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Binding of Oppositely Charged Surfactants to Poly(methacrylic acid) Brushes

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ABSTRACT: The interaction of poly(methacrylic acid) (PMAA) brushes with oppositely charged surfactants has been studied as a function of the polymer brush graft density, the surfactant concentration, and the surfactant alkyl chain length at neutral pH. The changes in the degree of dissociation of the polyacid α and in the amount of surfactant uptake β were determined from infrared and multiple-angle ellipsometry measurements, respectively. The brush shrinks already strongly at a surfactant concentration of around 10^{-5} mol L^{-1}, despite that the surfactant uptake in this regime is still low. A strong surfactant uptake sets in only above a critical concentration, which is slightly below the critical micelle concentration (cmc) of the respective surfactant. A comparison of dissocation α and surfactant uptake β reveals that the surfactant is not exclusively bound electrostatically by an exchange of the carboxylic acid protons for surfactant ions, but also through hydrophobic interactions. The influence of surfactant concentration, alkyl chain length, and graft density on the complexation behavior is studied.

1. Introduction

Polyelectrolyte−surfactant complexes have received much attention lately, on the one side from the scientific community as there are strong mutual interactions between its components which give raise to some interesting fundamental questions on the behavior of charged molecules and from the other side from groups interested in practical applications due to the unique materials properties of such systems. Polyelectrolyte−surfactant complexes have been used to adjust rheological properties, to enhance solubilization of hydrophobic materials, or to improve the mildness of surfactants in personal care products.[1] Recent investigations propose the use of these materials for the formation of metal nanoparticles[2] and for the fabrication of novel shape memory networks.[3]

The interaction of alkyltrimethylammonium and alkylpyridinium salts with poly(acrylic acid) (PAA) and poly(methacrylic acid) (PMAA) either in dilute solution[4−11] or as a cross-linked polymer gel[12−19] has been studied for various degrees of neutralization of the weak polyacids. Generally, in the presence of these polymers, the surfactant associates into aggregates at a concentration, denoted as the critical association concentration (cac), which is 2−3 orders of magnitude lower than the critical micelle concentration (cmc) of the corresponding surfactant solution. The polymeric counterions prevent an entropically unfavorable enrichment of surfactant counterions close to the surfactant aggregate surface. From a polymer-centered viewpoint, at the cac, the surfactant binds in a cooperative fashion to the polymer; i.e., the interaction between neighboring surfactant molecules facilitates the binding of surfactant in the vicinity of previously adsorbed surfactant.[20,21] The cooperative binding is accompanied by a strong shrinkage of the polyacid: gels exhibit a collapse (a more gradual volume transition is found when the gel is macroscopic and the monomer units are in excess compared to the surfactant), and polymer chains in solution show phase separation or a drop in the hydrodynamic radius upon surfactant binding. Although this cooperative binding is driven mainly by electrostatic interactions, hydrophobic interactions may play a significant or even dominant role when the polyacid is used at low degrees of dissociation α. If the polyacid was in the fully protonated form ($\alpha = 0$), addition of the surfactant led to a slight increase in the dissociation so that α values of $\alpha \approx 0.1-0.2$ were obtained. If a significant portion of the polyelectrolyte was already deprotonated before surfactant addition ($\alpha \geq 0.2$), α did not change during addition. It is believed that this behavior allows to maximize contributions from both electrostatic and hydrophobic interactions. However, a direct comparison of the different systems is difficult as the system properties depend also strongly on the concentration of added salt. As salt was added in most investigations, a quantitative comparison of the systems used in the different publications is somewhat difficult.

In the case of polymer brushes, polymer chains are end-grafted to a surface such that the distance between two anchoring points is significantly smaller than the radius of gyration of the same polymer chain in solution. This leads to energetically unfavorable segment−segment repulsions and a stretching of the polymer chains. How this conformational constraint affects the binding of oppositely charged surfactants to PMAA brushes and how the swelling of the brushes changes during this binding process will be the subject of this publication.

To our knowledge, only one experimental investigation that deals with the interaction of weak polyacid brushes and oppositely charged surfactants has been published up to now.[22] In this paper, Cohen Stuart et al. have studied the adsorption of alkyltrimethylammonium salts on PAA at pH = 8.5 by optical reflectometry. They found that the shape of the binding isotherms strongly depended on the graft density of the brush and that, above a certain graft density, the binding was noncooperative and limited to degrees of binding much lower than those for the binding to free PAA in solution. Theoretical data in the area of surfactant binding to

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polymer brushes are up to now limited to neutral polymer brushes.[23,24] In this case, the surfactant is only incorporated into the brush by hydrophobic interactions, and the authors find a decreasing degree of binding with increasing graft density.

In the present publication we study the adsorption of alkyltrimethylammonium salts of three different chain lengths on PMAA brushes of different graft density at $\alpha = 0$ and neutral pH. We follow the change in the degree of dissociation α of the carboxylic acid groups upon binding of the surfactant by infrared measurements and compare this to the degree of binding β which we calculate from changes in thickness. Furthermore, using multiple-angle ellipsometry, we study the swelling behavior of a PMAA brush in the presence of dodecyltrimethylammonium chloride solutions and relate it to the binding isotherm which is obtained simultaneously.

2. Experimental Section

2.1. Materials. Silicon wafers (CrysTec, Germany; 750 μm thick; polished on both faces) were cleaned with a stream of high-velocity dry ice particles (Tectra, Germany) prior to the immobilization and used as substrates for measurements of the dry complexes (IR, AFM, ellipsometry). High refractive index lanthanum glass prisms (LaSFN9, $n_D = 1.845$; Hellma, Germany) were used as substrates for measurements of the swollen polymer brushes. They were activated prior to the initiator deposition by repeated dipping into 1 mol L^{-1} H_2SO_4 and subsequent rinsing with deionized water and methanol (p.a. grade). Methacrylic acid (Fluka, Germany) was purified by vacuum distillation over a vigreux column and stored under nitrogen at −20 °C. Water was deionized with a Millipore system (resistivity $\geq$18.2 MΩ cm^{-1}) immediately prior to use. Octyltrimethylammonium bromide (OTAB; Fluka, Germany), dodecyltrimethylammonium chloride (DDTAC; Fluka, Germany), and octadecyltrimethylammonium bromide (ODTAB; Fluka, Germany) were of p.a. grade and used as received.

2.2. Synthesis of PMAA Brushes and Complex Formation. Figure 1 shows the synthesis of PMAA brushes via a surface-initiated free radical chain polymerization and the subsequent complex formation with oppositely charged surfactants.The "grafting from" procedure was described in detail previously.[25−27] First, a self-assembled monolayer of an initiator was covalently attached to the surface of silicon wafers or LaSFN9 glass prisms via reaction of the monochlorosilane moieties with surface hydroxyl groups. To generate sufficient hydroxyl groups on the glass substrate, an activation with 1 mol L^{-1} H_2SO_4 (3 × 1 min) was performed immediately prior to the immobilization. The azo function of the surface-bound initiator molecules was used in the second step to thermally initiate the radical polymerization of methacrylic acid in water (silicon wafers: 10 vol %; glass prisms: 50 vol %). The reaction mixture was carefully degassed by repeated ultrasonication and the application of vacuum before the initiator-functionalized substrates were added under nitrogen. Then, the Schlenk flasks were placed in a thermostat at 60.0 ± 0.1 °C for a given time. By varying the conversion of the surface-attached initiator through adjustment of the polymerization time ($t_{1/2} \approx 20$ h[26]), the number of end-grafted polymer chains per area, i.e., the graft density, can be controlled while keeping the molecular weight constant. Free polymer is also formed in solution as the initiator molecules decompose into two radicals, one surface-bound and one free in solution. Therefore, the PMAA-grafted substrates were carefully extracted in methanol and water for ≈15 h, respectively, to remove free polymer chains. The precise direct measurement of the molecular weight of the surface-attached polymer by gel permeation chromatography (GPC) was not feasible, given that the higher molecular weight fraction of the polymer was beyond the exclusion limit of available GPC columns and also beyond the limits of available GPC standards. However, using the known initiator decomposition kinetics, the number-averaged molecular weight M_n can be calculated from a plot of the film thickness d as a function of the polymerization time as was shown in a recent publication.[28] The molecular weight of the surface-attached polymer was estimated to be around $(4 \pm 1) \times 10^6$ g/mol for 10 vol % methacrylic acid and is expected to be somewhat higher for 50 vol %. Note, however, that the degree of polymerization was in any case very high (≈ 50 000 ± 10 000) and that the exact value is not crucial for the interpretation of the experimental findings. To form the polyelectrolyte surfactant complexes, the polymer brush modified substrates were placed in an aqueous solution of the surfactant for 15 h at room temperature. Then, the sample was carefully rinsed with deionized water and dried in air. Concentrations c were chosen such that $c <$ cmc for all surfactants (0.2 mol L^{-1}, OTAB;[29] 18 mmol L^{-1}, DDTAC;[30] 0.3 mmol L^{-1}, ODTAB[31]). For the investigation of the swelling behavior, DDTAC concentrations were extended above the cmc, up to 0.1 mol L^{-1}. All solutions were clear so that a simple sedimentation of the surfactant can be excluded.

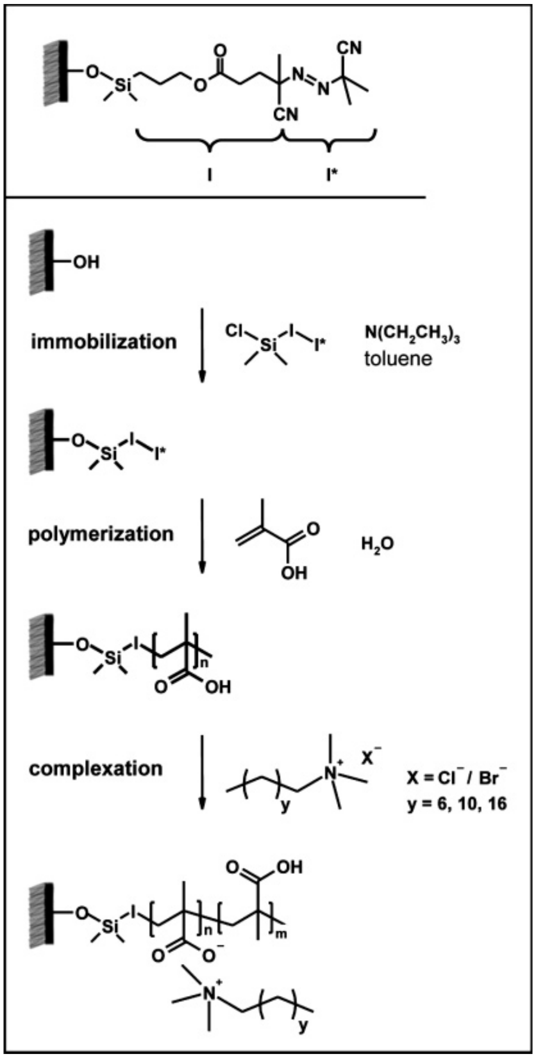

Figure 1. Schematic depiction of the "grafting-from" approach. Immobilization: a monolayer of azo-initiators is self-assembled on a silicon oxide or glass surface. Polymerization: the covalently attached initiator is used to surface-initiate a free radical polymerization by thermal cleavage. Complexation: after extraction in methanol and water, the brush is placed in a solution of the surfactant to form a stable polyelectrolyte−surfactant complex.

2.3. Instrumentation. Transmission Fourier transform infrared (FTIR) spectra were recorded on a Bio-Rad Excalibur spectrometer with a resolution of 4 cm^{-1}. Careful purging of the sample compartment with nitrogen was necessary to reduce water-OH and carbon dioxide bands from the gas phase to allow for a quantitative evaluation of the carbonyl absorption bands. To determine the dry layer thicknesses, null ellipsometric measurements were carried out on an ELX-2 ellipsometer (Riss, Germany) at an incident angle of 70°. The light source was a He−Ne laser with a wavelength of 632.8 nm and an intensity of 3 mW. AFM images were recorded in tapping mode on a DI nanoscope multimode 3100 instrument. To determine the swollen PMAA brush thicknesses, ellipsometric measurements were performed on a home-built multiple-angle null ellipsometer in an attenuated total reflection geometry. The laser beam (632.8 nm, 3 mW) was coupled into a high refractive index glass (LaSFN9) prism from the backside and was reflected at the base of the prism where the polymer brush was grown. Automated minimizations were performed at predefined angles. The setup was described in detail previously.[32,33] The refractive index profile of the swollen polymer brush was modeled by using a complementary error function. The model parameters (layer thickness, interface width, refractive index of the layer, offset in Δ due to birefringence) were optimized such that the calculated Δ- and Ψ-traces best fit to the experimental curves. The swollen brush thickness was defined as twice the normalized first moment of the refractive index profile, which is equal to a box profile of the same thickness and the same integrated area. In addition to the swollen layer thickness, the model calculations yield the zeroth moment of the refractive index profile, i.e., the total refractive index increment

$$\Delta\bar{n} = \int_0^\infty (n(z) - n_{\mathrm{solv}})\,\mathrm{d}z \qquad (1)$$

with the refractive index $n(z)$ of the swollen polymer layer at the distance z from the surface and the refractive index of the solvent $n_{\mathrm{solv}} = 1.33$ in aqueous solution. The amounts of surfactant and of polymer segments in the layer can be derived from the refractive index increments originating from the bound surfactant ions, $\Delta\bar{n}_{\mathrm{DDTA}}$, and from the PMAA polymer segments, $\Delta\bar{n}_{\mathrm{PMAA}}$, by relating the refractive index increments to the respective molar volumes v_{DDTA} and v_{PMAA} of the surfactant ion and the polymer repetition unit. One can then calculate the degree of binding

$$\beta = \frac{\Delta\bar{n}_{\mathrm{DDTA}}/v_{\mathrm{DDTA}}}{\Delta\bar{n}_{\mathrm{PMAA}}/v_{\mathrm{PMAA}}} = \frac{(\Delta\bar{n}_{\mathrm{PSC}} - \Delta\bar{n}_{\mathrm{PMAA}})/v_{\mathrm{DDTA}}}{\Delta\bar{n}_{\mathrm{PMAA}}/v_{\mathrm{PMAA}}} \qquad (2)$$

of dodecyltrimethylammonium ions to the swollen brush as the number of bound surfactant ions per polymer repetition unit (regardless of the degree of dissociation of the latter). $\Delta\bar{n}_{\mathrm{PSC}}$ denotes the refractive index increment originating from the polymer−surfactant complex. $\Delta\bar{n}_{\mathrm{PMAA}}$ and $\Delta\bar{n}_{\mathrm{PSC}}$ can be obtained from measurements of the pure PMAA brush swollen in aqueous solution and from the same brush swollen in surfactant solution of a given concentration. The molar volumes $v_{\mathrm{DDTA}} = M_{\mathrm{DDTA}}/\rho_{\mathrm{DDTA}}$ and $v_{\mathrm{PMAA}} = M_{\mathrm{PMAA}}/\rho_{\mathrm{PMAA}}$ can be calculated from the molar masses $M_{\mathrm{DDTA}} = 228.4$ g mol^{-1} and $M_{\mathrm{PMAA}} = 86.1$ g mol^{-1} and the densities $\rho_{\mathrm{DDTA}} = 0.81$ g cm^{-3} and $\rho_{\mathrm{PMAA}} = 1.12$ g cm^{-3} of the dodecyltrimethylammonium ion and the PMAA repetition unit. The value of ρ_{DDTA} was taken from the isomeric compound pentadecylamine.

3. Results

3.1. Characterization of the Complexes. Figure 2 shows a comparison of the infrared spectra of a fully protonated PMAA brush, an almost fully deprotonated PMAA brush, KBr pellets of the pure surfactants, and PMAA brush surfactant complexes obtained at different concentrations and surfactant alkyl chain lengths as denoted in the figure. The protonated poly(carboxylic acid) shows a characteristic carbonyl absorption band in the infrared spectrum at 1705 cm^{-1} (dotted line). After deprotonation, the absorption bands due to the asymmetric and symmetric stretching vibrations ν_{asym}(COO$^-$) and ν_{sym}(COO$^-$) of the carboxylate polyion are shifted to 1558 and 1396 cm^{-1} (dash−dotted lines), respectively.[28] The infrared spectra of the surfactants show absorption bands caused by CH stretching vibrations at 3017, 2918, and 2849 cm^{-1} and absorption bands at 1487, 1472, and 1464 cm^{-1} originating from the ammonium group (dashed lines). After adsorption of the surfactant to the brush, bands from both surfactant and polymer are found, confirming the formation of a polyelectrolyte brush surfactant complex. It is also qualitatively visible that the degree of surfactant binding increases with concentration and alkyl chain length. Note that the carboxylate band intensity increases at the expense of the carboxylic acid band intensity as more surfactant is bound to the brush. This indicates that the binding process is accompanied by a release of protons, as will be discussed in section 3.2.

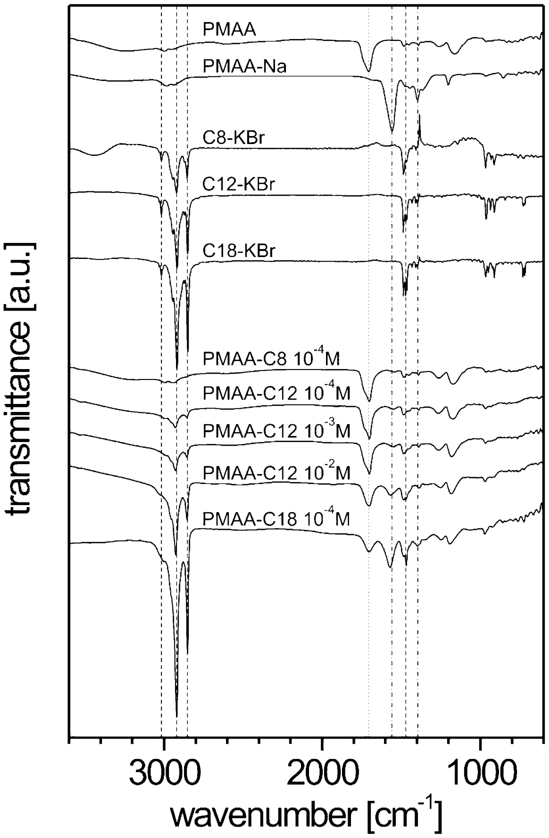

Figure 2. From top to bottom are shown infrared spectra of a PMAA brush at pH 3 and pH 12 (carboxylic acid and carboxylate stretching vibrations are marked with a dotted and dash−dotted lines, respectively), spectra of OTAB, DDTAC, and ODTAB as obtained from KBr pellets (characteristic bands are marked with dashed lines), and spectra of PMAA brush surfactant complexes at different surfactant concentrations and alkyl chain lengths as indicated in the figure.

In Figure 3, AFM micrographs of PMAA brushes (239 nm dry thickness; $\Gamma = 0.062$ μmol m^{-2}) that were placed in (a) deionized water, (b) 0.1 mmol L^{-1} OTAB, (c) 0.1 mmol L^{-1} ODTAB, (d) 0.1 mmol L^{-1} DDTAC, and (e) 10 mmol L^{-1} DDTAC are given. All images are 1 × 1 μm, and the rms roughnesses are (a) 0.4, (b) 1.3, (c) 1.2, (d) 4.0, and (e) 0.9 nm, indicating that for all conditions the complex formation led to a roughening of the brush surface. Different structures and roughnesses were observed for the different complexes; however, no clear trend with respect to the surfactant concentration or alkyl chain length was observed. Obviously, the optimization of electrostatic and hydrophobic interactions

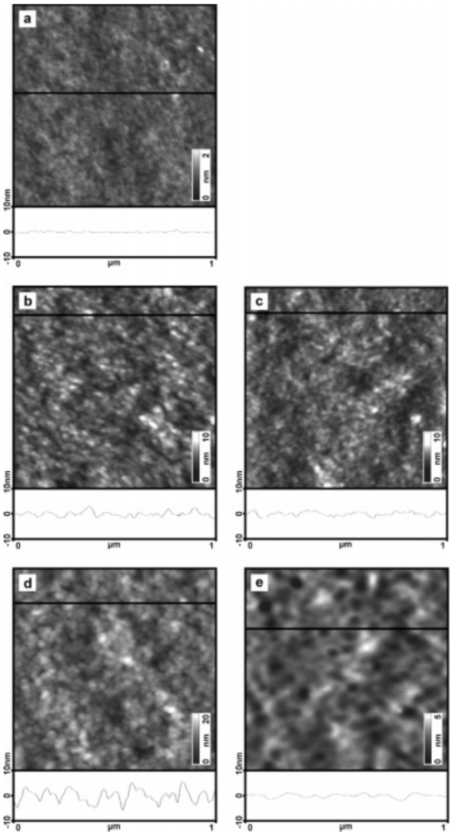

Figure 3. AFM micrographs of PMAA brushes (239 nm dry thickness; $\Gamma = 0.062$ μmol m^{-2}) after equilibration with (a) deionized water, (b) 0.1 mmol L^{-1} OTAB, (c) 0.1 mmol L^{-1} ODTAB, (d) 0.1 mmol L^{-1} DDTAC, and (e) 10 mmol L^{-1} DDTAC and drying.

causes different drying conditions of the film and thus different roughnesses. Comparable, for sodium polyacrylate gel complexes different ordered structures have been reported depending on the alkyl chain length of the oppositely charged surfactant.[12–14,17] The dry complexes often showed lamellar structures with the internal structure of the lamellae being strongly affected by the structure of the surfactant.[18] In the case of a sodium polyacrylate brush, the formation of a highly ordered lamellar subphase upon cooperative binding has been suggested.[22]

3.2. Influence of the Graft Density on Complex Formation. In this section the surfactant adsorption is studied as a function of the polymer brush graft density. PMAA brushes were grown on silicon wafers (polished on both faces) with the following graft densities Γ: 0.118, 0.081, 0.062, 0.052, 0.042, 0.032, 0.021, 0.016, and 0.011 μmol m^{-2}. The corresponding anchoring distances D were 3.7, 4.4, 5.1, 5.6, 6.2, 7.1, 8.7, 10.1, and 12.4 nm. The change in thickness upon complex formation was followed by ellipsometry, and infrared spectra were recorded to determine the chemical composition of the complexes.

Surfactant Concentration. Figure 4 exemplarily shows the infrared spectra in the CH and carbonyl absorption regions of the complexes with (a) 0.1 mmol L^{-1} DDTAC, (b) 1 mmol L^{-1} DDTAC, and (c) 10 mmol L^{-1} DDTAC. The graft densities Γ were 0.118, 0.081, 0.062, 0.032, and 0.011 μmol m^{-2} (D = 3.7, 4.4, 5.1, 7.1, and 12.4 nm), from top to bottom. From left to right, i.e., from low to high concentration and from top to bottom, i.e., from high to low graft density, the intensity of the CH absorption bands increases relative to the carbonyl bands intensity, indicating increasing amounts of adsorbed surfactant. Major changes were observed when going from 1 (b) to 10 mmol L^{-1} DDTAC (c). Furthermore, the CH absorption band at the highest DDTAC concentration shows the strongest dependence on the graft density. This is also reflected in a change in the carbonyl absorption region of the infrared spectra. With decreasing graft density, the carboxylic acid band intensity decreases at the expense of the carboxylate band intensity. This indicates that the binding occurs at least to some extent electrostatically with a release of protons and chloride ions. One can quantify this neutralization reaction by integrating the carboxylic acid and the carboxylate band intensities. Knowing the ratio of the extinction coefficients of the carboxylate and the carboxylic acid peak $\epsilon(\mathrm{COO^-})/\epsilon(\mathrm{COOH}) = 1.8 \pm 0.3$, one can calculate the degree of dissociation according to

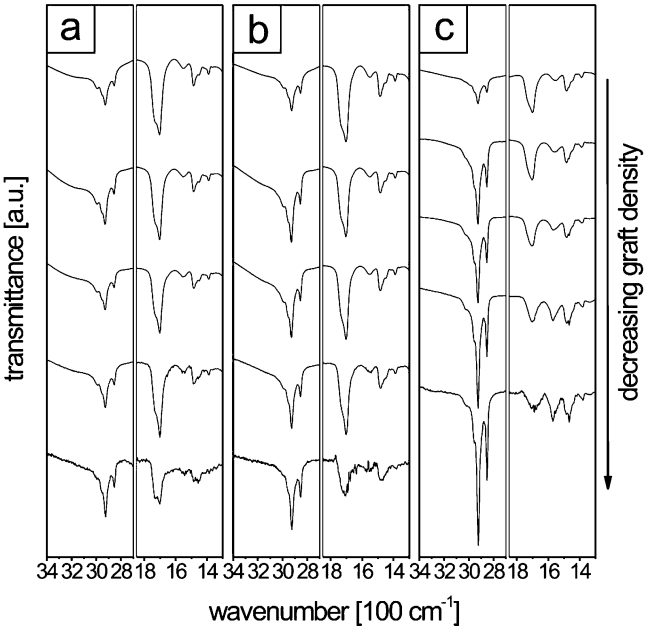

Figure 4. Exemplary infrared spectra (only the CH and carbonyl absorption regions are shown) of PMAA brush complexes with (a) 0.1 mmol L^{-1} DDTAC, (b) 1 mmol L^{-1} DDTAC, and (c) 10 mmol L^{-1} DDTAC. The graft densities Γ are 0.118, 0.081, 0.062, 0.032, and 0.011 μmol m^{-2} (D = 3.7, 4.4, 5.1, 7.1, and 12.4 nm), from top to bottom.

$$\alpha = \frac{[\mathrm{COO^-}]}{[\mathrm{COO^-}] + \epsilon_{\mathrm{COO^-}}/\epsilon_{\mathrm{COOH}}[\mathrm{COOH}]} \qquad (3)$$

The details of the calculation procedure have been discussed previously.[28] The quantitative evaluation of the spectra from Figure 4 is depicted in Figure 5a, where α is plotted as a function of the polymer brush graft density. The qualitative findings from the visual inspection of the infrared spectra are well reproduced in the dependencies of α on the polymer brush graft density and the surfactant concentration. α increases with increasing concentration for all graft densities. Whereas the difference in α between the lower concentrated solutions is small, a dramatic increase is observed when the concentration is increased to 10 mmol L^{-1}. For the lower concentrated solutions, α does not exceed a value of 0.15 at any graft density, and the graft density has little influence on the surfactant adsorption. However,

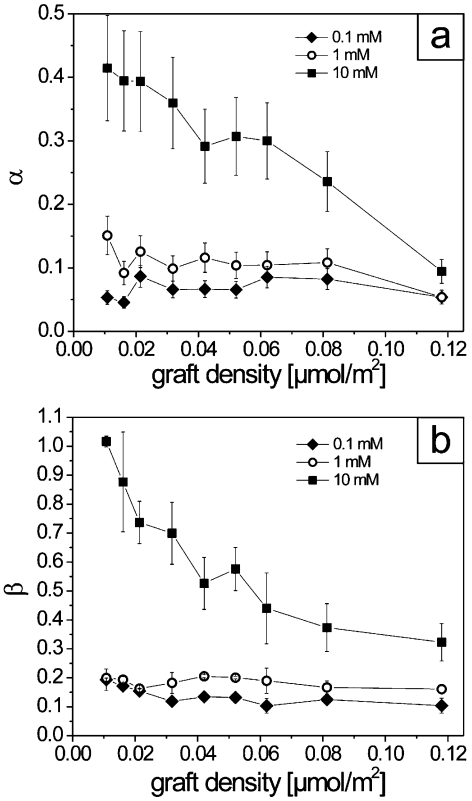

Figure 5. Degree of dissociation α (a) and degree of binding β (b) of PMAA brushes after equilibration with DDTAC solutions of 0.1 mmol L^{-1} (diamonds), 1 mmol L^{-1} (open circles), and 10 mmol L^{-1} (squares) as a function of the PMAA brush graft density.

in the case of 10 mmol L^{-1} DDTAC solution, α drops from a value of 0.41 for the lowest to a value of 0.09 for the highest graft density, indicating that the adsorption is increasingly suppressed with increasing graft density.

In principle, one could also calculate the degree of binding β, which is defined as the number of surfactant ions per monomer unit, from an integration of the CH absorption bands in the infrared spectra before and after surfactant adsorption. However, the strong overlap of the CH absorption bands with the broad band originating from the carboxylic acid OH stretching vibrations and the change in intensity of this band upon complexation prevents a meaningful integration of the spectra. On the other hand, we can calculate the total uptake of surfactant β from the increase in thickness of the PMAA brushes upon surfactant adsorption. Note that in the definition of β we do not differentiate between dissociated and undissociated monomer units as in the present case this is subject to change. One uncertainty, which remains if surfactant is taken up, is the whereabouts of the surfactant counterion. Depending on whether the surfactant is taken up via an ion exchange process or via hydrophobic interactions, the counterions do or do not leave the brush. Counterions which are coadsorbed with hydrophobically bound surfactant will contribute to the brush mass. For the following discussions it is assumed that all surfactant binds electrostatically, i.e., that no surfactant counterions are incorporated into the brush. This will cause a small systematic error, which leads to a slight overestimation of β. However, the error caused by this is small, and we cannot easily account for this effect as the exact number of coadsorbed surfactant counterions is unknown. On the basis of these assumptions, the thicknesses of the brush before adsorption L_1 and after adsorption L_2 of the surfactant are given by

$$L_1 = \frac{\Gamma M_n^{\mathrm{PMAA}}}{\rho} \tag{4}$$

$$L_2 = \beta\left(\frac{\Gamma M_n^{\mathrm{PSC}}}{\rho}\right) + (1-\beta)\left(\frac{\Gamma M_n^{\mathrm{PMAA}}}{\rho}\right) \tag{5}$$

Here M_n^{PMAA} describes the number-averaged molecular weight of the PMAA molecules in the brush and M_n^{PSC} the number-averaged molecular weight of the polymer–surfactant complex, i.e., of deprotonated PMAA and the surfactant cations. The graft density Γ remains unchanged upon adsorption. Assuming that changes in the density ρ are negligible, β can be calculated by dividing L_2 through L_1:

$$\beta = \frac{(L_2/L_1) - 1}{(M_n^{\mathrm{PSC}}/M_n^{\mathrm{PMAA}}) - 1} \tag{6}$$

Figure 5b shows β as a function of the graft density. β shows the same qualitative trends with increasing graft density as α. β increases with increasing concentration for all graft densities, and the by far most pronounced increase in β is observed when the concentration is increased to 10 mmol L^{-1}. Again, for the most concentrated solution, β drops from 1.0 to 0.32 with increasing graft density, showing that an increase in graft density strongly limits the surfactant binding. For the lower concentrated solutions, β remains below 0.2 for all graft densities, and similar to the trend for the degree of dissociation α, only little influence of the graft density on the surfactant uptake was observed. A closer inspection of β and α reveals that the values for β are generally higher than the corresponding α values. Even though the experimental error is not small and β might contain a systematic error as discussed above, it should be noted that the effect is very large and beyond all experimental errors. We did not observe a simple linear trend in the β/α ratio; however, β values were mostly on the order of 1.5–2.5 times higher than the corresponding α values. A larger difference is observed for the 10 mmol L^{-1} DDTAC solution at the highest graft density where β/α = 3.4.

Surfactant Alkyl Chain Length. To investigate the influence of the surfactant alkyl chain length, we have used three different surfactants with C_8, C_{12}, and C_{18} alkyl substituents and performed analogous measurements for the determination of α and β. Figure 6 shows the infrared spectra of the PMAA brush complexes with 0.1 mmol L^{-1} solutions of (a) OTAB, (b) DDTAC, and (c) ODTAB. The graft densities Γ were 0.118, 0.081, 0.062, 0.032, and 0.011 μmol m^{-2} (D = 3.7, 4.4, 5.1, 7.1, and 12.4 nm), from top to bottom. As expected, the alkyl chain length has a strong influence on the adsorption behavior. The longer the alkyl chain length, the stronger is the binding to the brush at all graft densities as indicated by an increase in the CH absorption band intensity. A dramatic increase is observed when the alkyl chain length is increased from C_{12} to C_{18}. Moreover, in the case of ODTAB, the amount of adsorbed surfactant strongly increases with decreasing graft density. This is reflected not only in an increase in the CH absorption band intensity but also in a strong

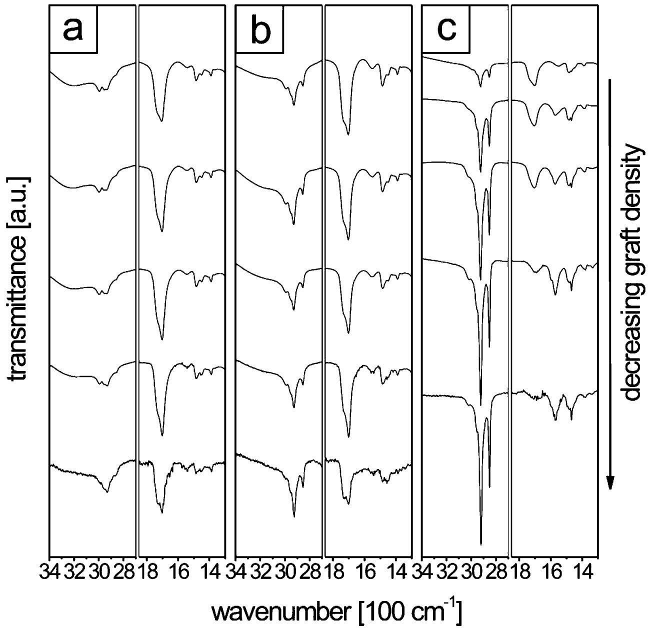

Figure 6. Exemplary infrared spectra (only the CH and carbonyl absorption regions are shown) of PMAA brush complexes with (a) 0.1 mmol L^{-1} OTAB, (b) 0.1 mmol L^{-1} DDTAC, and (c) 0.1 mmol L^{-1} ODTAB. The graft densities Γ are 0.118, 0.081, 0.062, 0.032, and 0.011 μmol m^{-2} (D = 3.7, 4.4, 5.1, 7.1, and 12.4 nm), from top to bottom.

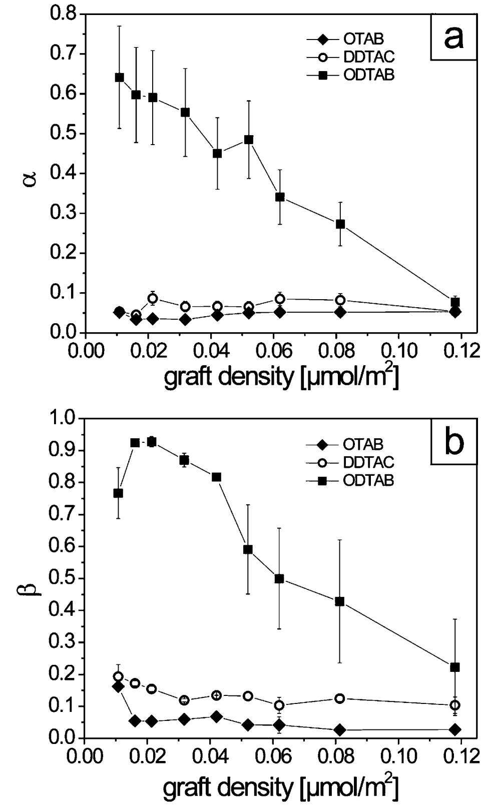

Figure 7. Degree of dissociation α (a) and degree of binding β (b) of PMAA brushes after equilibration with 0.1 mmol L^{-1} solutions of OTAB (diamonds), DDTAC (open circles), and ODTAB (squares) as a function of the PMAA brush graft density.

increase of the carboxylate band intensity at the expense of the carboxylic acid band intensity.

In Figure 7a, α is plotted as a function of the graft density of the PMAA brush for the three surfactants. The quantitative evaluation of the infrared spectra confirms the qualitative findings of the visual inspection. α increases with increasing alkyl chain length at all graft densities, however, only for the longest alkyl chain α values above 0.1 were observed, and only for this surfactant, α strongly depends on the graft density of the brush. From the lowest to the highest graft density, α decreases from 0.64 down to 0.08.

The degree of binding β was again determined from ellipsometric thickness measurements and is given in Figure 7b as a function of the PMAA brush graft density. The dependence of β on the surfactant alkyl chain length and on the brush graft density is closely related to the trend observable concerning the dissociation of the brush. β increases with increasing surfactant alkyl chain length with a drastic increase from DDTAC to ODTAB for all graft densities. The difference between OTAB and DDTAC is more clearly reflected in the surfactant uptake β than in the degree of dissociation α. Similar to the situation for α only the uptake of the surfactant with the longest alkyl chain depends strongly on the graft density. With increasing graft density, β decreases from 0.93 to 0.22.

3.3. Swelling Behavior and Binding Isotherm. To relate surfactant binding and the swelling behavior of PMAA brushes, we have studied a 37 nm (dry thickness) PMAA brush ($\Gamma \approx 0.01-0.02$ μmol m^{-2}; $D \approx 9-12$ nm) in DDTAC solutions of increasing concentration. The swollen brush thickness as well as the degree of surfactant binding were derived from multiple-angle null ellipsometric measurements, as described in section 2.3. At each concentration, the solution was renewed several times, and measurements were performed until the swollen brush thickness remained unchanged. Each measurement took ≈30 min.

The ellipsometric spectra for the PMAA brush in equilibrium with increasingly concentrated DDTAC solutions are shown in Figure 8; the corresponding evolution of the swollen thickness with concentration and the binding isotherm are given in Figure 9. The determination of the value of $\Delta\bar{n}_{\mathrm{PMAA}}$ (compare section 2.3) is associated with a certain error. From different model calculations of the ellipsometric spectra we estimate this error to be in the range of 20%, corresponding to an error in the highest β value of ±0.2. Note that an error in $\Delta\bar{n}_{\mathrm{PMAA}}$ only slightly stretches or compresses the binding isotherm; however, the overall shape and the main features remain unaffected. When the brush swollen in deionized water is brought into contact with a 10^{-5} mol L^{-1} DDTAC solution, the brush strongly deswells to less than 1/3 of its original thickness. From 10^{-5} mol L^{-1} up to 3 mmol L^{-1}, all Δ- and Ψ-traces are of similar shape, indicating that no dramatic thickness changes occur. The degree of binding increases very slowly to a value of $\beta = 0.22$ accompanied by a slight reduction in the swollen thickness by 16%. However, when the surfactant concentration was increased to 10 mmol L^{-1}, a drastic change in the ellipsometric spectra is observed. β strongly increases to a value of 0.66, and the swollen thickness decreases by another 34% to 180 nm. With further increasing concentration, the swollen brush thickness again increases to 312 nm at 0.1 mol L^{-1} accompanied by an additional increase in β to 0.9.

The kinetics at the lowest concentration are examined in more detail in Figures 10 and 11. Figure 10 shows the Δ- and Ψ-traces of the PMAA brush swollen in

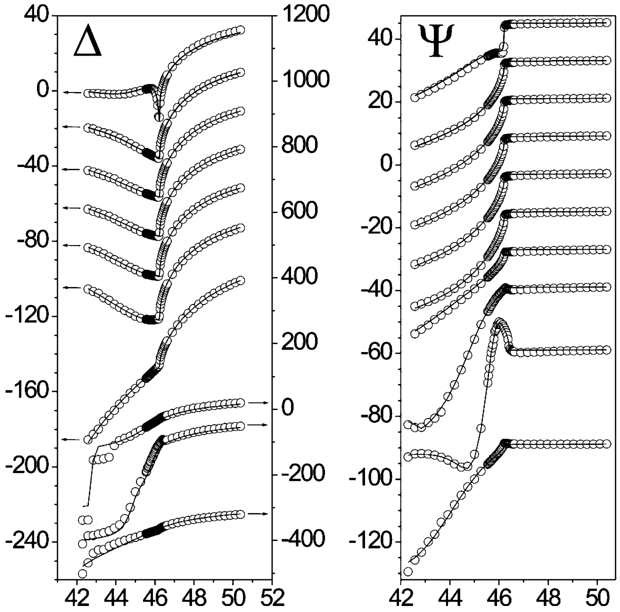

Figure 8. Ellipsometric spectra (Δ and Ψ as a function of the incidence angle) of a 37 nm (dry thickness) PMAA brush swollen in aqueous solutions of DDTAC at different concentrations. The spectra at the very top and the very bottom of each graph correspond to the brush swollen in deionized water before and after the adsorption of DDTAC, respectively. From the second spectrum to the second undermost, the concentrations were 10^{-5}, 10^{-4}, 3×10^{-4}, 10^{-3}, 3×10^{-3}, 10^{-2}, 3×10^{-2}, and 10^{-1} mol L^{-1}. Δ- and Ψ-traces were offset for clarity. The solid lines represent model calculations using a complementary error function to describe the refractive index profile at the interface.

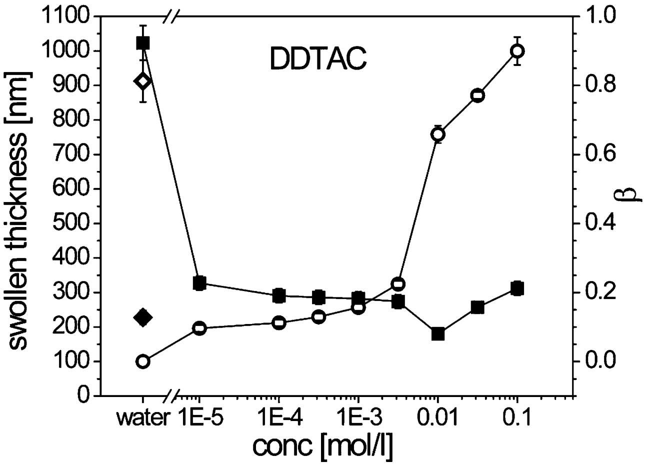

Figure 9. Swollen thickness (squares) and degree of binding β (open circles) of a PMAA brush (dry thickness = 37 nm) in contact with aqueous solutions of DDTAC as a function of the concentration. The brush was first swollen in pure, deionized water and then equilibrated with increasingly concentrated solutions of DDTAC. The swollen thickness in water (full diamond) and the total surfactant uptake β (open diamond) after surfactant exposure and repeated exposure of the monolayer to deionized water are also given.

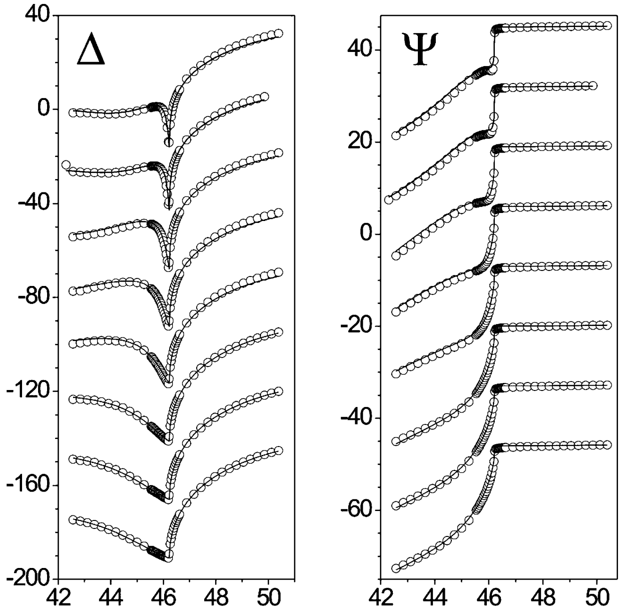

Figure 10. Representative ellipsometric spectra (Δ and Ψ as a function of the incidence angle) of a 37 nm (dry thickness) PMAA brush swollen in 10^{-5} mol L^{-1} aqueous solutions of DDTAC at different times. The spectra at the very top of each graph correspond to the brush swollen in deionized water. From the second spectrum to the bottom, the spectra were recorded at 0.5, 1, 2, 3, 5, 7.5, and 10 h after injection of the surfactant solution. Δ- and Ψ-traces were offset by −25° and −13°, respectively. The solid lines represent model calculations using a complementary error function to describe the refractive index profile at the interface.

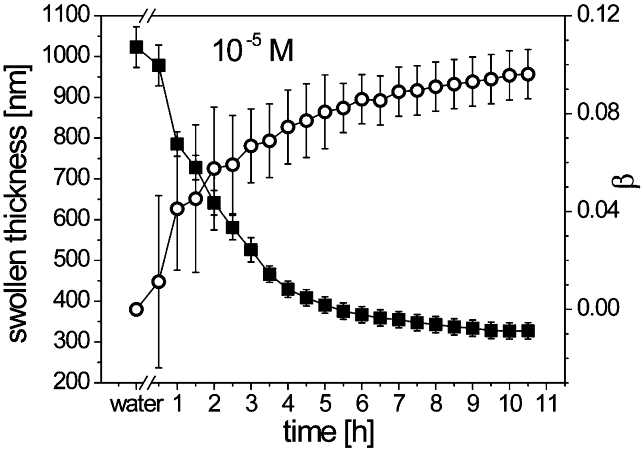

Figure 11. Swollen thickness (squares) and degree of binding β (open circles) of a PMAA brush (dry thickness = 37 nm) in contact with 10^{-5} mol L^{-1} aqueous solutions of DDTAC as a function of time. The first point corresponds to the brush swollen in deionized water.

deionized water (topmost graph) and in 10^{-5} mol L^{-1} solutions of DDTAC at different times (0.5, 1, 2, 3, 5, 7.5, and 10 h from top to bottom). Below the critical angle, the slopes of both the Ψ- and the Δ-trace are related to the swollen brush thickness with a steeper slope being indicative of a higher brush thickness for both functions.[33] From a visual inspection of the spectra it is obvious that the brush strongly deswells with time already at this low surfactant concentration. The corresponding plot of the evolution of the swollen brush thickness and the degree of binding β is shown in Figure 11. Within ≈10 h, the brush shrinks from ≈1023 to 327 nm, by more than 68%. At the same time β shows an inverse trend and levels off at a value of ≈0.1. At 10^{-5} mol L^{-1}, the number of surfactant molecules in the cell (cell volume was ≈1.5 mL) is of the same order of magnitude as the number of surface-bound polymer repetition units. Therefore, a depletion of the surfactant solution in the course of each measurement is likely. To ensure that the brush is in equilibrium with a 10^{-5} mol L^{-1} concentrated solution at the end of the kinetic experiment, the solution was renewed before every

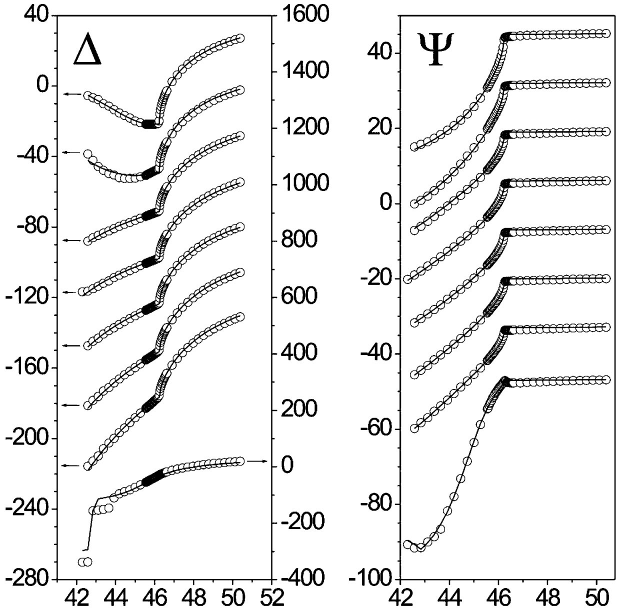

Figure 12. Ellipsometric spectra (Δ and Ψ as a function of the incidence angle) of a 37 nm (dry thickness) PMAA brush swollen in 10 mmol L^{-1} aqueous solutions of DDTAC at different times. The spectra at the very top and the very bottom of each graph correspond to the brush swollen in 3 and 32 mmol L^{-1} DDTAC solution, respectively. From the second spectrum to the second undermost, the spectra were recorded at 0.5, 1, 1.5, 2, 2.5, and 3 h after injection of the surfactant solution. Δ- and Ψ-traces were offset by −25° and −13°, respectively. The solid lines represent model calculations using a complementary error function to describe the refractive index profile at the interface.

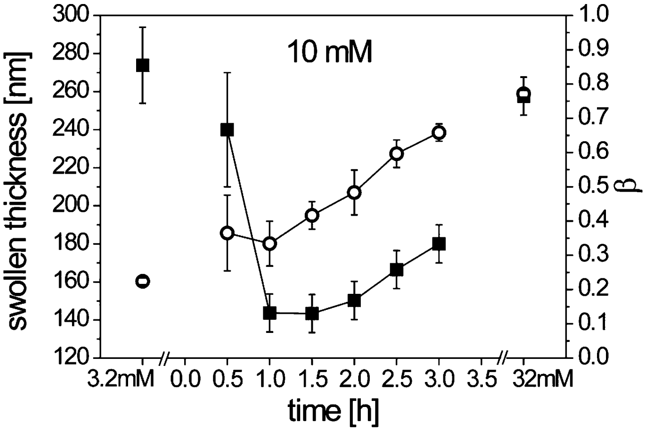

Figure 13. Swollen thickness (squares) and degree of binding β (open circles) of a PMAA brush (dry thickness = 37 nm) in contact with 10 mmol L^{-1} aqueous solutions of DDTAC as a function of time. The first and the last point correspond to the brush swollen in 3 and 32 mmol L^{-1} DDTAC solution, respectively.

second measurement. The periodic renewal of the solution should not influence the position of the equilibrium. The time, however, which is needed to reach an equilibrium is probably longer than that of a brush in contact with an infinite reservoir of 10^{-5} mol L^{-1} DDTAC solution. Interestingly, the swollen thickness shows a minimum at 10 mmol L^{-1} DDTAC. The brush thickness values at 0.3 and 32 mmol L^{-1} are very close, and at first glance, one might think that the brush remains largely unchanged in this concentration range. However, as we have seen, this is exactly the range where β strongly increases, and this is indeed reflected in a dramatic change of the Δ- and Ψ-traces between the two concentrations although the swollen thickness remains almost constant (Figure 8). To clarify the situation at 10 mmol L^{-1} DDTAC, the evolution of the ellipsometric spectra, the swollen thickness and β are shown in Figures 12 and 13 as a function of time. Whereas β almost linearly increases, the swollen brush thickness decreases, passes through a minimum at 143 nm, and then increases again. As a result, at 32 mmol L^{-1} the swollen brush thickness reaches a value which is very close to that at 3.2 mmol L^{-1}. These findings can only be explained by a change in the composition of the swollen polymer layer in the course of this experiment. Except for surfactant, the only species which is present in the swollen polymer layer and which is not covalently linked to the surface are water molecules. Therefore, the binding of surfactant, which is reflected in the increase in β, must be accompanied by a release of water molecules. This indicates that with increasing uptake of surfactant hydrophobic interactions become stronger, essentially leading to a dehydration or, equally, to a deswelling of the brush. Therefore, the evolution of the swollen brush thickness is governed by two opposing trends: First, the incorporation of hydrophobic surfactant leads to a dehydration of the brush which is reflected in a reduction of the swollen thickness by almost 50%. Then, the significant uptake in mass due to increasing surfactant binding leads to an increase in thickness. For comparison, in the case of PMAA brushes on silicon wafers of comparable graft density, the adsorption of DDTAC at 10 mmol L^{-1} resulted in an increase in dry thickness of about 200−250%.

To describe the situation more clearly, we have calculated the true swelling factor $Q = d_{\mathrm{swollen}}/d_{\mathrm{PSC}}$. Usually, for the calculation of a swelling factor, the swollen brush thickness d_{swollen} is referenced to the dry thickness d_{start} of the initial polymer brush before complex formation. However, as in the present case major amounts of material are becoming adsorbed, the inherent assumption that the zeroth moment stays constant in the course of the experiment is no longer true. Therefore, the true swelling factor is referenced to the thickness d_{PSC} which is the dry layer thickness after surfactant exposure and consequently surfactant uptake. d_{swollen} is directly measured and d_{PSC} can be calculated from β and the dry thickness d_{start} according to

$$d_{\mathrm{PSC}} = \beta \frac{M_{\mathrm{PSC}}}{M_{\mathrm{PMAA}}} d_{\mathrm{start}} + (1 - \beta) d_{\mathrm{start}} \qquad (7)$$

The data from Figures 9 and 13 are redrawn in Figure 14 in terms of the true swelling factor. Evidently, the major deswelling already at 10^{-5} mol L^{-1} DDTAC is confirmed in Figure 14a. Moreover, however, it becomes clear that, after the swollen brush thickness only slightly decreases with further increasing concentration, it undergoes a second deswelling at 10 mmol L^{-1}, where the strong increase in β was observed. In the course of this experiment, Q decreases from 27 to 7.0, i.e., by 74% when water is exchanged for 10^{-5} mol L^{-1} DDTAC solution. Then, in the second step at 10 mmol L^{-1}, Q declines from 4.6 to 1.8 or by a further 61% and only slightly increases again to 2.5, when the DDTAC concentration is further increased above the cmc to 0.1 mol L^{-1}. Figure 14b shows that in the course of the surfactant adsorption at 10 mmol L^{-1} DDTAC the true

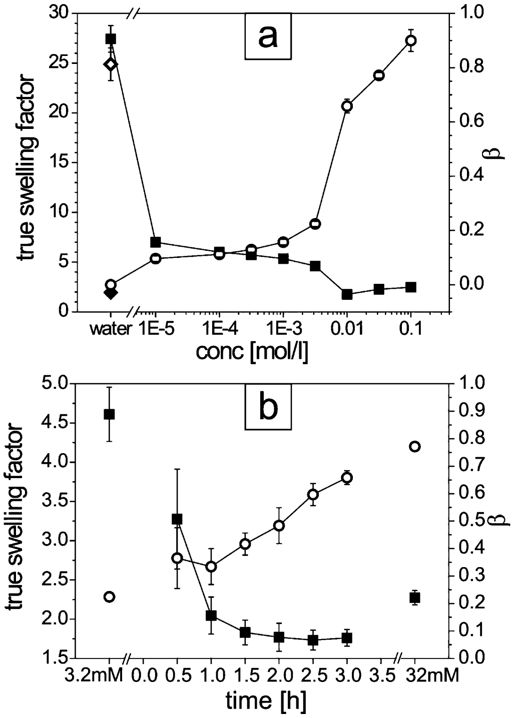

Figure 14. True swelling factor (squares) and degree of binding β (open circles) of a PMAA brush (dry thickness = 37 nm) in contact with (a) aqueous solutions of DDTAC as a function of the concentration and (b) 10 mmol L^{-1} aqueous solutions of DDTAC as a function of time. The data are redrawn from Figures 9 and 13 in terms of the true swelling factor.

swelling factor, unlike the swollen brush thickness (Figure 13), constantly decreases and remains even at the highest surfactant concentrations very low. Clearly, a massive adsorption of surfactant leads to a strong increase in d_{PSC} which accounts for the reduction in Q.

Finally, after the adsorption of DDTAC at the highest concentration (0.1 mol L^{-1}), the surfactant solution was replaced by deionized water. The respective ellipsometric spectra, the swollen thickness, Q, and β are included in Figures 8, 9, and 14a. A slight reduction in mass (β) is accompanied by a slight reduction in the swollen thickness. β is still very high (0.81), and the swollen brush thickness is 228 nm, 78% lower than the initial thickness of the brush swollen in deionized water. Q only takes a value of 1.9, close to its minimum value of 1.8, which corresponds to a reduction by 93% relative to the initial swelling factor. This clearly proves that no reswelling occurred if the brush was exposed to pure water. From d_{swollen} and Q, the dry thickness of the polymer–surfactant complex is calculated as 120 nm, a factor of more than 3 higher than the initial dry thickness, indicating that the complex is stable in deionized water.

Moreover, to see whether surfactant counterions can be replaced by a competitive interaction of the carboxylate groups with an inert salt, a PMAA brush was collapsed with 0.1 mol L^{-1} DDTAC and subsequently treated with deionized water and then with increasingly concentrated aqueous solutions of sodium nitrate (five exchange cycles at each concentration). No change in the ellipsometric spectra was observed upon addition of up to 0.1 mol L^{-1} inert salt, indicating that no significant amount of surfactant is released. At 1 mol L^{-1} a slight reswelling was found. However, the exchange of surfactant counterions for sodium ions at this concentration was far from complete. Even after exposure to this solution of high ionic strength, the brush exhibited after drying a significantly higher thickness than before surfactant complexation. We suppose that this behavior is due to the strong hydrophobic binding of the surfactant in addition to the purely electrostatic interactions typically found in the case of alkaline ions. The surfactant binding leads to a strong dehydration of the brush (associated with a strong deswelling) and the formation of strongly hydrophobic pockets which become largely inaccessible for water molecules, thus leading to a (largely) irreversible binding of the surfactant.

4. Discussion

For the understanding and practical application of polyelectrolyte brush–surfactant systems, two questions are of utmost importance, namely at what surfactant concentration major changes in the brush structure occur and how much surfactant is taken up.

Concerning the first question, the PMAA brush shows a strong deswelling upon interaction with DDTAC solutions already at very low surfactant concentrations where the degree of binding of the surfactant is low ($\beta < 0.1$). This corresponds directly to the situation with free polymer of similar structure in solution where addition of a small amount of such a surfactant causes phase separation to occur.[4] The same is true for water-swollen PAA gels at degrees of dissociation between $\alpha = 0.2$ and 1, which show a collapse at a critical concentration of added oppositely charged surfactant.[15,16,19] For the brush system studied here, the volume transition occurs at a concentration which is ≈3 orders of magnitude below the cac despite the fact that the increase in surfactant incorporation during the shrinkage of the brush is low. It is likely that this behavior can be attributed to the considerable increase of the hydrophobicity of the PMAA brushes when more and more protons are exchanged for long alkyl chain bearing counterions. When roughly 10% of the protons of the carboxylic acid groups are replaced by surfactant ions, the brush has reached a (quasi-?)equilibrium state. If β is plotted as a function of the square root of time (graph not shown), a linear relation is only found during the first 4 h, indicating that simple Fickian surfactant diffusion can be the rate-limiting step only during this first adsorption period. At longer times (compare Figure 10), surfactant diffusion may still be rate controlling. The non-Fickian behavior might arise from a gradual change in the chemical potential in the complexes and a concomitant change in the driving force for surfactant binding as a function of β. This change in the chemical potential results from a maximization of the hydrophobic interactions in the polymer–surfactant complex, which in turn requires a reorganization of the polymer chains and a displacement of water molecules from the brush. This conformational reorganization could also control the adsorption kinetics at longer times. It is interesting to note that even after very prolonged exposure to the surfactant solution the brush remains relatively strongly swollen, and even after significant surfactant uptake the brush still contains roughly 80–85 vol % water despite the strong hydrophobicity of the counterions.

To answer the second question, i.e., how much surfactant is taken up upon exposure of the brush to a surfactant solution, brushes of different graft density

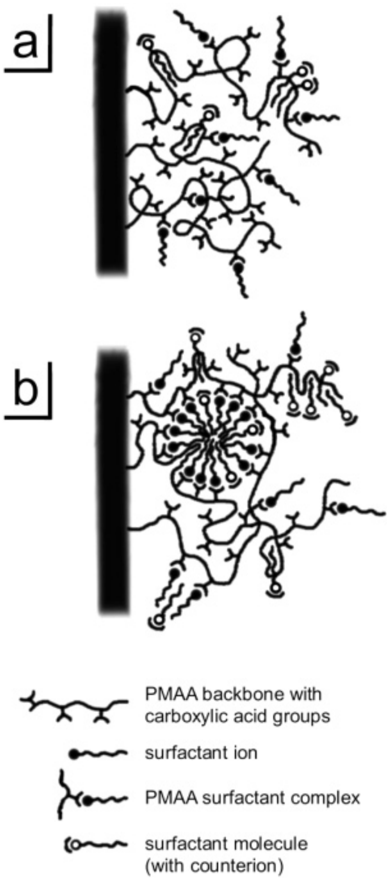

Figure 15. Schematic illustration of the binding of oppositely charged surfactant to PMAA brushes in the noncooperative (a) and the cooperative (b) binding regime.

were exposed to surfactant solutions whose concentration was also systematically varied. It was observed that the degree of binding β was low at concentrations below 3 mmol L^{-1} and strongly increased at 10 mmol L^{-1} DDTAC. Such a process where previously adsorbed surfactant molecules facilitate the adsorption of further surfactant is commonly denoted as cooperative binding. The strong increase in β was confirmed in two independent measurements, the increase in thickness of the dry polymer layers and the change in the total refractive index increment of the swollen polymer layers upon complexation. The degree of dissociation α, determined by infrared measurements, showed a similar trend. However, at all concentrations, i.e., in the noncooperative and in the cooperative binding regime, β was higher than α by a factor of $\approx$1.5−2.5, and with increasing concentration the difference between the absolute values of β and α became larger. This indicates that a fraction (on the order of 50%) of the surfactant is not bound electrostatically with a release of protons and surfactant counterions, but rather through hydrophobic interactions.

A schematic illustration how the processes can be envisioned on a molecular scale is shown in Figure 15. Below 10 mmol L^{-1} (Figure 15a), the surfactant binds in a noncooperative fashion, both electrostatically to carboxylic acid units and through hydrophobic interactions to the polymer backbone. The former process is accompanied by a release of protons and surfactant counterions, whereas in the latter process, surfactant counterions are incorporated into the polymer−surfactant complex. At around 10 mmol L^{-1}, cooperative binding occurs (Figure 15b). In this regime, again, both binding modes (electrostatic and hydrophobic) are present. No implication is made about the degree of association. However, it is likely that most of the surfactant associates into micelles or other surfactant aggregates rather than being bound in form of unimers. Sections of the hydrophobic polymer backbone may take part in the micelle formation as indicated in the figure; however, no information is so far available about the detailed structure of the micelles. This type of binding isotherm is well-known from studies of PMAA in solution.[5,6] For these systems a low cooperativity was found upon addition of surfactant at low concentration, followed by cooperative binding at higher concentrations.

We now compare the onset of cooperativity, i.e., the critical association concentration (cac) at which the presence of surfactant molecules facilitates the incorporation of further surfactant molecules, for a polyelectrolyte brush interacting with oppositely charged surfactant to the cac of similar systems where the polyelectrolyte is used free in solution or as a polymer gel. In the case of PMAA brushes, the DDTAC concentration where cooperative binding takes place is close to the cmc of this surfactant in water (18 mmol L^{-1}).[30] Usually, in the case of polyelectrolytes interacting with oppositely charged surfactants, cooperative binding is found at a concentration which is several orders of magnitude lower than the cmc of the corresponding surfactant in polymer-free solution.[34] This comparison between the literature results on free polymers and gels and the results obtained here on brushes is not trivial as the former studies focus on fully neutralized polyacids or strong polyelectrolytes, and additionally all measurements were carried out in highly diluted polymer solutions.

An interesting case is a comparison of the brush data presented here with the measurements of Hansson on free polymers in solution and gels.[12] Hansson has shown that the cac of dodecyltrimethylammonium bromide (DDTAB) interacting with sodium polyacrylate approximately linearly increases with the polymer concentration. Cross-linked sodium polyacrylate gels in the higher concentrated regime of this plot and sodium polyacrylate solutions in the lower concentrated regime all fall approximately on the same line, indicating that the surfactant assembly is largely unaffected by the exact polymer configuration, including the presence of cross-links. The average segment concentration in a brush depends of course on how strongly the brush is shrunken due to the presence of surfactant. If we calculate the average polymer segment concentration in the PMAA brush in the experiment with 3 mmol L^{-1} DDTAC (i.e., at the concentration closest to the onset of cooperative binding), we obtain on average over the whole brush $\approx$1.7 mol L^{-1}. If we extrapolate Hansson's plot to very high polymer concentrations, we obtain at this value a corresponding cac which is on the order of 10 mmol L^{-1}. This corresponds indeed to the surfactant concentration where we observed the onset of cooperative binding. Apparently, the polymer segment concentration is decisive for the cac whereas the exact conformation of the polymer is of minor importance. Therefore, the fact that in the case of PMAA brushes the cac is close to the cmc of the surfactant seems to be a result of the high polymer segment concentration in the brush.

Though the polyelectrolyte brush behaves similar to polyelectrolytes in solution with respect to the position of the cac, we observed pronounced differences in the way the degree of dissociation changes upon surfactant uptake. If bulk PAA, PMAA, or PAA gels are used in the fully protonated form ($\alpha = 0$), the addition of positively charged surfactant leads in all cases to an increase in α from 0 to 0.1–0.2.[4–6,16] If, however, the polyacid was partially neutralized to $\alpha \geq 0.2$ before the addition of surfactant, α did not further increase upon complexation. This indicates that at values of α in the range of 0.1–0.2 favorable contributions from electrostatic and hydrophobic interactions reach a maximum. In contrast to this, in the present investigation, the increase in α of the PMAA brushes upon addition of the surfactant was much more pronounced. The increase depended on the surfactant concentration and on the graft density of the brush and reached to values of up to 0.7 for the highest surfactant concentration and the lowest graft density. A reason for the striking difference might be the ionic strength of the solutions. Whereas in the above-mentioned studies on free polymers in solution and gels an inert salt was added in excess (several 10 mmol L^{-1}), only surfactant molecules were allowed to interact with the PMAA brushes. In such weak polyacid brushes, at very low ionic strength, protons are effectively confined inside the polymer brush to fulfill the electroneutrality condition. Even a very small charge density in the brush generates a high potential which opposes further dissociation so that charges on the tethered chains are effectively neutralized by protons. An increase in ionic strength, through the addition of an inert salt, however, facilitates the dissociation of the acid groups. Positively charged ions now penetrate into the brush and concomitantly allow protons to leave the brush. This leads to an increase in the degree of dissociation with increasing salt concentration in the so-called osmotic brush regime.[35] These purely electrostatically driven effects may even be reinforced if specifically interacting counterions are introduced as was shown in a recent publication.[28] The addition of monovalent silver ions, for instance, leads to a very strong dissociation of the carboxylic acid groups. Likewise, in the case of surfactant salts, both the osmotically driven exchange of protons for surfactant counterions and the specific binding of these counterions through the hydrophobic alkyl chain lead to high degrees of dissociation of the PMAA brushes. Interestingly, the binding of ODTAB leads to higher degrees of dissociation than the binding of DDTAC. The stronger specific interactions due to the longer alkyl chain length of ODTAB are likely to be the reason for this behavior.

A further important question is how the surfactant binding depends on the graft density of the PMAA brushes. The increasing suppression of the surfactant binding with increasing graft density in the cooperative binding regime is the result of two effects. First, the entropic constraints imposed by a densely grafted brush increase with the graft density. Accordingly, as the graft density increases, it will be increasingly energetically unfavorable for larger objects such as incorporated surfactant micelles to reside in the film. In that respect, the results obtained here agree with theoretical considerations of Currie et al., who predict a decreasing amount of surfactant adsorption onto neutral polymer brushes with increasing graft density.[23] Second, in the case of a weak polyacid, such as PMAA, a higher graft density results in higher carboxylic acid monomer unit concentrations in the brush. As the graft density increases, self-screening of the charges occurs, and the brushes become more and more neutral, effectively decreasing the acidity of the carboxylic acid groups. This effect opposes an electrostatic binding of the surfactant and could also be the reason for the preferential adsorption through hydrophobic interactions at the highest graft density.

Finally, we wish to comment on the influence of the surfactant alkyl chain length on the cac. Although we studied the adsorption of ODTAB onto PMAA brushes only at one concentration, 0.1 mmol L^{-1}, the strong binding and the strong dependencies of α and β on the graft density are very similar to the results obtained in 10 mmol L^{-1} DDTAC solution. This clearly indicates that the onset of cooperative binding, i.e., the cac, is shifted to lower surfactant concentrations by $\approx$2 orders of magnitude as the result of an elongation of the surfactant alkyl chain length by six C atoms, from C_{12} to C_{18}. Interestingly, the cmcs of the two surfactants show a similar dependence on the alkyl chain length. In similarity to the DDTAC case, the cac for the interaction of ODTAB with the PMAA brushes is therefore located at a value which is only slightly below the cmc of this surfactant in aqueous solution (0.3 mmol L^{-1}).[31] The fact that the cac scales with the surfactant alkyl chain length in the same manner as the cmc is in accordance with the findings of Cohen Stuart et al.[22] and indicates that in the process of cooperative binding of surfactant to the polymer brush surfactant aggregates are formed which have structures similar to those of surfactant micelles in solution.

5. Conclusions

Poly(methacrylic acid) brushes strongly interact with oppositely charged surfactant molecules. Already at concentrations of around 10^{-5} mol L^{-1}, the brush shrinks very strongly despite the fact that the amount of surfactant taken up at this concentration is relatively low. If the surfactant concentration is increased beyond these very low values, the total amount of surfactant absorbed by the brush increases up to concentrations of several mmol L^{-1} only slightly. At a critical concentration, slightly below the cmc of the surfactant, however, the brush takes up large amounts of surfactant and considerably shrinks further. At high surfactant concentrations the degree of binding reaches values close to 1. This corresponds to an increase in mass and accordingly in dry thinkness of the polymer layer of more than 250% due to the much higher molecular weight of the surfactant (228 g/mol) compared to the molecular weight of the repeat unit of the polymer (86 g/mol). In total, the concentration at which the shrinkage of the brush is strongest (10^{-5} mol L^{-1}) and where the highest amount of surfactant is taken up (10 mmol L^{-1}) are strongly decoupled. The brush is now strongly dehydrated, and many water molecules are replaced by surfactant. As the brush contains now strongly hydrophobic pockets, it cannot be reswollen in surfactant-free water, so that the surfactant uptake is completely irreversible. It is interesting to note that, especially in the high concentration regime and at the highest graft density, the surfactant is not only bound through electrostatic interactions, but a certain fraction of molecules are adsorbed through hydrophobic interactions. Furthermore, the surfactant uptake in the high concentration regime is strongly influenced by the graft density of the brush. These findings underline the fact that the interpretation of swelling data of polyelectrolyte brushes has to be made with great care and that even minute amounts of charged surfactants can have a very pronounced effect on the structure and properties of surface-attached polyelectrolyte chains.

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References and Notes

(1) Goddard, E. D.; Ananthapadmanabhan, K. P. In *Polymer-Surfactant Systems*; Kwak, J. C. T., Ed.; Surfactant Science Series 77; Marcel Dekker: New York, 1998.
(2) Bronstein, L. M.; Platonova, O. A.; Yakunin, A. N.; Yanovskaya, I. M.; Valetsky, P. M.; Dembo, A. T.; Makhaeva, E. E.; Mironov, A. V.; Khokhlov, A. R. *Langmuir* **1998**, *14*, 252−9.
(3) Guan, Y.; Cao, Y. P.; Peng, Y. X.; Xu, J.; Chen, A. S. C. *Chem. Commun.* **2001**, 1694−5.
(4) Fundin, J.; Hansson, P.; Brown, W.; Lidegran, I. *Macromolecules* **1997**, *30*, 1118−26.
(5) Kiefer, J. J.; Somasundaran, P.; Ananthapadmanabhan, K. P. *Langmuir* **1993**, *9*, 1187−92.
(6) Katsuura, H.; Kawamura, H.; Manabe, M.; Kawasaki, H.; Maeda, H. *Colloid Polym. Sci.* **2002**, *280*, 30−7.
(7) Kogej, K.; Theunissen, E.; Reynaers, H. *Langmuir* **2002**, *18*, 8799−805.
(8) Svensson, A.; Piculell, L.; Cabane, B.; Ilekti, P. *J. Phys. Chem. B* **2002**, *106*, 1013−8.
(9) Kasaikin, V. A.; Zakharova, J. A. *Colloids Surf. A* **1999**, *147*, 107−14.
(10) Shimizu, T. *Colloids Surf. A* **1995**, *94*, 115−23.
(11) Shimizu, T. *Colloids Surf. A* **1994**, *84*, 239−48.
(12) Hansson, P. *Langmuir* **1998**, *14*, 2269−77.
(13) Hansson, P. *Langmuir* **1998**, *14*, 4059−64.
(14) Hansson, P.; Schneider, S.; Lindman, B. *J. Phys. Chem. B* **2002**, *106*, 9777−93.
(15) Goransson, A.; Hansson, P. *J. Phys. Chem. B* **2003**, *107*, 9203−13.
(16) Sasaki, S.; Fujimoto, D.; Maeda, H. *Polym. Gels Networks* **1995**, *3*, 145−58.
(17) Sasaki, S.; Koga, S. *Macromolecules* **2004**, *37*, 3809−14.
(18) Kabanov, V. A.; Zezin, A. B.; Rogacheva, V. B.; Khandurina, Y. V.; Novoskoltseva, O. A. *Macromol. Symp.* **1998**, *126*, 79−94.
(19) Jeon, C. H.; Makhaeva, E. E.; Khokhlov, A. R. *Macromol. Chem. Phys.* **1998**, *199*, 2665−70.
(20) Piculell, L.; Lindman, B.; Karlström, G. In *Polymer-Surfactant Systems*; Kwak, J. C. T., Ed.; Surfactant Science Series 77; Marcel Dekker: New York, 1998.
(21) Linse, P.; Piculell, L.; Hansson, P. In *Polymer-Surfactant Systems*; Kwak, J. C. T., Ed.; Surfactant Science Series 77; Marcel Dekker: New York, 1998.
(22) Pyshkina, O.; Sergeyev, V.; Zezin, A.; Kabanov, V.; Gage, D.; Cohen Stuart, M. A. *Langmuir* **2003**, *19*, 2000−6.
(23) Currie, E. P. K.; van der Gucht, J.; Borisov, O. V.; Cohen Stuart, M. A. *Langmuir* **1998**, *14*, 5740−50.
(24) Currie, E. P. K.; van der Gucht, J.; Borisov, O. V.; Cohen Stuart, M. A. *Pure Appl. Chem.* **1999**, *71*, 1227−41.
(25) Prucker, O.; Rühe, J. *Macromolecules* **1998**, *31*, 592−601.
(26) Prucker, O.; Rühe, J. *Macromolecules* **1998**, *31*, 602−13.
(27) Prucker, O.; Rühe, J. *Langmuir* **1998**, *14*, 6893−8.
(28) Konradi, R.; Rühe, J. *Macromolecules* **2004**, *37*, 6954−61.
(29) Uzu, Y.; Saito, Y.; Yokoi, M. *Bull. Chem. Soc. Jpn.* **1989**, *62*, 1370−2.
(30) Baar, C.; Buchner, R.; Kunz, W. *J. Phys. Chem. B* **2001**, *105*, 2906−13.
(31) Bonilha, J. B. S.; Chiericato, G.; Martins-Franchetti, S. M.; Ribaldo, E. J.; Quina, F. H. *J. Phys. Chem.* **1982**, *86*, 4941−7.
(32) Habicht, J.; Schmidt, M.; Rühe, J.; Johannsmann, D. *Langmuir* **1999**, *15*, 2460−5.
(33) Biesalski, M.; Rühe, J.; Johannsmann, D. *J. Chem. Phys.* **1999**, *111*, 7029−37.
(34) Hansson, P.; Lindman, B. *Curr. Opin. Colloid Interface Sci.* **1996**, *1*, 604−13.
(35) Israëls, R.; Leermakers, F. A. M.; Fleer, G. J. *Macromolecules* **1994**, *27*, 3087−93.

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