

The Influence of an Acid-base-equilibrium on the Adsorption Behaviour of a Weak Polyampholyte

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Abstract

A weak diblock polyampholyte PMAA-*b*-PDMAEMA, poly(methacrylic acid)-*block*-poly((dimethylamino)ethyl methacrylate), was investigated as a model system for the influence of an acid-base-equilibrium of a phthalic acid buffer system on the polyelectrolyte adsorption behaviour. The adsorption of polyampholyte from aqueous solution onto silicon surfaces is known to be strongly influenced by the parameters of the polymer solution and the properties of the polyampholyte itself like block ratio or molecular weight. In the case of the investigated polyampholytes, the main parameter with the most significant influence on the adsorption is the pH. The big influence of pH on adsorption results from the charges of the polymer chains and the substrate, which are determined by the pH. Therefore, it should be useful to investigate the influence of a buffer system on the polyampholyte adsorption. On the one hand the buffer system enables to determine the pH of the aqueous polyampholyte solution more precisely. On the other hand the concentrations of different phthalic species like the phthalic acid, the hydrogen phthalate and the phthalate are strongly influenced by pH. These different species were observed to have a strong influence on the adsorption behaviour of the polyampholyte, so the adsorption as function of pH was observed to be also determined by the acid-base-equilibrium of the buffer system. The adsorbed amount of polyampholyte dried after the adsorption process was determined using ellipsometry, while the surface topography of these adsorbed layers were characterized by atomic force microscopy (AFM).

Keywords

adsorption, buffer, ellipsometry, polyampholyte, polyelectrolyte

Introduction

Polyelectrolytes containing a huge amount of oppositely charged functional groups are called polyampholytes. Both the behaviour of polyampholytes in solution and in adsorption processes are well discussed in literature during the last years [1, 2]. In aqueous solutions it has to be distinguished between permanently charged species and those polyampholytes, which charges are determined by the pH of the solution. In the second case, the polymer is called weak polyampholyte and the pH is one of the most important parameters that determine the adsorption behaviour [3, 4]. Therefore, investigations on the influence of other adsorption parameters like polymer concentration, substrate properties, the addition of salt to the polymer solution or the polymer characteristics should be performed as a function of pH of the polymer solutions [5].

For such investigations it should be useful to fix the pH by adding a buffer system like phthalic acid to the adsorption solution. Especially the adsorption of proteins as a function of pH and different types of buffers was discussed intensively in literature in the last few years [6-8]. Such a buffer system contains of different charged species in a ratio which is determined by the pH. The addition of charged species, especially bi- or multivalent ions is known to have a strong influence on the adsorption behaviour of polyampholytes [9-11]. Therefore, the present study reports on the adsorption of a weak polyampholyte under presence of a buffer system, which acid-base-equilibrium determined the concentration of additional species in the adsorption solution.

Experimental Section

Materials

All experiments were performed with the weak diblock polyampholyte PMAA-*b*-PDMAEMA, poly(methacrylic acid)-*block*-poly((dimethylamino)ethyl methacrylate) (Figure 1). Two types of PMAA-*b*-PDMAEMA with different molecular weight and block ratio were used. The bigger polyampholyte P1 contains a block ratio of PMAA: PDMAEMA 90:10 and a molecular weight of 68000 g/mol. The second smaller polyampholyte P2 is characterized by a molecular weight of 15000 g/mol and a block ratio of PMAA: PDMAEMA 33 :67.

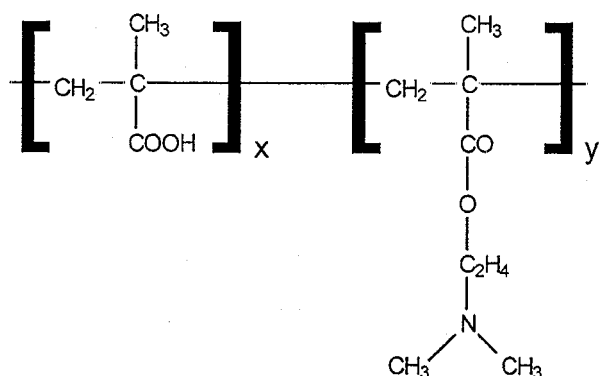


Figure 1 Schematic structure of the polyampholyte PMAA-*b*-PDMAEMA.

The synthesis of the polymer by an anionic polymerization process and the characterization using gel permeation chromatography (GPC) and ¹H-NMR spectroscopy are reported in literature [12-14]. The isoelectric points (IEP) of the investigated polyampholytes were determined by electrophoretic measurements. Polyampholyte P1 contains a p*H*_{IEP} = 3.8 and P2 contains p*H*_{IEP} = 8.5 [5,15,16].

The adsorption experiments were performed on alkaline pretreated silicon wafers containing a native silicon oxide layer of around 2 nm. For the alkaline pretreatment the silicon wafers were placed in an aqueous mixture of NH₃ and H₂O₂ at 70 °C for at least 30 minutes. After this alkaline treatment the wafers were rinsed with Milli-Pore water several times and dried with nitrogen. The IEP of the alkaline pretreated silicon wafers was determined using streaming potential measurements to be at p*H*_{IEP} = 3.8 [5, 17–19]. An IEP around p*H* = 3.8 is typical for silicon wafers pretreated by an alkaline procedure using NH₃ and H₂O₂. An acidic pretreatment using H₂SO₄ and H₂O₂ leads usually to lower values of p*H*_{IEP} [20]. For oxidized silicon wafers p*H*_{IEP} values of 4.1 were reported. These values were determined experimentally using two different methods the zeta-potential measurements and direct force measurements [21].

Adsorption Experiments

All adsorption experiments were performed from aqueous solutions containing 0.13 g/l polyampholyte and 0.01 mol/l of potassium hydrogenphthalate C₈H₅O₄K. The p*H* of these polymer solutions was set to values in a range of 2.5 up to 9.9 by adding HCl_{aq} or NaOH_{aq} in small amounts. Dependent on the p*H*, three different phthalic species can occur in this solution. There are the phthalic acid PH₂, the deprotonated hydrogenphthalate PH⁻ and the double deprotonated phthalic ion P²⁻ (Figure 2). The presence of those species in solution is determined by two acid-base-equilibria with p*K*₁ = 2.9 and p*K*₂ = 5.5 [22]. Therefore, below p*H* < 2.9 the phthalic acid is the predominant species, while between 2.9 < p*H* < 5.5 the hydrogenphthalic ion and at p*H* > 5.5 the phthalic ion is predominant. After setting the p*H* of the polyampholyte solution the silicon substrates were placed into this solution for at least 10 hours. Afterwards, the silicon substrates were taken out of the solution, rinsed with Milli-Pore water several times and dried with nitrogen.

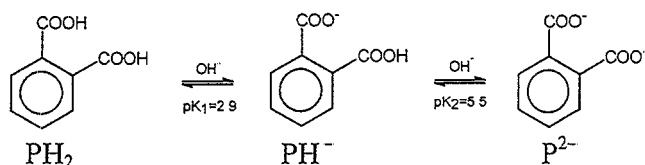


Figure 2. Acid-base-equilibrium of the phthalic acid PH_2 , the hydrogen-phthalate PH^- and the phthalate P^{2-}

Analogous investigations were performed with polyampholyte solutions containing 0.01 mol/l NaCl instead of $\text{C}_8\text{H}_5\text{O}_4\text{K}$. Kinetic measurements were performed in a teflon cell [23]. The silicon substrate was placed into this cell in an aqueous solution with 0.01 mol/l $\text{C}_8\text{H}_5\text{O}_4\text{K}$, and the ellipsometric angles were detected. After constancy of the ellipsometric angles the adsorption process was started by adding the polyampholyte to the aqueous solution.

Ellipsometry

The adsorbed amount of dried polyampholyte after the adsorption process was determined using null ellipsometry in PCSA arrangement. All ellipsometric measurements were performed with a commercially available null ellipsometer Multiskop (Optrel Berlin) [24]. The layer thickness d of the polyampholyte on the substrate was calculated from both ellipsometric angles ψ and Δ by using a multilayer model for homogeneous polymer films. The adsorbed amount of dried polyampholytic films was calculated by $A = d \cdot \delta$ with δ as the mass density of the polyampholyte. In case of kinetic measurements in solution, the adsorbed amount A was calculated with the equation of de Feijter [25]

$$A = d \cdot \frac{n_1 - n_0}{dn/dc}$$

d is the ellipsometrically measured thickness in aqueous solution, n_0 and n_1 are the refractive indices of the aqueous solution and the polyampholyte, dn/dc is the refractive index increment of the polyampholyte in water.

Atomic Force Microscopy (AFM)

Atomic force microscopy (AFM) was used to characterize the surface topographies of dried adsorbed polyampholytic layers. All AFM investigations were performed using a commercially available device (Multimode Nanoscope III / Digital Instruments). To minimize any damage of the polyampholyte layer the force microscopy was performed in the tapping mode TM with resonance frequencies in the range of 280 up to 320 kHz. The used AFM tips were made from microfabricated silicon.

Results and Discussion

Adsorption Behaviour as Function of pH

The adsorbed amount A of the polyampholyte P1 was determined ellipsometrically in a pH range from 2.5 up to 7.1. Altogether three adsorption maxima were observed at pH = 2.9 ($A = 7.5 \text{ mg/m}^2$), at pH = 4.1 ($A = 3.0 \text{ mg/m}^2$) and at pH = 5.2 ($A = 1.0 \text{ mg/m}^2$).

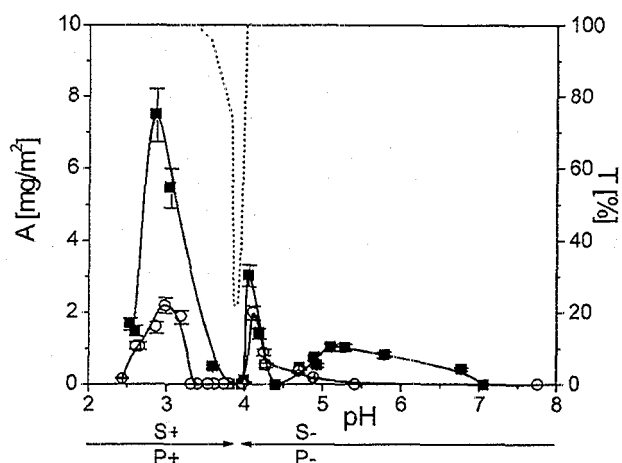


Figure 3. Adsorbed amount A of polyampholyte P1 as a function of pH obtained from solutions with 0.01 mol/l C₈H₅O₄K (solid squares ■) and from solutions with 0.01 mol/l NaCl (open circles ○). The solid and the dashed lines are shown as a guide for the eye. The transmission T of the polyampholyte solutions is also shown as a function of pH (dashed line). Below the graph arrows indicate, where the substrate surface S and the polymer P carry a positive or negative net charge.

Also two adsorption minima containing no detectable adsorbed amount were determined in the pH range from 3.8 to 4.0 and at pH = 4.4 (Figure 3). In the pH area around the isoelectric point (IEP) of the polyampholyte a polymer precipitation occurred in the polyampholytic solution. This precipitation could be detected as a reduction in the transmission of a red laser light crossed the polymer solution (Figure 3). Such an agglomeration and phase separation near the IEP is quite typical for weak polyampholytes [9, 26, 27]. Each of the three adsorption maxima appeared in a pH range, where a different phthalic species is predominant. Both maxima at lower pH were observed near the IEP of the polyampholyte P1 $pH_{IEP} = 3.8$, while at the IEP a minimum in adsorption was detected. Such an adsorption behaviour with adsorption maxima nearby and a minimum directly at the IEP is quite typical for the adsorption of a weak polyampholyte on silicon substrates [9, 15]. As reported earlier the IEP of the polyampholyte is determined by the block ratio PMAA:PDMAEMA of the polyampholyte [1.5]. Therefore the main influence of the position of the adsorption maxima as a function of pH is given by the polyampholyte properties itself. Towards the IEP the net charge P1 decreases, so the repulsive interactions between the polymer chains decrease and an adsorption in a bigger amount is possible. Therefore, an increasing adsorbed amount results in both adsorption maxima. Directly at the IEP the net charge P1 is zero and in this case, also the attraction to the substrate decreases and a minimum in adsorption occurred [15]. Additional ionic components in the polymer solution like mono-, bi- or multivalent ions screen the electrostatic interactions between the polymer chains. Therefore, often an increased adsorbed amount was observed under the presence of additional added ions. In case of the medium adsorption maximum at pH = 4.1 the predominant species in solution is PH^- a monovalent negatively charged ion and the monovalent positive K^+ .

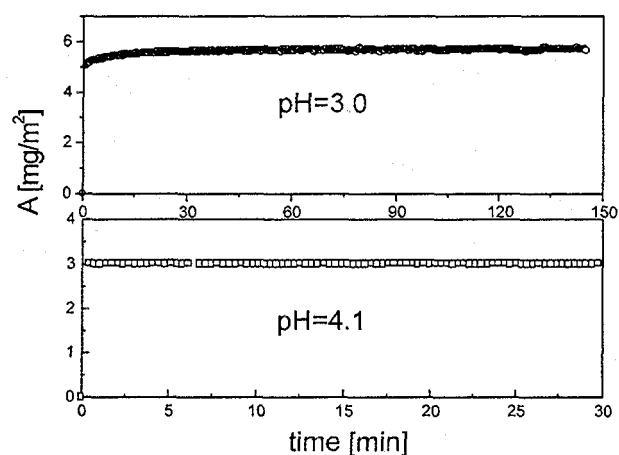


Figure 4. Adsorbed amount A of the polyampholyte P1 as a function of time. The adsorption was performed from polyampholyte solutions containing different pH-values.

So mainly monovalent ions are present in solution and the maximal adsorbed amount with $A = 3.0$ mg/m² is quite similar like the amount, if the adsorption was simply performed in the presence of NaCl (Figure 3). The maximum at lower pH = 2.9 contains an increased adsorbed amount up to $A = 7.5$ mg/m². In this pH region the concentration of PH⁻ is reduced and the PH₂ concentration is increased. Additionally the monovalent ions Na⁺, K⁺ and Cl⁻ are still present in solution. This means only the increased PH₂ concentration induces an increase in the adsorbed amount at pH = 2.9 compared to the maximum at pH = 4.1 and compared to an adsorption only under presence of NaCl (Figure 3). Therefore, this increase in adsorbed amount could not be explainable by changed electrostatic conditions in the polymer solution. In this case, an additional influence of the PH₂ species should be expected. The phthalic acid contains two COOH groups, which are able to form hydrogen bonds, so the PH₂ could form hydrogen bonds to different parts of one polymer chain and between different polymer chains. The third maximum at pH = 5.2 is placed in a pH area, where the concentration of the double ionic species P²⁻ increased in solution. An increase in adsorbed amount under presence of such a bivalent ion is explainable by an increased screening of repulsive electrostatic interactions between the polymer chains, so the polymer can adsorb in a higher density, which results in a bigger adsorbed amount [28, 29]. Ellipsometric measurements were also performed *in situ* under aqueous polymer solutions. Even under adsorption conditions leading to a maximum in the adsorbed amount near the IEP of the polyampholyte, the adsorption process was finished after a few minutes and the adsorbed amount was observed to be stable for a longer period of time (Figure 4). Therefore, a continuous polyampholyte adsorption leading to the formation of polymer multilayers should not be expected, even if the adsorption was performed in pH areas near the most significant adsorption maxima [30]. Adsorbed polymer amounts of more than 2 mg/m² are normally not caused by the adsorption of single polymer chains adsorbing in a polymer monolayer [5]. Higher adsorbed amounts of polymer up to 10 mg/m² or more different pH-values.

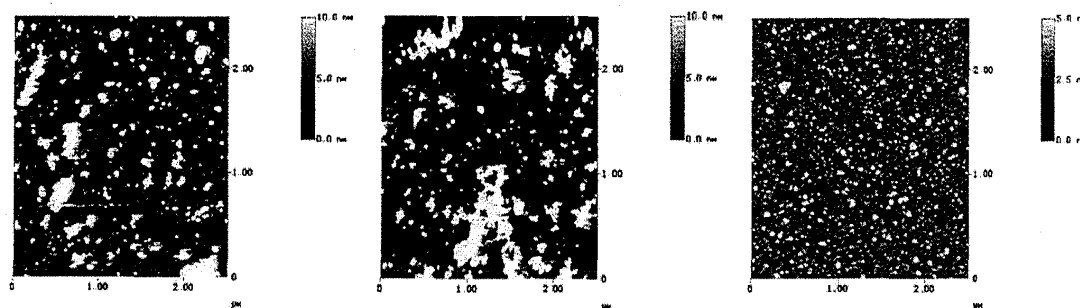


Figure 5. AFM topographies of dry polymer films adsorbed from polyampholyte solutions containing

The pH-values and the adsorbed amount A is shown directly above the AFM images. The scan area was set to 2.5 µm x 2.5 µm. and layer thicknesses of around 10 nm have been found in case of grafted polymer layers and for blockpolymer layers [31-34]. As reported in previous studies, the investigated polyampholyte is known to form bigger agglomerates in solution, which could adsorb directly from solution onto the silicon substrate [5, 15, 35]. This behaviour is quite similar to the adsorption of whole poly electrolyte complexes from aqueous solution [36, 37]. After the adsorption process performed with the aqueous polyampholyte solution, the silicon wafers were placed out of this solution and were rinsed intensively with Milli-Pore water. In this way any polymer containing solution was removed from the silicon surface and could not cause polymer structures via a drying process of a polymer containing solution on the silicon surface. The direct adsorption of bigger aggregates could lead to higher adsorbed amounts and also to increased inhomogeneous topographies of the adsorbed polymer layers (Figure 5). Especially in case of pH values near the IEP of the polyampholyte, the polyampholyte tends to form aggregates and precipitation [38], because of the attractive electrostatic interactions between the oppositely charged polymer blocks. According to this aggregation of the polyampholyte, the AFM topographies of the polyampholyte layers adsorbed at pH = 3.1 and pH = 4.2 show polymer aggregates with diameters up to some hundred nanometers. In contrast to this, the AFM topography of

the sample prepared near the third maximum at pH = 5.1 exhibited no such large agglomerated polymer structures at the interface. In this pH area agglomeration resulting from direct electrostatic attraction of both polymer blocks should not be preferred. Therefore, the less adsorbed amount containing the third maximum compared with the two adsorption maxima near the IEP could be also explained by a decreased trend to form polymer aggregates via electrostatic interactions in pH areas away from the IEP of the polyampholyte.

Influence of Polymer Block Ratio on the Adsorption Behaviour

The poly ampholyte P1 is characterized by a large negatively charged PMAA block and a pH_{IEP} of 3.8. What happens now, if the block ratio is changed to a larger positively charged PDMAEMA block? To answer this question, the adsorption behaviour of the polyampholyte P2 was investigated under the presence of the phthalic buffer system. The polyampholyte P2 contains a larger PDMAEMA block compared with the block ratio of P1 and a pH_{IEP} of 8.5.

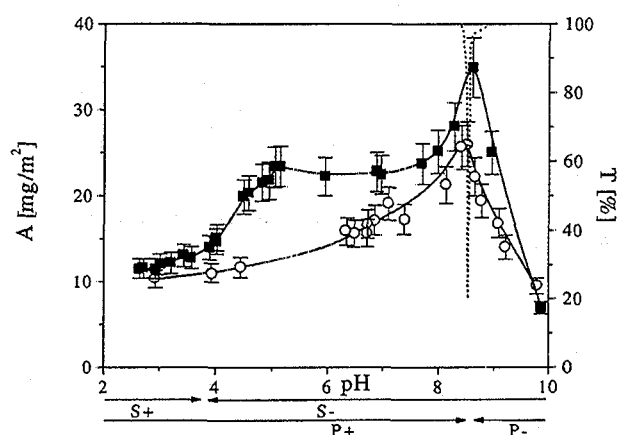


Figure 6 Adsorbed amount A of polyampholyte P2 as a function of pH obtained from solutions with 0.01 mol/l $C_8H_5O_4K$ (solid squares ■) and from solutions with 0.01 mol/l NaCl (open circles ○). The solid and the dashed lines are shown as a guide for the eye. The transmission T of the polyampholyte solutions is also shown as a function of pH (dashed line). Below the graph arrows indicate, where the substrate surface S and the polymer P carry a positive or negative net charge.

Under the presence of the phthalic buffer system the adsorbed amount of P2 was significantly increased over the whole investigated pH range compared with the adsorption performed only under presence of NaCl (Figure 6). Altogether, the adsorption behaviour as a function of pH can be separated into different pH areas. At low pH values from 2.7 up to 3.9 a smooth increase in the adsorbed amount from 11.6 mg/m² up to 14.0 mg/m² was observed. From pH 3.9 to 5.1 a drastic increase in the adsorbed amount up to 23.3 mg/m² was detected, while between pH 5.1 up to 7.7 a plateau area with quite similar adsorbed amounts around 23.5 mg/m² appeared. At the IEP of the polyampholyte P2 at $pH_{IEP} = 8.5$ a significant maximum in adsorption with $A = 34.9$ mg/m² was observed. Especially the drastic increase in adsorption from pH 3.9 to 5.1 and the high adsorbed amounts in the plateau area are significantly different from the lower adsorbed amount after an adsorption performed only under NaCl presence, while around pH 3 quite similar adsorbed amounts of around 11 mg/m² were observed (Figure 6). In this pH area around pH 3 monovalent ions like PH^- , Cl^- , Na^+ and K^+ are predominant in the polyampholyte solution, so the ionic strength should be quite similar to the one of the analogous NaCl containing polyampholyte solution. With increasing pH the concentration of the bivalent species P^{2-} also increased in the buffered polyampholyte solution. Therefore, the electrostatic repulsion between the charged polymer chains should also be reduced and the polyampholyte could adsorb in a higher amount. From pH values more than 5.5, P^{2-} is the clear predominant species in the acid-base-equilibrium of the phthalic buffer system (Figure 2). This predominance of P^{2-} corresponds to the high adsorbed amounts in the plateau area from pH 5.1 to 7.7. The maximum in adsorption at the IEP of the polyampholyte P2 at pH = 8.5 should not be only explained by the appearance of P^{2-} . At the IEP the

net charge of the polyampholyte is zero, so an adsorption in the largest amounts should be expected, especially if the **IEP** of the polyampholyte is placed in at alkalic pH and the adsorption is performed on a strongly negatively charged substrate [15, 39]. The adsorption behaviour of the polyampholyte P2 with a larger PDMAEMA block is significantly influenced by the presence of the phthalic buffer system in the aqueous polymer solution. An increase in the adsorbed amount of P2 was observed over the whole investigated pH range. A similar behaviour was also observed for the polyampholyte P1 but in case of P1 the appearance of a new third adsorption maximum at higher pH values could be the most significant result caused by the buffer system.

Conclusions

The adsorption of the weak polyampholyte PMAA-*b*-PDMAEMA on silicon substrates was investigated under the influence of an acid-base-equilibrium presented by a phthalic buffer system. The adsorption behaviour was investigated as a function of pH and demonstrates that the presence of the phthalic buffer significantly influenced the adsorption compared with the adsorption under single presence of NaCl. The pH range, where the adsorption experiments were performed, could be divided into different pH areas dominated by one of the three phthalic components phthalicacid, hydrogenphthalate or phthalate. Furthermore, it can be assumed that the polyampholyte do not adsorb in multilayers and the high adsorbed amounts at the adsorption maxima were characterized by big adsorbed polymer aggregates observed by AFM.

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