Salt Effect on Cationic Polyacrylamide Conformation on Mica Studied by Single Molecule "Pulling" with Scanning Probe Microscopy

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The effect of salts on adsorbed polyelectrolyte conformations has been studied extensively over the past three decades. Previous researchers have proposed that increasing salt concentration results in larger loops and tails for weak polyelectrolytes adsorbed on a surface. However, no experimental verification of this theory has been published. In this work, we present experimental verification acquired by "pulling" single molecules of a polyelectrolyte from a mica surface using a scanning probe technique. We also present a new method for analyzing changes in adsorbed polymer tail lengths. We demonstrate that increasing solution salt concentration correlates with both loop and tail lengths of an adsorbed low charge density cationic polyacrylamide on a mica substrate.

1. Introduction

The effects of electrolytes on polymer adsorption have been a study of great interest over the past two decades.[1–25] Much of this interest is due to the presence of salts in many industrial applications where polymers are used. Salts can affect the conformation and amount of adsorbed ionic and nonionic polymers.[1] According to Shubin and Linse, salts influence adsorbed polymer conformation by

- screening of electrostatic attractions between the polymer and the surface,
- screening of electrostatic repulsion between similarly charged groups,
- competition between electrolyte ions and polymers for space near the charged surface, and
- competition for adsorption sites between the electrolyte and the polymer.[2]

It is expected that these effects would be the most pronounced on polyelectrolytes.[26] Similarly, Fleer et al.[1] suggested a weak salt effect for uncharged polymers and charged surfaces. They expected the addition of salt to increase the amount of charged polymers adsorbed on uncharged surfaces and to decrease the amount of charged polymer adsorbed onto an oppositely charged surface unless the polymer adsorbs via a nonelectrostatic mechanism.

Electrolytes in solution have the ability to affect polyelectrolytes in different ways depending on the polymer's properties. They can screen electrostatic interactions and also compete for electrostatic adsorption sites. If a polyelectrolyte has a high charge density, there will be a large amount of repulsion between charged groups in the polymer chain. This will cause the polymer to occupy a large area upon adsorption and thereby reduce the number of polymer molecules which can adsorb on the surface. Adding salt to the solution screens these electrostatic forces allowing polymers to move closer to one another and increasing the adsorbed amount on the surface.[2]

The competition for adsorption sites is not as important, in this situation, as the multiple charged sites on the polymer allow most groups on the polymer backbone to adsorb. Van de Steeg et al. showed, through simulations, that salt ions are also able to displace highly charged polymers.[27] This illustration of the opposite case points to the effect that slight differences in experimental settings can yield different results. For the case of low charge density polymers, adsorption to a surface is based on the interaction of a few charged groups with the oppositely charged surface. Here the competition for adsorption sites can interfere with polymer adsorption resulting in decreased adsorption with increasing salt concentration.[2] Much of this effect has been shown through different modeling techniques. Dobrynin et al. used scaling theory to predict the effect of salt concentration on adsorbed amount of different polyelectrolytes.[7] Hoda and Kumar used Brownian dynamics, which is an intermediate coarse grained simulation technique, to do this.[5] Carrillo and Dobrynin used molecular dynamics simulations to analyze this situation.[6] Scheutjens and Fleer's self-consistent mean field theory was used by Shubin and Linse to again observe the salt effect on adsorbed polymers.[2]

To date, modeling and experimental work has focused on how salt impacts the amount of polymer adsorbed. Very little work has addressed the impact of salt on adsorbed polymer conformation. This is because most of the techniques, including dynamic light scattering, neutron reflectivity, and surface force analysis with a force-balance apparatus, used to determine adsorbed polymer layer thickness are incapable of revealing details of a single adsorbed polymer's conformation.[4,28–30]

The impact of salt on hydrodynamic thickness is an open question. Both Wang and Audebert and Meadows et al. found that as the salt concentration was increased, the hydrodynamic thickness decreased[4,29] whereas Takahashi, Dahlgren et al., Rojas et al., and Shubin and Linse found the opposite.[2,11,12,25,28] Wang and Audebert and Meadows et al., suggested that the increase in salt concentration screens out the electrostatic interactions between the polymer chains and also the polymer and substrate surface.[4,29] Because the charged group interactions are screened the polymer can occupy a more compact structure than would be allowed if the electrostatic interactions were present.

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SCHEME 1: SPM Tip Modification and Polymer Adsorption[a]
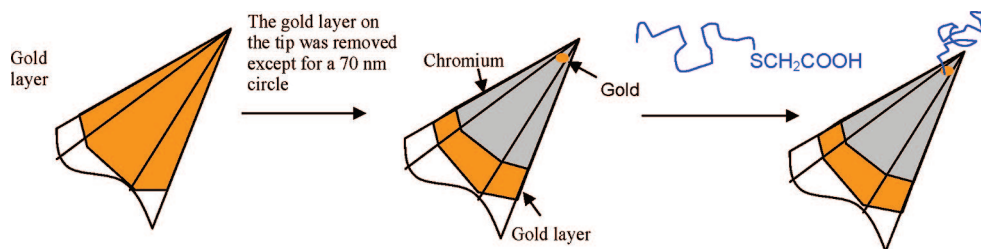
Takahasi, Shubin, and Linse counter that as competition for surface adsorption sites increases, the polymer will extend away from the surface which could increase the adsorbed polymer's loop lengths.[2,28] Work done by Dahlren et al. and Rojas et al. also found this polymer extension from a surface with increasing salt concentration using a surface force technique.[11,12,25] With light scattering and NMR measurements, Flood et al.[8,29] reported that the monovalent salts did not have a noticeable effect on the train portion of adsorbed poly(ethylene oxide), a nonionic polymer.[8,31] However, with increasing valence charges of salt ions, they found the competition for adsorption sites became noticeable.

Shubin and Linse[2] found that with increasing electrolyte, the adsorbed layer thickness, as measured by ellipsometry, increased. After performing self-consistent mean field theory modeling, they proposed, that the increase in layer thickness was due to larger loops and tails. Until now, no direct experimental verification of this prediction has been published.

Previous researchers have taken many different approaches to determine details of an adsorbed polymer's conformation.[32] Recently, Gaub et al., Senden et al., Walker et al., and others have conducted large amounts of work using scanning probe microscopy to attempt direct measurements of the characteristics of an adsorbed polymer's conformation.[17,18,33−41] Hugel et al. and Haschke et al. investigated the effects of electrolyte concentration on the attachment force between a polymer and a substrate.[17,38] This previous research provides a significant amount of information regarding these adsorbed polymer interfaces. However, as discussed in our previous work, none of these researchers has been able to ensure that only a single molecule was being observed.[30]

Previously, we reported the development of a technique which ensures single molecule "pulling" using scanning probe microscopy.[30] In this work, we have introduced a new data analysis technique allowing the determination of changes in adsorbed polymer tail length. Using these techniques we have experimentally evaluated the salt effect on three specific details of an adsorbed polymer's conformation: (1) the number of polymer attachment points to a surface; (2) the change in loop length distribution; (3) the change in the adsorbed polymer's tail length. We have also investigated the effects of size and valence charge of the dissociated salt ions on adsorbed polymer conformation.

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 leaves a single thiolglycollic acid group at one end of the polymer. The molecular weight as given by Ciba Specialty Chemicals was 1.04×10^6 g/mol (determined by gel permeation chromatography) and the radius of gyration, R_g, was found to be 151.3 nm (determined by static light scattering) at the tip functionalization conditions. The polymer consists of 15 wt % MAPTAC monomeric units and 85 wt % acrylamide monomeric units. All tests were done in Barnstead deionized water with varying salt concentrations on freshly cleaved V-1 grade mica surfaces from SPI Supplies. Sodium chloride from Mallinckrodt AR, lithium chloride (Reagent+ 99%) from Sigma Aldrich, cesium chloride (99.9% metals basis) from AlfaAesar, and magnesium chloride hexahydrate from Aldrich were used as obtained. Salt solutions were prepared by dissolution of the specific salt in deionized water (Barnstead).

Instrumentation. Scanning probe microscopy (SPM) pulling experiments were performed using an Asylum Research MFP3D system. The cantilevers used were modified MikroMasch CSC17/Cr−Au[30] with spring constants between 0.05 and 0.3 N/m. As discussed in our previous work, it is critically important that only one polymer molecule is bonded to the SPM cantilever tip.[30] The grafting of thiol group terminated cationic polymers on a SPM cantilever tip for polymer adsorption studies has been previously reported.[16,17] However, the method used by these researchers could not guarantee that only a single polymer was being analyzed. It is equally important that the polymer molecule is bonded on the SPM cantilever tip by only one terminal end. To ensure only one polymer can adsorb on the SPM tip ion beam milling was used to remove the gold layer on the cantilever tip except for a small 70 nm circle approximately 40 nm from the apex of the leading face of the tip. The process of cantilever fabrication and single polymer adsorption are illustrated in Scheme 1. More detailed information can be found in our previous publication.[30]

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 one minute. The tips were then rinsed in Barnstead deionized water and mounted for testing. The freshly cleaved mica surface has a reported anionic charge on approximately 1% of the surface area when placed in Barnstead deionized water.[42] A few drops of water or salt solution were then placed on the mica surface. Next, the SPM tip was lowered down to the surface at a rate of 2 μm/s until a deflection of 10nm was reached. At this point the tip was allowed to dwell on the surface for five minutes and then was retracted at 2 μm/s. To ensure clean and accurate force plots, the data acquisition rate used was 50kHz. All retractions were extended the full range of the *z* piezo to ensure complete polymer desorption from the surface. Following retraction, the data was analyzed to determine polymer detachments and the distances between them. A minimum of 200 data points was required for desorption event selection as described in more detail in our previous work.[30]
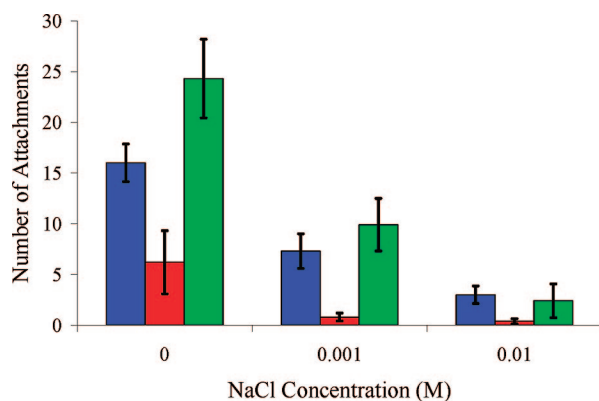
Figure 1. Effect of dissociated NaCl ions competing for adsorption points with the MAPTAC/acrylamide copolymer on a mica surface. Three different bars representing repeats using a new polymer. Error bars represent the 90% confidence range of the mean.

Figure 2. Effect of dissociated $MgCl_2$ ions competing for adsorption points with the MAPTAC/acrylamide copolymer on a mica surface. Error bars represent the 90% confidence range of the mean.

For each experiment a polymer functionalized cantilever was first tested in Barnstead deionized water. Then the tip was retracted and the water solution was removed with a pipet and a few drops of the lowest salt concentration to be tested were added to the mica surface. The tip was then allowed to equilibrate in the salt solution for approximately 5 min. Following this, the tip was brought to the surface and testing began again. Testing was always performed from low to high salt concentrations. For most of the testing presented a single polymer was analyzed under different electrolyte concentrations. However, when determining the effects of different salts a new cantilever and polymer were used to ensure no electrochemical damage occurred to the small gold circle at the end of the cantilever tip. The results of different polymer molecules were never combined or compared directly as differences in the molecules molecular weight could affect the results.

3. Results and Discussion

This study investigated an adsorbed polymer's conformation through determination of the number of polymer attachment points, the loop length distributions of an adsorbed polymer, and the change in the adsorbed polymer's tail length. These measurements provide an improved description of the tail and loop portions of adsorbed polymer's conformation.

Number of Polymer Attachment Points. Figure 1 illustrates the resulting trend of polymer desorption events with increasing NaCl concentration. It is found that as the concentration of sodium ions in the liquid phase increases, the number of polymer attachment points decreases. At salt concentrations greater than or equal to 0.1 M (data not shown), no desorption events were found.

Figure 2 correlates the number of attachments of the polymer to mica with a divalent salt, $MgCl_2$. For the divalent magnesium ion, no polymer adsorption points are found if the concentration of $MgCl_2$ is equal or greater than 0.01M.

The effect of cation size was also examined. Similar to NaCl, the number of polymer attachment points decreases with increasing concentration of either LiCl or CsCl. At concentrations greater or equal to 0.1 M no attachment points were detected. No apparent difference on the number of polymer attachment points with the radius of the salt cation was found.

Dissociated salt cations will compete with the cationic polyacrylamide molecule for adsorption sites on an anionic mica surface. Thus, increasing salt concentration should block polymer adsorption and increase loop and tail lengths. Ad-
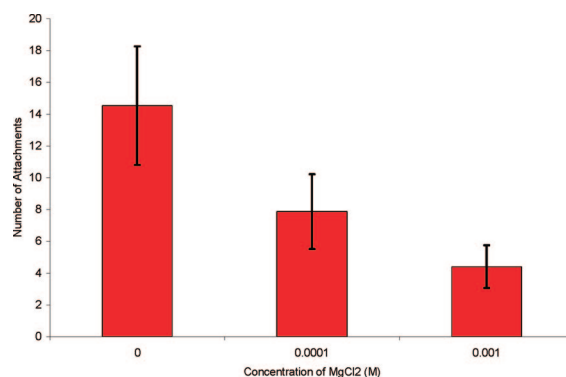
ditionally, the increase in the salt concentrations will reduce the electric double layer thicknesses of both cationic polymer and anionic substrate, resulting in weakening of electrical attraction between two opposite charged substances. As these ions screen the interaction of the polymer with the substrate, the polyelectrolyte molecules have fewer attachment points to the substrate due to the decreased electrostatic interactions.

As the salt ion concentration increased, its ability to fill the vacant anionic sites, left by the potassium ions, increases. For the case of a salt concentration greater than 0.01 M, this can be interpreted to mean that the sodium ions competing for the anionic oxygen sites, on the surface of the mica, have diffused into the electric double layer reducing the opportunity for the polymer to adsorb on the surface. This reduction in polymer attachment points was predicted by van de Steeg et al. and Shubin and Linse,[2,27] and experimentally verified here.

Adsorbed Polymer Loop Length Distributions. The loop length distributions for the salt effect using NaCl are shown in Figure 3. The loop lengths were determined by measuring the distance the AFM cantilever traveled away from the surface, perpendicularly, between adsorption points. The selection of desorption points was described in detail in our previous work.[30] This measurement technique gives the length of a stretched polymer chain, or the contour length of the loop. In this work, the same polymer molecule was tested at three different salt concentrations. It was found that the average number of attachment points decreases with increasing salt concentration, in agreement with the prediction of Shubin and Linse.[2]

Figure 3 depicts the loop length distribution as a function of [NaCl]. While it was possible to extract the mean loop length (first moment) from the distributions, it was difficult to identify changes in the distribution or the higher moments thereof in Figure 3. The same increases were found for all of the salts tested regardless of the cation size. These results are shown in Table 1. The mean loop lengths under different salt conditions we were able to confirm the increase of adsorbed polymer loop lengths with increasing salt concentration. While this experiment can provide no information on how extended the loop is from the surface it is presumed that longer loop lengths would be more extended.

The change in the average loop length values for the LiCl test, given in Table 1, show a decrease in adsorbed polymer loop length at the 0.001 M concentration. Although this is unexpected, it is plausible that the polymer could adsorb with shorter loop lengths in any of these conditions. The 0.01 M LiCl concentration tests produced the expected trend validating the argument for increasing adsorbed polymer loop lengths with increasing salt concentration.
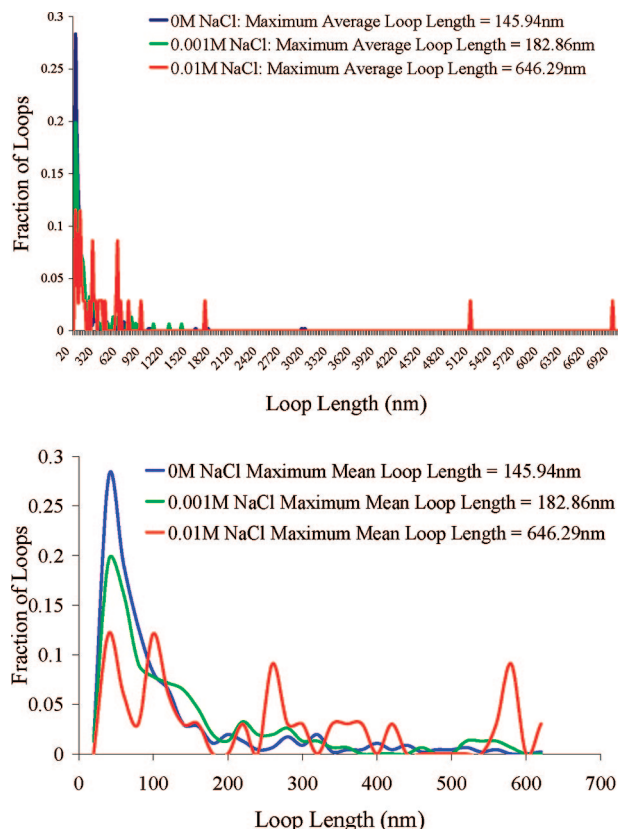
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Figure 3. Effect of NaCl concentration on the loop length distribution of a single MAPTAC/acrylamide copolymer on a mica surface. Enlarged portion of the smaller loop lengths to show shift with toward larger loops with increasing salt concentration.

TABLE 1: Mean Loop Lengths for Each Salt and Concentration Range Studied

concentration (M)	loop length (nm)			
	NaCl	LiCl	CsCl	MgCl$_2$
0	145.94	108.79	107.45	158.52
0.0001				172.48
0.001	182.86	88.56	114.11	191.54
0.01	646.29	157.47	316.00	

Change in Adsorbed Polymer Tail Length. Not only the loop length of an adsorbed polymer will change as a function of salt concentration, the tail length of the adsorbed polymer will also change as this condition is varied. This change in adsorbed polymer conformation has been a topic of interest to many researchers. Shubin and Linse predicted that increases in salt concentration would also increase the length of adsorbed polymer tails.[2] The work of Bauer et al. under the assumption of Nelson et al., supports this theory that the tail length increases with increasing salt concentration.[43,44] However, no research, to date, has been able to infer information on the length of adsorbed polymer tails, not to mention the effect of salt concentration on this, using atomic force microscopy.

To date, there have been no published reports of the use of AFM to determine the loop length change of an adsorbed polymer on a substrate at different conditions. We present herein compelling evidence that direct measurement of a polymer's tail length can be made by simply "pulling" an adsorbed polymer from a surface when one end of the polymer is covalently attached to an SPM tip. We have previously reported an approach for attaching a single polymer molecule to the apex of an SPM tip.[30] With our experimental technique, the distance
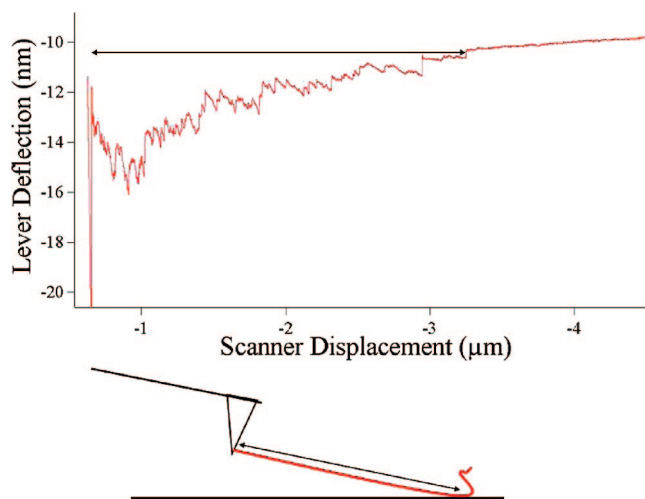

Figure 4. Schematic of how the length of a polymer chain leading up to the last adsorption point can be found. The distance to the last desorption point for this polymer, in Barnstead deionized water on mica, is 2626.4nm.
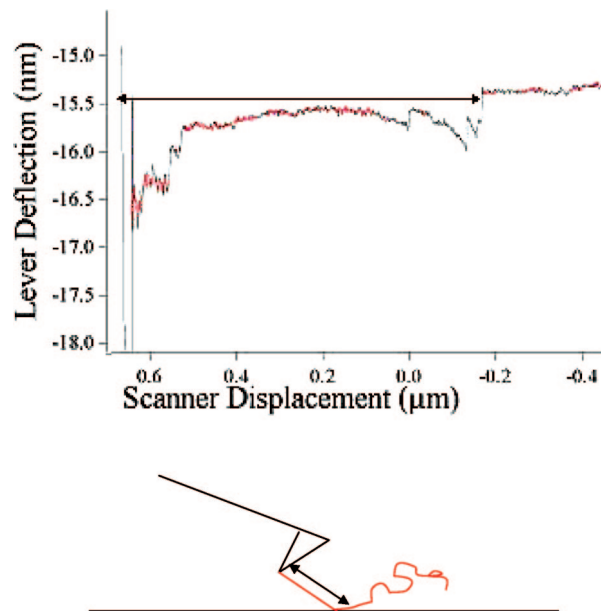

Figure 5. Schematic of the same polymer chain shown in Figure 4 in a 0.001 M NaCl solution on a mica surface. Here the distance to the last desorption point is 834.66nm.

from the point where the tip is removed from the surface during retraction and the last desorption point on the AFM force curves obtained, represents the straight chain length of the polymer that is involved in all of the loops on the surface plus the tail covalently bonded to the tip. Figures 4 and 5 illustrate how this is done.

In Figure 4, the distance from the tip to the last polymer adsorption point was found to be 2626.4 nm. This shows that the polymer is at least 2626.4 nm long. Figure 5 was obtained from the same polymer used in Figure 4. It is shown that the distance to the last adsorption point is significantly shorter at 834.66 nm. The acrylamide copolymer used in this research remains intact through several hundreds of attachment/detachment cycles. As such, any decreases in the length to the last adsorption point are attributed to an increase in the length of the free tail portion of the adsorbed polymer. For the specific case in Figures 4 and 5, the tail of the polymer increased by 1791.74 nm by increasing the salt concentration of the liquid environment.
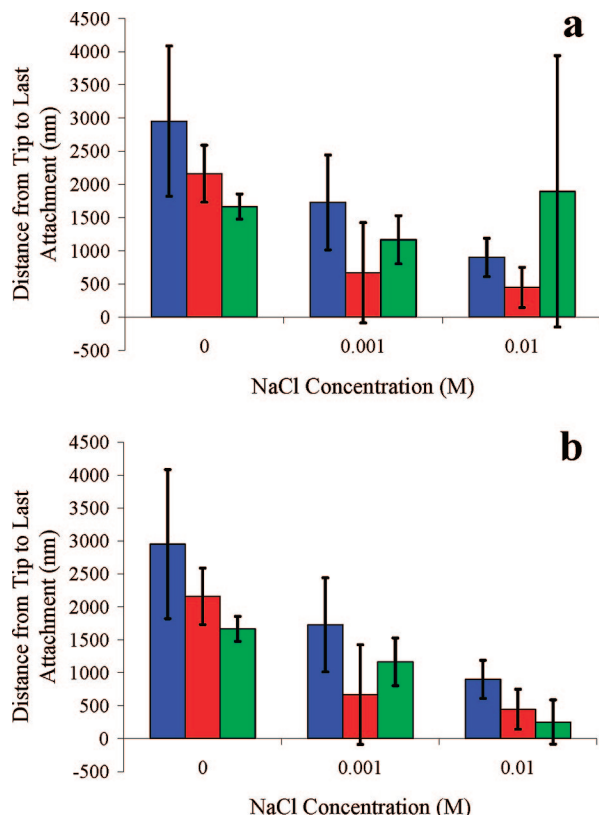
Figure 6. Effect of NaCl concentration on the free tail length of a MAPTAC/acrylamide copolymer on mica. The separate columns represent different repeats of the same experiment using a new polymer molecule. (a) All data. (b) Plot after the removal of two outlying points from the 0.01 M NaCl green column. Error bars show the 90% confidence range of the mean.

Figure 6a illustrates the use of this new technique to observe the salt effect of NaCl on the tail length three individual MAPTAC/acrylamide copolymers. The distance measured in Figure 6 is the total polymer length less the tail length and consequently is a measure of the tail length. This is only a qualitative measure of the tail length because the actual length varies with the angle of the tip to the last attachment point. However, this qualitative metric when averaged over the measurements in Figure 6 should provide trends in the tail length as a function of salt conditions. As the column height decreases in this figure the adsorbed polymer tail length is increasing. It is apparent, from Figure 6a, the free tail portion of the adsorbed polymer is growing with increasing salt concentrations. However, the error bars can make this visualization difficult. It is important to note that after evaluating all of the SPM data for the salt effect of NaCL study only two of 84 data points showed a decrease in the tail length with increasing salt solution. These two points caused the increase found in the green column at 0.01 M NaCl. In this set of data, the previous longest distance to the last adsorption point measured was 2256.5 nm. The two distances, in the 0.01 M condition, were 8273.7 and 7011.3 nm. If these two points are removed from the data set the trend is easily illustrated, as shown in Figure 6b. The reasoning for this surprising result will be discussed in the following discussion.

Figure 7 illustrates the increasing tail length trend for the three other salts analyzed. In these experiments, decreases in tail length with increasing salt concentrations were found similar to the case described previously.

With our new SPM-based method for determining changes in an adsorbed polymer's free tail length, we have demonstrated
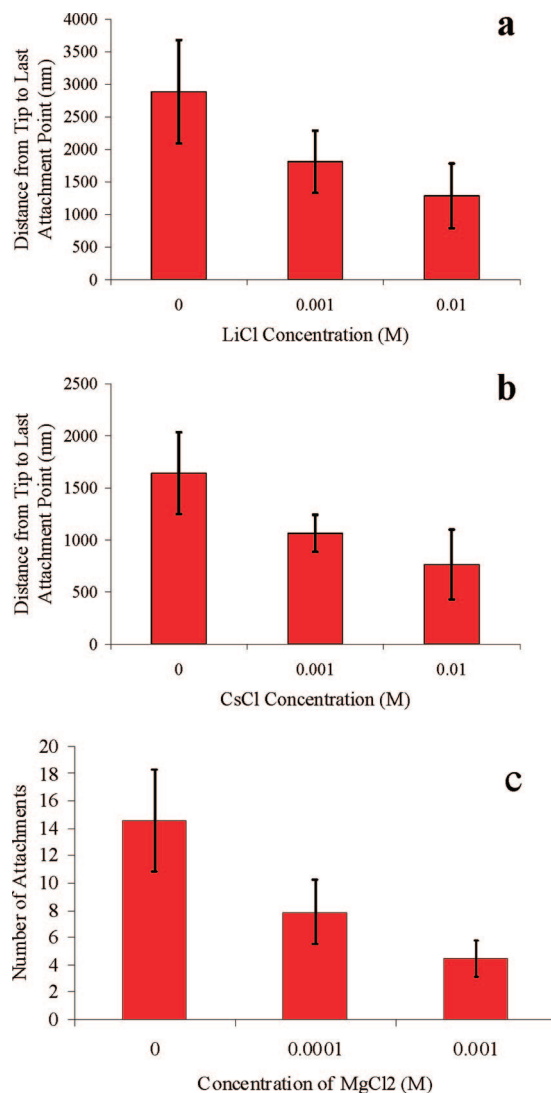

Figure 7. Effect of salt concentrations on the free tail length of three different individual MAPTAC/acrylamide copolymer molecules: (a) lithium chloride; (b) cesium chloride; (c) magnesium chloride. Error bars show the 90% confidence range of the mean.

that increasing salt concentration increases the tail segment length of an adsorbed polymer. This work complements that of Douglas et al. in their discussion of the heterogeneity of the conformations of adsorbed polymer layers.[45] They have shown that as a polymer adsorbs from solution, it will constantly change, thereby not allowing the use of equilibrium states for comparison of conformations. It was also predicted by Scheutjens et al. that the tail length distribution will be very broad.[46] Prior to this work, no other research has been able to experimentally confirm that the tail length of an adsorbed polymer increases with increasing salt concentration.

4. Conclusions

This study presents, experimental evidence of the salt effect on the conformation of an adsorbed low charge density cationic copolymer on a mica surface using our single molecule "pulling" technique. We verified that with increasing salt concentration: 1) the number of polymer adsorption points decreases; 2) the adsorbed polymer loop lengths increase; 3) the adsorbed polymer tail length increases. These results have added support to the current interpretation of the effect of salt concentration on adsorbed polymer conformation.

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