Diblock polyampholytes at the silicon/water interface: Adsorption at various modified silicon substrates

Boris Mahltig,[a] Robert Jerome[b] and Manfred Stamm[a]

[a]*Institut fur Polymerforschung Dresden e.V., Hohe Straße 6, D-01069 Dresden, Germany.*

[b] *Centre for Education and Research on Macromolecules, University of Liège, Sart-Tilman B6, B-4000 Liège, Belgium*

ABSTRACT

The adsorption behaviour of the ampholytic diblock copolymer poly(methacrylic acid)-*block*-poly((dimethylamino)ethyl methacrylate), PMAA-*b*-PDMAEMA, was investigated on differently prepared silicon surfaces. All adsorption experiments were performed from aqueous solutions as a function of pH. The polyampholyte amount adsorbed was determined ellipsometrically, while the topographies of the adsorbed polymer were investigated using scanning force microscopy (SFM). Three polyampholyte systems with similar molecular weight around 60000 g mol^{-1} and different block ratios were adsorbed on three different types of silicon substrates. Depending on the pretreatment the silicon substrates contained different isoelectric points (IEP) and hydrophobicity. The adsorbed amount, as a function of pH, was characterized by maxima and minima near the IEP of the polyampholytes. In the case of polyampholytes containing an IEP close to the IEP of the silicon substrates, the nature of the substrate strongly influenced the adsorption behaviour. Even a complete erasure of one adsorption maximum could be observed in some cases. In contrast to this, polyampholytes with an IEP in a pH area far away from the IEP of the substrates adsorbed in a quite similar manner on the different substrates.

1. INTRODUCTION

Polyampholytes are polymers containing a large amount of oppositely charged functional groups.[1] Distinction must be made between polyampholyte types carrying permanent charges and other species with acidic or alkaline functional groups containing charges as a function of pH. The arrangement of the charged groups can also be different, for example, there are statistical or diblock polyampholytes and polyampholytes with charged groups grafted at a polymer backbone. [2-4] The behaviour of polyampholytes in solution and in adsorption processes has been studied experimentally and theoretically by many authors.[3,5-10]

This article concerns the adsorption of the diblock polyampholyte poly(methacrylic acid)-block-poly((dimethylamino) ethyl methacrylate), PMAA-*b*-PDMAEMA, on differently pretreated silicon substrates. The solution behaviour of this polymer system is characterized by the formation of micelles and larger agglomerates resulting from hydrophobic and electrostatic interactions.[11,12] The adsorption process of PMAA-*b*-PDMAEMA from aqueous solution is strongly determined by the conditions in the polymer solution, the pH and salt concentration especially, have a significant influence on the adsorption. The polyampholyte amount adsorbed from aqueous solution as a function of pH shows maxima and minima near the IEP of the polyampholyte.[13,14] The molecular weight and the block ratio were also found to influence the adsorption.[15] However, up to now the influence of the silicon substrates has not been investigated. Here the adsorption behaviour of polyampholytes with similar molecular weight of around 60000 g mol^{-1} and different ratios of the blocks PMAA and PDMAEMA are reported. In all cases the adsorption on differently prepared silicon substrates was carried out from aqueous solutions as a function of pH. The adsorbed amount was determined by ellipsometry. Three kinds of different silicon substrates were used. These substrates contained different isoelectric points and hydrophobicity depending on the pretreatment. The topography of the adsorbed polyampholyte was investigated using SFM.

2. EXPERIMENTAL

2.1. Materials

For all adsorption experiments ampholytic diblock copolymers poly(methacrylic acid)-*block*-poly((dimethylamino)ethyl methacrylate), PMAA-*b*-PDMAEMA, with molecular weights around 60000 g mol^{-1} were used (Fig. 1). These polyampholytes were synthesized by anionic polymerization. The characterisation was performed using gel permeation chromatography (GPC) and ^{1}H-NMR.[16-18] The IEPs of the dissolved polyampholytes were determined by electrophoretic measurements as reported elsewhere.[19]
Three polyampholytes with different weight ratios of the two blocks PMAA and PDMAEMA were used. The different block ratios caused a change in the IEP of the polyampholytes. Both the block ratio and the IEP of the polyampholytes used are shown in Table 1.

Fig. 1: *Structural units of PMAA-b-PDMAEMA.*
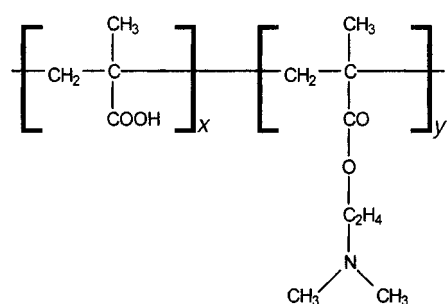
Table 1: *Polyampholytes*

Polyampholyte	Molecular weight /g mol^{-1}	Copolymer composition PMAA : PDMAEMA	Isoelectric point pH$_{IEP}$
B1	68000	84:16	3.8
B2	62000	55:45	5.9
B3	63000	29:71	8.9

Fig. 2 : *The adsorbed amount A of the polyampholyte Bl as a function of the pH of the adsorption solution.*
The adsorption was performed on differently pretreated silicon substrates (alkaline(■), acidic (●) , hydrophobic(▲)).. The solid and the dashed lines are shown as a guide for the eye. The transmission *T* of a red laser light through the polyampholyte solution as a function of pH is shown as a dotted line. The arrows below the graph indicate whether the polyampholyte P carries a positive or negative net charge.
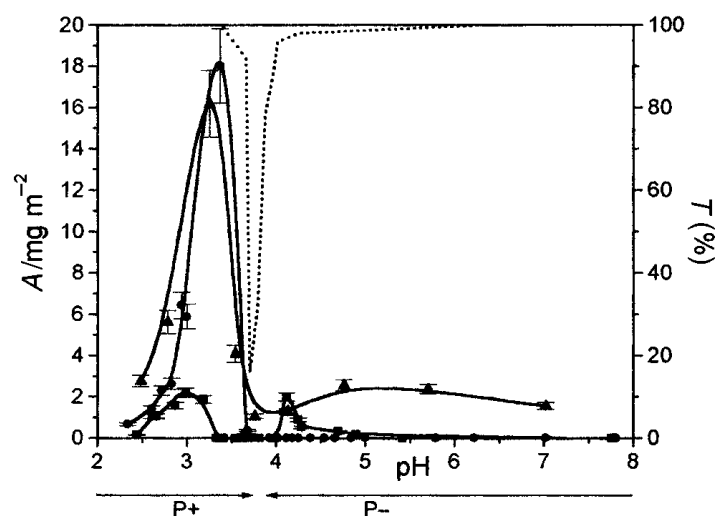
All adsorption experiments were performed on silicon wafers containing a native silicon oxide layer of approximately 2 nm. The properties of the silicon surface were determined by the pretreatment of the silicon oxide layer. Two different cleaning procedures were used to achieve different isoelectric points of the substrates. The alkaline treatment was carried out with an aqueous solution of H_2O_2 and NH_3. The silicon wafers were placed in this solution at 70°C for 30 min. For acidic cleaning the silicon substrates were treated for 15 min with an aqueous mixture of H_2O_2 and H_2SO_4 at 80 °C. After both procedures the wafers were rinsed with MilliQ water and dried with nitrogen.

To increase the hydrophobicity of the substrates silanization with *tert*-butyldiphenylmethoxysilane was used. All silanizations were performed directly after the alkaline treatment of the substrates.[20,21] In a first step the wafers were rinsed with acidic ethanol (95% ethanol, 4.97% water, 0.03% acetic acid) and than placed into acidic ethanol containing 5% of the methoxysilane. After 15 min the wafers were rinsed again with acidic ethanol, dried with nitrogen and kept for at least 12 h at 80 °C in a vacuum. The silanized substrates were then rinsed with THF, ethanol and MilliQ water several times. The isoelectric points of all substrates were determined using electrokinetic measurements[19] and are listed together with the contact angle of water in Table 2.

2.2. Sample preparation

All adsorption experiments were performed in aqueous solutions containing 0.01 mol 1^{-1} NaCl and 0.13 g 1^{-1} of the polyampholytes Bl, B2 or B3. As reported earlier, the adsorption behaviour of PMAA-*b*-PDMAEMA as a function of polymer concentration could be described using the Langmuir model for adsorption.[14,19] A polyampholyte concentration of more than 0.1 g 1^{-1} being sufficient to reach the plateau area of the adsorption isotherm. Therefore, the adsorbed amount is only slightly influenced by the polyampholyte concentration, if the polymer concentration is set to values greater than 0.1 g 1^{-1}.

Table 2: *Substrates*

Substrate	Contact angle	Isoelectricpoint pH_{IEP}
Alkaline cleaning	40°	3.9
Acidic cleaning	10°	2.9
Hydrophobic silanization	80°	3.9

The adsorption experiments were performed from solutions of pH 2.3-10.3. The pH was adjusted by adding HCl_{aq} or $NaOH_{aq}$ in small amounts. After adjusting the pH, the polymer solution was stirred and the silicon substrate was placed in the solution for at least 10 h, sufficiently long to reach the adsorption equilibrium of PMAA-fc-PDMAEMA.[14,19] The substrate was then rinsed with MilliQ water several times to remove the polymer solution and any unadsorbed precipitate from the substrate surface and then dried with nitrogen. The adsorbed polymer layers were investigated using ellipsometry and SFM.

2.3. Ellipsometry

The amount of adsorbed polyampholyte was determined ellipsometrically. All measurements were performed with a null ellipsometer in a polarizer-compensator-sample-analyser (PCSA) arrangement (Multiskop, Optrel Berlin).[22] As light source a He-Ne laser (2 = 632.8 nm) was used, while the angle of incidence was set to 70°. To calculate the thickness of the adsorbed polymer layer from the ellipsometric angles A and Ψ a multilayer model for homogeneous films on top of the silicon wafer was used.[23] The adsorbed amount A was calculated by the measured layer thickness d in air and the mass density δ of the adsorbed polymer:

$$A = d\delta \qquad (1)$$

2.4. Scanning force microscopy

Force microscopy was used to investigate the topographies of the dried polyampholytic films. The measurements were performed with a commercial SFM (Multimode Nanoscope III/ Digital Instruments). All SFM topographies were taken in the tapping mode™ to reduce any damage of the polyampholyte layer by tip contact.

3. RESULTS AND DISCUSSION

The adsorbed amount of polyampholyte B1 on different substrates is shown in Fig. 2 as a function of the pH of the adsorption solution. Transmission through the polyampholytic solution measured with a red laserlight as a function of pH showed contained a minimum at the IEP of the polyampholyte Bl. This minimum results from precipitation of the polyampholyte at the IEP and is quite typical for weak polyampholytes.[9,12] At the IEP the polyampholyte carries a net charge of zero, so the precipitation could also be described as an expulsion of the net uncharged polymer from the aqueous liquid.

In the case of alkali-treated substrates, the adsorption showed two maxima of similar height at pH 3.0 and 4.1 near the IEP of the polyampholyte. At the IEP no adsorption was found. The adsorption on acid-cleaned wafers showed only one large maximum at pH 3.4, while at pH >3.7 no adsorption was found. In the case of hydrophobic substrates, two adsorption maxima at pH 3.3 and 4.8 were found and also at the IEP of the polyampholyte a small adsorbed amount, $A = 1.1$ mg m^{-2}, was observed. The first maximum at lower pH was much larger than the second maximum at higher pH values.

The alkaline substrates were characterized by an IEP at $pH_{IEP} = 3.9$, which is quite similar to the IEP of the polyampholyte B1 at $pH_{IEP} = 3.8$. In every case, the adsorbing polymer B1 carried a net charge of the same sign as the alkaline substrate. Nevertheless adsorption was understandable, if the oppositely charged block acts as an anchor block, while the other block was placed away from the substrate dangling in solution.[5,24] The increase in the adsorbed amount towards the IEP may be explained by a decrease in the net charge of the polyampholyte, which reduces the repulsive interactions between adsorbed polyampholyte chains and leads to an increase in the amount adsorbed.[14,25] At the IEP the net charge of the polyampholyte is zero, so the electrostatic attraction to the substrate is reduced and the minimum in adsorption near the IEP is therefore explainable.[13] A change to acidic substrates induced a shift of substrate IEP from $pH_{IEP} = 3.9$ to 2.9. So between pH 2.9 and 3.8 substrate and polyampholyte B1 carry opposite net charges. In this pH area the attraction of acidic substrates to B1 was increased compared to the alkaline substrates and an increase in the adsorbed amount up to $A = 18.0$ mg m^{-2} was observed. Such large adsorbed amounts cannot be explained by adsorption of single polymer chains. Earlier studies reported the preformation of larger polymer aggregates in PMAA-*b*-PDMAEMA solution. The adsorption of these aggregates directly from solution onto the substrate surface has also been observed.[19,26] Similar adsorption behaviour was also reported for polyelectrolytes with a hydrophobic polymer block.[27] In contrast to the adsorption of single polymer chains the adsorption of larger aggregates from solution can lead to an increased adsorbed amount and also to larger structures observed in the polymer film. This phenomenon could be compared with the adsorption of whole polyelectrolytic complexes preformed in solution by aggregation of oppositely charged homopolyelectrolytes.[28-30]

A second adsorption maximum of polyampholyte Bl at higher pH was not observed on acidic substrates due to the increased negative net charge. Around pH 4.2 the polyampholyte Bl also carried a negative net charge, so an increase in the negative net charge of the acidic substrate leads to more electrostatic repulsion between substrate and polyampholyte. Therefore, a second adsorption maximum is not favoured for Bl on acid-cleaned substrates. The hydrophobic substrates also have an IEP of $pH_{IEP} = 3.9$, which is similar to that of alkaline substrates and the polyampholyte Bl. While the maximum at higher pH showed a quite similar height to the maxima on alkaline substrates, the first maximum at pH 3.3 was significantly increased on hydrophobic substrates. Because of the same substrate IEP, this behaviour could not be explained by changes in the electrostatic interactions between substrate and polymer. An explanation could be found in hydrophobic interactions, which have higher affinity to one of the polymer blocks. In the charged PDMAEMA block the nitrogen atom carrying the positive charge is shielded by two methylene groups and is therefore more hydrophobic than the deprotonated PMAA block. The increased affinity to the PDMAEMA block with the same net charge as the substrate could lead to an increase in the adsorbed amount. Similar behaviour probably occurred at the IEP, because on hydrophobic substrates adsorption was found in the IEP area. Substrate and polyampholyte Bl carry a net charge near zero but the increase in substrate hydrophobicity leads to a hydrophobically driven adsorption at the IEP.[31]

What happens now, if the block size of the PDMAEMA block increases and the IEP of the polyampholytes increases? To answer this question the adsorption of the polyampholytes B2 and B3 was investigated as a function of pH. The adsorbed amount as the average of the two adsorption maxima is shown as function of the PDMAEMA fraction in the polyampholyte (Fig. 3). Fig. 4 shows the difference in adsorbed amount of both maxima as a function of the PDMAEMA weight ratio for different polyampholytes.

In every case, the adsorbed amount increased with increasing PDMAEMA block size. This was explained by two trends working in the same direction. On the one hand, with increasing positively charged PDMAEMA block, the attraction to the mostly negatively charged silicon substrate increased. On the other hand, an increasing PDMAEMA fraction caused a shift of the IEP of the polyampholyte to more alkaline pH. So the adsorption maxima near the IEP were also shifted to higher pH. At more alkaline pH the silicon carries an increased negative charge so the attraction to the PDMAEMA at the pH area around the IEP was also increased.[13,15] Both these trends explain the strong increase in adsorption with PDMAEMA fraction on alkali-cleaned silicon substrates. In the case of acidic or hydrophobic substrates the increase is reduced. Here only one trend should have a significant influence on the adsorption behaviour. An increasing PDMAEMA block leads also to more attractive interactions between polyampholyte and substrate in the case of adsorption onto the almost negatively charged acidic or hydrophobic silicon substrates but the change in substrate characteristics should be less pH dependent. The acidic silicon substrates are negatively charged for pH values higher than 2.9, so an increase in pH will not have such a large influence on the substrate charge as in the case of the alkaline wafers. The adsorption behaviour on hydrophobic wafers is determined by the charge and the hydrophobic character of the substrate. Because of the near-independence of hydrophobicity on pH, the influence of the PDMAEMA fraction on the adsorption maxima should be decreased.

On alkaline silicon substrates the height of both adsorption maxima were quite similar. In contrast to this, the adsorption maxima on acidic or hydrophobic substrates were markedly different in the case of Bl. This difference decreased from the polyampholyte Bl to B3, which showed adsorption maxima of similar height.

In fact, the influence of substrate preparation on the adsorption process is especially significant, if substrate and polyampholyte have IEP in the same pH area. In this case, both adsorption maxima appeared in pH areas where the substrates had different characteristics. An exception is the adsorption of Bl on alkaline substrate which both have nearly the same IEP. Depending on the pH, a positively charged Bl is adsorbed on the positive substrate or, at lower pH, a negatively charged Bl is adsorbed on a negative substrate. Here the substrate charge switched to the opposite net charge and the net charge of B1 switched analogously, so the adsorption conditions are mirrored. In the case of the adsorption of B3, the pH area where the main adsorption took place is far away from the substrate IEP. In this pH area, around pH 8, all three types of substrate are clearly negatively charged, so in every case the polyampholyte B3 should adsorb on substrates with almost similar conditions.

Fig. 3: *The adsorbed amount A_{max} of the investigated polyampholytes at the adsorption maxima as a function of the PDMAEMA weight fraction.* The adsorption was performed on differently pretreated silicon substrates (alkaline (■), acidic (●), hydrophobic (▲)).
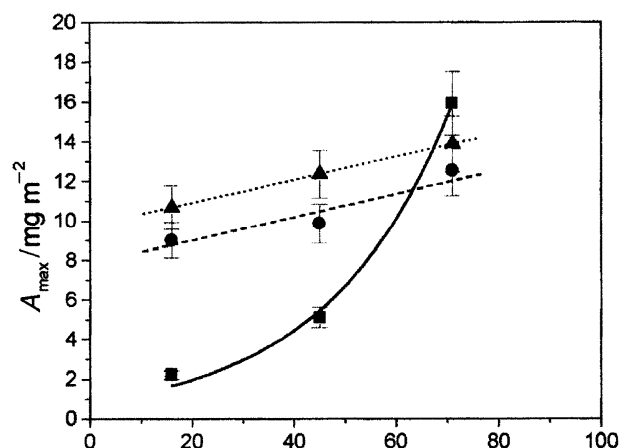
Fig. 4: *The difference between both adsorption maxima A$_{diff}$ of the investigated polyampholytes as a function of the PDMAEMA weight fraction.* The adsorption was performed on differently pretreated silicon substrates (alkaline (■), acidic (●), hydrophobic (▲)).
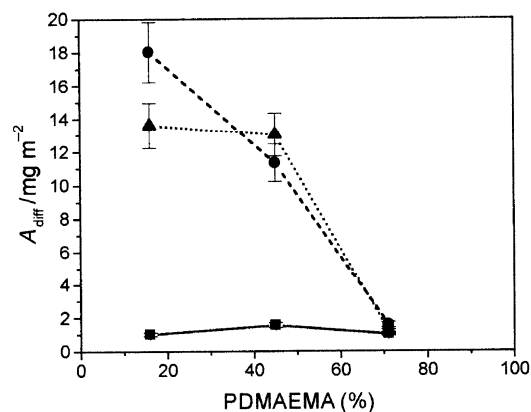
Fig. 5: *SFM topographies of the adsorbed polyampholyte B1 on differently pretreated substrates;* A: on alkali-cleaned substrate (pH 3.0, A = 2.4 mg m^{-2}); B: on acid-cleaned substrate (pH 2.7, A = 2.3 mg m^{-2}); C: on hydrophobic substrate (pH 2.8, A = 5.6 mg m^{-2}).
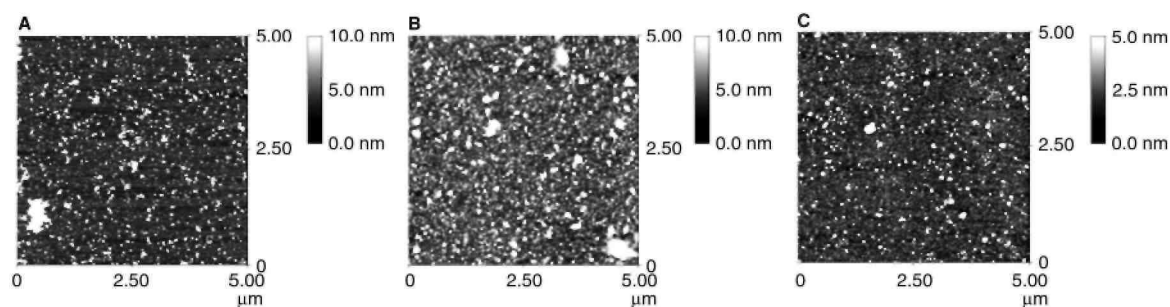
The topography of the adsorbed polyampholytes on the different substrates was investigated using SFM. Fig. 5 shows the SFM of the polyampholyte B1 on the three differently modified substrates adsorbed from aqueous solutions of pH around 3. In every case the topography of the adsorbed polyampholyte is strongly determined by adsorbed agglomerates with lateral diameters up to some hundred nm. Such topography is typical for the polyampholyte B1 and could result from the adsorption of whole agglomerates directly from solution onto the substrate.[13,15]

According to these topographies, earlier studies reported an analogous adsorption behaviour for the polyampholytic system PMAA-*b*-PDMAEMA and explained the formation of larger agglomerates at the silicon surface by the preformation of polyampholytic agglomerates in aqueous solution and the complete adsorption of these structures directly from solution.[19,26] Therefore, it should be concluded that the surface topography is mainly determined by the solution behaviour of the polyampholyte, while the native of the substrate has less influence on the topography.

4. CONCLUSIONS

The adsorption of the polyampholytic copolymer PMAA-*b*-PDMAEMA was investigated from aqueous solutions on three differently pretreated silicon substrates. In every case the adsorbed amount depends strongly on the pH of the polyampholyte solution. The nature of the silicon substrate is also found to have a significant influence on the adsorption behaviour. In particular, when the substrate and polyampholyte have similar IEP the adsorption is strongly influenced by the substrate characteristics.

Acknowledgements

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