

Adsorption and Structure Formation of Semi-Rigid Polyelectrolytes

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Abstract

The adsorption of a negatively charged semi-rigid sulfonated poly(*para*-phenylene) s-PPP on silicon oxide was studied. While the adsorption of s-PPP on native negatively charged silicon oxide is unfavourable, the switching of the substrate charge by previous adsorption of a highly positively charged, flexible polyelectrolyte enables the adsorption of s-PPP.

The amount of polymer adsorbed from aqueous solution was determined by ellipsometry. Scanning force microscopy (SFM) was used to investigate the lateral structures of the adsorbed polymer. SFM confirms the presence of wormlike structures at the interface. The length scale of these detected structures is significant larger than the persistence length of single chains in solution. Therefore the direct adsorption of whole agglomerates observed in solution can be expected.

Key words: polymer, adsorption, SFM, ellipsometry, poly-*para*-phenylene

Introduction

Polyelectrolytes are macromolecules containing charged functional groups. The polyelectrolyte behaviour in solution and at solid/liquid interfaces is the topic of many recent reports.^{1–3} The understanding of such processes contains a high impact for industrial applications like paper production or washing powders.^{4,5} Due to the applications of poly(*para*-phenylene) (PPP) derivatives as liquid crystals, the self assembly and adsorption behaviour of these semi-rigid polymers are of interest. The adsorption of different uncharged PPP is widely investigated on several types of materials like copper, gold or glass,^{6,7} while the adsorption of polyelectrolytic PPP is less reported.⁸ Theoretically the behaviour of stiff polymers at solid/liquid interfaces is described for uncharged⁹ and charged polymer systems.^{10–12} These theoretical predictions for charged stiff polymers are fixed on the adsorption of single polymer chains, while the solution behaviour of PPP is also determined by the formation of agglomerates.^{13–15} The adsorption of polyelectrolytes is determined by both the adsorption of single polymer chains and multi-chain aggregates.¹⁶ Therefore, it is of interest to investigate experimentally the adsorption behaviour of semi-rigid polyelectrolytic species, which are known to form also polymer aggregates in solution.

This study reports on the adsorption of a negatively charged semi-rigid sulfonated poly(*para*-phenylene) s-PPP on silicon. The used s-PPP is known to form wormlike aggregates in aqueous solutions.¹³ For analogous negatively charged PPP with additional hydrophobic alkylgroups also a wormlike hierarchical structure formation in aqueous solution was determined. Also the complex formation of s-PPP at the air-water interface is discussed in literature.¹⁸

Experimental Section

Sample preparation

All adsorption experiments were performed with a sulfonated poly(*para*-phenylene) derivative s-PPP (Figure 1). The molecular weight of the used s-PPP was $M_n = 9900$ g/mol. The synthesis by a palladium catalysed coupling reaction and the determination of the molecular weight using gel permeation chromatography (GPC) and membrane osmometry are described in literature.^{19–21}

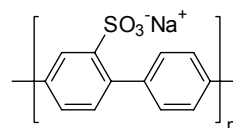


Figure 1. Structural unit of the sulfonated poly(*para*-phenylene) s-PPP.

As substrates for the adsorption experiments silicon wafers with a native silicon oxide layer of typically 2 nm were used. Prior all experiments the substrates were cleaned using an alkaline cleaning procedure.²² For cleaning the silicon wafers were placed into a bath of H₂O₂, NH₃ and Millipore water for 30 minutes at 70°C. Afterwards the wafers were rinsed with Millipore water and were dried with nitrogen. The silicon wafers treated by this procedure carry a pH dependent surface charge. This surface charge is above the isoelectric point p*H*_{IEP}=3.8 of the silicon substrate negative.²³ To enable the adsorption of the as well negatively charged s-PPP the silicon surface was modified. First a highly positively charged, flexible polyelectrolyte P+ (Figure 2) was adsorbed on the silicon wafer.

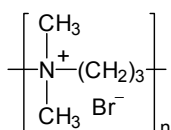


Figure 2. Structural unit of the positively charged polyelectrolyte P+.

This prior adsorption was performed from aqueous polymer solution containing 0.128 g/L P+ and 0.01 mol/L NaCl at a pH of 10.4. The high pH of 10.4 is chosen, because the net charge of the silicon surface depends on the pH (IEP=3.8). The adsorption of strong positively charged polymers should be favoured at higher pH due to the stronger negative charge of the silicon.⁸ The silicon substrates were placed in this adsorption solution for 12 hours, afterwards rinsed with Millipore water and dried under nitrogen. In this way modified silicon wafers contain a p*H*_{IEP}=6.9. To perform the adsorption of s-PPP the modified wafers were placed for 12 hours in an aqueous solution of s-PPP. This second adsorption solution contained s-PPP concentrations from 0.003 g/L to 0.09 g/L and 0.01 mol/L NaCl at a pH of 9.5. Finally, the wafers were rinsed with Millipore water again to remove any loosely attached polymer residues. Drying with nitrogen is performed afterwards.

Ellipsometry

The amount of adsorbed polymer was determined using a null ellipsometer in a polarizer-compensator-sample-analyser (PCSA) arrangement.²⁴ A He-Ne laser with $\lambda=632.8$ nm was used as light source. The angle of incident was set to 70°. The thickness of the adsorbed polymer layer *d* was calculated from the ellipsometric angles ψ and Δ using a multilayer model for a homogeneous film on the silicon wafer.²⁵ For the multilayer model altogether four layers were taken into account: silicon, silicon oxide, adsorbed polymer P+ and adsorbed polymer s-PPP. Ellipsometric measurements

were performed before and after every adsorption step. The adsorbed amount *A* was calculated from the layer thickness *d* determined in air after the adsorption process by $A=\delta d$. $\delta=1.3$ kg/L is the mass density of the adsorbed polymer layer gained as mean value from PPP bulk-material.²⁶

Scanning force microscopy (SFM)

The scanning force microscopy SFM was used to study the lateral structures of the dried adsorbed polymer films. All investigations were performed with a commercially available SFM (Multimode Nanoscope III / Digital Instruments) under temperature of 20°C. SFM topographies were taken in the tapping modeTM to minimize any damage of the polymer layer caused by tip contact. The measurement frequency was set from 280 to 330 kHz. The used tips were made from microfabricated silicon and are commercially available (Nanosensors).

Results and discussion

Adsorption experiments were performed from aqueous solutions containing a s-PPP concentration in a range of 0.003 g/L to 0.09 g/L. The adsorbed amount reached a plateau value of around 0.9 mg/m² at low polymer concentrations of 0.01 g/L. An adsorption of the negatively charged polymer s-PPP is only observed after the first adsorption of the positive polymer P+. No adsorption is determined on pure silicon wafers. The electrostatic net charge of the wafer surface is negative, so an adsorption of the as well negative charged polymer is not favoured. The first adsorption of the positively charged polymer is therefore necessary to enable the adsorption of s-PPP. To evaluate the adsorbed amount as function of the polymer concentration the Langmuir adsorption isotherm was used (Figure 3).

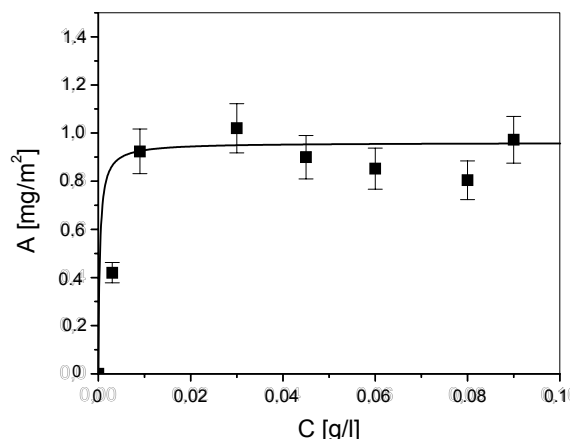


Figure 3. Adsorbed amount *A* of s-PPP as a function of the polymer concentration *C*. The solid line shows a fit based on the Langmuir adsorption model.

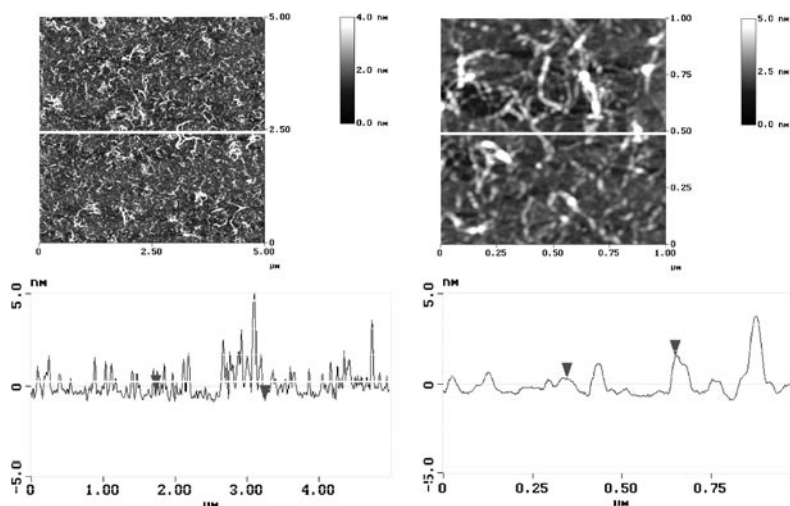


Figure 4. SFM images of adsorbed s-PPP ($C_{s\text{-PPP}}=0.06$ g/L; $A=0.9$ mg/m²). The cross sections of the SFM figures are shown below these images.

The Langmuir adsorption model describes the adsorbed amount $A(c)=A_{\infty}[Kc/(1+Kc)]$ as a function of polymer concentration c .²⁷ With A_{∞} as the adsorbed amount at an infinite high polymer concentration. $K=k_{\text{ads}}/k_{\text{des}}$ is the ratio of the rate for adsorption k_{ads} and desorption k_{des} of the polymer chains. The Langmuir fit performed with the value $A_{\infty}=0.96$ mg/m² leads to approximately $K=3000$. Therefore the adsorption process is expected to be much more dominant than desorption. The consistency of the adsorption isotherm with the Langmuir model and the low adsorbed amount around 0.9 mg/m² are a strong hint that the adsorption of s-PPP occurs in polymer monolayers.²⁸ Nevertheless weak attachment of further polymer layers could be possible but these loosely attached polymer chains would be removed by rinsing in the end of the sample preparation process. The Figure 4 shows typical SFM images of dried adsorbed s-PPP on silicon. The polymer was adsorbed from aqueous solution with a s-PPP concentration of $C_{s\text{-PPP}}=0.06$ g/L and an ellipsometrically determined adsorbed amount of $A=0.9$ mg/m². These images are representative for other s-PPP films adsorbed from aqueous solutions containing different s-PPP concentrations (Figure 5).

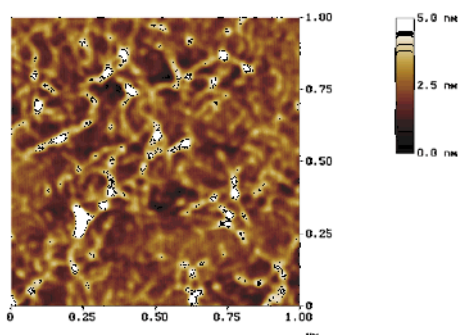


Figure 5. SFM image of adsorbed s-PPP ($C_{s\text{-PPP}}=0.03$ g/L).

The maximum height of the polymer film, determined from cross sections of SFM images, reaches nearly 5 nm and a root mean square roughness of approximately 2.5 nm was determined. The relatively small roughness of adsorbed polymer suggested that the adsorption of s-PPP occurs in a flat polymer conformation and together with the small adsorbed amounts an adsorption in monolayers should be also estimated. In contrast to the cross section of the adsorbed s-PPP the topography of SFM figures exhibit significantly wormlike structures (Figures 4). The diameter of the adsorbed wormlike structures is around 10 nm, while their length scale can reach values up to some 100 nm. This length scale is significantly higher than the persistence length of single polymer chains in solution.¹³ The polymer s-PPP is known to form wormlike aggregates in solution¹³ and analogously to the adsorption of whole spherical polyelectrolytic aggregates¹⁶ also the adsorption of whole wormlike aggregates should be expected. Therefore it could be concluded that the negatively charged poly(*para*-phenylene) derivative s-PPP is observed to adsorb in wormlike structures on modified silicon directly from solution.

Conclusions

Negatively charged semi-rigid sulfonated poly(*para*-phenylene) s-PPP is adsorbed on modified silicon. Investigations with ellipsometry and SFM show an adsorbed amount of less than 1 mg/m² in a flat conformation. The SFM topography exhibits wormlike structures of adsorbed polymer with length scales significant larger than the persistence length of single polymer chains in solution. Therefore the adsorption of wormlike s-PPP aggregates from solution is expected.

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Povzetek

Proučevali smo adsorpcijo negativno nabitega semi-rigidnega sulfoniranega poli(para-fenilena) na silicijevem oksidu. Ker adsorpcija zaradi naravnega negativnega naboja silicijevega oksida ni favorizirana, smo najprej spremenili naboj substrata z adsorpcijo pozitivno nabitega fleksibilnega polielektrolita, kar je nato omogočilo adsorpcijo sulfoniranega poli(para-fenilena). Množino adsorbiranega polimera smo določali z elipsometrijo, strukturo adsorbiranega polimera pa smo kontrolirali z mikroskopom na atomsko silo. Ugotovili smo, da je adsorbirani polielektrolit na površini prisoten pretežno v iztegnjeni obliki, da pa je povprečna dolžina bistveno večja od dolžine verige v raztopini. Privzamemo lahko, da poteka direktna adsorpcija celotnih v raztopini opaženih aglomeratov.