

Adsorption of polyampholyte copolymers at the solid/liquid interface: the influence of pH and salt on the adsorption behaviour

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Abstract

Polyampholytes are macromolecules that contain oppositely charged groups. We have studied the adsorption of the polyampholyte diblock copolymer poly(methacrylic acid)-*block*-poly((dimethylamino)ethyl methacrylate), PMAA-*b*-PDMAEMA, on oxidized silicon surfaces. The amount of polymer adsorbed from aqueous solution of different pH and salt concentration was measured by ellipsometry. The influence of the added salts NaCl, Na₂SO₄ and CaCl₂ was determined. In every case adsorption took place, although the polyampholyte and the substrate exhibit the same sign of net charge. For all types of salt, the adsorbed amount shows two maxima close to the isoelectric point (IEP) of the polymer as a function of pH. Directly at the IEP of the polyampholyte, no adsorption was found. The measured dependences can be explained by the adsorption of one or the other of the two blocks depending on acidity and ionic strength. Furthermore, the lateral structure of the dried films was investigated by scanning force microscopy (SFM).

Introduction

In the last few years, there has been great interest in polyelectrolytes in solution and at the solid/liquid interface.^{1,2} The adsorption of polyelectrolytes is an important component in many industrial processes like paper production, waste water and sewage sludge treatment.^{3,4} Processes containing polyelectrolytes or ionic macromolecules at solid/liquid interfaces are found in biology and medicine as well. Parameters like the pH, the type of added salt and the salt concentration in the polyelectrolyte solution influence the adsorption process.⁵⁻⁸ Thus, it is of fundamental interest to determine the adsorption behaviour of polyelectrolytes as a function of the solution conditions. Up to now there have been many investigations on polyelectrolytes and statistical polyampholytes in solution and on the behaviour of polyelectrolytes at interfaces.⁹⁻¹³ Only a few investigations^{14,15} have dealt with the adsorption of diblock polyampholytes. The influence of the type of salt added has rarely been investigated.¹⁶

Our investigations concern the adsorption of the ampholyte diblock copolymer poly(methacrylic acid)-*block*-poly((dimethylamino)ethyl methacrylate), PMAA-*b*-PDMAEMA, from a dilute aqueous solution onto oxidized silicon surfaces. We investigated the amount of polymer adsorbed as a function of pH. The influence of different types of salt and the variation of the salt concentration were also studied. The electrostatic interactions in the system are strongly influenced by the salt concentration and the pH. The adsorption of polyampholytes from solution onto a solid/liquid interface results from the electrostatic interaction between the charged blocks of the polymer and the charged surface of the substrate.

Hydrophobic or steric interactions are discussed as having an influence on the adsorption as well. The charge densities of the two blocks of the investigated polymer (PMAA-*b*-PDMAEMA) and of the surface of the substrate depend strongly on the pH in the adsorption solution. In addition, the type of salt added to the solution influences the electrostatic interaction. Bivalent ions, which are able to form chelate complexes with polyampholytes,² are expected to change the electrostatic interactions drastically. The adsorption behaviour as a function of pH, the conformation of the polymer in solution and its conformation at the surface are determined by the two isoelectric points (IEP) of the silicon substrate and the polyampholyte.

In the present paper, we report on a block polyampholyte that has nearly the same IEP as the silicon substrate. For this case, the polyampholyte has the same net charge as the surface over the entire pH range. One possible explanation for adsorption is that the oppositely charged block of the polymer acts as an anchor to the surface, while the other block is dangling in the solution. The adsorbed amount of the polymer layers was measured by ellipsometry and the lateral structures were determined by scanning force microscopy (SFM). The polymer structure in solution was investigated by dynamic light scattering. The transmission of red laser light through the

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polymer solution was measured as a function of pH by light scattering. All measurements were performed after the adsorbed amount had reached the adsorption equilibrium.

Experimental

Sample preparation

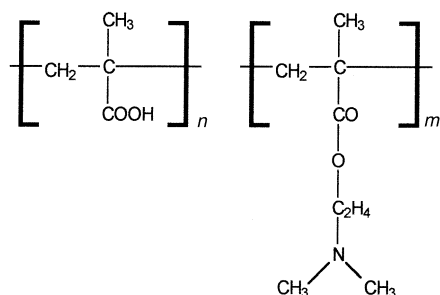
All adsorption experiments were performed with the ampholytic diblock copolymer poly(methacrylic acid)-*block*-poly((dimethylamino)ethyl methacrylate), PMAA-*b*-PDMAEMA (Fig. 1). The synthesis by anionic polymerization and the determination of the molecular weight and the block distribution of this copolymer by gel permeation chromatography (GPC) and nuclear magnetic resonance spectroscopy ($^1\text{H-NMR}$) are described in the literature.¹⁷⁻¹⁹ The molecular weight of the used polymer is $M_w = 68000 \text{ g mol}^{-1}$. The ratio of the PMMA to the PDMAEMA block is 90:10.

As substrates for the adsorption, silicon wafers Si(100) with a native oxide layer of approximately 2 nm thickness were used. Prior to the adsorption experiments, all substrates were cleaned by the following procedure: First, the wafers were placed in dichloromethane in an ultrasonic bath for 15 min at about 40 °C to remove the organic surface contamination. Next, the wafers were rinsed with Milli-Pore water and treated with an oxidation bath of H_2O_2 , NH_3 and Milli-Pore water at 70 °C for 30 min. Afterwards, the wafers were rinsed again with Milli-Pore water and dried with pure nitrogen.

The adsorption experiments were carried out in a specially designed Teflon cell. In the first step the cell was filled with the solution used for the adsorption experiment. This solution contained the polyampholyte at a concentration of 0.128 g l^{-1} . The concentration of low-molecular-weight salt was 0.01 or 0.04 mol l^{-1} . NaCl, Na_2SO_4 and CaCl_2 were used.

The pH of the solution was changed by adding acid (HCl) and base (NaOH) in an amount that is negligible in comparison with the salt concentration of 0.01 mol l^{-1} . After setting the pH, the solution was stirred gently and the silicon substrate was placed in the cell for at least 10 h, which is sufficiently long to reach equilibrium adsorption conditions for the used system as we reported elsewhere.¹⁴ Next, the sample was taken out of the cell and rinsed with Milli-Pore water several times to remove unadsorbed precipitation from the wafer. Milli-Pore water can be regarded as a good solvent for unadsorbed polyampholyte molecules. After drying of the wafer with nitrogen, the adsorbed polymer layer was investigated by ellipsometry and SFM. All experiments were performed at room temperature.

Fig. 1 Schematic drawing of the structural units of the used polyampholyte (PMAA left and PDMAEMA right).



Dynamic light scattering

The polymer in solution was investigated by dynamic light scattering (DLS). Polyampholyte solutions with varied pH and added salt were investigated. For these measurements a commercially available ALV 3000 digital correlator with a 400 mW krypton ion laser ($\lambda = 647 \text{ nm}$) was used. All measurements were performed with a scattering angle of 90° at room temperature.

The determined autocorrelation function of the scattered intensity, $g_q(t)$, is for monodisperse spheres given by the following exponential function²⁰

$$g_q(t) = \exp(-D_{\text{sol}} q^2 t)$$

where D_{sol} is the translational diffusion coefficient of the polymer particles in solution, q is the magnitude of the scattering vector and t is the time delay. The Stokes-Einstein equation enables one to calculate the hydrodynamic radius R_h of the particles from D_{sol} as

$$R_h = \frac{kT}{6\pi\eta D_{\text{sol}}}$$

where k is the Boltzmann constant, T is the temperature and η is the viscosity of the solvent.

Ellipsometry

The adsorbed amount was determined by null ellipsometry. All measurements were performed with a computer controlled null ellipsometer in a polarizer-compensator-sample-analyser (PCSA) arrangement.²¹ As a light source, a He-Ne laser ($\lambda = 632.8$ nm) was used. To obtain the best sensitivity for our system, the angle of incidence was set to 70.0° . The measured ellipsometric angles Ψ and Δ enable the calculation of the thickness d of the adsorbed polymer layer by using a multilayer model for a homogeneous isotropic film on top of the silicon wafer.²² For dried samples, which were measured in air after the adsorption process, the adsorbed amount is $A = \delta d$, with δ the mass density of the adsorbed polymer layer. The roughness of the adsorbed polymer layers causes only a small error in the measured adsorbed amount as reported in the literature.²³ The transmission of the adsorption solution was measured with the He-Ne laser of the ellipsometer.

Scanning force microscopy (SFM)

To investigate the topography of the dried adsorbed films, a commercially available SFM (Autoprobe CP/Park Scientific Instruments) was used. The cantilevers are made from micro-fabricated gold coated silicon. All measurements were performed in the non-contact mode at a chosen frequency of $f = 75$ kHz to minimize damage to the soft polymer layer caused by any tip contact. Measurements were taken at different positions of the sample, to ensure the regularity of our results.

Results and discussion

The investigation of the polymer in solution by dynamic light scattering has shown the coexistence of small and large structures, which can be connected to single polymer chains and polymer agglomerates in solution. For example, we observed in solution with 0.01 mol l^{-1} NaCl at pH 4.8 particles with a diameter of 11 nm and 95 nm, and at pH 2.8 particles with a diameter of 12.5 nm and 57 nm.

Polymer precipitation also occurs in our system and is determined from the decrease of the transmission of the solution. The transmission behaviour of different adsorption solutions, as shown in Figs. 2 and 3, is strongly influenced by the pH and the added salt in the solution. By rinsing after the sample preparation, the precipitate was removed from the sample and only the remaining adsorbed polymer was further investigated.

The adsorption from polymer solutions in a pH range without precipitation was investigated *in-situ* by ellipsometry. In each of these cases the adsorbed amount reached an equilibrium value after different adsorption times.

If the polymer solution shows precipitation the corresponding decrease in transmission prevents *in-situ* measurements by ellipsometry. For these cases samples were treated with the same solution for different times, and after rinsing the adsorbed amounts were determined from the dried sample by ellipsometry. Therefore the measured polymer amount is given by the adsorbed polymer only and not by the precipitated polymer.

Adsorption from a solution containing NaCl

Polymer adsorption from a solution containing NaCl was investigated at two different salt concentrations (0.01 mol l^{-1} and 0.04 mol l^{-1}). In both cases the adsorbed amount of the polyampholyte depended strongly on the pH of the solution. In Fig. 2, the adsorbed amount as a function of pH for 0.01 mol l^{-1} is shown. It exhibits two maxima at pH 3.0 and 4.1 in the pH range of 3.3 to 4.0, no adsorption is detectable. Simultaneously the transmission is reduced to 16% at pH 3.7, whereas for other pH values the transmission of the adsorption solution is mostly 100%.

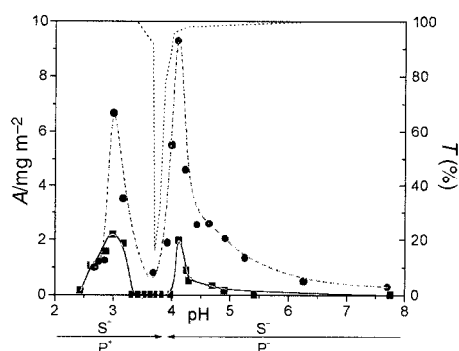
At the higher NaCl concentration of 0.04 mol l^{-1} , the adsorbed amount exhibits a quite similar curve shape as a function of pH as compared to the lower salt concentration (Fig. 2). However, the adsorbed amount is distinctly increased at every pH. In addition, the transmission of this solution shows a similar behaviour to the one with the lower NaCl concentration.

The adsorption minima and the minima in transmission of the polymer solution, caused by the precipitation of the polymer, were measured in the same pH range. Precipitation is typical for polyampholytes at the IEP.^{2,24}

The IEP of the used silicon substrate was determined by zeta-potential measurements at pH 3.9. Therefore, the polymer and the surface exhibit the same sign of the net charge independently of the actual pH value. The observed adsorption behaviour is explainable by an adsorption geometry in which the oppositely charged polymer block is attached to the substrate surface, while the other block is dangling in solution.^{7,25} The observed

decrease in the adsorbed amount at $\text{pH} < 2$ and $\text{pH} > 7$ can be explained by an increase of the charge on the polymer and substrate, while the oppositely charged polymer block loses its charge. Therefore the decrease of the attractive interaction and the increase of the repulsive forces together cause a decrease in adsorbed polymer.

Fig. 2 Adsorbed amount A of the polyampholyte obtained from a solution with $0.01 \text{ mol l}^{-1} \text{ NaCl}$ (solid squares) and from a solution with $0.04 \text{ mol l}^{-1} \text{ NaCl}$ (solid circles). The solid and the dashed lines are shown as guides for the eye. Also shown is the transmission T of the solutions (dotted line) as a function of pH . The arrows below the graph indicate where the silicon surface S and the polyampholyte P are carrying a positive or negative net charge.



Quite recently, polyampholytes with a different charge distribution and isoelectric point have been investigated.^{6,7,26} In the reported sample system the maximum of adsorbed polymer was observed at the IEP of the polymer. These results agree well with our observation of two maxima close to the IEP. On approaching the IEP, the amount of charges in the polyampholyte decreases, which leads to a screening in electrostatic repulsion between the polyelectrolyte segments as well. Therefore, the polymer can adsorb at a higher density, which causes a larger adsorbed amount.²⁷ This explains the measured increase in the adsorbed amount of the polymer towards the IEP and the maxima in the adsorbed amount close to the IEP. In contrast to this we observe a minimum in the adsorbed amount directly at the IEP. This behaviour can be explained by a similar IEP of polymer and substrate. At the common IEP, the substrate has a charge density that is close to zero as well. This leads to a low electrostatic interaction of the polymer and surface. Other authors report adsorption at the IEP of the substrate and interpret the driving force for adsorption to be non-electrostatic.⁸ These forces are obviously not strong enough in our system to lead to an adsorption of the precipitated polymer at the IEP, so after preparation the precipitated polymer is rinsed away from the substrate. Further experiments to clarify the adsorption mechanism are in progress.

The charge of a polyelectrolyte is shielded in aqueous solution by low-molecular-weight ions. This effect is described in the Debye-Huckel model by the screening length

$$\kappa^{-1} \sim 1/\sqrt{I}$$

with the ionic strength I given by the following equation :

$$I = \frac{1}{2} \sum_i z_i^2 m_i$$

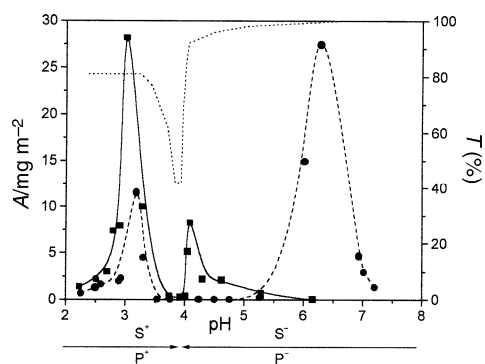
where z_i is the charge and m_i the molality of the ions in solution. Therefore, the increase of the salt concentration leads to a decrease in electrostatic repulsion between the polyelectrolyte chains and the polymer can adsorb in a higher density, which causes a larger adsorbed amount.^{9,27,28}

Adsorption from solutions containing the bivalent salts Na_2SO_4 and CaCl_2

In the presence of the bivalent salts Na_2SO_4 and CaCl_2 the adsorbed amount of polyampholyte exhibits two maxima, and in the region between these maxima no adsorption takes place as well. The total amount is higher as compared to the one from the solution with the same salt concentration of the monovalent salt NaCl (Fig. 3). Comparing the adsorption behaviour between Na_2SO_4 and CaCl_2 , particular differences are obvious. The adsorbed amount is strongly influenced by the pH . In the presence of Na_2SO_4 the peak at $\text{pH} 3.0$ is bigger than the one at $\text{pH} 4.1$. In the case of Na_2SO_4 the transmission of the adsorption solution shows a minimum of 42% at $\text{pH} 3.8$ and does not reach 100%. In contrast to CaCl_2 the transmission does not reach values above 10%.

The increase in the adsorbed amount in the presence of bivalent salts is explainable with the increase of ionic charge in solution as well. The enhanced adsorption and the polymer precipitation in the presence of Na_2SO_4 at a pH below the IEP can be explained in agreement with the Debye-Huckel model. The bivalent ion SO_4^{2-} causes a better shielding of the positively charged part of the polyampholyte. At a pH below the IEP the polyampholyte carries a positive net charge, so the effect of shielding and the increase in adsorption by the added SO_4^{2-} ions is larger than at pH above the IEP. The enhanced increase in the adsorbed amount in the presence of the bivalent metal ion Ca^{2+} cannot be explained by the Debye-Huckel model alone. Furthermore we have to take into account that bi- or multivalent metal ions are able to form chelate complexes with polyampholytes.^{2,29} Also short range electrostatic attractions between the polymer and the bivalent ions were discussed.³⁰ These effects reduce the electrostatic repulsion drastically and lead to a strong polymer precipitation and the high adsorbed amount in the presence of Ca^{2+} .

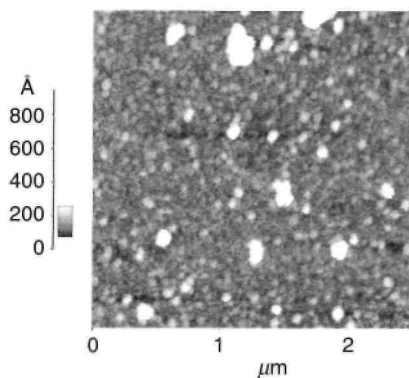
Fig. 3 Adsorbed amount A of the polyampholyte obtained from a solution with $0.01 \text{ mol l}^{-1} \text{ Na}_2\text{SO}_4$ (solid squares) and from a solution with $0.01 \text{ mol l}^{-1} \text{ CaCl}_2$ (solid circles). The solid and the dashed lines are guides for the eye. Also shown is the transmission T of the solution containing Na_2SO_4 (dotted line) as a function of pH. The arrows below the graph indicate where the silicon surface S and the polyampholyte P are carrying a positive or negative net charge.



Lateral structures at the adsorbed polymer layers

Fig. 4 shows a typical example for the topography of an adsorbed polymer layer measured by SFM. This layer was adsorbed from a solution at pH 3.0 containing $0.04 \text{ mol l}^{-1} \text{ NaCl}$. The adsorbed amount determined by ellipsometry is 6.7 mg m^{-2} . The surface consists of spherical structures with diameters between 50 nm and 300 nm. The height of these structures reaches up to 80 nm. The adsorption of polymer agglomerates instead of single chain adsorption¹⁵ may explain the large spherical structures. This is in good agreement with the formation of larger polymer structures in solution, detected by dynamic light scattering.

Fig. 4 Topography of an adsorbed polymer film measured with SFM at a scan area of $2.5 \times 2.5 \mu\text{m}^2$. The film was adsorbed from a solution containing $0.04 \text{ mol l}^{-1} \text{ NaCl}$ with pH 3.0. The adsorbed amount measured by ellipsometry is 6.7 mg m^{-2} .



Conclusions

The adsorption of PMAA-*b*-PDMAEMA with a block ratio of 90:10 on silicon substrates was investigated as a function of pH, salt type and salt concentration. The chosen block ratio causes the same isoelectric point IEP of polymer and silicon surface. The similarity of the IEPs explains the unusual adsorption profile with a minimum in the adsorbed amount at the IEP.

The increase of adsorption in the presence of bivalent salts, or with higher salt concentration, was shown to be in agreement with theoretical predictions. Lateral structures seen by SFM indicate the adsorption of polymer agglomerates instead of the adsorption of single polymer chains.

Acknowledgements

We thank H. Buchhammer from the Institute of Polymer Research, IPF, Dresden, for zeta-potential measurements, and B. Müller and S. Wiegand for their help with dynamic light scattering measurements. For helpful discussions we thank J. S. Gutmann and K. Page. This work was supported by the DFG Schwerpunkt 'Polyelektrolyte' (grant IIC10-322 1009). R. J. is grateful to the 'Services Fédéraux des Affaires Scientifiques, Techniques et Culturelles' for general support to CERM (grant PA14/11).

References

- 1 S. Förster and M. Schmidt, *Adv. Polym. Sci.*, 1995,120, 51.
- 2 S. E. Kudaibergenov, *Adv. Polym. Sci.*, 1999,144, 115.
- 3 H. Dautzenberg, W. Jaeger, J. Kötz, B. Philipp, C. Seidel and D. Stscherbina, *Polyelectrolytes*, Hanser Publishers, Munich, 1994.
- 4 N. Böhm and W.-M. Kulicke, *Colloid Polym. Sci.*, 1997, 275, 73.
- 5 G. R. Joppin, *J. Phys. Chem.*, 1978, 82, 2210.
- 6 Y. Kamiyama and J. Israelachvili, *Macromolecules*, 1992, 25, 5081.
- 7 V. Shubin and P. Linze, *J. Phys. Chem.*, 1995, 99, 1285.
- 8 N. G. Hoogeveen, M. A. Cohen Stuart and G J. Fleer, *Faraday Discuss.*, 1994,98,161.
- 9 A. V. Dobrynin, M. Rubinstein and J.-F. Joanny, *Macromolecules*, 1997,30,4332.
- 10 M. Skouri, J. P. Munch, S. J. Candau, S. Neyret and F. Candau, *Macromolecules*, 1994, 27, 69.
- 11 N. V. Sastry, J.-M. Séquaris and M. J. Schwuger, *J. Colloid Interface Sci.*, 1995,171, 224.
- 12 K. Lowack and C. A. Helm, *Macromolecules*, 1995, 28, 2912.
- 13 C. Amiel, M. Sikka, J. W. Schneider, Y.-H. Tsao, M. Tirrell and J. W. Mays, *Macromolecules*, 1995, 28, 3125.
- 14 H. Walter, C. Harrats, P. Müller-Buschbaum, R. Jérôme and M. Stamm, *Langmuir*, 1999,15, 1260.
- 15 H. Walter, P. Müller-Buschbaum, J. S. Gutmann, C. Lorenz-Haas, C. Harrats, R. Jérôme and M. Stamm, *Langmuir*, submitted.
- 16 Y. Zhang, M. Tirrell and J. W. Mays, *Macromolecules*, 1996, 29, 7299.
- 17 S. Creutz, P. Teyssié and R. Jérôme, *Macromolecules*, 1997, 30, 6.
- 18 S. Antoun, P. Teyssié and R. Jérôme, *Macromolecules*, 1997, 30, 1556.
- 19 S. Creutz, J. v. Stam, S. Antoun, F. C. De Schryver and R. Jérôme, *Macromolecules*, 1997, 30, 4078.
- 20 R. Pecora and B. J. Berne, *Dynamic Light Scattering*, John Wiley & Sons, New York, 1976.
- 21 H. Motschmann, M. Stamm and C. Toprakcioglu, *Macromolecules*, 1991,24,3681.
- 22 R. M. A. Azzam and N. M. Bashara, *Ellipsometry and Polarized Light*, North Holland, Amsterdam, 1987.
- 23 F. Tiberg and M. Landgren, *Langmuir*, 1993, 9, 927.
- 24 C. S. Patrickios, L. R. Sharma, S. P. Armes and N. C. Billingham, *Langmuir*, 1999,15, 1613.
- 25 R. R. Netz and J.-F. Joanny, *Macromolecules*, 1998, 31, 5123.
- 26 M. A. Cohen Stuart, G J. Fleer, J. Lyklema, W. Norde and J. M. H. M. Schcutjens, *Adv. Colloid Interface Sci.*, 1991, 34, 477.
- 27 H. G. M. van de Steeg, M. A. Cohen Stuart, A. de Keizer and B. H. Bijsterbosch, *Langmuir*, 1992, 8, 2538.
- 28 S. A. Sukhishvili and S. Granick, *J. Chem. Phys.*, 1998,109, 6861.
- 29 C. Fenn-Barrabaß, A. Pohlmeier, W. Knoche, H. D. Narres and M. J. Schwuger, *Colloid Polym. Sci.*, 1998, 276, 627.
- 30 M. Olvera da la Cruz, L. Belloni, M. Delsanti, J. P. Dalbiez, O. Spalla and M. Drifford, *J. Chem. Phys.*, 1995,103, 5781.