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Tailoring the Charge Density of Surface-Attached Polyelectrolyte Brushes

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ABSTRACT: The preparation and swelling behavior of surface-attached charged statistical copolymer brushes are described. The brushes are prepared by free radical chain polymerization of monomer mixtures of 4-vinylpyridine (VP) and dimethylacrylamide (DMAA) using a surface bound azo-initiator (surface-initiated polymerization). So-prepared neutral PVP-*stat*-PDMAA copolymer brushes are then transferred into polyelectrolyte brushes through a polymer-analogous quaternization reaction of the respective PVP segments. By adjusting the ratio of the monomers added to the polymerization feed, the concentration of the corresponding polymer segments generated in the final surface-attached layer can be controlled, and thus, the charge density of the resulting polyelectrolyte copolymer brush can be determined. Finally, the swelling behavior of such polyelectrolyte brushes in aqueous solutions containing low molecular weight salts is investigated by using multiple-angle null ellipsometry. Depending on the charge density of the copolymers, the brushes exhibit a swelling behavior between that of a polyelectrolyte and a neutral polymer brush. Thus, the sensitivity of the layers against salt present in the surrounding medium can be precisely controlled.

Introduction

The manipulation of the physical and chemical interactions between a surface covered with macromolecules and its environment is perhaps the key factor in advancing the engineering of surfaces. To this respect, polymer brushes, i.e., macromolecules tethered with one end to a solid surface, have attracted considerable interest both in academia and in industry.[1−3] Moreover, if charged polymer molecules are considered, the resulting surface-attached polyelectrolyte brushes are expected to offer a powerful means by which to control a number of important interfacial properties, such as friction, interfacial tension, lubrication, adhesion, and wetting behavior.[4] The underlaying parameter that determines the interaction of such polyelectrolyte brushes with their surrounding is their ability to swell in appropriate solvents. In particular, systems where the swelling of the surface-attached layers can be triggered by external parameters such as the pH, the temperature, or the ionic strength of the medium are of utmost interest.[5]

With neutral polymer brushes at wet interfaces, the swelling of the surface-attched chains is determined by the balance of the osmotic pressure of the chain segments and the chain elasticity.[5] In contrast to this, the force that leads to chain stretching with polyelectrolyte brush systems is governed by the osmotic pressure entropy of the free mobile counterions inside the brush; hence, the swelling behavior of charged brushes is dominated by electrostatic contributions.[6,7] Besides parameters such as the grafting density and the molecular mass of the surface attached polymer chains, the amount of charges along the chains is the most important parameter that determines the swelling behavior of polyelectrolyte brushes.

Especially for biorelated studies and applications, such surface-attached charged brushes are of great interest due to their capability of swelling in an aqueous environment, which is the major requirement for any biological system.

Different pathways exist to adjust the charge density of a polyelectrolyte brush. For example, the charge density of surface-attached of “weak” polyacids or polybases can be adjusted by controlling parameters such as the graft density of the chains or by changing the external pH or the ionic strength of the solution. Both theoretical[8,9] and experimental investigations[10] describe the swelling behavior of weak polyacid brushes at planar surfaces as a function of the external pH.

However, if the brush consists of “strong” polyelectrolyte molecules, where the charge density on the chains does not depend on the external pH of the solution and also is independent of the graft density within the experimentally available range of graft densities, there are only few ways of how to control the amount of charged sites inside the brush.

For such systems, one can lower the amount of free charges inside the brush by screening the charges upon addition of low molecular weight electrolytes. Again, this has been shown both in theory[7,8] and in experiments.[11] Note, because many polyelectrolytes consist of a vinyl backbone with the charges being located in the side chain, the insolubility of the hydrophobic backbone in an aqueous environment poses a problem when the charges are being screened.[8] As a result, the brush shrinks very strongly, sometimes even close to the dry thickness as is shown in a parallel communication.[12] For many applications, however, it is crucial that even in the high screening limit, i.e., in the presence of significant amounts of salt in the surrounding medium, the brush remains in a sufficiently swollen state to allow

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further molecules, i.e., analytes, to enter the brush. Therefore, a strategy needs to be developed that allows to control the charge density of the brush independent of conditions of the surrounding medium.

In one approach, the charges could be introduced by a polymer-analogous reaction on a neutral polymer brush. The amount of ionic groups on the polymer chains can then be adjusted by controlling the conversion of the reaction. However, most neutral polymers, which can be transformed in such a way, are hydrophobic in nature. The sulfonation of polystyrene[13,14] or the quaternization of poly(vinylpyridines)[15,16] are typical examples. If these reactions are carried out to nonquantitative conversions, the polymer brushes will consist of hydrophobic as well as of hydrophilic segments. As a result, microphase separation can occur inside the layer, and the polyelectrolyte brush will have a complex internal structure and complicated swelling behavior.

Such difficulties, due to phase separation, could be avoided if, in another approach, polymer chains would be designed that consist of copolymer segments, where one carries a charged moiety and the other is neutral, but hydrophilic. Thus, the copolymer chains should be water swellable regardless of the composition. By controlling the distribution of the amount of neutral and charged polymer segments in the copolymer, the charge density on the surface-attached chains could be adjusted.

In this paper we follow the latter strategy and report on the synthesis and the characterization of surface-attached charged poly([*N*-methyl-4 vinylpyridine iodide]-*stat*-[dimethylacrylamide]) (MePVP-*stat*-PDMAA) copolymer brushes. The copolymer brushes were prepared using a surface-initiated polymerization, where monolayers of statistical neutral copolymers of 4-vinylpyridine (VP) and dimethylacrylamide (DMAA) were grown at planar solid substrates by radical chain polymerization using an surface-immobilized initiator.[17-19] The charged MePVP-*stat*-PDMAA copolymer brush was then obtained by a polymer-analogous quarternization of the VP segments in the layer (Figure 1). In a previous publication, we have shown that this reaction can be carried out under mild conditions and to quantitative conversion.[16] Finally, by using multiple-angle null ellipsometry, we studied the swelling behavior of the prepared copolymer brushes as a function of the amount of ionic segments incorporated into the brush structure and as a function of the external salt concentration.

Experimental Section

Preparation of the Copolymer Brushes. The synthesis and the immobilization of the initiator onto the solid substrates have been described in detail elsewhere.[17] As substrates for the attachment of the polyelectrolyte monolayers, LaSFN9 prisms (n = 1.844; Helma, Germany) and silicon wafers (Crystec, Germany; Aurel, Germany) having a 2.5 nm thick silicon oxide layer on the surface were used. The LaSFN9 prisms were activated prior to the modification by repeated dipping in 2 N sulfuric acid, rinsing with water (Milli-Q quality) and ethanol (p.a. grade, Sigma-Aldrich, Germany), and drying in a vacuum. The silicon wafers were used as obtained.

After the immobilization of the initiator, the substrates were transferred into Schlenk tubes and the chosen monomer mixture was added. From both monomers, 4-vinylpyridine (Fluka, Germany) and dimethylacrylamide (Sigma-Aldrich, Germany), the stabilizer was removed prior to use by distillation from copper(I) chloride in a vacuum. Through repeated freeze−thaw cycles all oxygen traces were removed from the solutions, and the Schlenk tubes were placed into a thermostat at $T = 60$ °C. After desired reaction times the substrates were taken out of the tubes and carefully rinsed with methanol, which is a good solvent for both polymers and subsequently extracted for at least 15 h with the same solvent in a Soxhlet extractor to remove all physisorbed polymer from the monolayers. The quaternization of the poly(vinylpyridine) (PVP) segments was carried out using methyl iodide as the quaternization agent. Under conditions chosen here ($t = 6$ h; $T = 45$ °C; 1.0 M methyl iodide/nitromethane) the reaction can be carried out to almost quantitative conversion (degree of quaternization: $f > 0.9$).[16] After the quaternization, the samples were rinsed extensively with nitromethane to remove all nonreacted quaternization agents and then dried in a vacuum.

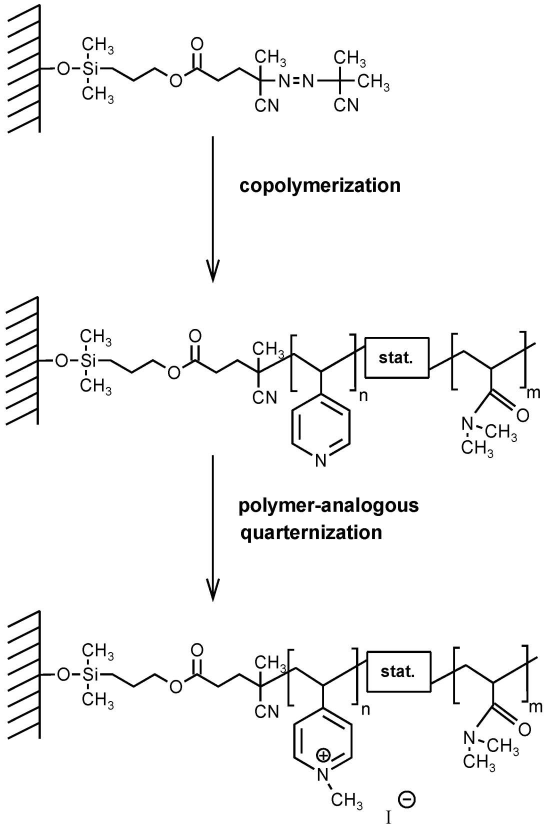

Figure 1. Synthesis of a positively charged poly([*N*-methyl-4-vinylpyridine-iodide]-*stat*-[dimethylacrylamide]) (MePVP-*stat*-PDMAA) copolymer brushes attached to a solid surface. In a first step a neutral copolymer brush (PVP-*stat*-PDMAA) is grown by using a self-assembled monolayer of an azo-initiator. Subsequently, the neutral brush is converted into a polyelectrolyte brush by a polymer analogous quaternization reaction on the PVP segments incorporated in the layer.

The number-average molecular weight of the copolymers cannot be obtained directly with sufficient accuracy without performing degrafting experiments on large surface area subtracts (>1 m^2). However, these values can be estimated by the knowledge of the dry layer thickness and the known decomposition kinetics of the initiator.[17]

$$M_{\mathrm{n}} = \frac{L_{\mathrm{dry}}\rho}{\sigma_{\mathrm{chains}}} = \frac{L_{\mathrm{dry}}\rho}{\Gamma_0 f(1-\exp\{-kt\})} \qquad (1)$$

Here M_{n} is the number-average molecular weight, L_{dry} is the measured dry thickness, $\Gamma_0 \approx 1.8$ μmol/m^2 is the surface concentration of the immobilized initiator, $f \approx 0.4$ is the radical efficiency, and $k = 9.6 \times 10^{-6}$ s^{-1} is the time constant for the decomposition of the initiator at a given temperature of $T =$ 60 °C. The latter parameters have been obtained from extensive studies and have been reported separately.[17]

For the samples shown below, the number-average molecular weight calculated from eq 1 is $5 \times 10^5 < M_n < 2 \times 10^6$. For example, the number-average molecular mass of a copolymer brush that is prepared with the surface-attached initiator and free radical polymerization for 3 h at 60 °C and having a measured dry thickness of 40 nm is calculated to $M_n \approx 6 \times 10^5$. Note, although this procedure only yields an estimate for the molecular mass of the surface-attached chains, any uncertainty in the molecular mass will not affect the outcome of the study shown below.

Characterization of the Copolymer Composition. To investigate the composition of the statistical copolymer, transmission FTIR spectra were taken on a Nicolet Magna 850 spectrometer from brushes having different ratios of the respective monomers in the feed. 1 mm thick silicon wafers (polished on both sides) were immobilized with the copolymer layers as described above. The surface-attached layers were extensively purged with nitrogen in the sample chamber to avoid any uptake of water during measurements. Typically, 750 scans were accumulated with a resolution of 4 cm^{-1}.

Characterization of the Swelling Behavior of the Copolymer Brushes. For the investigation of the swelling behavior of the copolymer brushes, multiple-angle null ellipsometry measurements were performed. The brushes were attached directly on the base of a high-refractive index prism (LaSFN9, $n = 1.844$), and ellipsometric spectra were measured as a function of the angle of incidence. The laser light is reflected from the backside of the brush, and the ellipsometric parameters Ψ and Δ that correspond to the change in amplitude and phase of the light upon reflection are measured as a function of the incidence angle. The obtained ellipsometric spectra can be analyzed either by Fresnel modeling[20] or by an inverse Fourier transformation of the data.[21] Note, in this paper we use the Fresnel modeling procedure only. The brush heights, given in the text, refer always to twice the first moment of the segment density profile.

Results and Discussion

Copolymer Composition. The chemical composition of the P(VP-*stat*-DMAA) copolymer brushes at the surface of silicon wafers was determined using FTIR spectroscopy. To this, a series of copolymer brushes were prepared under identical polymerization conditions (polymerization time and temperature) but with varying comonomer concentrations in the feed. For an evaluation of the copolymer composition, the integrals of the characteristic absorption bands for PVP at 1597 cm^{-1}, which corresponds to the pyridine ring vibrations ν(C=C), and for PDMAA at 1640 cm^{-1}, corresponding to the amide carbonyl vibrations ν(C=O), were determined. To determine the composition of the copolymers, the extinction coefficients or, more simply, the ratio of the two extinction coefficients is required according to the well-known Lambert–Beer law:

$$\frac{E_{\mathrm{PVP}}}{E_{\mathrm{PDMAA}}} = \frac{c_{\mathrm{PVP}}}{c_{\mathrm{PDMAA}}} \frac{\epsilon_{\nu(\mathrm{C=C})}}{\epsilon_{\nu(\mathrm{C=O})}} \frac{d}{d} = \left(\frac{n_{\mathrm{PVP}}}{n_{\mathrm{PDMAA}}}\right)\epsilon \qquad (2)$$

Here, E is the integral absorbance of the corresponding vibrations, ϵ are the molar extinction coefficients, c are the molar concentrations of the functional groups, d is the length of the pathway of the light through the layer (i.e., the dry thickness of the brush), and $n = c/V$ is the molar amount of the corresponding functional group. The ratio of the extinction coefficients ($\epsilon_{\nu(\mathrm{C=C})}/\epsilon_{\nu(\mathrm{C=O})} = \epsilon$) $\epsilon = 0.22 \pm 0.03$ of these bands was determined by measuring IR spectra from two samples of unattached copolymer of known composition. The composition of these samples had been determined separately by NMR spectroscopy.

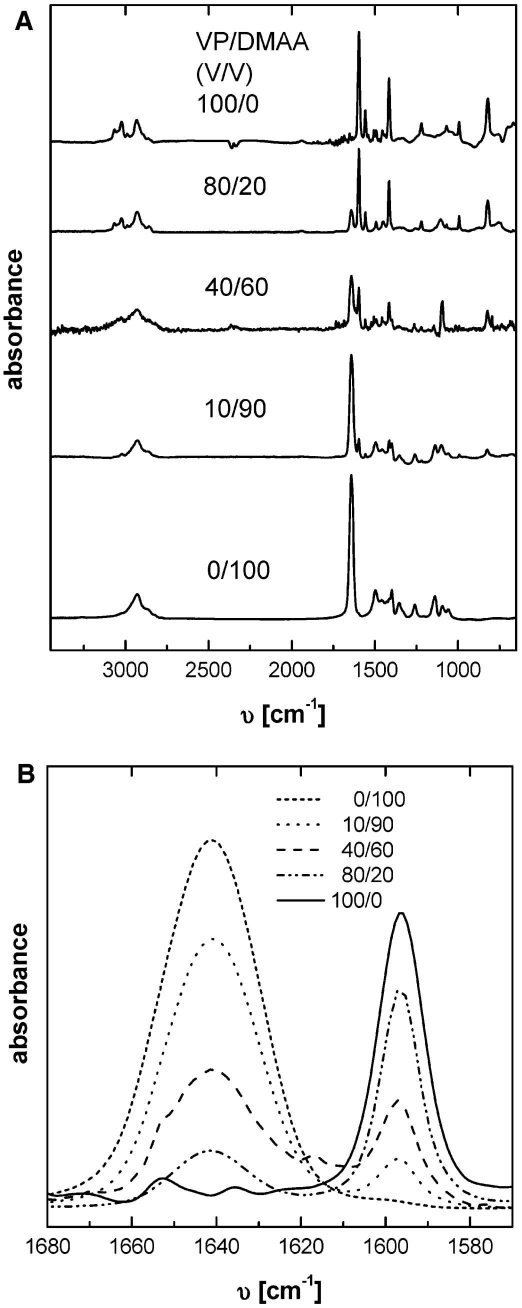

Figure 2. (A) FTIR transmission spectra of a series of neutral copolymer brushes (PVP-*stat*-PDMAA). The brushes are prepared by having different amounts of 4-vinylpyridine (VP) and dimethylacrylamide (DMAA) monomer in the polymerization feed, as denoted in the figure. (B) Detailed FTIR spectra obtained from (A).

In Figure 2, FTIR spectra of P(VP-*stat*-DMAA) brushes attached to silicon wafers are shown. The copolymer brushes had different ratios of the respective monomers in the feed during preparation. With increasing amount of DMAA in the monomer feed the height and the area of the absorption band at 1640 cm^{-1} increase while the integral intensity of the absorption band at 1597 cm^{-1} decreases (Figure 2B). In Figure 3 the amount of PVP segments of the surface-attached copolymer is shown as a function of the VP monomer content in the feed. Assuming that no significant changes in the density with varying copolymer composition occur, the copolymer compositions shown in Figure 3 were calculated from the integral intensities according to eq 2.

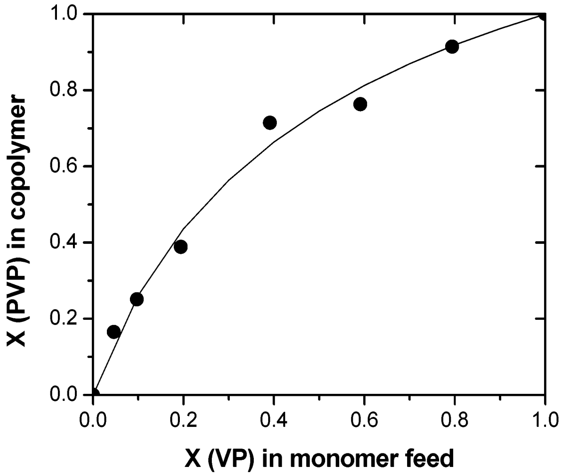

Figure 3. Amount of PVP segments incorporated in the statistical copolymer brush (PVP-*stat*-PDMAA) as a function of the amount of the VP monomer concentration used in the polymerization feed. The data are calculated from the integral intensities of FTIR spectra taken from the copolymer brushes. For more details see text. The solid line is a best fit to the data using eq 3. The copolymerization parameters obtained from the fit are $r_1 = 2.5 \pm 0.3$ and $r_1 = 0.3 \pm 0.1$.

Generally, the relation between the concentrations of the comonomers $[m_1]$ and $[m_2]$ in the feed and the concentrations of the appropriate segments $[M_1]$ and $[M_2]$ in the copolymer for a statistical copolymerization process is given by the following equation:[22]

$$\frac{[M_1]}{[M_2]} = \frac{[m_1](r_1[m_1] + [m_2])}{[m_2](r_2[m_2] + [m_1])} \tag{3}$$

Here r_1 and r_2 are the copolymerization parameters. Equation 3 holds as long as the mononer conversion of the copolymerization reaction is sufficiently low.[22] As all polymer chains are grown from the surface, the overall monomer conversion for the reactions described in this paper is less than 1%.

The copolymerization parameters can be evaluated via graphical methods (Finemann–Ross) as well as by fitting a simulated curve to the experimental data shown in Figure 3. For VP as m_1 and DMAA as m_2 copolymerization parameters of $r_1 = 2.5 \pm 0.3$ and $r_2 = 0.3 \pm 0.1$ yield the best fit to the experimental data. Similar results for the determination of the copolymerization parameters were obtained if graphical calculation methods, again, based on eq 3, were applied to the experimental data.

Quaternization of the Surface-Attached Copolymer Brushes. In Figure 4, transmission FTIR detailed spectra are shown that were obtained from polyelectrolyte brushes consisting of different amounts of quaternized VP segments as denoted in the figure. Because of the introduction of the charges, the maximum of the C=C adsorption band shifts to 1638 cm^{-1}.[16] In none of the samples the maximum of absorbance of the non-quaternized PVP segments at 1597 cm^{-1} can be detected anymore, indicating that the conversion of the reaction is quantitative in all cases. In addition, from a comparison of the overall integral intensity of the bands above 3000 cm^{-1} before and after the quaternization reaction, which are correlated to the aromatic C–H vibrations, it can be concluded that no significant amount of the surface-attached polymer chains was cleaved off the surface during the reaction. These results agree well with earlier investigations, carried out on the polymer-analogous quaternization reaction on PVP homopolymer brushes.[16]

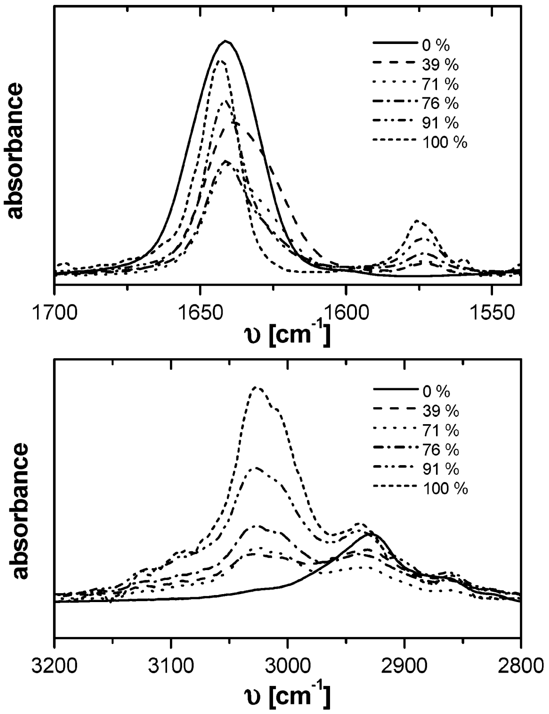

Figure 4. Detailed FTIR spectra obtained from statistical copolymer brushes (MePVP-*stat*-PDMAA) having different concentrations of charged MePVP and neutral PDMAA segments. The molar fraction of the MePVP segments in the brushes are given in the figure, where 100% corresponds to a pure MePVP brush and 0% to a pure PDMAA brush.

The results of atomic force microscopy (AFM) studies show that all brushes cover the surface of the substrate in a very homogeneous manner, and the rms roughness is in all cases below 1 nm, which is similar to the underlaying surface of the silicon wafers (data not shown).

Swelling Behavior of the Surface-Attached Copolymer Brushes. To study the swelling behavior of the surface-attached copolymer brushes, we have modified LaSFN9 glass prisms under identical conditions as described above. The dry thickness of the copolymer brushes L_{dry} has been measured prior to the swelling experiment by multiple-angle null ellipsometry. The brushes are then brought into contact with an aqueous environment containing a distinct amount of added salt, and ellipsometric measurements were performed. The swollen brush height was calculated from a Fresnel modeling of the raw data.[20]

Both the measured ellipsometric spectra and the model-fit calculations are shown in Figure 5 for three examples of the prepared statistical copolymer brushes having 100%, 39%, and 0% MePVP segments, respectively. It can be seen that the ellipsometric spectra of the pure MePVP brush in Figure 5 (spectra A) as well as the copolymer brush consisting of 39% MePVP (spectra B), and accordingly 61% PDMAA segments exhibit drastic changes of the curve-shape upon the addition of external salt. The changes are most prominent in the $\Delta(\Theta)$ curves. Because the number of interference patterns ($\Delta(\Theta)$ curves) as well as the slope of the $\psi(\Theta)$ curves close to the critical angle of total reflection is a measure for the swollen brush height, it

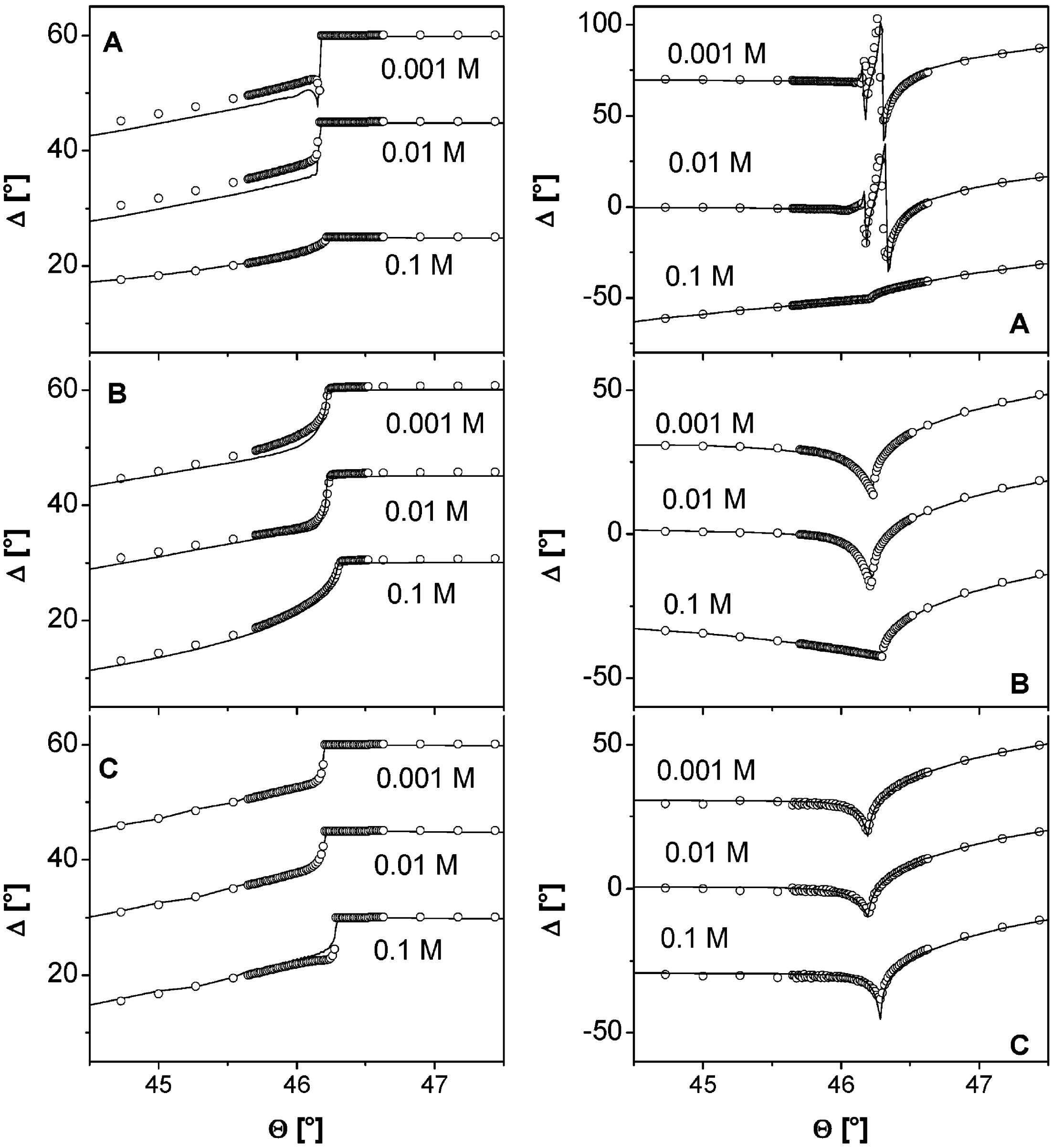

Figure 5. Ellipsometric spectra (ψ and Δ as a function of the angle of reflection Θ) of statistical MePVP-*stat*-PDMAA copolymer brushes having (A) 100%, (B) 39%, and (C) 0% MePVP segments. The spectra were recorded at different external salt (KI) concentrations denoted in the figure. Model-fit calculations are superimposed to the raw data as solid lines in the figure. For more details see text.

can be already concluded from the visual inspection of the data that both the MePVP brush as well as the MePVP-*stat*-PDMAA copolymer brush undergo large changes in the brush height upon the addition of salt. Note, because the changes in the spectra of the pure MePVP brush are much more pronounced, it can be furthermore concluded that also relative changes in the brush height of the swollen layer are much larger. Finally, the spectrum of the pure PDMAA brush does not change upon the addition of external salt, which leads to the conclusion that hardly any changes in the swollen brush height can be observed (Figure 5, spectra C). Note that a small shift in the position of the critical angle of total reflection can be attributed to a slight change in the refractive index of the contacting solution upon addition of large amounts of external salt. However, such a small shift influences neither the measurement nor the analysis of the data.

As we have recently shown in detail, from the model-fit calculations of the ellipsometric spectra (solid lines in Figure 5), the swollen layer height L_{swell} can be calculated.[20,21] Figure 6 shows the degree of swelling that is $Q = L_{\mathrm{swell}}/L_{\mathrm{dry}}$ as a function of the external salt concentration for six copolymer brushes having different amounts of ionic MePVP segments incorporated into the layer. Note, here we have used the degree of swelling instead of the absolute brush height to account for any differences in the molar mass of the surface-attached polymer chains of the copolymer brushes investigated.

In Figure 6A, which shows the spectra for pure MePVP, it can be seen why this class of polymers was chosen as a demonstration case for the copolymers in this paper. If exposed to external salt concentrations of $c_{\mathrm{S}} > 0.01$ mol/L (Figure 6A), the polyelectrolyte brush collapses to almost the dry layer thickness. In concrete terms this means that the degree of swelling changes from about $Q \approx 55$ at $c_{\mathrm{S}} < 0.01$ mol/L to $Q < 2$ at $c_{\mathrm{S}} > 0.06$ mol/L. Such a behavior has been already described in a previous publication and has been attributed to an association of the iodide ions with the charged sites on

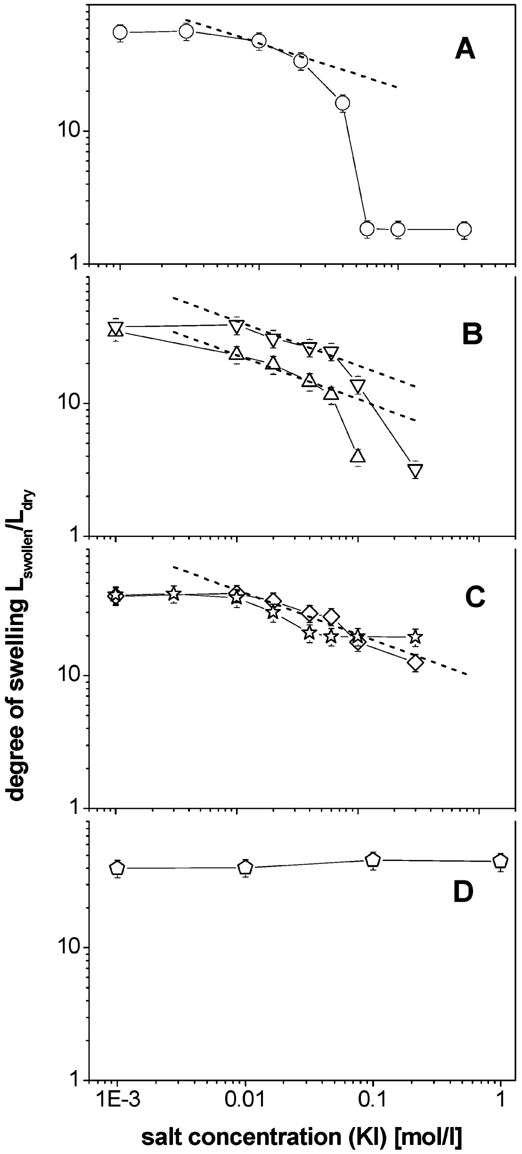

Figure 6. Degree of swelling $Q = L_{swell}/L_{dry}$ (L_{swell} = swollen brush thickeness and L_{dry} = dry brush thickness) as a function of the external salt concentration (salt: potassium iodide) of a MePVP brush (mole fraction of MePVP segments: A, 100%; B, △ = 91%, ▽ = 71%; C, ◇ = 39%, ☆ = 17%; D, 0%). The dashed lines qualitatively represent the predicted scaling relations as derived by mean-field theory.

the chains (leading effectively to a recombination of charges). The salt addition thus renders the chains more or less "neutral" and, accordingly, insoluble in the aqueous environment. Because of this reduced solubility, the brush height decreases strongly.

Already, when only small amounts of PDMAA segments are incorporated into the polymer (Figure 6B, having 91% and 71% MePVP segments, respectively), the concentration range, in which the transition between the fully swollen brush and the collapsed layer occurs, becomes much broader. In addition, the brush remains in a slightly swollen state, even at the highest salt concentration chosen ($Q \approx 3-4$ at $c_S \approx 0.1$ mol/L, at 71% MePVP).

This trend becomes even more pronounced if the charged segments are further diluted. It can be seen in Figure 6C, where copolymer brushes with 39% and 17% MePVP segments are shown. Upon addition of the salt only very small changes occur, and the brush remains in a highly swollen state even at the highest salt concentration ($Q \approx 15-20$ at $c_S \approx 0.1$ mol/L). The brush does not collapse anymore, but just shrinks to about half the initial swollen thickness.

If the brush consists of 100% PDMAA segments (Figure 6D), the brush height in aqueous solution remains, as expected, constant upon addition of the salt, regardless of the salt concentration of the environment.

Finally, we like to compare the data shown in Figure 6 qualitatively with predictions derived from mean-field theory for the scaling of the brush height with varying external salt concentration. When the external ion concentration exceeds the concentration of free ions trapped inside the brush, mean-field theory expects the brush height to shrink with the third root of the external salt concentration ($L \propto c_S^{-1/3}$). The theoretical predictions are superimposed as dashed lines on the data shown in Figure 6. The MePVP brush shown in Figure 6A collapses much faster as expected from the theory. We believe that this behavior of the brush can be attributed to the specific interactions between the iodide and the polymer segments, which leads to strong changes of the solubility of the MePVP brush, as described in detail in a parallel communication.[12]

If the charged segments of the brush are diluted by noncharged PDMAA segments, however, the response to addition of the salt is rather different. As shown in Figure 6B,C, the influence of salt on the brush height is in agreement with theoretical scaling predictions at external salt concentrations of $0.01 < c_S < 0.1$, as due to screening of all charges the polymer becomes more and more neutral, but remains water-soluble, even in the case of complete screening. Eventually, if the number of charges along the polymer chain becomes too small, the electrostatic interactions contribute only very little to the overall brush height, and the addition of salt has a weak or even no longer any effect on the swelling properties of the brushes.

Conclusions

The statistical copolymerization of 4-vinylpyridine and dimethylacrylamide by a surface-initiated radical chain polymerization using an immobilized azo-initiator leads after quaternization of the pyridine moities to surface-attached MePVP−PDMAA copolymer brushes with adjustable charge concentration along the polymer chain.

When the brush consists of mainly MePVP segments, the swelling behavior is dominated by the polyelectrolyte, and in the particular example chosen here, the brushes respond very strongly to the addition of external salt as here the screening of the charges is strongly coupled to the solubility of the system. With increasing amount of uncharged PDMAA segments the swelling behavior of the brush becomes more and more dominated by the neutral water-swellable segments and becomes less affected by electrostatic screening. Eventually, the swelling behavior of a neutral DMAA (homo)-polymer brush is unaffected by the addition of salt.

An interesting twist to this is that in highly charged brush systems most charges are self-screened ("Manning" condensation). The mobile fraction of ions, i.e., the remaining unscreened charges, has been estimated in high graft density brushes to less than 20%. Accordingly, upon dilution with uncharged units, the effective charge density per segment should increase quite strongly. This is corroborated by the fact that the onset of the decrease of the brush height, i.e., the concentration at which screening of charges becomes significant, is similar for all systems shown here (Figure 6). At this onset the external salt concentration equals the amount of free ions inside the brush. From this it can be concluded that the dilution of the charged repeat units with the uncharged comonomer is compensated by a decrease in the Manning condensation, so that the overall number of effective charges is more or less the same in all brushes shown here.

This study shows that the sensitivity of the swelling behavior of surface-attached polymer molecules against the presence of low molecular weight salt in an aqueous environment can be easily tuned by adjusting the charge density of the surface-attached macromolecules. This is particularly interesting for applications where the swellability of polymer layers is crucial for the functioning of a device. In the case of sensor devices strong changes in the layer thickness upon an external stimulus might be desired; however, if (bio)molecules are immobilized in such layers, strong changes in the solubility upon introduction of small amounts of charges in the environment might be not advantageous. The generation of copolymer brushes might be an interesting perspective for a simple way to control such properties.

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