Adsorption behaviour of semirigid polyelectrolyte chains

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A poly(para-phenylene) derivative (c-PPP), poly(2,5-dihexyl-1,4-phenylene-alt-2,5-bis(6-triethylammonium iodide)hexyl-1,4-phenylene), was investigated as a model system for semirigid, charged polymers. The adsorption on oxidized silicon surfaces was studied via ellipsometry and scanning force microscopy. The adsorption was performed from dilute aqueous solutions, and carried out as a function of pH and polymer concentration. The adsorbed amount determined by ellipsometry was found to be influenced by pH, as expected from the charge of polymer and silicon substrate. From adsorption isotherms, adsorption is expected to occur in monolayers, where chains are lying flat on the substrates. Dried monolayers contain a small roughness of 2 nm, as determined by scanning force microscopy. The kinetics of adsorption was studied in-situ by ellipsometry and a two stage adsorption process is proposed.

Introduction

Polyelectrolytes in solution and adsorbed at the solid/liquid interface are described in numerous reports [1, 2]. To find the optimal adsorption conditions, many parameters have to be taken into account, such as pH, salt concentration, polymer concentration and adsorption kinetics [3].The theoretical work of Matsuyama et al. on the adsorption of rigid-rod molecules describes the equilibrium properties of the adsorbed polymer chain as function of the solvent conditions and stiffness of the polymer chain [4]. Further theoretical studies cover stiff polyelectrolytes in solution and at the solid/liquid interface [5, 6]. Charged poly(para-phenylene) (PPP) derivatives can be taken as semirigid systems and have not been used as models for the adsorption of stiff polyelectrolytes so far. The behaviour of many different PPP derivatives in organic solvents is well described in literature [7, 8, 9]. Due to the application of PPP as liquid crystals, the determination of the chain conformation and the self assembly of the stiff polymers are of special interest. The adsorption of different uncharged PPP derivatives on copper and gold is described by Brunner, Steiner et al. [10, 11]. Other substrates like glass are also used for adsorption experiments from organic solvents [12]. Adsorption of uncharged polymers from organic solutions is mainly determined by a hydrophobic driving force [13].
In this paper we present the adsorption of a highly charged PPP derivative (c-PPP) from aqueous solution on a charged silicon substrate. The adsorption takes place in a pH range where the substrate and the polymer carry opposite electrical charges. In this case, the electrostatic attraction of polymer and substrate is expected to be the

main driving force for adsorption. The adsorbed amount of the thin polymer monolayer was determined by ellipsometry, while the lateral structures and the roughness of the layer were investigated by scanning force microscopy (SFM). The adsorption kinetics was studied in-situ by ellipsometry.

Experimental

Materials

All adsorption experiments were performed with the cationic polyelectrolyte poly(2,5-dihexyl-1,4-phenylene-alt-2,5-bis(6-triethylammonium iodide)hexyl-1,4-phenylene) (Scheme 1). The degree of polymerisation was n=40 determined from membrane osmometry. The synthesis of the PPP derivative by Pd catalysed polycondensation as well as the characterisation of the polymer by ^{1}H-NMR spectroscopy and membrane osmometry are well described in the literature [9].

For all adsorption experiments, silicon wafers were used. These wafers contained a native silicon oxide layer of approximately 2 nm. All substrates were cleaned by the same alkalic procedure using an aqueous mixture of NH_3 and H_2O_2 at 70°C for 30 minutes. After the alkalic bath the wafers were rinsed with MilliQ water and dried with nitrogen. The isoelectric point (IEP) of the alkalic cleaned wafers was determined by electrokinetic measurements to be at pH=3.8 [14].
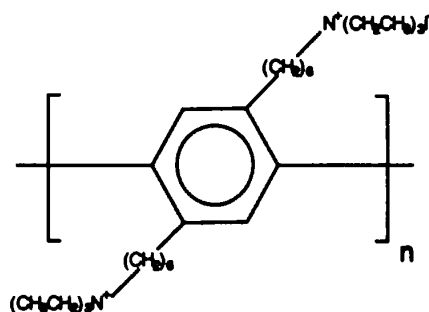
Scheme 1: Schematic drawing of poly(2,5-dihexyl-1,4-phenylene-alt-2,5-bis(6-triethylammonium iodide)hexyl-1,4-phenylene)

Ellipsometry

The amount of adsorbed polymer was determined by null ellipsometry. All ellipsometric measurements were performed with a null ellipsometer in PCSA arrangement [15]. The thickness d of the adsorbed polymer layer was calculated from the ellipsometric angles Ψ and Δ by using a multilayer model for a homogeneous polymer film containing a refractive index of n=1.5 placed on the silicon wafer [16]. The amount of adsorbed polymer A for dry samples measured under air is determined by $A = d\delta$ with δ=1.3 g/l as the mass density of the polymer. In case of ellipsometric measurements in solution, the adsorbed amount A was given by $A = d \cdot \dfrac{(n_1 - n_0)}{dn/dc}$. n_1

and n_0 are the refraction indices of the polymer and the aqueous solution, and

dn/dc=0,21 ml/g is the refraction index increment of PPP in water determined with a Michelson interferometer [15, 17].

Dynamic light scattering (DLS)

Dynamic light scattering measurements were used to determine the diffusion coefficient of the c-PPP chains in solution. The scattering system was built up from a commercial ALV 3000 digital correlator with a 400 mW krypton laser (λ=647 nm) as light source. The measurements of the autocorrelation functions were performed at c-PPP concentrations of 0.128 g/l and 0.032 g/l. The pH of the polymer solution was set to 9.4 and salt concentration was 0.01 mol/l NaCl. The analysis of the autocorrelation function gives the diffusion coefficient [18].

Scanning force microscopy (SFM)

We used scanning force microscopy SFM to study the roughness and the lateral structures of the dried adsorbed polymer films. For all investigations, a commercially available SFM (Multimode Nanoscope III / Digital Instruments) was used. SFM topographies were taken from different samples in the tapping mode™ to minimize any damage of the polymer layer caused by tip contact. The used commercially available SFM tips were made from microfabricated silicon (Nanosensors™). The resonance frequencies were set from 300 to 320 kHz.

Adsorption Experiments

The adsorption was carried out from a dilute aqueous polymer solution containing 0.01 mol/l NaCl. Different c-PPP concentrations from 0.00061 g/l to 0.128 g/l were used. The pH of the adsorption solution was varied from 3.2 to 10.8 by adding acid (HCl) or base (NaOH) in an amount that is negligible in comparison with the NaCl concentration of 0.01 mol/l.

After preparation of the adsorption solution, it was stirred gently, and the silicon wafers were submerged in it for at least 10 hours. Afterwards, the wafers were rinsed with Milli-Pore water and dried under nitrogen. The kinetic measurements were performed in a specially designed teflon cell. First the wafer was put into the cell under 0.01 mol/l aqueous NaCl solution, and the ellipsometric angles were detected until constancy was reached. Then the adsorption was started by adding of the polymer.

Results and discussion

Adsorption as a function of pH

The adsorption experiments were performed in a pH range from 3.2 to 10.8. The polymer concentration was set to 0.128 g/l and the concentration of added NaCl was set to 0.01 mol/l. Below a pH of 6.7, no adsorption was detected. In the pH range from 6.7 to 9.2 the adsorbed amount increased to approximately 0.8 mg/m^2 and reached a plateau at higher pH values (Figure 1). While the positive electrostatic charge of the polymer is expected to be essentially pH independent, the charge of the

silicon substrate is strongly influenced by the pH. Because the IEP of the siliconoxide layer covering the silicon substrate is located at pH=3.8, the wafer is negatively charged in the pH range, where the adsorption experiments were performed.

Adsorption was observed only in a pH range where substrate and polymer are oppositely charged. From this, we conclude that the adsorption is mainly caused by the electrostatic attraction of polymer and substrate. In the case of pH<3.8, the wafer and the substrate have the same electrostatic charge, and the electrostatic repulsion between them prevents adsorption [19]. With pH values larger than 3.8, the wafer is negatively charged, thus polymer and substrate attract each other. Also, strong electrostatic repulsion exists between the positively charged polymer chains. These repulsive forces provide a limit for the adsorption of the polymer. In the adsorbed polymer layer, the positive charge will be compensated by the negative charge of the wafer. This leads to a reduction of the repulsive interaction. While the negative charge of the wafer increases from the IEP at 3.8 toward higher pH, more positive charges on the polymer can be compensated, and the polymer can adsorb at higher density. This behaviour explains the increase in adsorption with increasing pH until the polymer density on the surface is no longer limited by the electrostatic repulsion, and a plateau is reached. In the pH area from 3.8 to 6.5, where no adsorption was observed, the silicon substrate is expected to be to lightly charged to compensate the positive polymer charges to prevent any repulsion between the polymer chains at the surface.

The plateau above pH=9.2 is due to the formation of a polymer monolayer on the wafer at highest polymer density. This monolayer consists of highly charged polyelectrolytes with a layer thickness less than 1 nm. The persistence length of poly-para-phenylene was calculated to be at approximately 20 nm [20], which means that the persistence length of an uncharged adsorbed polymer molecule is much larger than the layer thickness. Therefore the formation of a random polymer conformation with loops is not appropriate and the adsorption of the polymers in a flat rigid rod like conformation is expected [6].
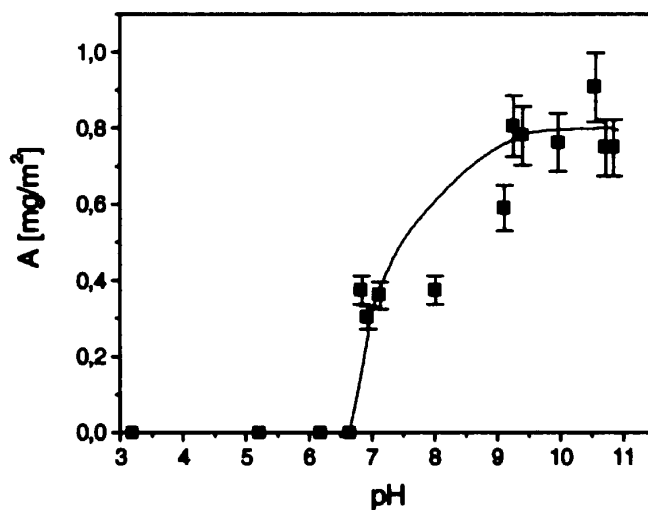

Figure 1: Adsorbed amount A as a function of pH. The solid line provides a guide for the eye.

Adsorption as a function of polymer concentration

Adsorption experiments are performed from solutions with pH=9.4 containing different polymer concentration from 0.00061 to 0.128 g/l. The adsorbed amount reaches a plateau at a low polymer concentration. The adsorption behaviour as function of polymer concentration is consistent with the Langmuir adsorption isotherm for monolayers (Figure 2). The Langmuir model describes the adsorbed amount $A(c_p)$ as a function of polymer concentration c_p by the following equation [21]:

$$A(c_p) = A_\infty \left(\frac{Kc_p}{1 + Kc_p} \right)$$

(1)

A_∞ is the adsorbed amount at an infinite high polyelectrolyte concentration, and $K = k_{ads}/k_{des}$ is the ratio of the rate for adsorption k_{ads} and desorption k_{des} of the polyelectrolyte chains. With $A_\infty = 0.8$ the Langmuir fit on the investigated polyelectrolyte leads to approximately K=500. So the adsorption process in equilibrium is much more dominant than desorption. This is explainable by strong electrostatic interaction between the oppositely charged polymer and the substrate. The consistency of adsorption isotherm with the Langmuir model gives further evidence of monolayer polymer adsorption [22].
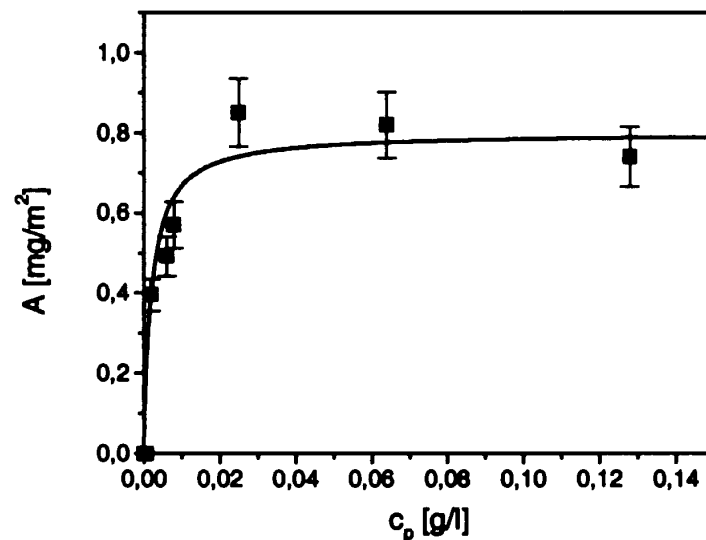

Figure 2: Adsorbed amount A as a function of polymer concentration c_p at pH = 9.4. The solid line is a fit based on the Langmuir adsorption model as explained in the text.

Lateral structures of the adsorbed polymer layers

Figure 3 shows a typical topography of a dried adsorbed polymer layer measured by SFM, where the polymer layer is adsorbed at a concentration of 0.128 g/l and at pH=10.0. It is representative for other polymer films adsorbed at different conditions.

The polymer film exhibits a small root mean square roughness of approximately 2 nm. The maximum height reaches 3.5 nm. The relatively small polymer roughness again indicates that polymer adsorption occurs in monolayers with a flat polymer conformation compared with the polymer persistence length of 20 nm.
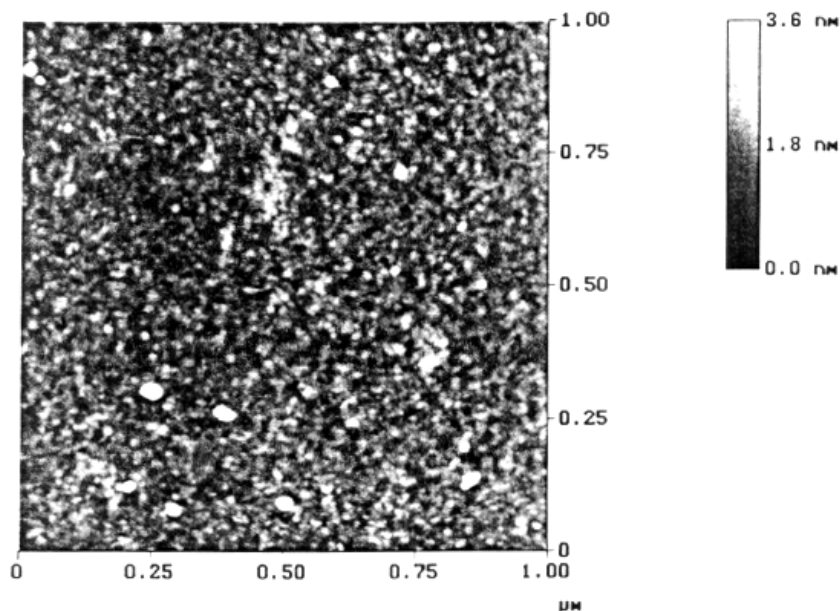

Figure 3: SFM-topography of a dry polymer film adsorbed from a polymer solution with c_p=0.128g/l and pH=10.0.

Adsorption kinetics

The adsorption kinetics of c-PPP was investigated from solutions containing polymer concentrations ranging from 0.008 to 0.128 g/l. For these experiments, pH was set to 9.4.

The adsorbed amount of c-PPP increases monotonically with time in all our measurements, and reaches a plateau value after a characteristic time depending on polymer concentration. Figure 4 shows the adsorbed amount for a range of polymer concentrations plotted with respect to time, t or square root of time, $\sqrt{t}$. Consistent with the literature for charged and uncharged surfactants, the time for adsorption increases with decreasing c-PPP concentration [23]. The time to reach equilibrium increases from a few minutes (c_p=0.128 g/l) to at least 2 hours (c_p=0.008 g/l). At low concentrations it takes a longer time until a certain number of chains diffuse to the substrate and adsorb [24].

The increase of adsorbed amount with $\sqrt{t}$ shows two regimes. At the beginning of the adsorption process, the adsorbed amount increases linearly with $\sqrt{t}$. This

behaviour is typical for a diffusion controlled adsorption process [15], in which the transport of the polymer to the substrate is limited mostly by the diffusion of the polymer in solution. In the second regime, the adsorption rate decreases because rearrangement of the adsorbed polymer layer must be taken into account, the surface charge is decreasing due to adsorbed chains and the number of available free sites for adsorption is decreasing. Consequently repulsion between chains becomes stronger.

For the first adsorption regime the diffusion coefficient of the polymer toward the surface D_{sur} can be calculated from the slope of the adsorbed amount A(t) as a function of the square root of time [15]:

$$A(t) = \frac{2}{\sqrt{\pi}} \cdot c_p \sqrt{D_{sur} t} \tag{2}$$

It should be noted that this equation does not explicitly takes the surface charges into account and has been derived under simplifying assumptions. The diffusion coefficients obtained are therefore only apparent diffusion coefficients. The calculated diffusion coefficients show no clear trend as a function of polymer concentration. The average of D_{sur} is 13.0 10^{-8} cm^2/s which is quite comparable with the diffusion coefficient D_{DLS}=9.2 10^{-8} cm^2/s found by dynamic light scattering in aqueous solution as the mean value from measurements at different polymer concentrations. The opposite charges of polymer and surface therefore seem not to play a major role in the kinetics of adsorption. i.e. the attractive forces may be only of short distance.
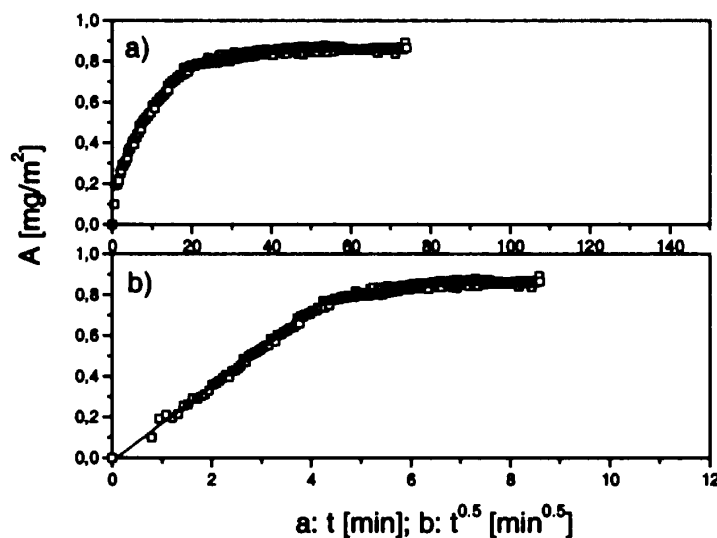

Figure 4: Adsorbed amount A obtained from a 0.025 g/l polymer solution at pH=9.4 plotted as function (a) of time, t and (b) square root of time, $t^{0.5}$.

Conclusions

The adsorption of the a highly charged PPP derivative poly(2,5-dihexyl-1,4-phenylene-alt-2,5-bis(6-triethylammonium iodide)hexyl-1,4-phenylene) on silicon substrates was investigated as a function of pH and polymer concentration. The PPP

derivative can be assumed to adsorb in monolayers with a flat conformation, thus producing a small roughness on the silicon surface.

The adsorption behaviour as function of pH demonstrates that the adsorption is connected with the electrostatic interaction between the polymer and the substrate. Adsorption was only observed in a pH range, where substrate and polymer are strongly oppositely charged. Further hydrophobic interactions may only play a marginal role.

The time to reach equilibrium was dependent on polymer concentration, and could take several hours. The adsorption kinetics was divided into two regimes. The first regime is characterized by a rapid adsorption process determined by diffusion of the polymer to the substrate. The following slower process was most likely governed by the decreasing surface charge, possible chain rearrangements of the surface and a saturation of available free adsorption sites on the surface.

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