Synthesis of a Poly(*p*-styrenesulfonate) Brush via Surface-Initiated Polymerization

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Received February 25, 2002

ABSTRACT: The synthesis of molecularly thin poly(*p*-styrenesulfonate) monolayers as an example for a negatively charged polyelectrolyte brush covalently attached to a planar solid surface is described. The polymer monolayers are generated directly at the surface of the substrate by using self-assembled monolayers of an azo initiator and radical chain polymerization of *p*-styrenesulfonate ethyl ester (ESS) monomer in situ. This “grafting from” approach yields surface-bound poly(*p*-styrenesulfonate ethyl ester) (PESS) molecules with high molecular weights and with high graft densities of the attached chains. The PESS monolayers can be transformed into a charged poly(*p*-styrenesulfonate) (PSS) monolayer through a polymer-analogous saponification reaction under mild conditions, and the reaction can be carried out to quantitative conversion. The thickness of the polyelectrolyte brush can be controlled from 2 to more than 35 nm in the dry, collapsed state.

Introduction

Polyelectrolyte (PEL) brushes are monolayers where charged polymer chains are tethered with one anchor group (or a small number of such groups) to a surface while the grafting density of the chains is high enough to induce interchain correlations. As a result of the electrostatic interactions, the polymer chains are stretched away from the surface and assume a so-called “brush”-like conformation.[1,2] Many research groups have focused their work on a theoretical elucidation of a polyelectrolyte monolayer, in which the charged molecules are terminally attached to a planar solid surface.[3−10] In general, polyelectrolyte brushes show a very rich and interesting phase behavior. As the conformation of the surface-attached chains depends on both interchain correlations and electrostatic interactions, such a system is expected to show a very interesting dependence of the physical properties on the structure and conformation of the polymers. The conformation of the polymer molecules in the monolayer and therefore the properties of the surface-attached film depend on the graft density, the molecular weight, and the charge density of the attached chains as well as the ionic strength of the surrounding medium to name just a few of the important parameters. Polymer brushes are of potential technological importance for the improvement of lubrication, adhesion, and wetting properties as well as for the stabilization of colloids against flocculation. In PEL brushes the stabilization of the colloids would be achieved with a combination of electrostatic and steric interactions.[10]

Despite strong theoretical interest in such systems now for more than a decade, there are only a limited number of examples known that describe the experimental realization of such surface-attached charged monolayers. In one example, Mir et al.[11] linked polystyrene molecules that were end-functionalized with a monochlorosilane group to a high area silica gel. Subsequently, they converted the neutral polystyrene layer into a poly(styrenesulfonate) layer through a polymer-analogous sulfonation reaction using a mixture of sulfuric acid and SO_3. The degree of sulfonation was $f = 0.64$. As the highest swollen thickness in good solvent, 75 nm was measured.[11] Also, Tran et al.[12,13] have used this technique to link poly(styrenesulfonate) (PSS) onto planar SiO_2 surfaces. Other synthetic strategies include the formation surface-attached polymer brushes via surface-initiated ATRP polymerization[14−16] as well as surface-attached polyelectrolyte brushes through photoemulsion polymerization.[17] For a more detailed overview about the fascinating field of surface-attached polymeric brush systems, the reader is referred to recent review articles.[18]

Several conditions have to be fulfilled in order to synthetically realize a polyelectrolyte brush. First, the graft density of the attached polymer films has to be sufficiently high. Second, the polymer has to cover the substrate material in a homogeneous manner. A third prerequisite is that the solubility of all parts of the chain is similar. Serious problems could arise from the latter if, for example, the polyelectrolyte is obtained through a polymer-analogous reaction of a water-insoluble polymer and the conversion of the neutral into the charged species is not quantitative. In this case microphase separations can occur inside the film as some parts of the chain are readily water-soluble and other parts consist of neutral segments, which are not soluble. Consequently, the polyelectrolyte monolayer will be phase-separated on a microscopic level and will become structurally inhomogeneous. It is obvious that a complete characterization of such a layer remains extremely difficult and that such a system can hardly be used as a model system to study the phase behavior of a polyelectrolyte brush. Therefore, it is an important target for the realization of a PEL brush system to obtain monolayers, where the degree of functionalization is high and well-known.

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10.1021/ma020301o CCC: $25.00

In principle, the generation of a polyelectrolyte monolayer, covalently attached to a solid surface, can be established using two different approaches. One, the "grafting to" technique, as shown by Mir et al.[11] and by Tran et al.,[12,13] uses the chemisorption of polymer chains from solution. Typically, the polymer molecules are functionalized with an anchor group at one end of the molecule and are linked to appropriate sites at the surface of the substrate.[19] Because of the fact that in such systems the polymer molecules have to diffuse to the surface against the concentration gradient built up by already attached chains, further film growth is kinetically hindered once the surface becomes significantly covered. Therefore, only relatively small amounts of polymer (typically between 1 and 5 nm film thickness) can be attached to the surface.[19,20]

Another approach, the so-called "grafting from" technique, uses initiators that are self-assembled onto a solid substrate. The polymer layer is then grown in situ from the surface.[21,22] Using this "grafting from" technique, a wide range of different functional polymer brushes can be obtained at planar and spherical solid surfaces with high graft density ($>1.5\ \mu mol/m^2$) and high molecular mass ($M_n > 10^6$) of the surface-attached chains.[21-23] In addition, the synthesis of various positively charged quarternized poly(4-vinylpyridine) brushes on planar silicon oxide surfaces has been reported in several communications.[23]

In this paper we describe the "grafting from" synthesis of a poly(styrenesulfonate) brush on planar siliconoxide surfaces. The monomer *p*-styrenesulfonate ethyl ester was polymerized at the surface with the immobilized initiator. The neutral polymer brush is then transferred through a polymer-analogous saponification reaction into the polyelectrolyte brush. The rate and conversion of the neutral surface-attached polymer chains into the corresponding polyelectrolytes are studied. A comparison between the reaction of surface-attached and nonattached polymer chains is made.

Experimental Section

Materials. The azo initiator used for the preparation of the self-assembled initiator monolayer was prepared in a three-step synthesis as described by Prucker and Rühe.[21] Toluene (p.a. grade) was dried over sodium−potassium alloy, and benzophenone was used as an indicator. As substrates for the deposition of the monolayers, silicon wafers (Aurel; Germany) were used, which had an approximately 2.5 nm thick silicon oxide layer on the surface. The monomer, *p*-styrenesulfonate ethyl ester (ESS), was prepared in a two-step synthesis according to procedures described by Woeste.[24] Briefly, the sodium salt of styrenesulfonic acid, which had been recrystallized from 50% aqueous ethanol prior to use, was converted into the corresponding alkyl ester by forming in a first step the silver salt of the acid. The silver sulfonate was purified by extraction with acetonitrile (p.a. grade). In a second step the sulfonate ethyl ester was formed through reaction of the silver salt with ethyl bromide.[25,26] The final product, the ESS monomer, was carefully extracted with methylene chloride and purified over a silica column (1:50, eluent acetonitrile).

Preparation of the Polymer Monolayers. The immobilization of the azo initiator at the surface of the silicon substrate was carried out in dry toluene at room temperature under argon. The reaction time was 15 h, and the concentration of the initiator was approximately 0.5 mmol/L.[27] Triethylamine (dried over $LiAlH_4$ and distilled prior to use) was added as acid scavenger and catalyst for the condensation reaction. Nonattached initiator and other byproducts of the reaction were removed after completion of the reaction by careful extraction with toluene and methanol.

After the formation of the initiator monolayers the substrates were transferred into Schlenk tubes, which were then filled with monomer and solvent. After removal of all oxygen traces from the solution under vacuum during repeated freeze thaw cycles, the tubes were placed into a thermostat at 60.0 ± 0.1 °C. The polymerization of ESS with the surface-attached initiator was carried out in acetonitrile using a monomer concentration of 30 vol %. After desired polymerization times the substrates were removed from the polymerization solution, rinsed with a good solvent for the resulting polymer (acetonitrile), and extracted for about 15 h with the same solvent in a Soxhlet extractor to remove any physisorbed polymer from the deposited polymer layer.

The saponification of the PESS monolayers was carried out in 0.5 M aqueous ammonium carbonate solution at 50−70 °C following the procedure described for the saponification of low molecular sulfonate esters and of free PESS in solution.[24,28,29] Reaction times were chosen between 7 and 60 h, including a additional heating period of 1 h in pure aqueous solution to remove the ammonium ions through outgassing of NH_3; otherwise, the surface-attached polyanionic PSS molecules contain NH_4^+ as counterions. After completion of the reactions the samples were rinsed twice with water and acetonitrile to remove reaction byproducts, such as ethanol and ammonium carbonate, and dried in a vacuum and in a closed chamber containing solid potassium hydroxide. The latter procedure ensures that residual water molecules are removed from the dry film and that no ambient water vapor enters the film.

Monolayer Characterization. For a qualitative characterization of the generated monolayers, Fourier transform infrared (FTIR) transmission measurements were carried out using a Nicolet Omnic 850 spectrometer. 1 mm thick silicon wafers polished on both sides were used as substrates. Typically 750 scans were accumulated with a resolution of 4 cm^{-1}. As the final polyelectrolyte monolayers are strongly hygroscopic, nitrogen purging of the sample chamber had to be carried out especially careful to keep the intensity of water adsorption bands low. Additional qualitative information about the layer composition was obtained 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 angle was set to 90° relative to the substrate surface. For the determination of the thickness of the monolayer X-ray reflectometry measurements were performed. The measurements were carried out using an instrument with a 18 kW rotating anode (Cu Kα, $\lambda = 0.154$ nm). The reflected intensities were measured as a function of the incidence angle from 0.2° to 2.0° relative to the sample plane. Above the critical angle a decrease of the intensity proportional to q^{-4} can be observed, which is modulated by periodic oscillations, the so-called Kiessig fringes. They originate from the interference of beams reflected at the polymer−air and polymer−substrate interfaces. The thickness of the sample and the roughness (rms roughness) of the various interfaces can be obtained with the help of a matrix formalism for the analysis of the data. Details of the instrumental setup, about the instrument performance, and of the model fit calculations are described elsewhere.[30]

For the determination of the dry thickness of the PESS brushes before and after saponification null ellipsometry measurements were carried out using a commercial ELX-1 ellipsometer (Riss, Germany). The commercial software supplied with the instrument was used to model the derived ellipsometric parameters in order to calculate the dry layer thickness using Fresnel formalism.

Results and Discussion

Figure 1 schematically describes the synthesis of the charged surface-attached polymer brushes. An azo initiator with a monochlorosilane headgroup was immobilized on the surface of a silicon (oxide) substrate. After the generation of the self-assembled initiator monolayer, the neutral PESS monolayer was formed by

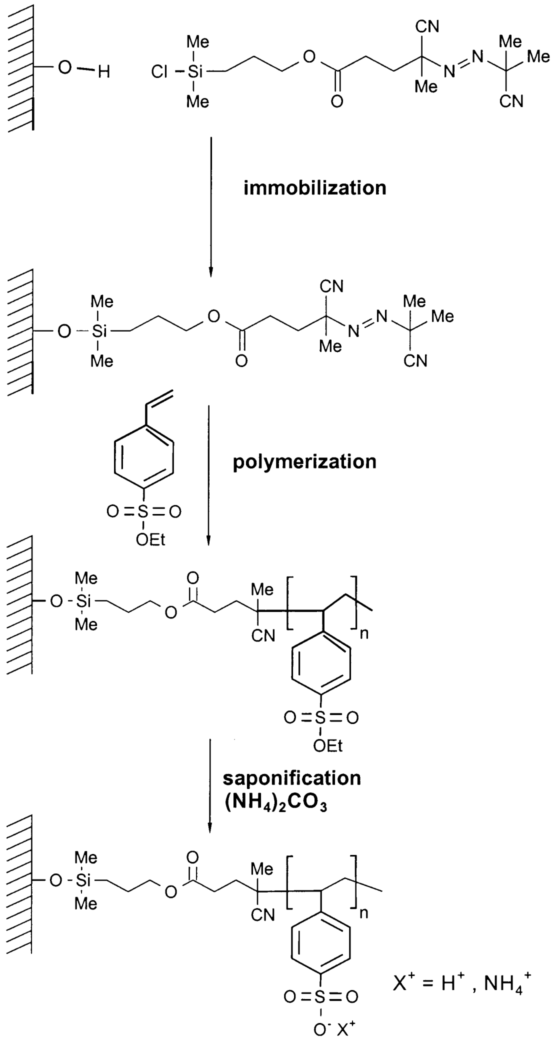

Figure 1. Synthesis strategy of negatively charged PSS monolayer covalently attached to planar silicon oxide surface by using a "grafting from" approach.

thermally induced radical chain polymerization of *p*-styrenesulfonate ethyl ester (ESS) monomer using the surface-attached initiator. The ester route was chosen as it has distinct advantages over the well-known direct sulfonation of polystyrene.[24] The sulfonation of polystyrene has to be carried out under rather drastic conditions (H_2SO_4/SO_3). Because of the harsh reaction conditions, a number of side reactions can take place. It is well-known that double (or even triple) substitution of the phenyl rings occurs even if conversion is well below 100%, and a large number of phenyl moieties remain still unchanged.[31-33] This makes the determination of the degree of functionalization and thereby the determination of the charge density on the polymer chain difficult. Further problems arise from the occurrence of degradation reactions such as breaking of polymer chains or partial cross-linking[31-33] and/or the cleaving off of polymer chains due to the strongly acidic medium. Both a decrease in molecular mass and the cleavage of chains from the surface would lead to a decrease of the resulting dry film thickness. The polymer-analogous cleavage of a sulfonate alkyl ester, on the other hand, which gives essentially the same final product, can be carried out under relatively mild conditions. No side reactions have been reported, and the saponification of such a polymer in solution can be carried out to almost quantitative conversion.[24]

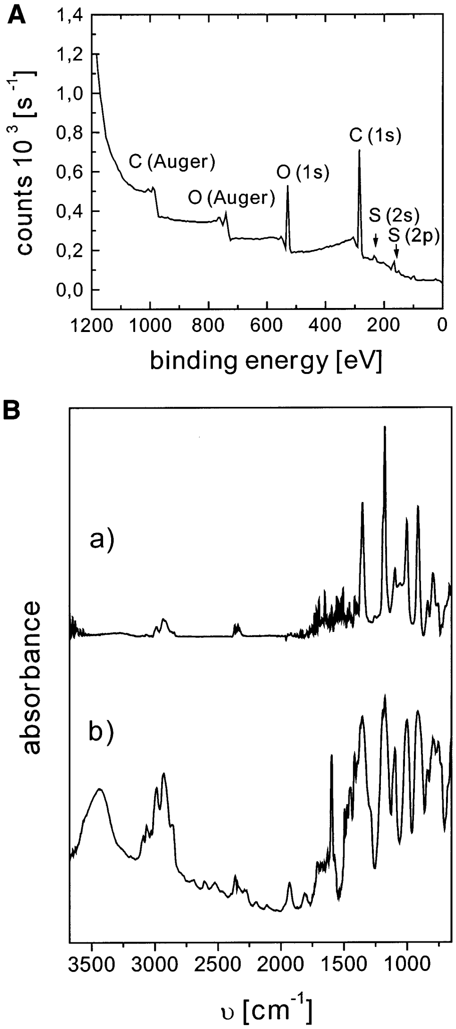

Figure 2. (A) XP spectrum of a 35 nm thick PESS monolayer on a silicon wafer. The monolayer was prepared on the wafer by radical chain polymerization of *p*-styrenesulfonate ethyl ester in acetonitrile solution, 1/2 (v/v) at $T = 60$ °C. After the polymerization the substrate was extracted with acetonitrile for 15 h. (B) Transmission FTIR spectra of (a) a PESS monolayer on silicon wafer, prepared under the same conditions as in (A). The films are deposited on both sides of a silicon wafer (polished on both sides). (b) The PESS bulk material in a KBr pellet.

The chemical identity of the surface-attached PESS monolayers was proven by FTIR and XPS measurements. The XP spectrum of an 35 nm thick (dry thickness) PESS layer on a silicon wafer is shown in Figure 2A. After the deposition of a PESS layer on the silicon substrate, the spectrum is dominated by the O(1s) signal at 520 eV, the C(1s) signal at 285 eV, and the S(2s/2p) signals around 200 eV due to the presence of the polymer. No signals from the underlying substrate are visible, indicating that the surface is homogeneously covered with the neutral polymer monolayer. Figure 2B shows the FTIR spectrum of a 35 nm thick PESS brush and the spectrum of bulk PESS (in KBr pellet). The transmission spectrum of the sample shows typical vibrational bands of the PESS that arise from the C−H stretching (around $\nu = 3000$ cm^{-1}). Also, the vibrational bands arising from the symmetric and asymmetric sulfonate ester vibrations at $\nu = 1355$ cm^{-1} and at $\nu = 1180$ cm^{-1} are detected. All other observed absorption bands are in good agreement with the bulk spectrum.

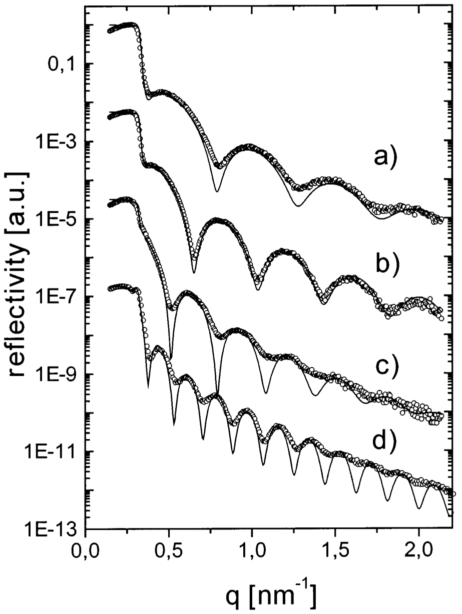

Figure 3. X-ray reflectometry spectra of (a) 12, (b) 15, (c) 20, and (d) 37 nm thick PESS monolayers on silicon wafers. The monolayers were prepared on the substrates by radical polymerization of *p*-styrenesulfonate ethyl ester in acetonitrile, 1:2 (v/v) at $T = 60$ °C for $t = 3$, 6, 9, and 15 h. After polymerization the substrates were extracted for 15 h in acetonitrile.

The thickness of the surface-attached polymer monolayer is a function of the number of polymer chains per surface area (graft density) and the molecular weight of the polymer chains.[21,34] As a consequence, the layer thickness can be controlled by adjusting polymerization parameters such as the polymerization time, the concentration of the monomer, and the grafting density of the initiator. When the concentration of the monomer and the reaction temperature are set to a fixed 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.

The neutral monomer ESS was polymerized with the surface-immobilized initiator using acetonitrile as solvent for different periods of time. The thickness of the prepared monolayers was measured by means of X-ray reflectometry experiments on the prepared samples. Examples of such X-ray-reflectivity curves are shown in Figure 3. All samples have been prepared individually under identical conditions; only the polymerization time was varied. Clearly, it can be seen that with increasing polymerization time the frequency of the Kiessig fringes increases, indicating an increase in the dry thickness of the surface-attached layers. Calculated reflectivity curves obtained from Fresnel modeling were compared to the experimental data. The model-fit calculations are superimposed to the data in Figure 3 as solid lines.

The outcome of the measurements and model calculations are summarized in Figure 4. The experimental error of the measurement technique is within the size of the symbols. Note that all substrates were extracted for at least 15 h after the deposition of the PESS layers with a good solvent for the free polymer (acetonitrile). The extraction is carried out to remove physisorbed polymer (originating from the second, free radical formed during decomposition of the azo compound or from chain transfer of surface-attached radicals to monomer or solvent and from thermal polymerization in solution). Control samples consisting of spin-cast films of the free polymer showed that during such an extraction procedure almost all polymer could be removed from the surface, and only films of a few nanometers thickness remained.[23] Besides dry thickness also the model calculations of the reflectivity measurements yield an average roughness of the interfaces studied. In this case here the root-mean-square roughness of the PESS monolayers was about 1 nm, which is only slightly higher than the roughness of the bare substrate.

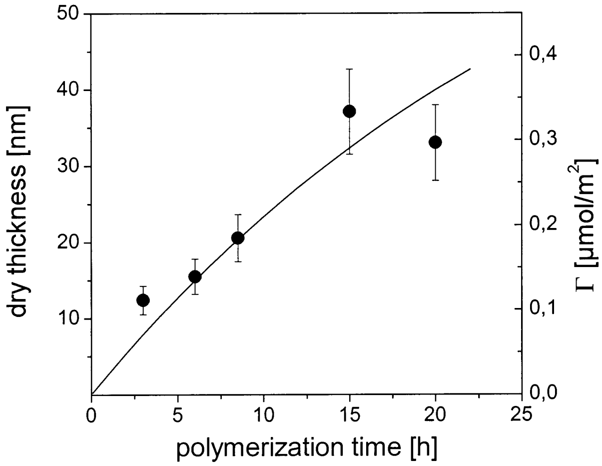

Figure 4. Thickness of PESS monolayer as a function of polymerization time, measured by X-ray reflectometry. The polymerization was carried out in acetonitrile solution, in a monomer concentration of *p*-styrenesulfonate ethyl ester of 1/2 (v/v) at $T = 60$ °C. After polymerization all substrates were extracted for 15 h with acetonitrile. The solid line represents the graft density Γ of the polymer molecules calculated from the decomposition kinetics and radical efficiency of the initiator.

The number of chains per surface area (graft density Γ) is expressed in mol/m^2. The film growth kinetics is well described by the relation $\Gamma(t) = f\Gamma_0(1 - \exp(-k_z t))$, where t is the polymerization time, Γ_0 is the graft density of the initiator, f is the radical efficiency factor, and k_d is the velocity constant of the initiator decomposition. The parameters entering the equation have been measured for the system styrene/toluene with the same surface-attached initiator as $\Gamma_0 = 1.8$ µmol/m^2, $f = 0.4$, and $k_z = 9.6 \times 10^{-6}$ s^{-1}.[21,22] Using these parameters, we have calculated the graft density (solid line in Figure 4) of the surface-attached PESS brush. The good agreement between the measured dry thickness and the calculated graft density shows that the latter can be reliably and reproducibly adjusted by the polymerization time. Note that the absolute values for Γ as well as a calculated dry thickness can only be given with the exact knowledge of the molecular mass of the surface-attached chains. A more quantitative description of detailed studies on the molecular mass of the surface-attached polymer molecules is in progress and will be reported separately.

After characterization of the polysulfonate ester monolayers the negative charges were introduced into the layer by cleavage of the sulfonate alkyl ester groups. The saponification reactions were carried out under mild conditions (aqueous solution of ammonium carbonate, 0.5 M; pH = 9.5; 70 °C), to prevent degrafting of the polymer chains from the silicon oxide surface. If the reactions were carried out using more strongly basic

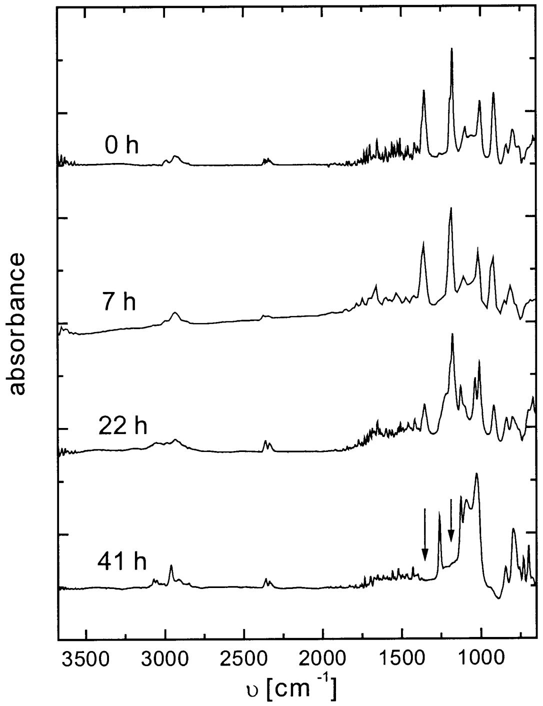

Figure 5. FTIR spectra of a 2 × 35 nm thick PESS monolayer attached to both sides of a silicon wafer. The spectra were measured during the saponification of the surface-attached PESS monolayer at a given reaction time (denoted in the figure). The reaction was carried out with 0.5 M $(NH_4)_2CO_3$ at $T = 70$ °C.

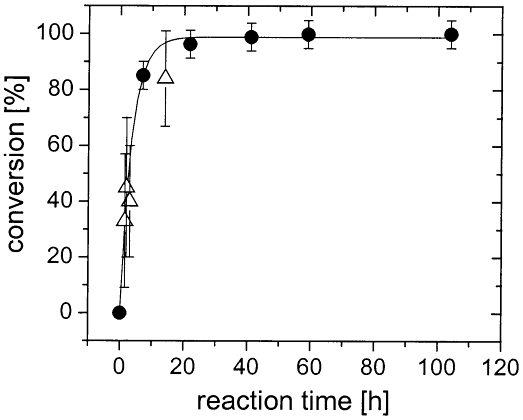

Figure 6. Conversion of the saponification reaction as a function of the reaction time of a 35 nm thick PESS monolayer on the surface of a silicon wafer (●). The reaction was carried out with 0.5 M $(NH_4)_2CO_3$ at $T = 70$ °C. The conversion was calculated by the integral intensity of the absorbance maximum at $\nu = 1355$ cm^{-1} (asymmetrical vibrational band of the PESS sulfonate ester). In addition, the conversion (Δ) calculated from the loss of mass during the saponification reaction of different PESS brushes is shown (see also Table 1).

Table 1. Conversion of the Saponification Reaction[a] Calculated from the Loss of Mass of the Monolayer

t_p [h]/t_s [h][b]	thickness PESS[c] [nm]	thickness PSS[c] [nm]	Δd [nm]	conv [%]
6/1.5	15.7	15.0	0.7 ± 0.5	33 ± 24
6/2	15.5	14.6	0.9 ± 0.5	45 ± 25
9/3	18.3	17.3	1.0 ± 0.5	40 ± 20
20/14	21.5	19.0	2.5 ± 0.5	84 ± 17

[a] The conversion is calculated from the thickness of the PESS layer and the mass ratio of the PESS/PSS repeat units. [b] t_p = polymerization time; t_s = saponification time. [c] The thicknesses of the monolayers were measured with ellipsometry.

conditions (pH > 11), high temperatures ($T > 80$ °C), and longer reaction times ($t > 40$ h), the substrates were not sufficiently stable, and a significant amount of the polymer chains was cleaved from the surface.

In Figure 5 transmission FTIR spectra of a PESS monolayer attached to both sides of a silicon substrate (film thickness 35 nm on both sides) are shown. The spectra were measured during the saponification after different periods of time as noted in the figure. The decrease of the ester vibrational bands of the PESS monolayer at $\nu = 1355$ cm^{-1} and $\nu = 1180$ cm^{-1} and the appearance of new adsorption bands at $\nu = 1025$ cm^{-1} and $\nu = 1130$ cm^{-1} indicate the cleavage of the ester bonds and the formation of the polymeric sulfonic acid. The spectrum of the resulting surface-attached free acid is in good agreement with the bulk spectrum.[35] The conversion of the reaction at different reaction times is shown in Figure 6. This conversion was calculated by two different methods. The first was FTIR spectroscopy. IR spectra were normalized to the CH vibrational bands above $\nu = 3000$ cm^{-1}. The conversion was then calculated from the sulfonate ester adsorption band at $\nu = 1355$ cm^{-1}, as this is the only characteristic adsorption band that has no significant overlap with other bands. From the complete disappearance of the band it can be concluded that after approximately 25 h the polymer-analogous saponification is quantitative.

In addition, the conversion of the saponification reaction can be calculated from the measurement of the loss of mass. As the mass per monomer unit is decreased during saponification from 212 g/mol for the sulfonate ester to 183 g/mol for the free acid, the PESS layer should show a significant decrease in the dry (solvent free) thickness. Therefore, sulfonate ester monolayers with different thicknesses were prepared. From the measurement of the dry thickness before and after transfer of the surface-attached PESS layer to the corresponding polyelectrolyte monolayer, the loss of adsorbed mass and, consequently, the conversion of the saponification reaction can be calculated (Table 1). The results of these calculations are also depicted in Figure 6.

Note that no significant decrease of the integral intensities of the C−H vibrational bands above $\nu = 3000$ cm^{-1} can be observed if the spectra are normalized to the sulfonate acid vibrational band at $\nu = 1025$ cm^{-1}. This suggests that no polymer molecules are cleaved off from the surface under the chosen reaction conditions.

Conclusions

Poly(*p*-styrenesulfonate) monolayers as examples for a negatively charged polyelectrolyte brush were prepared using a “grafting from” approach. Self-assembly of a radical chain initiator at the surface of the substrate and radical polymerization initiated from the surface-attached initiator allows the buildup of monolayers with high graft densities of the attached chains. By adjusting the polymerization time during formation of the neutral precursor brush, we are able to control the graft density of the surface-attached polyelectrolyte chains.

The transformation of the sulfonate ester groups under mild conditions leads to a surface-attached monolayer consisting of negatively charged poly(*p*-styrenesulfonate) (PSS) molecules. The reaction is quantitative, and no side reactions such as the loss of polymer molecules originating from an attack to the anchor groups or the sission of polymer chains can be observed.

The latter two show the excellent stability of the layer even under good solvent conditions. Moreover, the covalent attachment of the chains allows for the attachment of polyelectrolyte molecules independent of the surface charge of the substrate.

In conclusion, the generation of densely grafted PSS molecules through a polymer-analogous saponification of a sulfonate ester precursor system represents a further example for the synthetic establishment of charged polymeric monolayers covalently attached to planar solid surfaces. As already performed with positively charged polyelectrolyte brushes[36] as well as with surface-attached weak polyacid brushes,[37] interesting further studies will include the determination of the swelling behavior of such negatively charged brushes in various environments.

Acknowledgment. Dr. F. Kempkes and Dr. J. Habicht are thanked for X-ray reflectometry measurements and model-fit calculations. The German National Science Foundation (Deutsche Forschungsgemeinschaft, DFG; Schwerpunkt: "Polyelektrolyte mit definierter Molekülarchitektur") is thanked for financial support.

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MA020301O