Preparation and Characterization of a Polyelectrolyte Monolayer Covalently Attached to a Planar Solid Surface

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ABSTRACT: A novel concept for the synthesis of molecularly thin polyelectrolyte layers covalently attached to planar solid surfaces is introduced. The polymer monolayers are generated directly at the surface by using self-assembled monolayers of an azo initiator and radical chain polymerization in situ. This "grafting from" approach yields surface-bound polymer molecules with a high molecular weight and with high graft densities of the attached chains ("brush"-like state). As an example for the preparation of a positively charged polyelectrolyte "brush" at first a monolayer of poly(4-vinylpyridine) (PVP) was generated at the surface, which was subsequently quarternized to yield a poly[4-vinyl-*N*-*n*-butylpyridinium] bromide (BuPVP) monolayer. The thickness of this resulting cationic monolayer can be controlled in a wide range, starting from 2 nm to more than 1000 nm in the solvent-free state.

Introduction

The behavior of polyelectrolyte molecules in contact with a solid surface is fundamentally different from that of uncharged polymers. When the surface-attached layers consist of polymer molecules carrying charges, the structure and properties of the layers are dominated by the electrostatic interactions. Mutual repulsion between the charged polymer segments and electrostatic forces between the polyelectrolyte molecules and the surface to which the chains are attached (especially if the latter one also carries a charge) influence the strength of interaction with the substrate and the physical properties of the layers strongly.[1]

Generally, two different pathways can be followed to attach a polyelectrolyte (PEL) monolayer to a solid surface: one where the chains are physically bound (physisorption) and the other where the chains are attached through establishment of a covalent bond between the substrate and the polymer (chemisorption). In the case of an attachment through physical interactions, the amount of adsorbed polymer and the conformation of the attached chains are controlled by the charge density of the polymer,[2] the sign of the surface charge, the charge density,[3] and the ionic strength of the solution from which the polymer is physisorbed.[4−6] The electrostatic repulsion between PEL molecules in water opposes the accumulation of polymer chains at the surface, and highly charged polymers adsorb only in small amounts to the substrate. This repulsion can at least partially be overcome if the electrostatic forces are screened through increasing the ionic strength of the solution from which the PEL is physisorbed by addition of low molecular weight electrolytes. However, when the electrostatic interactions are strongly screened through addition of large amounts of salt to the polymer solution, the adsorbed amount of polymer is no longer determined by the electrostatic forces, but the adsorption process closely resembles that of the adsorption of neutral polymers at surfaces. For example, Marra et al.[6] have shown in studies of the adsorption of sodium poly(styrenesulfonate) (PSS) to silica that in the absence of salt hardly any polymer adsorbs. However, they noted that by addition of low molecular electrolytes, in this case NaCl and $MgCl_2$ up to a concentration of 3 M, the adsorbed amount of PSS can be increased to 1 mg/m^2. Generally, it can be stated that, regardless of the fact whether salt is added or not during the adsorption of polyelectrolytes, in both cases in a typical experiment the amount of polymer that is adsorbed is between 0.1 and 5 mg/m^2.[1]

A general problem of all physisorbed polyelectrolyte layers is the stability of the layers in different environments. The physisorbed polyelectrolyte monolayers can be desorbed, either by changing the sign of the surface charge (which leads to an electrostatic repulsion between the polymer segments and the substrate)[3] or by adsorption of a competing compound leading to a displacement of the polymer chains.[7,8] One way to improve the adhesion and to overcome problems caused by the electrostatic repulsion in the surface layer is to generate a chemical bond between the polyelectrolytes and the surface. In that case the polymer can only be removed from the surface if the bond is cleaved, which is connecting the polymer to the surface. Additionally, the attachment of the polymer molecules to the surfaces should be independent of the sign and density of the surface charge of the substrate.

Despite strong theoretical interest in such systems, to the best of our knowledge only one experimental realization of such a system has been described so far (although numerous studies on surface-attached uncharged systems have been carried out). Mir et al.[18] immobilized polystyrene, which had been functionalized with a dimethylchlorosilane end group, to the surface of a high surface area silica gel. Subsequent sulfonation of the polystyrene conditions with SO_3 led to the formation of a surface-attached poly(styrenesulfonate) monolayer. However, the authors noted that several difficulties persisted in the preparation of the PEL monolayer via this route due to problems with the sulfonation reaction as strongly acidic conditions are applied.[18] Furthermore, the sulfonation reaction remained incomplete (degree of sulfonation: $f = 0.64$), which should lead to a nonhomogeneous distribution of hydrophilic and hydrophobic segments inside the poly-

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mer layer. The resulting amount of surface-attached polyelectrolyte was not given in the paper by Marra et al. The thickness of the swollen layer was determined to be 75 nm.[18]

Such a "grafting to" approach to link a PEL molecule to a solid surface is very straightforward; however, it is generally limited insofar as only polymers with a rather moderate molar weight can be used. When high molecular weight compounds are used, not all "anchor" groups reach the surface, and the layer will consist of a mixture of physically and chemically attached polymer molecules. Furthermore, the thicknesses of layers obtained by "grafting to" are intrinsically limited. Once the surface starts to become significantly covered, the attachment of further chains becomes unfavorable for kinetic (and at high graft densities also for thermodynamic) reasons.[19] Due to this hindrance for the attachment of further chains, the polymer layers generated by this approach are limited to film thicknesses of only a few nanometers in the dry state, and the graft densities remain rather low if high molecular weight polymers are employed.

PEL layers with a high graft density (PEL "brushes") have attracted much interest recently from a theoretical point of view.[9−15] It is predicted that PEL brushes exhibit a scaling behavior (relation between molecular weight and the thickness of the surface-attached layers swollen in solvent) that is very different from that of uncharged brushes due to the electrostatic interactions. In monolayers consisting of uncharged molecules, the brush height increases with increasing graft density of the surface-attached chains and grows with increasing molecular weight of the surface-attached molecules.[16,17] The electrostatic interactions within the PEL brushes, however, can induce a much more complex scaling behavior as the brush height depends also on the density of charges on the chains and on the ionic strength of the surrounding medium. For example, it has been predicted by Pincus[9] that, under conditions where the graft density is low and the charge density is high, PEL brushes have a much stronger tendency to stretch than uncharged brushes. In contrast to this, if both the graft density and the charge density are very high, a behavior is predicted in which the height of the brush is proportional to the molecular weight of the surface-attached chains but *independent* of the graft density of the monolayer. A complete review of the theory of PEL brushes is beyond the scope of this article and is not attempted here, but these few examples already demonstrate that some very unusual scaling behavior of such chains should be expected. The extent to which the chains are stretched, however, will have a strong influence on the physical properties of the surface-attached polymer layers.

It has been recently shown that the intrinsic limitation of the thickness for attaching polymers to surfaces can be overcome if, instead of grafting preformed chains onto a surface, the polymer is generated directly at the surface in situ.[20,21] To achieve this, at first a self-assembled monolayer of initiator molecules is generated at the surface of the substrate. Subsequent polymerization in situ leads to very thick polymer films with high grafting densities ("grafting from"). In contrast to "grafting to" techniques only monomers have to react with the growing chain during polymerization, and no significant diffusion barrier exists.[20,21]

In this paper we report that by using this "grafting from" approach also polyelectrolyte monolayers can be prepared with high film thicknesses. As a first step a self-assembled monolayer of an azo initiator is prepared, and after addition of a noncharged monomer, the initiator is thermally activated and a covalently attached neutral polymer monolayer is generated (Figure 1). Afterward, the neutral polymer monolayer was converted into the polyelectrolyte monolayer through a polymer-analogous reaction.

Experimental Section

Materials and Experimental Procedure. The end-functionalized azo initiator was prepared in a three-step synthesis according to Prucker et al.[22] Glass slides (BK 7; Schott, Germany) were used as substrates for the deposition of the polymer layers. Onto the slides an approximately 50 nm thick silver and a 30 nm thick silicon oxide layer were evaporated prior to polymer deposition. As alternative substrates, silicon wafers (Aurel, Germany) with a natural silicon oxide layer were used. The immobilization of the initiator was carried out in dry toluene at room temperature under argon. The reaction time was about 15 h. The concentration of the initiator was approximately 0.5 mmol/L,[23] and triethylamine was used as catalyst for the surface attachment reaction. After completion of the immobilization reaction, nonattached initiator and other byproducts of the reaction were removed by careful extraction with toluene and methanol.

The polymerization of 4-vinylpyridine with the surface-attached initiator was carried out in benzene and in ethanol as solvents, at a concentration of 50 mol % monomer in benzene and 30 mol % monomer in ethanol. After the immobilization of the initiator, the substrates were transferred into Schlenk tubes, which were subsequently filled with the monomer and the solvent. After removal of all oxygen traces from the solution under vacuum during repeated freeze−thaw cycles, the Schlenk tubes were placed into a thermostat at 60.0 °C. After the desired polymerization times the substrates were removed from the polymerization solution, rinsed carefully, and extracted for at least 15 h in a Soxhlet extractor with methanol, which is a good solvent for poly(vinylpyridine) (PVP). This procedure was found to be necessary to remove all physisorbed polymer from the covalently bound polymer monolayer.

The quarternization of the PVP was carried out with *n*-butyl bromide in nitromethane at 65 °C following the procedure described by Fuoss and Strauss for the quarternization of free PVP in solution.[24] Reaction times were varied from 3 to 100 h. After completion of the quarternization reactions the samples were rinsed extensively with nitromethane, to remove all of the nonreacted quarternization agents, and dried in vacuum.

Instrumentation. For a qualitative characterization of the generated monolayers, Fourier transform infrared (FTIR) transmission measurements were carried using a Nicolet Omnic 850 spectrometer. For these measurements approximately 1 mm thick silicon wafers, which were polished on both faces, were used as substrates. Typically 750 scans were accumulated for each spectrum with a resolution of 4 cm^{-1}. Additional qualitative information about the structure of the deposited polymer layer was received by X-ray photoelectron spectroscopy (XPS). The measurements were carried out on a Fisions 220 spectrometer using Mg Kα radiation. The step width during accumulation of the spectra was 2 eV. The analyzer was set to an angle of 90°.

For the determination of the thicknesses of the surface-attached polymer layers surface plasmon and waveguide spectra were measured. The measurements were carried out in an ATR (attenuated total reflection) setup, as shown in Figure 2. Using a glass prism the p-polarized laser light (HeNe laser, 632.8 nm) was coupled into a silver film, which had been evaporated onto the glass substrates as described above. During angular scans the reflected intensity was measured

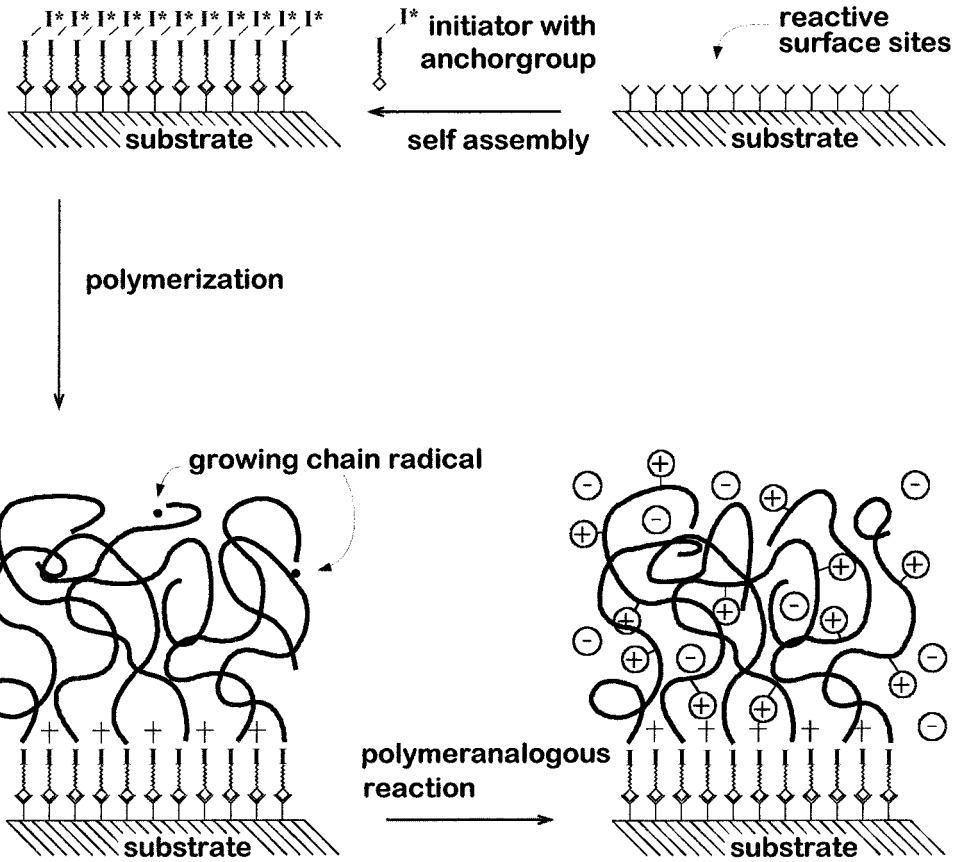

Figure 1. Preparation of a polyelectrolyte monolayer at a planar solid surface by generation of a covalently attached polymer monolayer of uncharged molecules and subsequent introduction of positive charges through a polymer-analogous reaction.

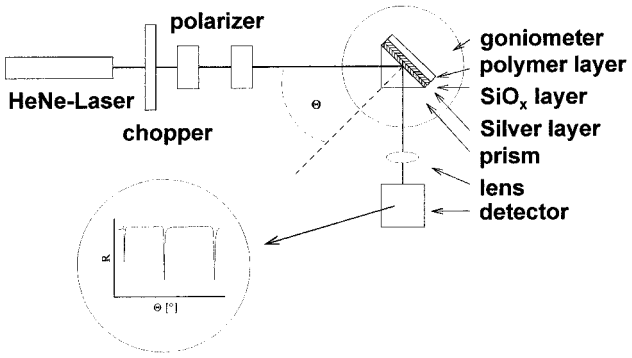

Figure 2. Setup for surface plasmon and waveguide spectroscopy measurements.

as a function of the angle of incidence (Θ). Each sample was measured in three to five locations before and after the surface modification. By comparison of a calculated reflection curve (Fresnel calculation, using a simple box model) and the experimental data, the thicknesses of the deposited polymer layer can be determined.[25] Waveguide spectroscopy experiments were carried out using both p- and s-polarized light. If at least two waveguided modes are observed, both thickness and refractive index n of the layer can be determined independently. Values of $n = 1.581 \pm 0.003$ were obtained for PVP and $n = 1.595 \pm 0.008$ for BuPVP.

X-ray reflectivity measurements were carried out using a 18 kW rotating anode instrument (Cu Kα, $\lambda = 0.154$ nm). For these measurements also silicon wafers were used as substrates. Details of the instrumentation and the model fit calculations have been described elsewhere.[26]

Results and Discussion

The polyelectrolyte monolayers were generated at the surface of the substrate as shown in Figure 3. In the first step an azo initiator with a dimethylchlorosilane headgroup was self-assembled on planar silicon oxide substrates. The use of a monofunctional silane compound prevents any cross-linking of the initiator molecules and the buildup of unspecific initiator multilayers. As only one group in the initiator molecule can react with the hydroxyl groups at the surface of the substrate, it allows for the formation of well-defined initiator monolayers. Initiator molecules, which are only physically attached to the substrate and which are not covalently linked to the surface, can be readily removed by solvent extraction. In the next step the PVP monolayer was generated by thermal activation of the attached initiator and radical chain polymerization directly at the surface in situ. The polymerizations were carried out in benzene and ethanol solution as described by Yocum and Nyquist[27] and by Boyes and Strauss[28] for the radical chain polymerzation of PVP in solution.

After preparation of the neutral PVP monolayers FTIR spectroscopy and XPS measurements were performed to prove the chemical identity of the attached molecules. The XP spectrum of an approximately 35 nm thick PVP layer on a silicon wafer is shown in Figure 4A. After deposition of a PVP layer on the wafer, the spectrum is dominated by the C(1s) signal at 285 eV and the N(1s) signal at 400 eV due to the presence of the polymer. No signals from the underlying substrate are visible, indicating that the surface is homogeneously covered. As we are able to prepare the PVP layer with high thicknesses, as will be shown further below, the polymer layers can be easily characterized by transmission FTIR spectroscopy. For this we prepared an approximately 2 × 35 nm thick PVP layer on both sides of a silicon wafer. The spectrum of this sample is shown

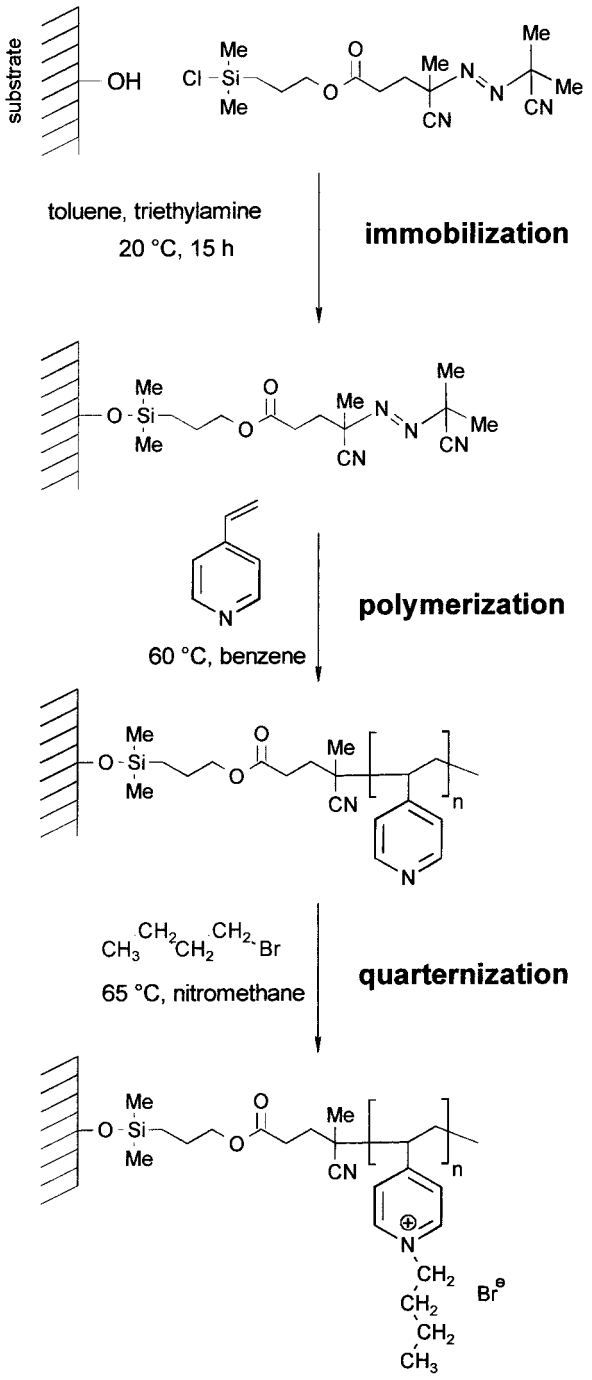

Figure 3. Synthesis of a cationic polyelectrolyte monolayer (poly[4-vinyl-*N*-*n*-butylpyridinium] bromide) covalently attached to a planar silicon oxide surface. First a neutral poly(vinylpyridine) monolayer is grown by using a self-assembled monolayer of an azo initiator. The layer is subsequently converted into the positively charged monolayer by a quarternization reaction.

in Figure 4B. The spectrum shows typical vibrational bands of the PVP such as the C−H stretching vibrations around 3000 cm^{-1} and the vibrational bands from the C=C double bonds of the pyridine ring at 1600 cm^{-1}. The area below 1500 cm^{-1} shows the typical absorption bands of the bulk spectrum of PVP.[29]

The thickness of the attached polymer monolayers is a function of the number of polymer chains attached per surface area (graft density) and the molecular weight of the attached polymer chains.[21] Both the graft density and the molecular weight of the attached chains and

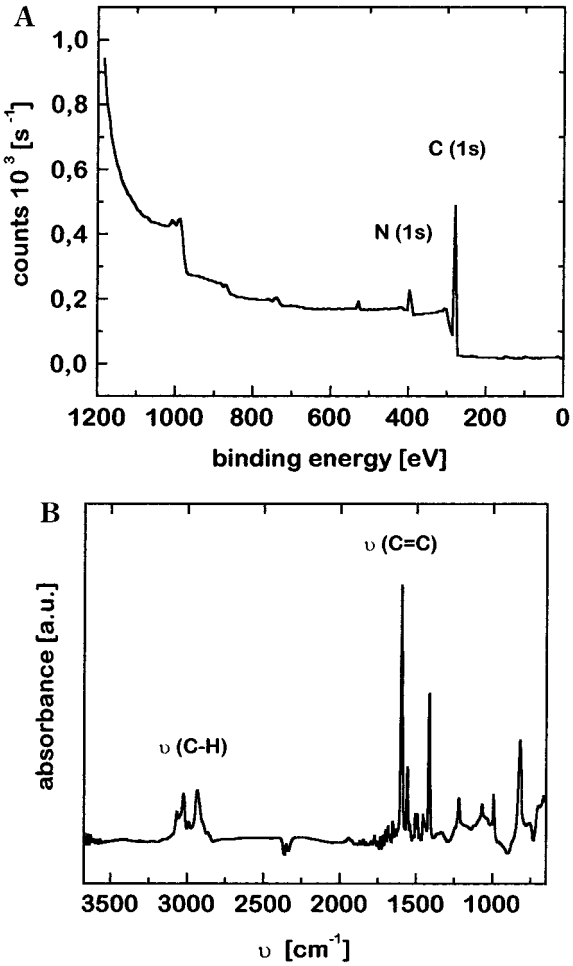

Figure 4. XP spectrum (A) and FTIR spectrum (B) of a 35 nm thick PVP monolayer attached to a silicon wafer. The monolayer was prepared on the wafer by radical chain polymerization of 4-vinylpyridine in ethanol for 6 h at 60 °C. After the polymerization the substrate was extracted with methanol for 15 h.

consequently the layer thickness can be controlled by adjusting the polymerization parameters. Examples are the polymerization time, which determines the number of activated initiator molecules and therefore the graft density of the attached chains, and the monomer concentration, which influences the molecular weight of the surface-bound polymer. When the concentration of the monomer and the reaction temperature are set to a constant value, the conversion of the initiator and therefore the polymerization time controls the graft density of the attached chains and as a result of that the thickness of the polymer layer. To determine the layer thicknesses, we have performed waveguide spectroscopy experiments on the prepared PVP monolayers. As an example three typical reflectivity curves of SiO_x substrates with attached monolayers are shown in Figure 5A. For the preparation of these samples 4-vinylpyridine (VP) was polymerized in a monomer concentration of 50% (v/v) in benzene for different periods of time. It can be clearly seen that with increasing polymerization time the resonance minimum of the first waveguide mode shifts to higher angles of incidence, and additional waveguide modes can be excited. The appearance of waveguide modes in the reflectivity curve can be taken as a first evidence that the coverage of the substrate by the polymer is complete. The positions of the waveguide modes allow to determine

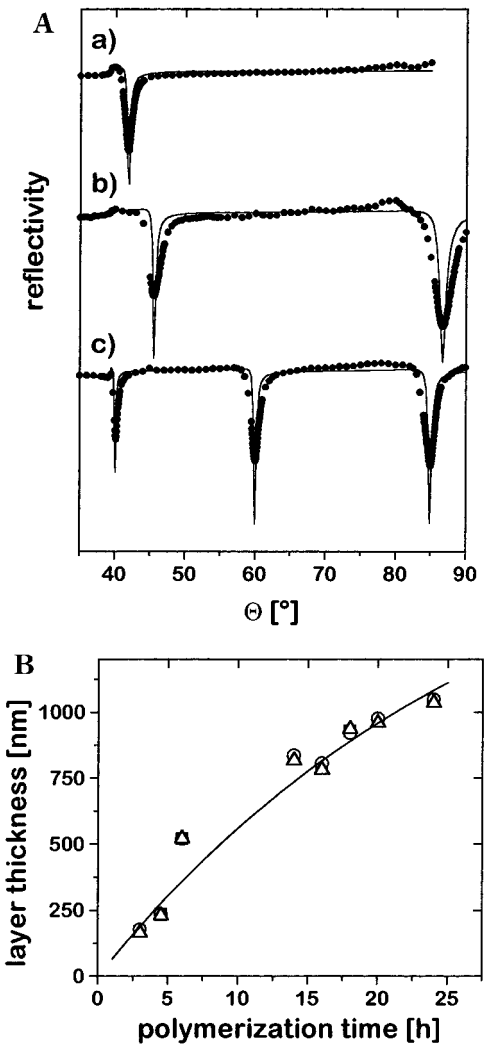

Figure 5. (A) Waveguide spectra (p-polarization) of (a) 230, (b) 520, and (c) 1030 nm thick PVP layers on glass/silver (50 nm)/SiO_x (30 nm) substrates. The layers were prepared on the substrates by radical polymerization of 4-vinylpyridine in benzene (50 mol %) at 60 °C for 4.5, 6, and 24 h. After polymerization the substrates were extracted for 15 h in methanol. The solid lines are the calculations according to the Fresnel equations. (B) Thicknesses of PVP monolayers as a function of polymerization time, measured by waveguide spectroscopy. The polymerization reactions were carried out at 60 °C in benzene using a monomer concentration of 50 mol %. After the polymerizations all substrates were extracted for 15 h with methanol. The solid line represents the graft density of the polymer molecules calculated from the decomposition kinetics and radical efficiency of the initiator.

the thickness and the refractive index of the polymer layer using Fresnel equations. The thicknesses of the obtained PVP layers as a function of the polymerization time are shown in Figure 5B. The different symbols represent the results of measurements on different spots of the same sample. The close agreement between the different data points show that the layer thickness is very similar in various areas of the substrate. The results of the waveguide spectroscopy experiments demonstrate that the thickness of the PVP layer can be easily controlled by adjusting the conversion of the initiator through choosing an appropriate polymerization time and that the film formation can be carried out in a well reproducible manner.

It should be specifically noted that the solid line shown in the graph is not a fit to the data points but represents the number of polymer chains calculated from the graft density of the azo initiator (1.8 μmol/m^2), the reaction time, the decomposition kinetics of the initiator ($k = 9.6 \times 10^{-6}$ s mol^{-1}), and a radical efficiency factor of 0.4.[21] All parameters have been measured previously[19,20] for the polymerization styrene with the same surface-attached initiator.

It should further be noted that all substrates were extracted for at least 15 h with a good solvent after the deposition of the PVP layers, to remove physisorbed polymer from the covalently attached polymer layer. Nonbonded material could originate from the second, free radical formed, from chain transfer, or from thermal polymerization in solution. It was recently shown that a simple rinsing procedure does not remove all polymer from the film; however, following such Soxhlet extraction procedure, it was shown that no physisorbed polymer remains in the film.[21] To demonstrate the difference between the stability of a layer of chemically attached PVP chains in comparison to one consisting of purely physisorbed PVP, both layers were deposited at the surface of a surface plasmon substrate and exposed to a good solvent for the polymer. To obtain a layer of physisorbed PVP, the polymer was spin-coated from methanol solution on the substrate. The thickness of the thus prepared layer was determined by waveguide spectroscopy and surface plasmon spectroscopy measurements before and after extraction with methanol in a continuous extraction procedure (Soxhlet extractor). The reflectivity curves obtained from these measurements are shown in Figure 6A. From the disappearance of the resonance signal of the waveguide mode, it can be concluded that after the extraction only a small amount of physisorbed PVP (film thickness <1 nm) remains on the substrate. The same experiment was carried out with a PVP layer prepared by polymerization of 4-vinylpyridine in benzene following the procedure described above. After polymerization, the substrate was extracted following the same procedure as for the spin-cast film. The reflectivity curves obtained from the waveguide spectroscopy measurements before and after deposition of the PVP on the substrate and after the extraction are shown in Figure 6B. As a result of the removal of a small amount of non-chemically attached PVP, the resonance angle of the waveguide modes shifts to slightly lower angles of incidence but remains constant after prolonged extraction, demonstrating the good solvent stability of the attached monolayers.

The subsequent quarternization of the PVP monolayer with *n*-butyl bromide in nitromethane similar to procedures described by Fuoss and Strauss[24] leads to monolayers of positively charged BuPVP molecules. The polymer-analogous transformation of the PVP monolayers into positively charged BuPVP layers was carried out under mild conditions using *n*-butyl bromide as the reagent and nitromethane as a solvent. At room temperature the reaction proceeds very slowly. A satisfactory reaction rate could be obtained using a temperature of 65 °C. Figure 7A shows FTIR spectra of an approximately 2 × 35 nm thick PVP layer measured during the quarternization after different reaction times as noted in the figure. When PVP is transformed into the cationic species, a second infrared adsorption band can be observed at 1640 cm^{-1} (for C═C double-bond stretching vibrations of the BuPVP) in addition to the band at 1600 cm^{-1} (C═C double-bond stretching vibrations of the PVP). At higher conversion the signals

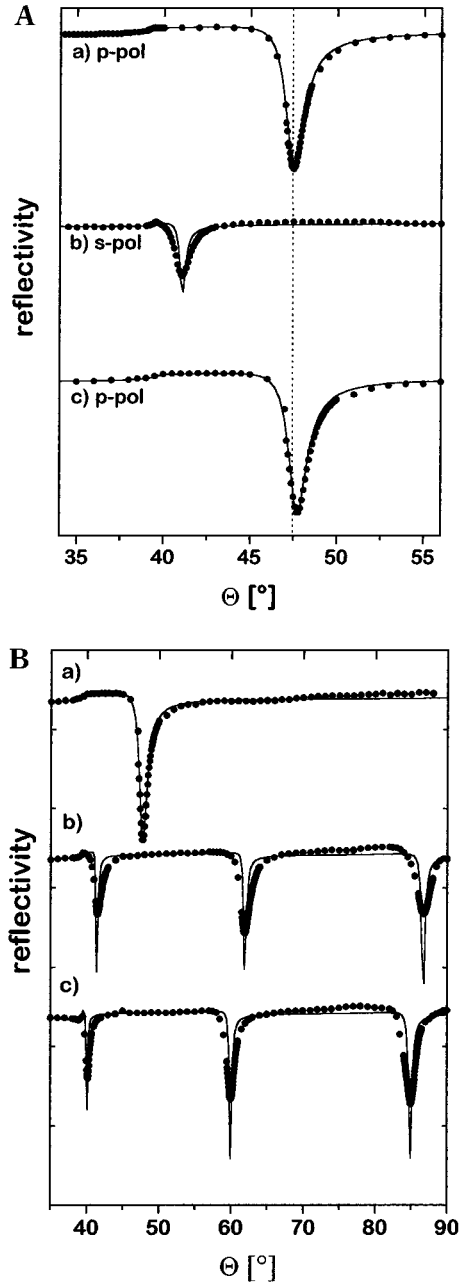

Figure 6. (A) Reflectivity curves obtained from surface plasmon (p-polarization) and waveguide (s-polarization) spectroscopy of a glass/Ag/SiO_x substrate (a) before and (b) after spin coating of a PVP layer from methanol solution and (c) after 15 h extraction with methanol. The film thickness after deposition was approximately 92 nm. After extraction 0.8 nm of the PVP film remains on the substrate. (B) Same experiments as in (A) before (a) and after deposition (b) of an covalently attached PVP monolayer and (c) after 15 h extraction with methanol. The PVP monolayer was generated by radical chain polymerization of 4-vinylpyridine in benzene 1:1 (mol %), at 60 °C for 24 h. The thickness of the PVP monolayer was 1045 nm before and 1030 nm after extraction.

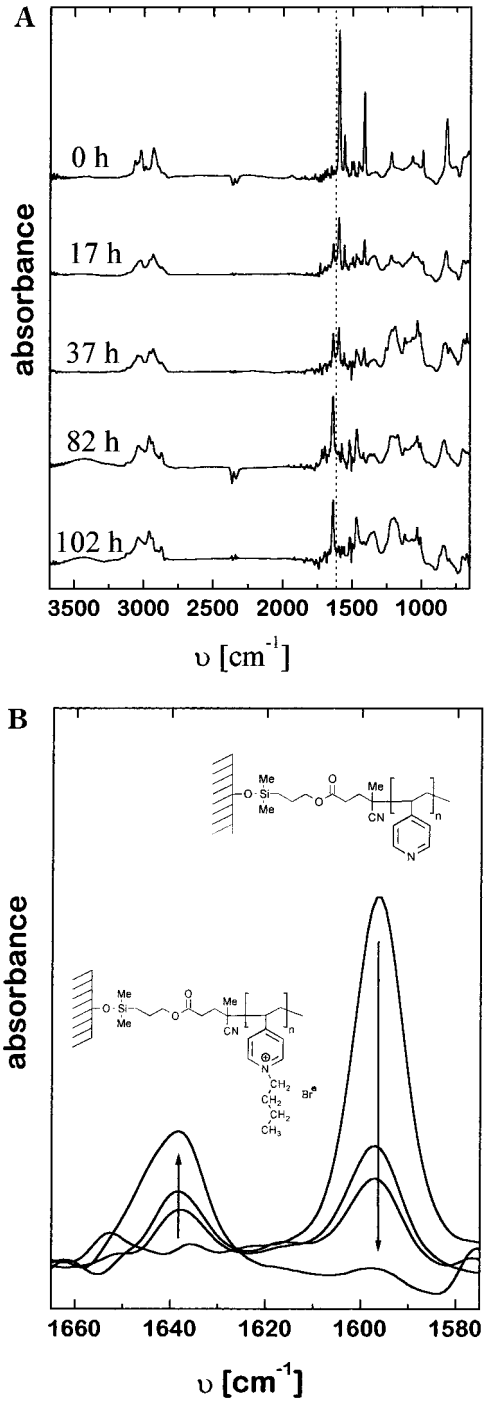

Figure 7. (a) FTIR spectra of a 2 × 35 nm thick PVP monolayer attached to both sides of a silicon wafer. The spectra were measured during the quarternization of a covalently attached PVP monolayer at given reaction times. The quarternization was carried out with 0.5 M *n*-butyl bromide in nitromethane at 65 °C. (b) Detailed FTIR spectra obtained from (a).

attributed to the unquarternized PVP cannot be detected any longer. To show the changes in the infrared spectra in more detail, the spectral region between 1665 and 1570 cm^{-1} of samples obtained after various reaction times are shown in Figure 7B. The conversion of the quarternization reaction can be calculated from the integrated intensities of the absorption maxima at 1640 and 1600 cm^{-1}. From the fact that no significant absorption at 1600 cm^{-1} can be detected after roughly 80 h of reaction time, it can be concluded that the reaction is almost quantitative. In Figure 8 the conversion of the quarternization reaction is shown as a function of the reaction time. The conversion has been calculated from the integration of the adsorption bands in the IR spectra. Additionally, the results of measurements from Fuoss and Strauss on the kinetics of the quarternization of PVP in solution are shown in Figure 8b.[24] The close agreement between the conversion in the surface-attached monolayers and the rate of quarternization in solution proves that the immobilization

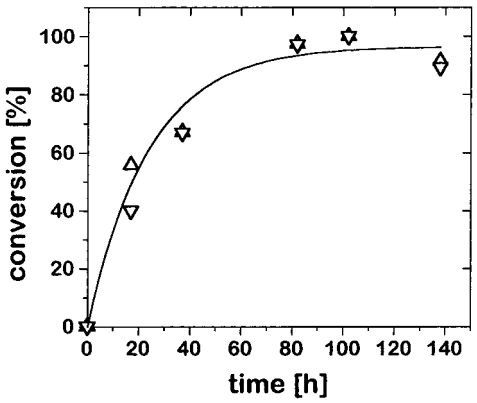

Figure 8. Conversion of the quarternization reaction as a function of the reaction time of a 2 × 35 nm thick PVP monolayer on a silicon wafer. The quarternization was carried out with 0.5 M *n*-butyl bromide in nitromethane at 65 °C. The conversions were calculated by measuring the integrated intensity of the maximum of absorbance from PVP at 1600 cm^{-1} (△) and from BuPVP at 1640 cm^{-1} (▽).

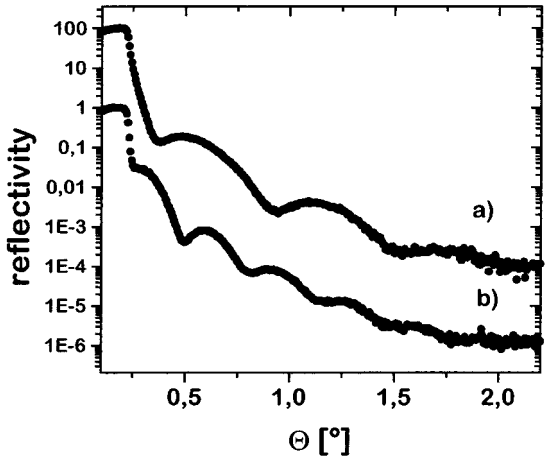

Figure 9. X-ray reflectometry curves of a 7.3 nm thick PVP brush on a silicon wafer (a) before and (b) after quarternization (thickness: 14.3 nm). The layer was prepared by polymerization in ethanol for 1.5 h at 60 °C and subsequent quarternization for 96 h at 65 °C in 0.5 M *n*-butyl bromide/nitromethane.

of the chains at the surface has no significant influence on the quarternization reaction. To receive additional quantitative information about the PVP and the BuPVP layer on the substrates, we have performed X-ray reflectometry experiments on a 7.3 nm thick PVP layer attached to a silicon wafer before and after quarternization (Figure 9). Such measurements give information about both the layer thickness and the roughness of the attached monolayers. From the X-ray reflectivity curves it can be seen that the roughnesses of the attached polymer layers are rather low. The rms (root-mean-square) roughness from the sample before and after quarternization was calculated to be approximately 1.1 nm, which is only slightly higher than that of the silicon wafer before the modification (0.5 nm).

Due to quarternization of the polymer (reaction time 80 h under the conditions described above), the thickness of the attached layer increases from 7.3 to 14.3 nm. This thickness increase is caused by the fact that the molecular weight of the repeat unit is increased from 106 g/mol (VP) to 245 g/mol (BuPVP) due to linkage of the *n*-butyl chains to the polymer and the incorporation of the bromine counterions into the layer. When this increase of the molecular weight of the polymer is used for calculation of the expected increase of the layer thickness, it has to be considered that during the quarternization of bulk (nonattached) PVP with butyl bromide the density of the polymer increases from 1.01 ± 0.02 to 1.20 ± 0.05 g/cm^3. Therefore, a thickness increase from 7.3 to 15.1 ± 0.6 nm would be expected if all repeat units of the polymer are converted. This result shows that during the quarternization reaction no polymer is lost and that no significant changes of the graft density (number of polymer molecules per surface area) occur.

The thickness increase of the polymer layer during the quarternization reaction can serve as an example that polymer layers prepared by the "grafting from" approach show a strong response toward low molecular weight compounds in their environment due to the large number of reactive sites present in the polymer layer. As the layers can be swollen in appropriate solvents and polymer-analogous reactions be carried out on the tethered molecules, it can be envisioned that the grafted monolayers can be used to quantify low molecular compounds present in a surrounding analyte. Whereas thickness changes due to chemical reactions in self-assembled low molecular weight monolayers are typically only on the order of a few angstroms, films as the ones described here can show a much stronger response to the presence of low molecular weight compounds. Thickness increases of dozens or even hundreds of nanometers caused by reaction with a low molecular present in the analyte can easily be achieved, making the measurement much more simple. This might render the "grafted from" polymer layers interesting components in sensor applications.

Conclusions

Polyelectrolyte monolayers that are covalently attached to a planar silicon oxide surface can be prepared using a self-assembled monolayer of an initiator and growth of the polymer at the surface of the substrate in situ. The self-assembly of an azo radical chain initiator containing a monochlorosilane anchor group onto a planar silicon oxide surface, polymerization of 4-vinylpyridine (VP) starting from the initiator monolayer, and subsequent quarternization allows the preparation of poly[*N*′-*n*-butyl-4-vinylpyridinium] bromide (BuPVP) monolayers with thicknesses greater than 1000 nm in the dry, solvent-free state. The graft density, the molecular weight, and the thicknesses of the prepared polyelectrolyte monolayers can be easily controlled by adjusting the polymerization conditions. The density of charges on the polyelectrolyte chains can be adjusted by choosing the appropriate reaction time during the quarternization reaction. If the proper reaction conditions are chosen, the uncharged polymers can be quantitatively transformed into the polyelectrolyte, and within the experimental error a degree of functionalization of $f = 1$ is obtained. The surface-attached polyelectrolyte monolayers obtained by this strategy can be used in further reaction steps for the incorporation of other counterions and for the buildup of more complex structures such as polyelectrolyte−tenside or polyelectrolyte−polyelectrolyte complexes in surface-attached monolayers as we will show in a separate communication.

The mass of the attached polymer monolayers is 2−3 orders of magnitude larger than that obtainable by established techniques of surface attachment such as

"grafting to" procedures or adsorption processes, where only mass coverage of 0.1−5 mg/m^2 can be obtained. In contrast to this the preparation of a polyelectrolyte monolayer by the described "grafting from" approach leads to amounts of the surface-attached polymer of up to 1000 mg/m^2.

Finally, it should be noted that not necessarily the polyelectrolyte monolayers have to be prepared in a two-step procedure (growth of an uncharged polymer and subsequent transformation into the polyelectrolyte in a polymer-analogous reaction), but also a direct polymerization of charged monomers can be performed as we will show in a following communication.

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