brush height). Topographic AFM images of brushes show that the adsorbed layers are not completely homogeneous, suggesting that the variation observed in consecutive AFM force measurements arises because the tip drifts over regions of high and low polymer density. To our knowledge, inhomogeneity of polymer brushes has not been explicitly addressed in direct force measurements by simulation or experiment, but such inhomogeneities are an important consideration in interpreting AFM data. The AFM $F-D$ profiles for the polyelectrolyte brush at fixed

---

* Address correspondence to either of these authors: tirrell@maroon.tc.umn.edu or frisbie@cems.umn.edu.

S0024-9297(97)01571-4 CCC: $15.00

salt concentration also show a distribution of interaction distances. Further, the profiles reveal a strong dependence of interaction distance on electrolyte concentration, in keeping with several recently published theoretical predictions.[6]

Experimental Method

Chemicals. The PVP−PS and PtBS−NaPSS diblock copolymers were synthesized by sequential anionic polymerization by Rastislav Levicky (University of Minnesota) and by Jimmy Mays (University of Alabama), respectively, according to procedures previously described in the literature.[1f,7] The PVP−PS diblock had a polydispersity ≤ 1.04. The molecular weights of the blocks were 15000 (PVP) and 90000 (PS) g/mol. The PtBS−NaPSS diblock had a polydispersity ≤ 1.04, an 87% sulfonation level, and block molecular weights of 4000 (PtBS) and 165000 (NaPSS) g/mol. All solvents were HPLC grade and were used directly from the bottle.

Adsorption of Polymer. PVP−PS brush samples were formed by immersing freshly cleaved, round, 1 cm diameter sheets of mica in a toluene adsorption solution of the polymer (40 μg/mL of solvent) for 3−4 days at 40 °C. The PtBS−NaPSS brush samples were prepared first by dissolution of the diblocks in Millipore water at a polymer concentration of 1 mg/mL for 1 week under stirring.[8] Freshly cleaved mica sheets were then immersed in a thrice-filtered (0.45-μm pore size) 1.0 M aqueous solution (100 μg of polymer/mL of solution) for a minimum of 20 h at room temperature.

AFM Force Measurements. All force measurements were made on a Digital Instruments Nanoscope III AFM equipped with a liquid cell. AFM probes were standard, commercially available Si_3N_4 cantilevers with integrated tips. The tips had a radius of curvature of 40 nm as measured by scanning electron microscopy and were cleaned prior to use in the AFM by immersing them in a warm solution of $NH_4OH/H_2O_2/H_2O$ (1:1:5) for 2 min. Samples were prepared for force measurements by removal from the adsorption solution followed by rinsing with copious amounts of toluene (in the case of PVP−PS adsorption) or water (in the case of PtBS−NaPSS adsorption). The samples were allowed to air-dry; this did not appear to introduce any variations in the measurements due to contamination. The dry samples were mounted on the piezoscanner of the microscope and the desired solvent was injected into the liquid cell. Teflon coated O-rings (Precision Associates, Inc., Minneapolis, MN) were used to seal the liquid cell. These O-rings were not noticeably swollen or degraded by any of the solvents used in the force measurements.

Before acquiring force curves, the brushes were allowed to equilibrate with the solvent. A 15-min equilibration time proved adequate, although times as short as 5 min and as long as 30 min were tried with no marked difference in the force curves recorded between 15 and 30 min. Typically, a total of 20 force curves were taken at different locations on each sample. Some variation in force curves was seen from location to location on each sample and from sample to sample, probably indicative of inhomogeneity of the brush density, consistent with our images in Figure 1 and recent publications which indicate these brushes actually adsorb in islands instead of forming completely homogeneous surfaces.[9]

Conversion of AFM Data to *F*/*R* vs Distance Plots. AFM force curves are generated in the format of Δd, change in cantilever deflection (nm), vs Δz, change in z-position (nm) of the sample. To compare directly the AFM and SFA data, we converted the AFM force curves to force/radius (F/R) vs tip−mica separation (D). Force is obtained by multiplying the cantilever deflection by the spring constant of the cantilever (0.58 N/m). The change in z-position is equal to the change in tip−mica separation plus the change in deflection, thus $\Delta z = \Delta D + \Delta d$. Rearranging, we obtain $\Delta D = \Delta z - \Delta d$ and need only set a zero point to obtain an actual tip−mica separation distance, D. The point of intimate contact with mica, $D = 0$, was defined as the point where the approach force curve first becomes linear in the high-force regime (small D regime); linear extrapolations of the baseline and the high-force regime were made on an enlarged version of each force curve to find this zero point.

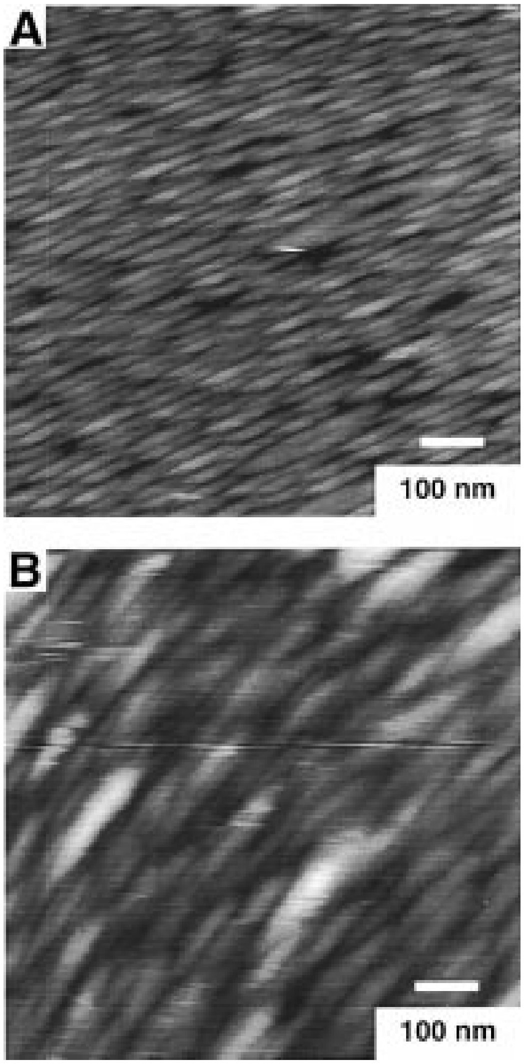


Figure 1. Contact mode AFM images of a PVP−PS brush in cyclohexane (A) and a PtBS−NaPSS brush in 0.016 M aqueous NaCl (B).

Results and Discussion

Figure 1A shows a contact mode AFM image acquired under cyclohexane of the PVP−PS layer on mica. Drift of the sample during the image acquisition gives the image a stretched appearance. Accounting for the stretching, the image reveals that the polymer has adsorbed in densely packed clumps or islands with diameters ∼50 nm. The radius of gyration of a single PS chain with a molecular weight comparable to the molecular weight of the PS block (90 000 g/mol) is about 5 nm in cyclohexane, such that these clumps represent groups of several chains. Images in toluene were more difficult to interpret due to greater chain stretching, which resulted in a slightly more homogeneous overall appearance, although regions of high and low density were still clearly visible.

We measured force−distance profiles of the PVP−PS layer in toluene, a good solvent for the PS block, using Si_3N_4 AFM tips and compared these data to SFA profiles taken on a similarly prepared brush (SFA data were obtained for a bare mica sheet interacting with a sheet bearing adsorbed polymer), Figure 2. The figure shows three traces of AFM F/R vs distance data (traces 1, 2,

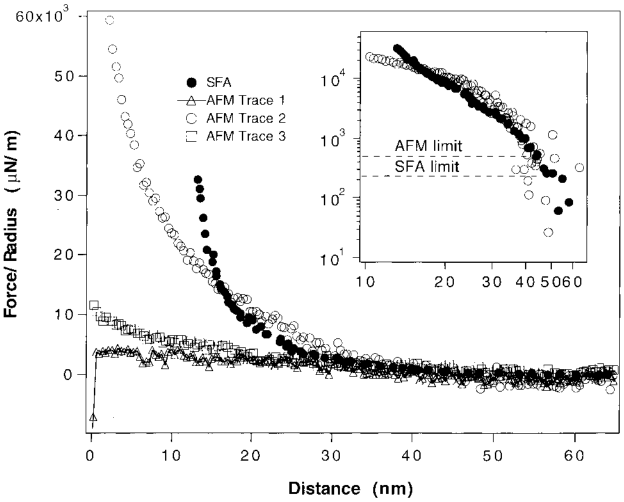


Figure 2. Comparison of AFM and SFA force profiles at a PVP−PS brush. Force/radius vs distance plots were obtained in toluene for a Si_3N_4 AFM tip interacting with a bare mica surface (AFM trace 1), a Si_3N_4 tip interacting with a PVP−PS brush (AFM traces 2, 3), and a bare mica sheet interacting with a PVP−PS brush (SFA data). Inset shows a log−log plot of AFM trace 2 and the SFA profile. The detection limits (noise level) associated with each technique are indicated by the dashed lines in the inset. “Distance” refers to tip−mica separation (for AFM data) or mica−mica separation (for SFA data). AFM tip radius = 40 nm as determined by SEM micrographs. SFA radius = 2 cm.

and 3) and one trace of similar SFA data. Trace 1 is the profile obtained for a bare Si_3N_4 AFM tip interacting with mica in toluene. This profile indicates essentially no tip−sample interaction until ∼2 nm separation, at which point the tip jumps to contact due to attractive van der Waals forces. Traces 2 and 3 are typical force profiles obtained for a bare Si_3N_4 tip approaching a brush-coated mica surface in toluene. A long-ranged repulsion due to the PVP−PS brush is evident in both profiles, but the brush compliances in the high compression regime are clearly very different (see below). We expect that in this nonpolar solvent environment these long-ranged repulsive interactions are due essentially to steric crowding of the polymer chains upon tip−brush contact.

Importantly, both traces 2 and 3 are shallower than the SFA data, in accord with the Murat and Grest prediction that splaying of the polymer chains underneath the tip results in shallower profiles. A log−log plot of F/R vs D in the inset of Figure 2 facilitates comparison of the SFA data and AFM trace 2. The interaction distance or brush height measured by AFM and SFA is determined as the point where the F/R value exceeds the respective detection limits of the two methods. These detection limits are 2×10^2 μN/m for the SFA giving an interaction distance of 50 nm and 5×10^2 μN/m for the AFM, corresponding to a measured interaction distance of 45 nm. The slightly smaller AFM interaction distance is perhaps not surprising since the onset of a detectable repulsive force may not occur until the tip is well within the periphery of the brush.

AFM traces 2 and 3 in Figure 2 are representative of a nearly bimodal distribution of force profiles observed on PVP−PS surfaces. A compilation of 60 curves from one experimental session resulted in two bands of force curves centered around traces 2 and 3. We believe that the distribution of force profiles we observe is consistent with the image of the brush in Figure 1A, which shows that the tip can distinguish between regions of high and low chain density, or clumps vs holes. Drift of the sample underneath the tip causes the tip to probe regions of differing chain density. When the tip is directly above a clump, we observe the steepest profiles (e.g., trace 2). When it falls between clumps, we observe the shallowest profile (e.g., trace 3). The fact that AFM trace 2 crosses the SFA data, i.e., larger F/R values are observed between ∼18 and 35 nm, may imply that the chain density is greater in an individual clump probed by the AFM than the *average* chain density between mica sheets as measured by the SFA. However, we caution against making strong conclusions regarding the origin of the “curve crossing” in Figure 2 since uncertainties in the $D = 0$ point for the AFM data and tip radius could account for the apparent difference in F/R values in the 18−35 nm regime. Irrespective of these uncertainties, the bimodal “on-island, off-island” response of our AFM measurements is clearly represented in Figure 2.

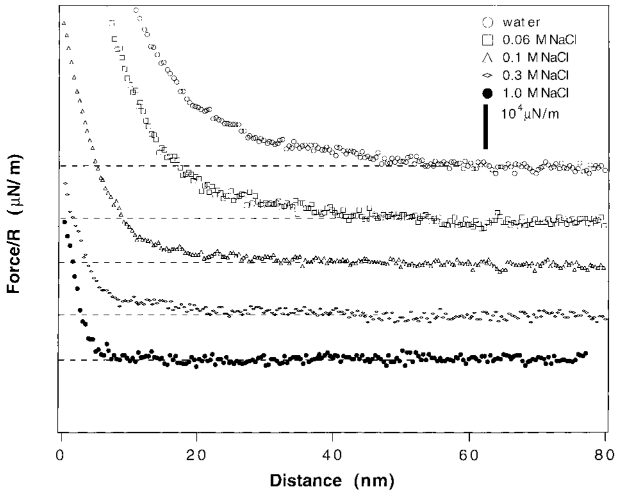


Figure 3. Force/radius vs distance curves for a bare Si_3N_4 AFM tip interacting with a PtBS−NaPSS brush in water, 0.06, 0.1, 0.3, and 1.0 M added NaCl. The vertical axis of each curve has been shifted so that the individual profiles can be seen more clearly.

Figure 1B shows a contact mode AFM image of the PtBS−NaPSS brush in 0.016 M NaCl. Again, sample drift in the microscope contributed to the apparent elongation of the groups of chains, but it can be seen that the average clump size is larger than in the case of the neutral brushes, as expected, due to better solvent quality and larger molecular weight of the NaPSS block in comparison to the neutral PS block. Force profiles of the polyelectrolyte brush taken at varying salt concentrations are represented in Figure 3, where the vertical axis has been shifted for each curve for the sake of clarity. Inspection of Figure 3 shows that repulsive forces are evident in all profiles, but the interaction distance decreases dramatically from no added salt to 1 M salt solutions. Profiles obtained at 0.1 M NaCl concentration showed no dependence on pH of the solution, indicating that these repulsive forces are not a consequence of potential double layer interactions between the Si_3N_4 tip and the charged polymer layer.[10,11] We conclude that the measured repulsive forces are indicative of steric interactions upon compression of the brush. Shrinking of the brush layer (and thus decreasing interaction distance) with increasing salt concentration can be attributed to screening of the charge

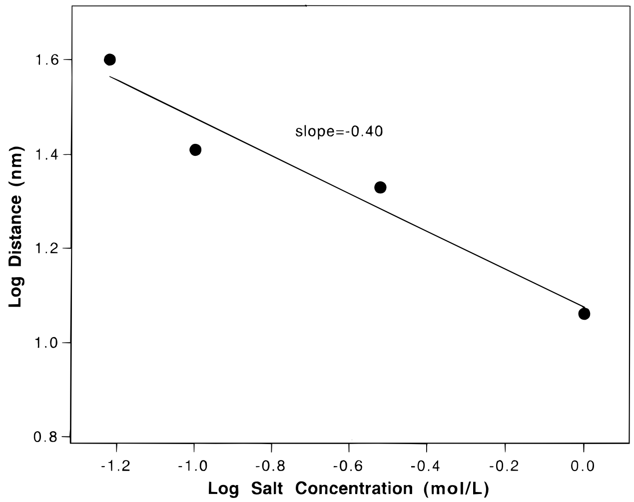


Figure 4. Log–log plot of interaction distance vs NaCl concentration determined from the AFM profiles for the PtBS–NaPSS brush in Figure 3. The line represents the best linear fit.

associated with the ionizable sulfonate groups on each NaPSS block.[6b,12] As salt is added, positive Na^+ ions form a cloud near the polyelectrolyte chains, partially screening the repulsive interactions between consecutive charges on the chains, allowing the chains to relax into a less stretched conformation.

A plot of log interaction distance vs log of the salt concentration based on the profiles in Figure 3 is shown in Figure 4. In water (no added salt) the interaction distance is observed to reach to almost 60 nm, while in 1 M salt, the interaction is diminished to slightly more than 10 nm. The slope of the plot in Figure 4 is −0.40, which is in good agreement with several recent theoretical predictions;[6,13] however, variations in measured interaction distance were observed for each salt concentration. The slope of the power law plot in Figure 4 varied from about −0.37 to −0.45 depending on the force curves chosen. Compilation of the force curves taken at different salt concentrations in one experimental session showed a continuous band of interaction distances. The remarkable result is that despite the heterogeneity which we see in images of the PtBS–NaPSS brushes, the variation in measured distance is small enough that our AFM measurements yield a very reasonable dependence of brush height on salt concentration. This result underscores the applicability of AFM force measurements to a wide variety of brush systems.

Conclusions

Direct comparison of force–distance profiles on a neutral brush by AFM and SFA confirms recent simulation and experimental results that the AFM profiles are less steep than corresponding SFA profiles in the region of high brush compression. This result is in accord with the simulation study of Murat and Grest which predicted chains would be splayed by the penetrating tip. AFM force–distance profiles of a polyelectrolyte brush reveal an expected strong dependence of interaction distance on salt concentration. The measured functional dependence of the interaction distance compares favorably with theoretical predictions.

Interestingly, consecutive AFM force measurements at the neutral PVP–PS brush show a bimodal distribution of interaction distances, which we ascribe to brush heterogeneity, i.e., regions of high and low polymer density. The observation of brush heterogeneity raises questions regarding interpretation of SFA force measurements at brush surfaces, since to date these experiments have been well explained by theories which consider the brush to be completely homogeneous. Furthermore, efforts to use polymer brushes in surface biocompatibilization and colloidal stabilization will benefit from increased understanding of the importance of brush heterogeneity to force profiles. With the AFM, it is possible to measure, through force–distance profiles and topographical images, brush heterogeneity on ~10 nm length scales. Future research using the AFM and SFA as complementary techniques should allow further insight into the nature of polymer brushes, brush heterogeneity, and polymer brush applications.

Acknowledgment. M.T. and C.D.F. thank the Center for Interfacial Engineering at the University of Minnesota for support of this work. M.T. also acknowledges the National Science Foundation (CTS-9616797) for financial support.

References and Notes

(1) (a) For a review, see: Patel, S. S.; Tirrell, M. *Annu. Rev. Phys. Chem.* **1989**, *40*, 597. (b) Watanabe, H.; Tirrell, M. *Macromolecules* **1993**, *26*, 6455. (c) Parsonage, E.; Tirrell, M.; Watanabe, H.; Nuzzo, R. G. *Macromolecules* **1991**, *24*, 1987. (d) Granick, S.; Patel, S.; Tirrell, M. *J. Chem. Phys.* **1986**, *85*, 5370. (e) Chen, C.; Dan, N.; Dhoot, S.; Tirrell, M.; Mays, J.; Watanabe, H. *Isr. J. Chem.* **1995**, *35*, 41. (f) Hadziioannou, G.; Patel, S.; Granick, S.; Tirrell, M. *J. Am. Chem. Soc.* **1986**, *108*, 2869.

(2) Watanabe, H.; Patel, S. S.; Argillier, J. F.; Parsonage, E. E.; Mays, J.; Dan-Brandon, N.; Tirrell, M. *Mater. Res. Soc. Symp. Proc.* **1992**, *249*, 255.

(3) (a) Overney, R.; Leta, D.; Pictroski, C.; Rafailovich, M.; Liu, Y.; Quinn, J.; Sokolov, J.; Eisenber, A.; Overney, G. *Phys. Rev. Lett.* **1996**, *76*, 1272. For other AFM studies of polymer modified surfaces, see: (b) Braithwaite, G.; Howe, A.; Luckham, P. *Langmuir* **1996**, *12*, 4224. (c) Biggs, S. *Langmuir* **1995**, *11*, 156. (d) Aime, J.; Elkaakour, Z.; Odin, C.; Bouhacina, T.; Michel, D.; Curely, J.; Dautant, A. *J. Appl. Phys.* **1994**, *76*, 754.

(4) Subramanian, G.; Williams, D. R. M.; Pincus, P. A. *Macromolecules* **1996**, *29*, 4045.

(5) Murat, M.; Grest, G. *Macromolecules* **1996**, *29*, 8282.

(6) (a) Pincus, P. *Macromolecules* **1991**, *24*, 2912. (b) Argillier, J.-F.; Tirrell, M. *Theor. Chim. Acta* **1992**, *82*, 343.

(7) Argillier, J.; Mao, G.; Tirrell, M.; Mays, J. Submitted to *Macromolecules*.

(8) Amiel, C.; Sikka, M.; Schneider, J. W., Jr.; Tsao, Y.-H.; Mays, J. W. *Macromolecules* **1995**, *28*, 3125.

(9) (a) Zhao, W.; Krausch, G.; Rafailovich, M.; Sokolov, J. *Macromolecules* **1994**, *27*, 2933. (b) Stipp, S. *Langmuir* **1996**, *12*, 1884. (c) Spatz, J.; Sheiko, S.; Moller, M. *Macromolecules* **1996**, *29*, 3220.

(10) Force profiles were taken at pH 4, 5, 6, 9, and 10 in 0.1 M NaCl. The pH was adjusted with HNO_3 or KOH. The isoelectric point for Si_3N_4 occurs at approximately pH 6, implying that the surface potential of the tip should have changed from positive to negative values in this pH range.

(11) Kamiyama, Y.; Israelachvili, J. *Macromolecules* **1992**, *25*, 5081.

(12) Wang, L.; Yu, H. *Macromolecules* **1988**, *21*, 3498.

(13) Vongoeler, F.; Muthukumar, M. *J. Chem. Phys.* **1996**, *105*, 11335.

MA971571N