Macromolecules **2007,** *40,* 4561−4567

Cationic Polyacrylamide Conformation on Mica Studied by Single Molecule “Pulling” with Scanning Probe Microscopy

Brett Brotherson,[†] Lawrence A. Bottomley,[‡] Peter Ludovice,[†] and Yulin Deng*,[†]

School of Chemical & Biomolecular Engineering and School of Chemistry and Biochemistry, Georgia Institute of Technology, Atlanta, Georgia 30332-0620

Received February 27, 2007; Revised Manuscript Received April 20, 2007

ABSTRACT: In recent years, scanning probe microscopy (SPM) has been used to gain information about the conformation of an adsorbed polymer. However, the experimental techniques used make interpretation of the data difficult or impossible without significant assumptions. In this work, an improved “pulling” method, which overcomes many of the limitations of traditional methods, is executed. The sequential adsorption/desorption of cationic polyacrylamide on freshly cleaved mica in deionized water was directly measured using these modified SPM experiments. Our method uses a specially etched tip which ensures only one polymer molecule is adsorbed on the cantilever tip, allowing more accurate interpretation of the results. The results were compared with previous studies showing the applicability of this modified technique to determine the conformation of an adsorbed polymer. The effect of cantilever tip retraction velocity from the surface was shown to be insignificant to the measured loop length distribution. For the first time, SPM was used to show the effects of dwell time on adsorbed polymer conformation.

1. Introduction

The conformation of an adsorbed polymer on a surface directly determines the properties and interactions of a surface with other particles or surfaces. Polymers are used in many industries to affect how colloidal materials interact. These industries include papermaking, water treatment, oil recovery, mining, and food processing. In all of these industries, better knowledge of adsorbed polymer conformation could greatly increase the efficiency and efficacy of surface modification in these industries. For this reason, the study of polymer surface conformations is an important concept in polymer science. One commonly used polymer in industrial practice is cationic polyacrylamide.

Polymers can adsorb to surfaces by two mechanisms: chemisorption and physisorption. Chemisorption includes mechanisms such as covalent bonding, while physisorption refers to mechanisms such as electrostatic interaction and van der Waals forces.[1] Once adsorbed on a surface a polymer’s conformation can be described by three different regions: loops, trains, and tails.[2] Adsorbed polymers will align in higher ordered structures depending on factors such as the molecular weight of the polymer, surface affinity, and polymer concentration. These structures are generally categorized as pancakes, mushrooms, or brushes.

There have been many different experimental techniques used, in past research, to determine the adsorbed conformation of a polymer on a surface. These methods include Brewster angle reflectivity, total internal reflectance fluorescence, dynamic light scattering, surface force analysis with a force-balance apparatus, nuclear magnetic resonance, neutron reflectivity, small-angle neutron scattering, and scanning probe microscopy.[3−8]

Brewster angle reflectivity is an optical test where light passes through different materials with different increasing refractive indices.[3] At the Brewster angle the sample will emit zero-plane-polarized reflected light. If another material of a different density is adsorbed on a surface, the Brewster angle will change. This technique has been used to determine the thickness of adsorbed polymer layers.[9] One limitation of this approach is that one must assume a constant density in an adsorbed polymer layer, which is not always true. Total internal reflectance fluorescence provides information about the thickness and conformation of an adsorbed polymer. In this technique, light is internally reflected through a waveguide. When this waveguide is coated with polymer containing fluorophores, the evanescent field excites the fluorophores in close proximity to the surface.[3] Thus, from the fluorescence intensity, a surface concentration of adsorbed polymer and thickness can be determined. Dynamic light scattering is a commonly used technique to measure the thickness of polymer layer adsorbed on a small particle surface.[10−16] The surface force balance can also be used for this purpose. When surfaces that are coated with an adsorbed polymer layer are brought near each other, repulsive or attractive interactions between the polymer layers can be detected by this device. The resolution for a force-balance apparatus is about 0.1 nm and is sensitive to forces as small as 10^{-8} N.[3,11]

The above approaches provide measures of the thickness of an adsorbed layer but not the conformation of the adsorbed polymer. Information about an adsorbed polymer’s conformation can be provided by nuclear magnetic resonance spectrometry. Cosgrove et al. have used nuclear magnetic resonance to determine the proportion of polymer present in the train regions of the conformation.[4−8] Cosgrove has also used a combination of both nuclear magnetic resonance and neutron reflectivity to gain information about the volume fraction profiles of adsorbed polymers.[4] Similar to light scattering, small-angle neutron scattering detects the intensity of scattered neutrons to image objects. With respect to polymers adsorbed on a surface, neutron reflection is used.[12−14] Using neutron reflection, Rennie et al. were able to determine the volume fraction of a polymer at varying distances from a surface.[13] This method, however, is very subjective to the amount of liquid the neutrons must travel through and the reflection that can occur from the solid surface.[12]

---

[*] To whom correspondence should be addressed. E-mail: yulin.deng@chbe.gatech.edu.

[†] School of Chemical & Biomolecular Engineering.

[‡] School of Chemistry and Biochemistry.

10.1021/ma070495d CCC: $37.00

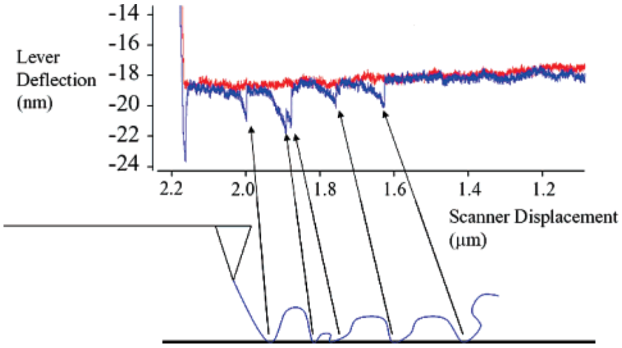

Figure 1. Force curve showing how polymer attachment points appear in a typical SPM test. As an attachment is approached you see a deflection of the lever visible by the large blue curves. As this attachment is released you see a quick straightening of the cantilever shown by the vertical line following the initial deflection.

Small-angle neutron scattering and neutron reflectivity can give the density of polymer at different distances from a surface; however, this method is also relatively inaccessible to most researchers. Scanning probe microscopy is readily available to most researchers and has the ability to measure the length of polymer between attachment points by performing "pulling" experiments.

In recent years, scanning probe microscopy (SPM) "pulling" experiments, or force pulls, have been used to gain information about the conformation of adsorbed polymers.[15−27] However, the experimental techniques used in many cases make the interpretation of the data difficult or impossible without significant assumptions. SPM "pulling" experiments are used to determine polymer loop lengths by observing the deflections of the cantilever as it is pulled away from a surface. Figure 1 shows a typical polymer desorption event and how it may reflect the adsorbed polymer's conformation. As the tip is pulled up from the surface, moving right in Figure 1, the polymer chain stretches out. When a desorption point is approached, the straight polymer chain now begins to deflect the cantilever until enough force is applied to cleave this attachment. At this point, a sudden decrease in deflection is seen.

In a SPM "pulling" experiment, the polymer can be attached to both the tip and substrate by either physisorption or chemisorption. Thus, there are three different scenarios in a "pulling" experiment: physisorption on both the tip and the surface, physisorption on one surface and chemisorption on the other, and chemisorption on both the tip and the surface. When polymers chemisorb to both surfaces, the force profile tracks cleavage of a covalent bond.[28] Many of the currently used techniques involve bringing a clean tip or a tip laden with physisorbed polymers to a surface that may or may not contain physisorbed polymers.[19,22−25] Figure 2 shows some of the many different possible scenarios of a "pulling" experiment like this.

Schemes a−c in Figure 2 illustrate possible scenarios of a single polymer being pulled from a surface. In the experiments done by Senden et al. and Levy et al., a polymer can adsorb and desorb in multiple places on the tip and the surface.[19,22−25] Only in Figure 2c can a true measurement of the polymer loop lengths, from one end of the chain to the other, be measured, and this depends on the attachment to the tip not detaching. In Figure 2b, the desorption events do not have to occur in any particular order. If desorption events followed the pattern 3, 4, 2, 5, 6, and then 7, not all events would be counted, and the distance between attachment points, describing a polymer on a single surface, would be incorrectly accounted for, due to the order of desorption. Figure 2d, which is very likely in previous experiments, allows the results to be significantly complicated by measuring the desorption events of multiple polymers on the same curve. In this case, it is very likely that large loop lengths would be screened out by detachments of different polymers. With these complications, it is impossible to determine to the loop length distribution of a single polymer. Figure 3 gives a detailed look at three possible scenarios of a polymer pull. It illustrates where the polymer could possibly adsorb in a physisorption-dominated experiment.

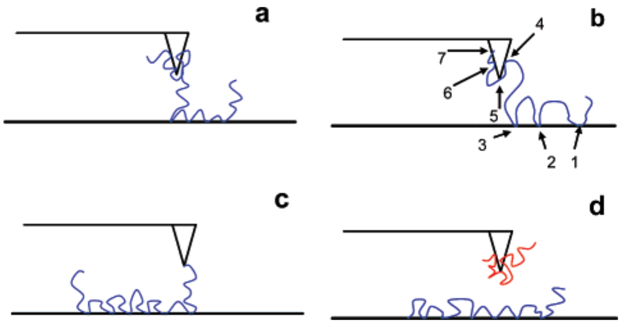

Figure 2. Possible polymer "pulling" scenarios with current SPM techniques used. (a) Polymer is bonded to the tip and surface in multiple places, each equally available for desorption. (b) Polymer bonded to tip and surface showing all points which could desorb during a SPM pull. (c) Polymer bonded by a terminal end on the cantilever. (d) Multiple polymers interacting as tip approaches and is retracted from the surface.

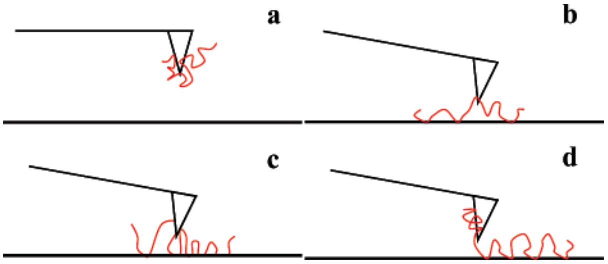

Figure 3. Possible scenarios for one physisorbed polymer. (a) Initial conformation on SPM tip. (b) Polymer adsorbs in two directions from the tip. (c) Polymer adsorption points alternate between the tip and the surface. (d) Polymer has multiple adsorption points to the tip and multiple points on the surface without alternation.

As shown in Figure 3, the initial conformation, shown in scheme a, can change to that of schemes b−d due to different adsorption and desorption possibilities. In Figure 3b, if the polymer does not desorb from the tip initially, it will yield small loop lengths due to the desorption of attachments on alternating sides of the cantilever tip. In Figure 3c the loop lengths could be altered by alternating desorption from the surface and the tip. Figure 3d shows another case were desorption from the surface and the tip are equally likely for a physisorbed polymer.

The examples in Figures 2 and 3 were complicated by the fact that a polymer can both adsorb and desorb from the tip and surface. This problem was improved with the "pulling" method developed by Haschke et al.[20, 21] Haschke ensured that each polymer could only adsorb on one terminal end, as seen in Figure 2c.[20,21] To do this, a gold SPM tip was used, and one terminal end of the polymer to be used contained a thiol group. This thiol linkage is a strong covalent bond which should be stable relative to the force necessary to remove the physisorbed attachments on the surface. In addition to this, it was found that polyacrylamide does not readily hydrogen bond to gold surfaces, making only one attachment point on the surface for each polymer.[20,21] This method made large improvements to the use of SPM to determine adsorbed polymer conformation.

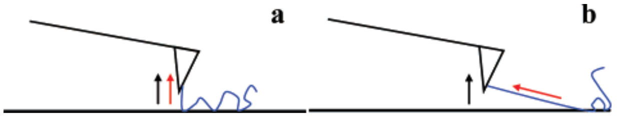

Figure 4. Geometric considerations for polymer force interpretation. (a) Force to remove polymer attachment can be related to the adsorption strength. (b) Force to remove polymer attachment, found by changes in cantilever deflection, is less than that required to remove the attachment due to the angle of the pull.

However, these workers were unable to control the number of macromolecules adsorbed on the tip. In the work done by Haschke et al., different concentrations of thiol-terminated polymers were tested at different "soak" times to show the effect of multiple polymers on a tip.[20,21] It was reasoned that at a very low concentration and adsorption time it could be assumed that only one polymer adsorbed on the tip.[20,21] While this increases the odds of a single chain being measured, it does not guarantee it. Any cluster or agglomeration of the polymer in solution would still result in multiple chains being attached without any way to tell. This issue is of particular importance because polyacrylamide, the polymer used in many studies, does tend to agglomerate.[29] It is important to note that polyacrylamide used for this work is cationic, which gives added stability against agglomeration through the interaction of the charged groups on the polymers. Without knowing the number of polymers on the tip, interpretation of the force curve desorption events to obtain loop lengths becomes nontrivial.

Previous literature has used the force necessary to pull a polymer attachment point from a surface to make reference as to the type of bonding responsible for the attachment.[19−25] Although this seems to be a straightforward deduction, there is at least one complication which has, for the most part, been disregarded. This is the geometry and spacing between the polymer attachment and the tip. Figure 4 illustrates how the force measured to pull a polymer from a surface is dependent on the position on the surface.

If the polymer only laid directly under the tip, the geometry of the pull would not affect the resulting force. However, with a polymer all the attachment points will not lie directly under the tip. Because some polymer attachment points could lay micrometers from the tip on the surface, the geometry of the pulling experiment will directly affect the force to remove the attachment. Thus, as the polymer attachment point lies at greater distances from the tip, the force to detach the polymer, detected by tip deflection, will decrease. This makes references to the force to detach the polymer questionable. For this reason, our work will only deal with deflections of the cantilever and not the forces necessary to deflect the cantilever.

In this paper, we have addressed the problems mentioned previously. Our approach ensures a single polymer on the cantilever tip. This was achieved by (1) introducing thiolglycollic acid group to one terminal end of the polymer, thereby forming a chemical bond with the cantilever tip surface; (2) verified that there was no unexpected adsorption of our modified polymer to the chromium surfaces of the tip; and (3) limited the area of possible adsorption sites available for the polymer to covalently attach to the tip.

2. Experimental Section

Materials. A high molecular weight copolymer of acrylamide and [(3-methacryoylamino)propyl]trimethylammonium chloride (MAPTAC) with one terminal SCH_2COOH group was synthesized by Ciba Specialty Chemicals. This polymer was functionalized with a terminal thiol group by using thioglycollic acid as a chain transfer agent which will leave a single thiolglycollic acid group at one end of the polymer. The molecular weight as given by Ciba Specialty Chemicals was 1.04×10^6g/mol (determined by GPC), and the R_g was found to be 151.3 nm (determined by SLS) at the tip functionalization conditions. All tests were done in Barnstead deionized water on freshly cleaved V-1 grade mica surfaces from SPI Supplies. SPM pulling experiments were performed using an Asylum Research MFP3D system. The cantilevers used were MikroMasch CSC17/Cr-Au. These cantilevers have a spring constant between 0.05 and 0.3 N/m, allowing for the detection of desorption events.

SPM Tip Fabrication. As mentioned previously, one of the major problems with SPM "pulling" experiments relates to where the polymer is being removed from. We employed Haschke's method of attaching the polymer to the tip.[20,21] A problem still left inadequately addressed was how many polymers are present on the tip. The starting point of this work involved developing a method to attach only a single polymer to each tip. To do this, we limited the size of possible adsorption sites available for the polymer to covalently attach to the tip. This was done using focused ion beam milling of the gold surface to remove the gold layer except for a 70 nm circle about 40 nm from the apex of the leading edge of the tip. For our cantilever tips, this left a small gold circle on an exposed chromium sublayer. The gold coating was removed about 6 μm up the tip surface to ensure any polymer adsorbed on the top of the cantilever tip cannot influence our results. A modified tip is shown in Figure 5.

Experimental Methods. Polymer-modified SPM tips were prepared for testing by soaking them in a 9.074×10^{-6} g/mol solution of polymer in water for 1 min. The tips were then rinsed in Barnstead deionized water and mounted for testing. The freshly cleaved mica surface has a reported anionic charge on about 1% of the surface area when placed in Barnstead deionized water.[30] The SPM tip was then lowered down to the surface at a rate of 2 μm/s until a deflection of 10 nm was reached. At this point the tip was allowed to dwell on the surface for a specified amount of time and then was retracted. To ensure clean and accurate force plots, the data acquisition rate used was 50 kHz. All retractions were extended the full range of the z piezo to ensure complete polymer desorption from the surface. Following retraction, the data were analyzed to determine polymer detachments and the distances between them.

Variables Evaluated. This paper also investigated the effect of the retraction rate on adsorbed polymer conformation. In past literature, the retraction rate of the tip from the surface has varied from 50 nm/s up to 10 μm/s.[20,22] In most cases, no reasoning was given for why these speeds were selected. Haschke et al. reported that a quick retraction velocity was necessary to prevent polymer readsorption during the pull.[20] When retracting the cantilever tip from the surface quickly the amount of data points possibly obtained is limited. With fewer data points, the force curve loses detail and makes the detection of desorption events much more difficult. We propose that the frequency of polymer conformation change occurs much faster than the retraction rates used in past and present research. To test this, we examined the effects of five different retraction velocities of 200 nm/s, 500 nm/s, 2 μm/s, 4 μm/s, and 10 μm/s on the polymer loop length distributions.

The SPM "pulling" experiments data may also be affected by the dwell time that the tip spends in contact with the surface. The effect of time on adsorbed polymer thickness was addressed using ellipsometry by Stromberg et al. on polystyrene.[31] They found that the thickness of the polymer layer initially increased then over time decreased. Cohen Stuart and Tamai were able to show the same type behavior of poly(vinylpyrrolidone) on glass using the streaming potential method.[32] Indirect measurements of this behavior have also been found observing decreases in flocculation over time.[33] This shows that polymer movement and reorganization on a surface can and does take place. No work, using SPM pulling experiments, has been done to attempt to detect and analyze polymer movement or relaxation on a surface with time. In this work, the effects of the dwell time on the results of SPM pulling experiments were investigated. We have looked at dwell times from as short as 0.0064

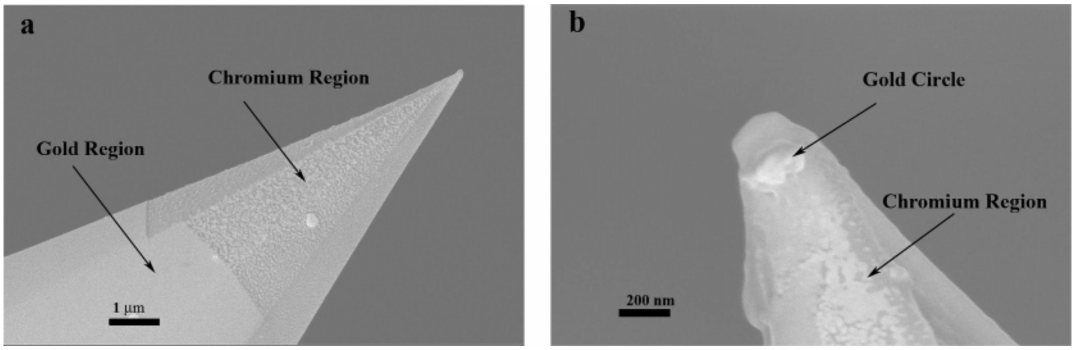

Figure 5. (a) SEM micrograph of modified tip showing the removal of gold as the apex is approached. (b) Closer view of the apex of the SPM tip showing the 70 nm gold circle.

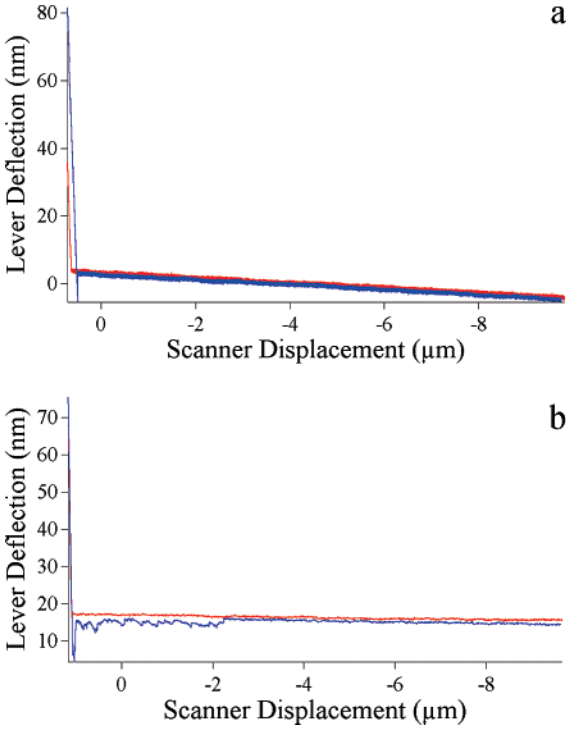

Figure 6. Verification of polymer tip interaction. (a) Chromium tip exposed to concentrated polymer solution. (b) Gold tip exposed to concentrated polymer solution.

s to 300 s to check the number of polymer attachment points and how they change with time.

3. Results

Verification of Methodology. In Figure 5 the gold layer was removed, leaving only the chromium sublayer. The composition of the SPM tip surface was confirmed using scanning Auger microscopy. It was important to verify that there was not any unexpected adsorption of our modified polymer to the chromium portion of the tip. To do this, a gold cantilever and a chromium cantilever were both tested with thiol-modified polymer and without polymer. Each cantilever was tested with polymer concentrations of 0 g/mL and a very high concentration of 6.98 $\times 10^{-4}$ g/mL. Figure 6 shows the force curves of both the gold and chromium tips after a treatment time of 1 min in the high concentration polymer solution followed by rinsing in Barnstead water. The tests clearly indicated that the polymer will only attach to the gold surfaces on our modified tips. It was also shown that physisorption of the polymer to the chromium surface of the tip was not present after rinsing in Barnstead water. This verifies that our technique of exposing the chromium sublayer is an effective method to prohibit polymer adsorption.

By leaving only a small area of gold on the tip available for polymer adsorption, it is very likely that only one polymer will be able to adsorb. This reasoning is supported by the cationic polyacrylamide's tendency to form "mushroom" conformations when tethered by one end to a surface. This will leave a large "mushroom" which will experience electrostatic repulsion between the cationic groups both within the polymer and with other polymers which may be trying to access the gold circle. This "mushroom" can be expected to shield the gold circle, prohibiting any additional polymers from adsorbing. Griebel et al. reported the radius of gyration, R_g, for a cationic polyacrylamide of a similar molecular weight and charge density to be 95 nm.[34] We found the R_g to be 151 nm at our tip functionalization conditions. This would result in a "mushroom" with a diameter of about 300 nm, which should easily cover the 70 nm gold circle left on the cantilever tip. This suggests that once a polymer is adsorbed on the gold circle on the tip of the cantilever, the adsorption of other polymer molecules to the gold circle is unlikely. Because the polymer does not chemically bond to the chromium surface, only one polymer molecule will adsorb on the surface by the chemical bond formation between gold and thiol end group on the polymer. This assumption was experimentally tested by exposing the SPM tips to polymer solutions of different concentrations and looking for changes in the force curves at higher concentrations. Figure shows a modified tip treated at a polymer concentration of (a) 9.074 $\times 10^{-6}$ g/mL and (b) 6.98 $\times 10^{-4}$g/mL. As can be seen in Figure 7, the increase in concentration does not significantly change the force curve. The lengths of which the attachment points were found in Figure 7b are similar to those of Figure 7a.

Retraction Velocity. Past literature, using "pulling" SPM experiments to determine polymer loop lengths, has employed a wide range of cantilever retraction velocities with very little explanation for the selected velocities.[20,22] In this work, we have investigated the effect of retraction velocity on the resulting polymer loop length distributions. Figure 8 shows the population distribution of an adsorbed polymer put into 20 nm bins. Bin sizes of 10, 20, 30, and 50 nm were all tested to ensure our results were not significantly affected by the choice of bin size. We selected 20 nm bins because it gave the most detail without significantly decreasing the frequency of events in each bin. All frequencies were reported as the percentage of loops which fell in respective bins. This allowed for comparison using statistical methods without needing to account for the number of loops. The minimum number of loops used in a distribution was 74, and the maximum number of loops was 517. The majority of the populations contained more than 100 loops, showing statistical significance.

Unlike Haschke et al., we have not removed parts of the population that are on either end of the distribution.[20] We have

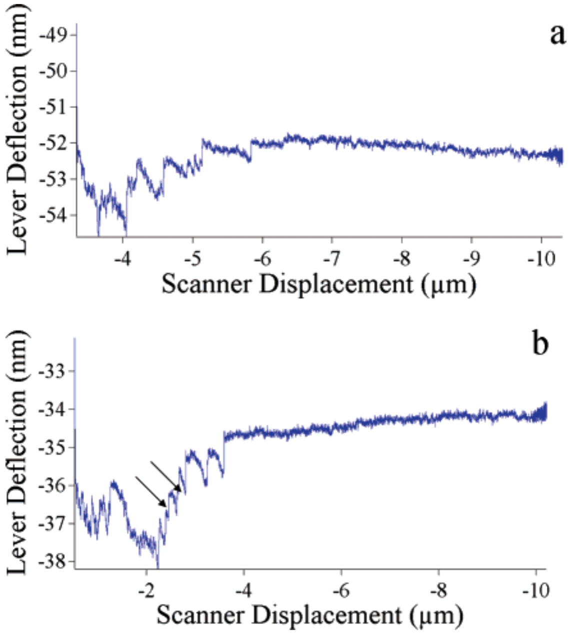

Figure 7. Effect of polymer concentration for cantilever tip functionalization. (a) Cantilever tip treated for 1 min in a 9.074 × 10^{-6} g/mL solution of polymer. (b) Tip used in (a) treated for an additional 5 min in a high polymer concentration solution of 6.98 × 10^{-4} g/mL.

included all points that passed the criteria for selection. We believe this to be important as a few very large loops can have profound effects on the interactions of the substrate this polymer is adsorbed, such as the collision efficiency in flocculation.[35] The large loop lengths found in this work may have resulted from nonuniform distribution of charged groups in our random copolymer and also encounters with nonuniform regions of the mica surface. The shape of the polymer loop length distribution is very similar to that found by Lévy and Maaloum, although the location is different which is most likely due to the methodology used and the polymers analyzed.[22,23] In Figure 8b−d, the population distributions have the same scale and shape. Figure 8a has a different scale but does retain the same shape. In order to compare these distributions, we chose to use a chi-squared test for homogeneity. This test can be used for non-normal distributions, which this clearly is. Evaluating with a significance level of 99.9995%, we were able to show that the populations for all retraction velocities were statistically the same. From this analysis, we have shown that within our testing limits the retraction velocity does not have an effect on the polymer loop length distribution. This allows researchers to choose which retraction velocity allows them to get the best data. For the rest of this work we chose a retraction velocity of 2 μm/s.

While our method overcomes the problem of multiple chains on the SPM tip, it does not deal with the fact the tip is not always positioned directly above the adsorbed polymer. The polymer location could be greatly displaced from the tip. The resulting angle dependence does mean that the actual loop length distribution may be shifted toward larger loop lengths.

Dwell Time. The effect of dwell time on adsorbed polymer conformation was also investigated. Cohen Stuart et al. have shown that a polymer will spread out on a surface over time.[32] This was done by measuring the change in thickness of the adsorbed polymer layer. We have verified polymer movement by monitoring the number of attachments found after different dwell times of the tip on the surface. Figure 9 shows that with increasing dwell time the number of attachment points on the surface increases. Figure 9 also shows that this number appears to plateau quickly, also seen by the Cohen Stuart and Tamai using streaming potential measurements.[32] Our results show that the number of attachment points of our polymer reach a statistical equilibrium at about 60−90 s of dwell time. This relaxation time is the same as the values, found previously, by Cohen Stuart and Tamai.[32]

Figure 9 shows that there is a large variation in the number of attachments with the same polymer at the same dwell time. This is most likely due to the instantaneous conformation of the polymer as it is put on the surface. If the polymer lies in a loose ball, it is possible that there could be multiple attachments in a small area. However, if the polymer is extended, the likelihood of having many attachment points decreases due to the amount of polymer that will come in contact with the surface. These effects cannot be avoided due to the polymers confined movement in solution away from the surface. However, with multiple tests we have been able to detect a trend, which even including the deviations shows a plateau event.

4. Discussion

Data Selection. To analyze the polymer conformation and lengths of polymer loops, a method that can correctly determine the desorption points from a force curve must be developed. Much of the past work simply states that only clear desorption events are selected which show a stretching of the polymer chain followed by a sharp detachment, shown in each of the peaks selected in Figure 1. However, it is, in practice, difficult to determine the "clear desorption events". First, the minimum magnitude of the deflection necessary to make a point must be found. Second, how many data points must be present to make up the stretching portion of an event should be determined. Lévy and Maaloum wrote an algorithm to automatically pick out desorption events based on the magnitude of the detachment relative to the noise of the freely vibrating chain.[23] By doing this, they have set criteria to select points and limited the number of false events which could be selected. Lévy and Maaloum required the deflection to be greater than the mean-squared deviation of the freely vibrating cantilever after the last desorption event.[23] For this work we looked to take this even further. We have set a requirement that the deflection of the lever must be greater than 3 times the average standard deviation of a freely vibrating lever and chain. This adds to our confidence that the deflections we see are not due to noise in the cantilever vibration. We have also begun to look at the effects of requirements on the stretching of the polymer chain relative to point selection. Table 1 shows how the selection of desorption events is altered by requiring different stretching lengths for acceptance.

Table 1 shows the effects of requirements on polymer stretching relative to desorption event selection. We have chosen to use only events which have a minimum of 200 data points leading to a desorption event. We believe this, in combination with our requirement on the magnitude of desorption events, will significantly reduce the chance of counting false desorption events. If the stretching criterion is increased to 1000 data points, then events that we believe to be significant, as illustrated by the arrows in Figure 7b, are not counted.

Comparison with Theory. A considerable amount of work has been done to theoretically model adsorbed polymer conformations.[36−40] With the development of SPM testing techniques, researchers are now able to determine what the loop length distribution for an adsorbed polymer actually is. It has been shown that the distribution of polymer concentration at

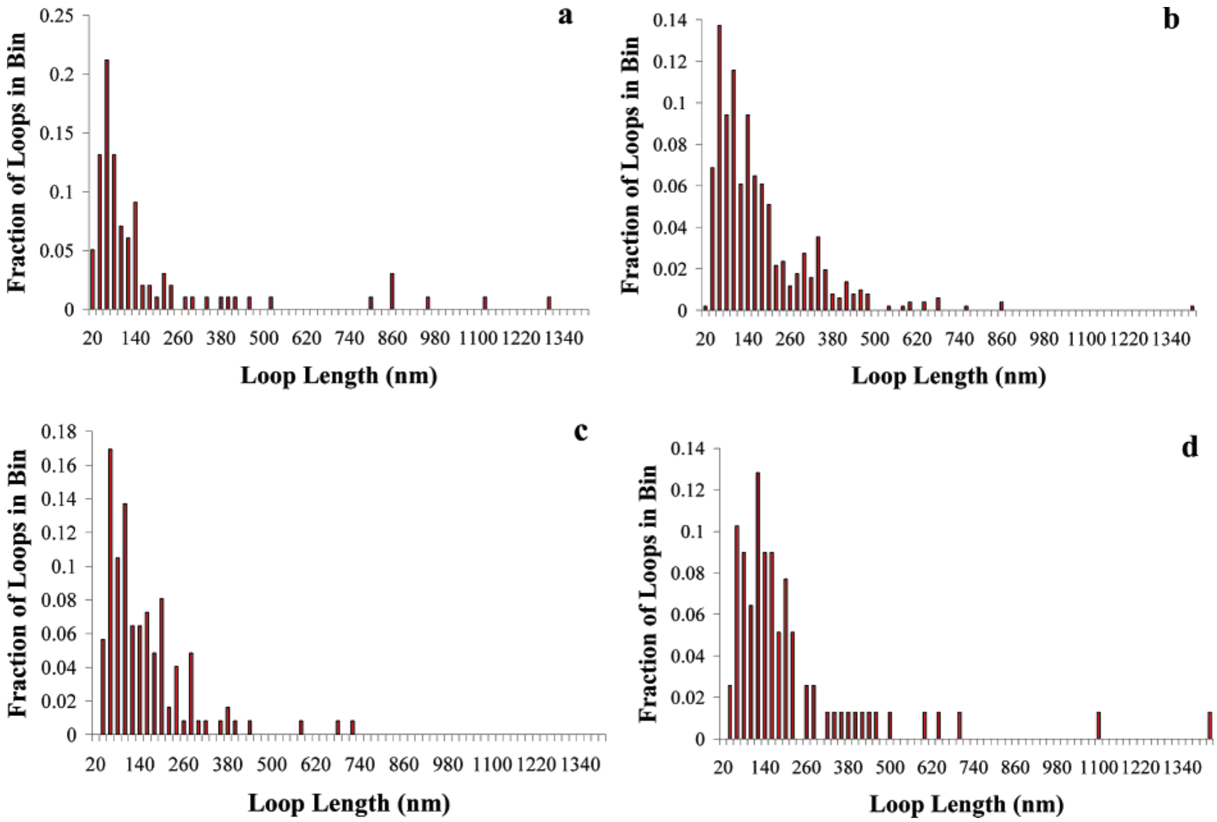

Figure 8. Loop length distribution for different retraction velocities: (a) 200 nm/s, (b) 2 μm/s, (c) 4 μm/s, and (d) 10 μm/s.

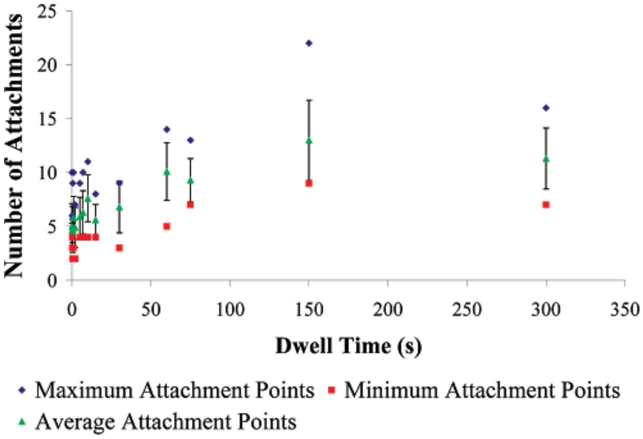

Figure 9. Effect of dwell time on number of polymer attachment points. Error bars show the standard deviation in the number of attachment points for each dwell time.

Table 1. Effect of Polymer Stretching Criteria on Selection of Desorption Events in Figure 7b

no. of points in stretch	no. of desorption events
50	19
100	19
200	14
500	9
1000	5

different lengths from the surface decays at different rates.[41] The central region where most of the polymer lies decays following a power law, but the distal region follows an exponential decay.[41] Previous work done by Senden et al. and Haschke et al. has looked to fit the obtained loop length distributions to the scaling models developed by Aubouy et al.[20,25,38,39] Aubouy et al. showed that the number of loops in a distribution with exactly n monomers scaled with $n^{-11/5}$ in the dilute regime and good solvent.[38] To compare the power law distribution of polymer loop lengths, the data were plotted on a log/log scale and the slope of the distribution was found, as shown in Figure 10.

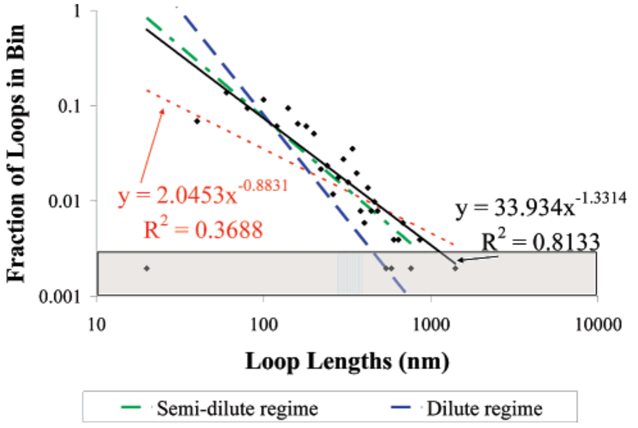

Figure 10. Loop length distribution for 2 μm/s retraction rate. The short-dashed trend line includes all points while the solid trend line only includes points in the unshaded region.

The short-dashed trend line in Figure 10 shows that when all points in our distribution are included, the power law does not fit very well. Past researchers have discarded small and large loop lengths to fit the central region of the distribution.[20] When this is done, the slope and fit of the power law distribution fit much better. The effect of this change is illustrated in the solid trend line in Figure 10 which shows that the central region of our polymer distribution does not fall in the dilute regime with a good solvent. This has been explained by Haschke et al. through confinement of the polymer between the tip and the surface, resulting in a transfer to the semidilute regime which would scale to $n^{-3/2}$.[20] Our data agree with this explanation, within the deviation of the distributions. However, we feel that even though the distal and proximal regions of the polymer distribution only account for a small fraction of the loop lengths, they are still valid data points and can be used to describe the overall distribution.

5. Conclusions

This study presents measurements of a single polymer's adsorption to a mica surface. This was achieved through a covalent attachment of one terminal end of an individual polymer molecule to our modified tip. The results indicated that the number of polymer adsorption sites can be detected using SPM. The loop lengths of cationic polyacrylamide on a mica surface have a broad distribution, and the distance between two adsorption sites varies from around 20 nm to over 1 μm. We have shown, using a chi-squared analysis, that the retraction velocity's effect on the size of polymer loops detected is negligible. Therefore, the use of slower pulls to gain more data points and more consistent interpretation is allowed. The movement of an adsorbed polymer on a mica surface over time using SPM was, for the first time, directly confirmed by testing the effect of dwell time on the number of polymer attachment points to a mica surface. The loop length distributions of the central region were shown to fall within predictions for a polymer in the semidilute regime in a good solvent. An investigation into the effects of site blocking on adsorbed random copolymer conformation is in progress.

Acknowledgment. The authors kindly acknowledge the following companies: Ciba Specialty Chemicals for providing the polymer for these experiments, MikroMasch for their assistance in fabricating the SPM tips used, Asylum Research for their generous support and provisions of code to run these experiments, Dr. Christine Kranz for her valuable discussions on FIB milling, and the Institute of Paper Science and Technology at Georgia Tech for providing the funding for this research.

References and Notes

(1) O'Shaughnessy, B.; Vavylonis, D. *Eur. Phys. J. E* **2003**, *11*, 213−230.
(2) Fleer, G. J.; Cohen Stuart, M. A.; Scheutjens, J. M. H. M.; Cosgrove, T.; Vincent, B. *Polymers at Interfaces*; Springer: Berlin, 1993.
(3) Sperling, L. H. *Introduction to Physical Polymer Science*; Wiley-Interscience: New York, 2001.
(4) Cosgrove, T. *J. Chem. Soc., Faraday Trans.* **1990**, *86*, 1323−1332.
(5) Cosgrove, T.; Fergie-Woods, J. W. *Colloids Surf.* **1987**, *25*, 91−99.
(6) Cosgrove, T.; Griffiths, P. C. *Adv. Colloid Interface* **1992**, *42*, 175−204.
(7) Barnett, K. G.; Cosgrove, T.; Vincent, B.; Burgess, A. N.; Crowley, T. L.; King, T.; Turner, J. D.; Tadros, T. F. *Polym. Commun.* **1981**, *22*, 283−285.
(8) Barnett, K. G.; Cosgrove, T.; Vincent, B.; Sissons, D. S.; Cohen, Stuart, M. A. *Macromolecules* **1981**, *14*, 1018−1020.
(9) Santore, M.; Fu, Z. *Macromolecules* **1997**, *30*, 8515−8516.
(10) Chu, B. *Laser Light Scattering*; Academic Press: New York, 1974.
(11) Taunton, H. J.; Toprakcioglu, C.; Fetters, L. J.; Klein, J. *Macromolecules* **1990**, *23*, 571−580.
(12) Higgins, J. S.; Benoit, H. C. *Polymers and Neutron Scattering*; Oxford University Press: New York, 1994.
(13) Rennie, A. R.; Crawford, R. J.; Lee, E. N.; Thomas, R. K.; Crowley, T. L.; Roberts, S.; Qureshi, M. S.; Richards, R. W. *Macromolecules* **1989**, *22*, 3466−3475.
(14) Forsman, W. C.; Latshaw, B. E. *Polym. Eng. Sci.* **1996**, *36*, 1114−1124.
(15) Ray, C.; Brown, J. R.; Akhremitchev, B. B. *J. Phys. Chem. B* **2007**, *111*, 1963−1974.
(16) Al-Maawali, S.; Bemis, J. E.; Akhremitchev, B. B.; Liu, H.; Walker, G. C. *J. Adhes.* **2005**, *81*, 999−1016.
(17) Al-Maawali, S.; Bemis, J. E.; Akhremitchev, B. B.; Leecharoen, R.; Janesko, B. G.; Walker, G. C. *J. Phys. Chem. B* **2001**, *105*, 3965−3971.
(18) Hugel, T.; Grosholz, M.; Clausen-Schaumann, H.; Pfau, A.; Gaub, H.; Seitz, M. *Macromolecules* **2001**, *34*, 1039−1047.
(19) Chatellier, X.; Senden, T. J.; Joanny, J.-F.; Di, Meglio, J.-M. *Europhys. Lett.* **1998**, *41*, 303−308.
(20) Haschke, H.; Miles, M. J.; Koutsos, V. *Macromolecules* **2004**, *37*, 3799−3803.
(21) Haschke, H.; Miles, M. J.; Sheppard, S. *Single Molecule* **2002**, *3*, 171−172.
(22) Levy, R.; Maaloum, M. *J. Phys.: Condens. Matter* **2004**, *16*, 7199−7208.
(23) Levy, R.; Maaloum, M. *Ultramicroscopy* **2005**, *102*, 311−315.
(24) Senden, T. J.; di Meglio, J.-M.; Auroy, P. *Eur. Phys. J. B* **1998**, *3*, 211−216.
(25) Senden, T. J.; di Meglio, J.-M.; Silberzan, I. *C. R. Acad. Sci. IV* **2000**, *1*, 1143−1152.
(26) Bemis, J. E.; Akhremitchev, B. B.; Walker, G. C. *Langmuir* **1999**, *15*, 2799−2805.
(27) Conti, M.; Bustanji, Y.; Falini, G.; Ferruti, P.; Stefoni, S.; Samori, B. *ChemPhysChem* **2001**, *2*, 610−613.
(28) Garnier, L.; Gauthier-Manuel, B.; van der Vegte, E. W.; Snijders, J.; Dadziioannou, G. *J. Chem. Phys.* **2000**, *113*, 2497−2503.
(29) Hecker, R.; Fawell, P. D.; Jefferson, A. *J. Appl. Polym. Sci.* **1998**, *70*, 2241−2250.
(30) Pashley, R. M. *J. Colloid Interface Sci.* **1981**, *80*, 153−162.
(31) Stromberg, R. R.; Tutas, D. J.; Passaglia, E. *J. Phys. Chem.* **1965**, *69*, (11), 3955−3963.
(32) Cohen Stuart, M. A.; Tamai, H. *Macromolecules* **1988**, *21*, 1863−1866.
(33) Yu, X.; Somasundaran, P. *J. Colloid Interface Sci.* **1996**, *178*, 770−774.
(34) Griebel, T.; Kulicke, W.-M.; Hashemzadeh, A. *Colloid Polym. Sci.* **1991**, *269*, 113−120.
(35) Behl, S.; Moudgil, B. M.; Prakash, T. S. *J. Colloid Interface Sci.* **1993**, *161*, 414−421.
(36) de Gennes, P.-G. *Scaling Concepts in Polymer Physics*; Cornell University Press: Ithaca, NY, 1979.
(37) de Gennes, P.-G. *Macromolecules* **1981**, *14*, 1637−1644.
(38) Aubouy, M.; Guiselin, O.; Raphael, E. *Macromolecules* **1996**, *29*, 7261−7268.
(39) Aubouy, M. *Phys. Rev. E* **1997**, *56*, 3370−3377.
(40) Scheutjens, J. M. H. M.; Fleer, G. J. *J. Phys. Chem.* **1980**, *84*, 179−190.
(41) de Joannis, J.; Park, C.-W.; Thomatos, J.; Bitsanis, I. A. *Langmuir* **2001**, *17*, 69−77.

MA070495D