

Desorption Behaviour of Regular Adsorbed Polyampholytic Layers

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Abstract

The desorption behaviour of the diblock polyampholyte PMAA-*b*-PDMAEMA, poly(methacrylic acid)-*block*-poly((dimethylamino)ethyl methacrylate), preadsorbed on silicon substrates was investigated under the influence of several desorption agents. The investigated polyampholyte is known to adsorb in regular structures directly from aqueous solutions onto silicon substrates. While the adsorption process is mainly determined by electrostatic interactions, two kinds of desorption mechanism should be assumed. The first mechanism is based on changed electrostatic conditions caused for instance by a strong change in pH of the aqueous solution. The other mechanism is observed after treatment with hydrophobic organic solvent, which leads to the desorption of hydrophobic adsorbed polyampholyte chains, while the electrostatically attached ones will not be influenced. To complete the desorption experiments with organic solvents also adsorption experiments from analogous polyampholytic solutions in the same organic solvents were performed. The amount of polymer at the substrate surface after adsorption or desorption experiments was determined using ellipsometry. Atomic force microscopy (AFM) was used to investigate the surface topography of dried samples after the desorption process.

Keywords

adsorption, AFM, desorption, ellipsometry, micelles, polyampholytes, polyelectrolytes

Introduction

Adsorption and desorption phenomena of charged polymers are the topics of many articles published recently [1-8]. Charged polymers usually called polyelectrolytes, while polyampholytes are a special type of poly electrolyte with positively and negatively charged functional groups [9]. Experimental investigations on the adsorption behaviour of statistical, diblock or triblock polyampholytes were reported [10—18]. Also theoretical descriptions of polyampholytes in solutions and at interfaces have been done [2, 3, 12, 19-24]. Higgs and Joanny in 1991 [25] give a description of polyampholyte behaviour as function of the ratio of positively to negatively charged groups. While the adsorption phenomena of polyampholytes were intensively discussed experimentally and theoretically, the desorption behaviour of those polymer systems is less noticed in literature [6,15].

Polymer desorption in general means a process, which leads to a decreased amount of adsorbed polymer at the solid/liquid interface. Altogether, there are many different reasons for a desorption process following the polymer adsorption. After the polymer adsorption from a polymer solution onto the solid/liquid interface, a possible route for desorption is the removal of the polymer from the liquid phase. In this case, the polymer being in equilibrium with the solution should be also removed from the interface but especially polyelectrolytes adsorbed on oppositely charged surfaces exhibit a high adsorption energy, because of the strong electrostatic interactions to the surface. Therefore, the removal of polyelectrolytes from the liquid phase will lead only to the desorption of a small portion of adsorbed polymer [6]. To start a desorption of higher polymer amounts, the conditions in the liquid phase have to be changed drastically. Le Bene et al. reported from the desorption of permanently charged polyelectrolytes by an increasing salt concentration in the aqueous liquid phase [15]. In this case, the electrostatic attraction of polyelectrolyte and solid surface was reduced, because of the increased

Debye screening resulted from increasing ionic strength. Also the solubility of the charged polymer could be improved by adding salt to the aqueous medium. Similar results were reported by Rojas et al. [26, 27] on positively charged copolymers. They reported that beside the increasing in concentration simple salt like NaCl the addition of the charged surfactant SDS is much more effective to reach desorption. This phenomenon was explained by an additional complex formation between surfactant and polymer.

Analogously also a change in pH could induce a change in electrostatic interactions between poly electrolyte and substrate surface. Therefore a pH dependent desorption should be especially favoured, if the poly electrolyte and the substrate carry functional groups, which charges are determined by the pH of the aqueous phase [6].

Other studies concern the desorption of uncharged endat-tached polymers. This polymer type could be replaced from the solid surface by displacers of low molecular weight like THF or acetone [28]. In this case, the desorption results from the higher affinity of the low weight species to the substrate,

compared to the polymer substrate interactions. A similar behaviour is also reported for¹ uncharged polymers at surfaces, which could be easily replaced by charged polymers containing a higher' affinity to the substrate [29].

Polymer desorption could not only be induced by the replacement of one polymer type by another polymer species with higher electrostatic affinity to the substrate. Also polymer chains could be replaced by polymers with similar chemical structure containing only a higher molecular weight [30]. In this case, the desorption could not be explained by changed polymer substrate interactions, so an entropically driven desorption process should be stated [31].

This article will report the desorption behaviour of a diblock polyampholyte PMAA-*b*-PDMAEMA, poly(methacrylic acid)-*block*-poly((dimethylamino)ethyl methacrylate), The used diblock system with a molecular weight of 15000 g/mol and a block ratio of PMAA: PDMAEMA 33 :67 is well characterized and known to adsorb in highly regular adsorbed structures [32]. Previous studies report also on the high stability of these polyampholyte layers under treatment with phosphate buffered protein solutions [33]. High adsorbed amounts of around 16 mg/m² on silicon substrates and regular adsorbed structures facilitate investigations on the desorption by ellipsometry and atomic force microscopy (AFM). While ellipsometry was used to detect the decrease in polymer amount at the interface caused by desorption, AFM allowed the observation of changes in the topography of the adsorbed polymer films.

To investigate the desorption caused by drastic changes in electrostatic conditions NaOH_{aq} and HCl_{aq} were used as desorption agents. For investigations on hydrophobically driven desorption organic solvents like THF and toluene were used as desorption agents. In this case, also adsorption experiments from organic polyampholyte solutions were performed to complete the description under the influence of organic solvents.

Experimental Section

All desorption experiments were performed on previously adsorbed layers of the polyampholyte poly(methacrylic acid)-*block*-poly((dimethylamino)ethyl methacrylate), PMAA-*b*-PDMAEMA (Figure 1). The used diblock poly ampholyte contains a molecular weight of 15000 g/mol, a block ratio PMAA: PDMAEMA of 33:67 and an isoelectric point (IEP) of pH_{IEP} = 8.5 [32, 34]. This polymer was synthesized using a sequential anionic polymerization process. The molecular weight and the block ratio were determined by size exclusion chromatography and ¹H-MNR spectroscopy, respectively [35-37]. The investigated polyampholyte type is known to adsorb on silicon substrates in regular structures [32]. It was presented in previous studies that the regularity of the adsorbed structures results from the adsorption of whole polyampholytic micelles directly from aqueous solution onto the silicon substrate [32, 38].

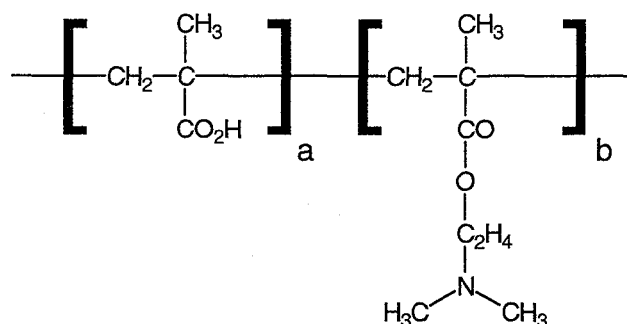


Figure 1. Chemical structure of the investigated polyampholyte PMAA-*b*-PDMAEMA.

The silicon wafers were alkaline pretreated by using a mixture of NH_3 and H_2O_2 in MilliQ water. After this cleaning procedure the IEP of the silicon substrate was determined to be $\text{pH}_{\text{IEP}} = 3.8$ [38,39]. For all desorption experiments the adsorbed polyampholyte layers were prepared using the same procedure. At first an aqueous adsorption solution containing 0.13 g/L polyampholyte and 0.01 mol/L NaCl was prepared. The pH of these polymer solutions was set to values around $\text{pH} \approx 6.8$. The silicon substrates were placed in this solution for at least 10 hours, which is quite long enough to reach the equilibrium in adsorption [33, 40]. Afterwards the wafers were taken out of the solution, rinsed with MilliQ water and dried with nitrogen. Under the used adsorption conditions the adsorbed polyampholyte layer contains adsorbed amounts around 16 mg/m^2 [32]. This adsorbed amount is stable in aqueous solution in a pH range from 2.5 up to 10.0 and such high adsorbed amounts enables an easier detection of desorption using ellipsometry. A previous study concerns the secondary adsorption of proteins on such preadsorbed polyampholyte layers. The adsorbed layers of PMAA-*b*-PDMAEMA were observed to be stable under treatment with phosphate buffered protein solution and no replacement of polyampholyte by adsorbing protein molecules was determined [33]. The desorption was performed using four different desorption agents NaOH_{aq} , HCl_{aq} , toluene and THF. Also the stability of the polyampholyte films were checked under the presence of the cationic and anionic surfactants dodecyltrimethylammoniumbromide $\text{C}_{15}\text{H}_{34}\text{BrN}$, sodiumdodecylsulfate $\text{C}_{12}\text{H}_{25}\text{NaO}_4\text{S}$ and under the presence of a highly positively charged poly electrolyte P^+ (Figure 2).

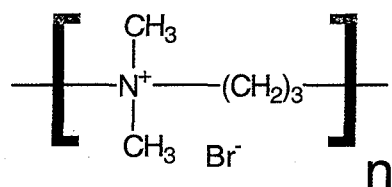


Figure 2. Chemical structure of the positively charged poly electrolyte P^+ with $P_n = 30$.

Desorption experiments with NaOH_{aq} and HCl_{aq} were performed directly after the polyampholyte adsorption process. The pH of the polymer solution was set to 13.5 or 1.0 by adding NaOH_{aq} or HCl_{aq} , respectively. To perform the desorption with NaOH_{aq} and HCl_{aq} the samples were placed into the liquid for at least 2 hours.

Because of the immiscibility of toluene and water, the desorption of polyampholyte with toluene could not be performed by adding toluene to the aqueous polymer solution. In case of desorption experiments with toluene, dried silicon wafers containing an adsorbed polyampholyte layer were placed into toluene. The desorption with THF was performed in two different ways. On one hand the THF was added directly after the adsorption process to the aqueous polymer solution, so the desorption was performed under the presence of polyampholyte in the liquid. On the other hand the desorption was started by adding polyampholyte coated silicon substrates to THF/ H_2O mixtures without any dissolved polyampholyte. In both cases different THF/ H_2O ratios in the range of 0% up to 100% THF amount were investigated. For desorption with organic solvents the samples were placed into them for at least 10 hours.

To complete the investigations concerning the desorption with the organic solvents toluene and THF also adsorption experiments were performed from analogous solutions. The polyampholyte adsorption from organic solvents was performed on alkaline cleaned silicon wafers by placement in toluene, THF or THF/H₂O mixtures containing 0.3 g/l PMAA-*b*-PDMAEMA. After at least 10 hours the silicon substrates were taken out of the organic solution, rinsed with MilliQ water and dried with nitrogen. To check the stability of the adsorbed polyampholyte films under treatment of surfactants, dried polyampholyte coated silicon substrates were placed for at least 10 hours in aqueous solutions containing 33 g/l dodecyltrimethylammoniumbromide C₁₅H₃₄BrN and 10 g/l sodiumdodecylsulfate C₁₂H₂₅NaO₄S. An analogous procedure was performed with an aqueous solution of the positively charged polyelectrolyte P⁺, the poly electrolyte concentration was increased up to C = 24 g/l. After rinsing with MilliQ water and drying with nitrogen all samples were investigated by ellipsometry and atomic force microscopy (AFM).

The ellipsometry was used to determine the amount of polyampholyte on the silicon substrate. All ellipsometric measurements were performed with a commercially available computer controlled null ellipsometer in a polarizer-compensator-sample-analyser (PCSA) arrangement (Multi-skop, Optrel Berlin) [41]. A red He-Ne laser was used as light source ($\lambda = 632.8$ nm) and the angle of incident was 70°. To calculate the polymer layer thickness d from the ellipsometric angles ψ and Δ a multilayer model for a homogeneous film covering the silicon wafer were used. The amount of adsorbed polymer on the substrate A was calculated from the layer thickness d by $A = \delta d$. $\delta = 1.27$ is the mass density of the polyampholyte layer.

The atomic force microscopy (AFM) was used to investigate the topography of dried polyampholytic layers after the desorption process. All investigations were performed in the tapping mode (TM) using a commercial AFM (Multimode Nanoscope III/Digital Instruments). The frequencies for AFM measurements were set between 270 to 330 kHz.

Dynamic light scattering measurements DLS were performed to determine the hydrodynamic dimensions of polyampholytic structures in solution. The measurement setup was built up from a commercial ALV 3000 digital correlator and a 400 mW krypton laser ($\lambda = 300$ nm) as light source. The diffusion coefficients of the solved polymer structures were gained by analysis of the autocorrelation function. The hydrodynamic diameter of these polymer structures in solution was calculated from the diffusion coefficient using the Stokes-Einstein equation [42].

Results and Discussion

Adsorbed amounts of polyampholyte on the silicon substrates after treatment with different desorption agents are presented in Table 1. The ellipsometrically determined amount is given in [mg/m²] and in percentage [%] of remaining polyampholyte with respect to initially adsorbed amount. No desorption was observed after treatment with C₁₂H₂₅NaOS_{aq} up to concentrations of 10 g/l and with C₁₅H₃₄BrN_{aq} up to concentrations of 33 g/l. Le Berre et al. reported recently on the desorption process of polyampholytes caused by an increasing NaCl concentration [1.5]. In contrast to these investigations, no desorption of PMAA-*b*-PDMAEMA was induced by an increased salt concentration of C₁₂H₂₅NaOS or C₁₅H₃₄BrN, so the adsorbed polyampholyte PMAA-*b*-PDMAEMA should be quite more stable at the silicon surface than the polyampholyte system presented earlier by Le Berre. Also no change in adsorbed amount was detected after treatment with the highly positively charged polyelectrolyte P⁺ up to concentrations of C = 24 g/l. The poly electrolyte P⁺ contains a high density of permanently positively charged functional groups and is therefore expected to have strong attractive electrostatic interactions to the negatively charged silicon substrate [5, 31]. Despite these strong attractive interactions between P⁺ and the substrate no displacement of the preadsorbed polyampholyte PMAA-*b*-PDMAEMA by the polyelectrolyte P⁺ was obvious. Both the stability of the adsorbed polyampholyte layer against highly concentrated surfactants or positive polyelectrolytes indicate the high stability of the adsorbed PMAA-*b*-PDMAEMA layer at the silicon surface under aqueous conditions at pH around 7.

What happens now, if the polyampholyte layer is treated with an aqueous medium under drastic alkaline or acidic conditions? The increase in pH to 13.5 leads to a drastic desorption up to only 10% of remaining polyampholyte, while the decrease in pH to 1.0 leads only to a reduction up to 49%. The investigated polyampholyte exhibits an IEP of pH_{IEP} = 8.5 and the silicon substrate of pH_{IEP} = 3.8.

At pH = 1.0 both the polyampholyte and the substrate carry a positive net charge and repulsive

electrostatic interactions induce a desorption of polyampholyte. The same situation is analogously observed for adsorption experiments performed on alkalic cleaned silicon wafers from liquid media containing different ratios of THF and water. The adsorbed polymer amount decreased significantly with increasing THF concentration in solution. With 50% THF the amount of adsorbed polyampholyte is near¹ zero ($A = 0.2 \text{ mg/m}^2$), while at higher THF concentrations the adsorbed amount is increased again up to $A = 4.2 \text{ mg/m}^2$ (Figure 7). This minimum in adsorbed amount should be explained by the solubility of the polyampholyte in THF/water mixtures. First with increasing THF concentration the solubility of the polyampholyte increases, so the adsorbed amount decreases. If the THF amount further increased to values higher than 50% the polyampholyte solubility should decrease again and therefore the adsorbed polymer amount is increased. An analogous minimum in adsorbed amount is not observed after both desorption experiments, because the previous polyampholyte layer was adsorbed from aqueous solution and those polyampholyte chains, which are directly electrostatically attached to the silicon substrate should not be desorbed under the presence of organic solvents.

The AFM topography of the adsorbed polyampholyte layer after THF treatment contains a decreased rms-roughness of 1.7 nm compared with the situation before the desorption experiment, while the adsorbed structures contain similar parameters in size and shape (Figures 2 and 8). As described in a previous article, these remaining adsorbed structures result from a desorption of only hydrophobic adsorbed polymer chains, while the directly electrostatically attached polyampholytic chains remain on the substrate surface as a kind of remaining "micelle stump" [32]. In contrast to this regular topography after desorption, a much more irregular surface topography was observed after adsorption of polyampholyte from pure THF solutions. Also PMAA-*b*-PDMAEMA solved in THF formed aggregates with hydrodynamic diameters from 50 nm to 60 nm determined by DLS. Despite of the presence of polyampholytic aggregates in solution, the adsorption of these whole aggregates directly from solution onto the silicon surface was not observed to lead to regular surface structures. Analogously to the polyampholyte adsorption from toluene solutions a structural correlation of polyampholyte aggregates could not be observed at the surface for adsorption from THF solution. The reason for this behaviour should be found again in the difference in hydrophilicity of the solvent THF and the silicon substrate.

Conclusions

Altogether the highly regular adsorbed PMAA-*b*-PDMAEMA layers were observed to be of high stability against desorption in contact with aqueous solutions under moderate pH conditions, even under presence of high concentrated surfactants or highly charged poly electrolytes. In general, a desorption can be induced with two different strategies. On one hand a drastic change in pH to acidic or alkaline values leads to a switching of net charges of the adsorbed polyampholyte layer and the silicon substrate. Therefore, the electrostatic interactions between substrate and adsorbed polymer become repulsive and a polyampholyte desorption would be favoured. On the other hand a polyampholyte desorption could be reached by the treatment with hydrophobic solvents like toluene or THF. These hydrophobic solvents should not influence the electrostatic interactions between adsorbed polymer and the silicon substrate but they are able to lead to the desorption of hydrophobically adsorbed polyampholyte segments.

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