

## Adsorption Characteristics of Stoichiometric and Nonstoichiometric Molecular Polyelectrolyte Complexes on Silicon Oxynitride Surfaces

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Adsorption properties of stoichiometric and nonstoichiometric polyelectrolyte complexes (PECs) have been investigated by means of dual polarization interferometry (DPI) and X-ray photoelectron spectroscopy (XPS). Poly(sodium styrenesulfonate) (NaPSS) of molecular weight 4300 g/mol was used as polyanion, and two bottle-brush copolymers possessing different molar ratios of the cationic segment methacryloxyethyltrimethylammonium chloride (METAC) and the nonionic segment poly(ethylene oxide) methyl ether methacrylate (PEO<sub>45</sub>MEMA) were used as polycations. They are referred to as PEO<sub>45</sub>MEMA:METAC-25 and PEO<sub>45</sub>MEMA:METAC-50, where the last digits denote the mol % of charged main-chain segments. The time evolution of the adsorbed amount, thickness, and refractive index of the PEC layers were determined in aqueous solution using DPI. We demonstrate that cationic, uncharged, and negatively charged complexes adsorb to negatively charged silicon oxynitride and that maximum adsorption is achieved when small amounts of PSS are present in the complexes. The surface composition of the adsorbed PEC layers was estimated from XPS measurements that demonstrated very low content of NaPSS. On the basis of these data, the PEC adsorption mechanism is discussed and the competition between PSS and negative surface sites for association with the cationic polyelectrolyte is identified as a key issue.

### Introduction

Polyelectrolyte complexes (PECs) are formed when a solution of cationic polyelectrolytes is mixed with a solution of anionic polyelectrolytes.<sup>1,2</sup> This self-assembly process is largely driven by electrostatics and the entropy gain due to counterion release.<sup>3</sup> The same mechanism is also of importance for the association between oppositely charged polyelectrolytes and surfactants,<sup>4</sup> colloidal particles,<sup>5</sup> and biomolecules.<sup>6</sup> Complex formation between oppositely charged polyelectrolytes has attracted a great deal of interest, mainly due to the use of PECs in a range of applications covering biotechnology,<sup>7,8</sup> medicine,<sup>7</sup> surface coatings,<sup>9</sup> and papermaking.<sup>10–13</sup> PECs have also found use in large-scale industrial applications as flocculants<sup>14</sup> and binders,<sup>15</sup> and it has

been found that the stability and rheology of colloidal suspensions can be significantly enhanced by employing PECs instead of polyelectrolytes.<sup>16</sup>

Soluble nonstoichiometric PECs are normally formed when polyelectrolytes are mixed with an excess of one type of polyion charge (either positive or negative). Systematic studies of the formation and structure of nonstoichiometric PECs have been reported by the groups of Tsuchida,<sup>17</sup> Dautzenberg,<sup>18</sup> and Kabanov,<sup>2,19</sup> and computer simulations performed by Linse<sup>20,21</sup> and Khokhlov<sup>22</sup> have increased our fundamental understanding significantly. The nonstoichiometric PECs are normally divided into two categories: (i) highly aggregated complexes consisting of several polyelectrolyte chains that are stabilized by the polyion in excess, which charges the PEC surface and prevents macroscopic precipitation; (ii) water-soluble molecular complexes that can form when special conditions are met.<sup>20</sup>

Stoichiometric polyelectrolyte complexes contain equal amounts of positive and negative charges. They are usually insoluble and precipitate out of solution upon formation.<sup>23</sup> However, the precipitation of stoichiometric PECs can be prevented if a hydrophilic nonionic block (e.g., poly(ethylene oxide) (PEO)) is attached to at

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(1) Philipp, B.; Dautzenberg, H.; Linow, K.-J.; Kotz, J.; Dawydoff, W. *Prog. Polym. Sci.* **1989**, *14*, 91.

(2) Kabanov, V. A. *Usp. Khim.* **2005**, *74*, 5.

(3) Bucur, C. B.; Sui, Z.; Schlenoff, J. B. *J. Am. Chem. Soc.* **2006**, *128*, 13690.

(4) Bain, C. D.; Claesson, P. M.; Langevin, D.; Meszaros, R.; Nylander, T.; Stubenrauch, C.; Titmuss, S.; von Klitzing, R. *Adv. Colloid Interface Sci.* **2010**, *155*, 32.

(5) Kötz, J.; Kosmella, S.; Beitz, T. *Prog. Polym. Sci.* **2001**, *26*, 1199.

(6) Cooper, C. L.; Dubin, P. L.; Kayitmazer, A. B.; Turksen, S. *Curr. Opin. Colloid Interface Sci.* **2005**, *10*, 52.

(7) Hartig, S. M.; Greene, R. R.; Dikov, M. M.; Prokop, A.; Davidson, J. M. *Pharm. Res.* **2007**, *24*, 2352.

(8) Hamman, J. H. *Mar. Drugs* **2010**, *8*, 1305.

(9) Zhang, L.; Sun, J. *Macromolecules* **2010**, *43*, 2413.

(10) Gernandt, R.; Wågberg, L.; Gärdlund, L.; Dautzenberg, H. *Colloids Surf., A* **2003**, *213*, 15.

(11) Gärdlund, L.; Wågberg, L.; Gernandt, R. *Colloids Surf., A* **2003**, *218*, 137.

(12) Ankerfors, C.; Lingstrom, R.; Wågberg, L.; Odberg, L. *Nordic Pulp Pap. Res. J.* **2009**, *24*, 77.

(13) Gärdlund, L.; Norgren, M.; Wågberg, L.; Marklund, A. *Nordic Pulp Pap. Res. J.* **2007**, *22*, 210.

(14) Bolto, B.; Gregory, J. *Water Res.* **2007**, *41*, 2301.

(15) Mihai, M.; Dragan, E. S. *Colloids Surf., A* **2009**, *346*, 39.

(16) Petzold, G.; Mende, M.; Lunkwitz, K.; Schwarz, S.; Buchhammer, H. M. *Colloids Surf., A* **2003**, *218*, 47.

(17) Eishun Tsuchida, Y. O. K. S. *J. Polym. Sci., Part A: Polym. Chem.* **1972**, *10*, 3397.

(18) Thunemann, A. F.; Muller, M.; Dautzenberg, H.; Joanny, J. F. O.; Lowne, H. Polyelectrolyte Complexes. In *Polyelectrolytes With Defined Molecular Architecture II*; Springer: Berlin, 2004; Vol. 166, p 113.

(19) Kabanov, A. V.; Kabanov, V. A. *Bioconjugate Chem.* **1995**, *6*, 7.

(20) Hayashi, Y.; Ullner, M.; Linse, P. *J. Phys. Chem. B* **2004**, *108*, 15266.

(21) Ryden, J.; Ullner, M.; Linse, P. *J. Chem. Phys.* **2005**, *123*.

(22) Kramarenko, E. Y.; Pevnaya, O. S.; Khokhlov, A. R. *J. Chem. Phys.* **2005**, *122*.

(23) Tsuchida, E. *J. Macromol. Sci., Chem.* **1994**, *A31*, 1.

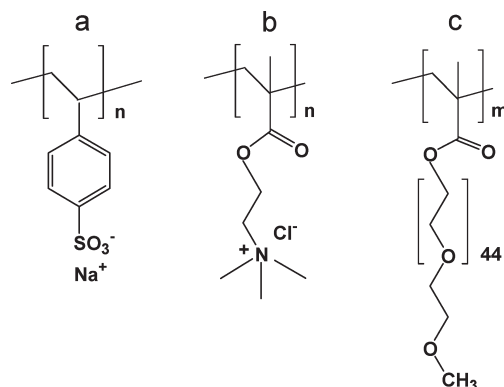
least one of the polyelectrolytes.<sup>24,25</sup> In such a case uncharged water-soluble PECs are formed, comprised of a water-insoluble core (the insoluble PEC) surrounded and stabilized by a hydrophilic PEO corona. Bottle-brush polyelectrolytes, with a charged backbone and hydrophilic PEO side chains, provide an alternative strategy to prepare water-soluble stoichiometric PECs with oppositely charged linear polyelectrolytes.<sup>26–28</sup>

In contrast to the abundant work on polyelectrolyte association in bulk, the literature on the adsorption properties of PECs at solid–liquid interfaces is limited. In early studies, PEC adsorption was investigated on silica particles.<sup>29,30</sup> More recently, investigation of PEC adsorption has been performed on macroscopic planar substrates using surface sensitive techniques such as quartz crystal microbalance (QCM)<sup>31,32</sup> and DPI.<sup>33</sup>

The adsorption of nonstoichiometric PECs, prepared from the cationic poly(diallyldimethylammonium) chloride and the anionic maleic acid-*co*-propene copolymer, on a silica wafer surface has been studied by direct force measurements utilizing an atomic force microscope. Drastic changes in the interaction forces were found due to PEC adsorption.<sup>34</sup> The adsorption behavior of PECs formed by assembly of weak polyelectrolytes, poly(methacrylic acid) and poly[(dimethylamino)ethyl methacrylate], has also been studied and compared to adsorption of the ampholytic diblock copolymer PMAA-*b*-PDMAEMA on silica surfaces.<sup>35</sup>

Regular and consecutive adsorption of negatively and positively charged PECs on planar silica surfaces have also been studied systematically.<sup>36</sup> More recently, the surface properties of centrifuged nonstoichiometric PEC dispersions were investigated at polyelectrolyte multilayer-modified silicon surfaces, and the adsorption data were fitted by the classical Langmuir model.<sup>37</sup> The adsorption kinetics of PECs on silica has been investigated by Kekkonen and co-workers, and they suggest five different types of adsorption kinetics.<sup>38</sup> A recent study by Saarinen et al.<sup>39</sup> compared the surface properties achieved with polyelectrolyte multilayers and PECs on silica and cellulose surfaces. Further, nonstoichiometric PEC nanoparticles have been assembled into multilayer films on flat substrates,<sup>9,40</sup> using the layer-by-layer method.

Youyong Xu and co-workers have recently presented an AFM study on water-soluble complexes formed by assembly of cationic cylindrical polyelectrolyte brushes and linear anionic polyelectrolytes, and a transition in PEC geometry was demonstrated.<sup>41</sup>



**Figure 1.** Schematic representation of the molecular structure of the segments in the polyelectrolytes used: (a) NaPSS, (b) METAC, and (c) PEO<sub>45</sub>MEMA.

The present work aims at clarifying the adsorption properties of sterically stabilized PECs that are soluble as molecular complexes at all stoichiometries due to the presence of a high density of poly(ethylene oxide) side chains. Particularly, we aim to understand how the adsorbed mass and the structure of the adsorbed layer depend on the PEC stoichiometry and how the composition of the adsorbed layer differs from that of the PECs present in solution.

The report presents results for mixtures of poly(sodium styrenesulfonate) (NaPSS) with two different cationic bottle-brush copolymers with different charge density. The adsorption of stoichiometric and nonstoichiometric PECs on silicon oxynitride was investigated using DPI and XPS. The physical characteristics of the adsorbed layers, i.e., adsorbed mass, layer thickness, and refractive index, were determined from DPI measurements. However, DPI does not provide any chemical information. For this reason XPS was employed to elucidate the composition of the adsorbed layer. Results from these two techniques provide insights into the mechanism of PEC adsorption and a detailed picture of the structure of the adsorbed layer.

## Materials and Methods

**Materials.** Poly(sodium styrenesulfonate) (NaPSS) standard ( $M_w = 4300 \text{ g mol}^{-1}$ ,  $M_w/M_n = 1.2$ ) was purchased from Fluka and used as received. Copolymers of methacryloxyethyltrimethylammonium chloride (METAC) and poly(ethylene oxide) methyl ether methacrylate (PEO<sub>45</sub>MEMA) with two distinct molar ratios were synthesized by free-radical copolymerization as reported previously.<sup>42</sup> This results in close to random copolymers, having a polydispersity index of around 2–3, typical for polymers prepared by this method. Henceforth, PEO<sub>45</sub>MEMA:METAC-*X* represents the general abbreviation of these brush copolymers. The subscript 45 refers to the number of ethylene oxide units in the side chains, and *X* denotes the molar percentage of charged units in the mainchain (*X* = 50, 25 in this study).

The molecular structures of the monomer units are schematically depicted in Figure 1. The short and linear polyanion NaPSS is composed of only one type of monomer, as illustrated in Figure 1a. The two types of monomer units in the bottle-brush copolymers are shown in Figure 1b,c. The polyions used in this study are classified as strong polyelectrolytes.

The water used in all experiments was first pretreated with a Milli-RO 10 Plus unit and then further purified with a Milli-Q PLUS 185 system. The resistivity after the treatment was 18.2 MΩ cm, and the total organic carbon content of the water did not exceed 2 ppb. Sodium chloride was purchased from Fluka.

(42) Naderi, A.; Iruthayaraj, J.; Vareikis, A.; Makuska, R.; Claesson, P. M. *Langmuir* **2007**, *23*, 12222.

- (24) Cohen Stuart, M. A.; Hofis, B.; Voets, I. K.; de Keizer, A. *Curr. Opin. Colloid Interface Sci.* **2005**, *10*, 30.
- (25) Sotiropoulou, M.; Bokias, G.; Staikos, G. *Biomacromolecules* **2005**, *6*, 1835.
- (26) Larin, S. V.; Pergushov, D. V.; Xu, Y.; Darinskii, A. A.; Zezin, A. B.; Muller, A. H. E.; Borisov, O. V. *Soft Matter* **2009**, *5*, 4938.
- (27) Shovsky, A. V.; Varga, I.; Makuska, R.; Claesson, P. M. *J. Dispersion Sci. Technol.* **2009**, *30*, 980.
- (28) Shovsky, A.; Varga, I.; Makuska, R.; Claesson, P. M. *Langmuir* **2009**, *25*, 6113.
- (29) Kramer, G.; Buchhammer, H. M.; Lunkwitz, K. *Colloids Surf., A* **1997**, *122*, 1.
- (30) Buchhammer, H.-M.; Petzold, G.; Lunkwitz, K. *Langmuir* **1999**, *15*, 4306.
- (31) Ankerfors, C.; Ondaral, S.; Wågberg, L.; Ödberg, L. *J. Colloid Interface Sci.* **2010**, *351*, 88.
- (32) Olanya, G.; Iruthayaraj, J.; Poptoshev, E.; Makuska, R.; Vareikis, A.; Claesson, P. M. *Langmuir* **2008**, *24*, 5341.
- (33) Swann, M. J.; Peel, L. L.; Carrington, S.; Freeman, N. J. *Anal. Biochem.* **2004**, *329*, 190.
- (34) Estel, K.; Kramer, G.; Schmitt, F. J. *Colloids Surf., A* **2000**, *161*, 193.
- (35) Mahltig, B.; Gohy, J. F.; Jerome, R.; Buchhammer, H. M.; Stamm, M. *J. Polym. Sci., Part B: Polym. Phys.* **2002**, *40*, 338.
- (36) Reihls, T.; Müller, M.; Lunkwitz, K. *Colloids Surf., A* **2003**, *212*, 79.
- (37) Reihls, T.; Müller, M.; Lunkwitz, K. *J. Colloid Interface Sci.* **2004**, *271*, 69.
- (38) Kekkonen, J.; Lattu, H.; Stenius, P. *J. Colloid Interface Sci.* **2001**, *234*, 384.
- (39) Saarinen, T.; Österberg, M.; Laine, J. *Colloids Surf., A* **2008**, *330*, 134.
- (40) Schuetz, P.; Caruso, F. *Colloids Surf., A* **2002**, *207*, 33.
- (41) Xu, Y.; Borisov, O. V.; Ballauff, M.; Muller, A. H. E. *Langmuir* **2010**, *26*, 6919.

**Dynamic Light Scattering.** Bulk properties of the individual polyelectrolytes and the PECs were determined by means of laser light scattering. Dynamic light scattering (DLS) measurements were conducted with a Brookhaven Instruments (USA) device, which consists of a BI-200SM goniometer and a BI-9000AT digital autocorrelator. A water-cooled argon ion laser, Lexel 95 model 2, was used as light source. The laser was used at a wavelength of 514.5 nm and emitted vertically polarized light at a maximum power of 840 mW. In DLS mode the signal analyzer was used in a “multi tau” mode; i.e., the time axis was logarithmically spaced to span the required correlation time range. The autocorrelation functions were measured at an angle of 90° in 218 channels using a 100  $\mu\text{m}$  pinhole size.

The measured autocorrelation functions were analyzed by the CONTIN and the second-order cumulant methods. The samples were found to be polydisperse, having a wide monomodal size distribution. Despite the polydispersity of the samples, the mean hydrodynamic diameter (the first cumulant of the second order cumulant expansion) is used for the presentation of the changes in the hydrodynamic size distribution. This can be done since neither the composition of the copolymer nor the complex formation changed significantly the character of the size distribution, as evidenced by the CONTIN analysis. For polydisperse systems, the first cumulant represents the  $z$ -average of the diffusion coefficient.<sup>43</sup> At finite concentrations and  $q$  values, an apparent diffusion coefficient is obtained ( $D_{\text{app}}$ ), and by using the Einstein–Stokes equation, the apparent hydrodynamic radius of the PEC particles could be determined

$$R_H = \frac{kT}{6\pi\eta D_{\text{app}}} \quad (1)$$

where  $k$  is the Boltzmann constant,  $T$  the absolute temperature,  $\eta$  the viscosity of the medium, and  $R_H$  the hydrodynamic radius. The autocorrelation functions were analyzed with the software supplied by Brookhaven Instruments. The results of 30 consecutive measurements were averaged for each PEC sample.

**Electrophoretic Mobility Measurements.** The electrophoretic mobility of the aggregates was measured using a Zeta-sizer 2000 device (Malvern Instruments, UK) in 5 mM NaCl solution at  $T = 25^\circ\text{C}$ . The instrument was calibrated prior to measurements using Malvern Zeta Potential transfer standard (code DTS-1050).

**Dual-Polarization Interferometry.** Dual-polarization interferometry (DPI) is a relatively new technique, able to measure changes in thickness and refractive index of adsorbed layers *in situ* and in real time. The instrument used was an AnaLight Bio200 from Farfield Sensors Ltd. (Manchester, UK). The instrument consists a helium–neon laser (emitting light at 632.8 nm), a means to select plane-polarized light, a sensor constructed using two optical waveguides stacked one on the top of the other, and a camera. A detailed description of the instrument is provided by Swann et al.<sup>33</sup> The core of this instrument is the substrate surface, which is a sandwichlike chip structure of two horizontally stacked waveguides made of silicon oxynitride, i.e., nitrogen-doped silica. This substrate is preferred due to its excellent optical properties with low absorption losses in the visible and near-IR region combined with a high refractive index (about 1.5). Silicon oxynitride has an isoelectric point at pH 3, and the zeta-potential at pH 6 is about  $-50$  mV as determined by streaming potential measurements.<sup>44</sup> When plane-polarized laser light is shone on the short end of the surface, it splits and travels separately through the two waveguides (sensing and reference). As it emerges on the other side of the chip, the two signals interfere with each other, and this interference is detected by a camera as a fringe pattern in the far field. The evanescent field emitted by the sensing

**Table 1. Refractive Index Increment of Polyelectrolytes and Polyelectrolyte Complexes**

substance	$dn/dc$ ( $\text{cm}^3/\text{g}$ )
NaPSS	0.180
PEO <sub>45</sub> MEMA:METAC-50	0.144
PEO <sub>45</sub> MEMA:METAC-25	0.139
PEO <sub>45</sub> MEMA:METAC-50/NaPSS 2:1	0.142
PEO <sub>45</sub> MEMA:METAC-50/NaPSS 1:1	0.140
PEO <sub>45</sub> MEMA:METAC-50/NaPSS 1:2	0.138
PEO <sub>45</sub> MEMA:METAC-25/NaPSS 2:1	0.137
PEO <sub>45</sub> MEMA:METAC-25/NaPSS 1:1	0.135
PEO <sub>45</sub> MEMA:METAC-25/NaPSS 1:2	0.134

waveguide into the solution is affected by changes in the index of refraction and by adsorption onto the surface. Hence, the light propagating through the sensing waveguide is somewhat changed relative to the light traveling through the reference waveguide. This difference is detected as a shift in the fringe pattern in the far field, and these shifts are alternately and continuously recorded for both horizontally and vertically polarized light. By assuming formation of a homogeneous and isotropic adsorption layer, a unique solution for the thickness and refractive index of the layer can be calculated from the measured DPI signals.<sup>45</sup> The adsorbed mass was calculated using eq 2 and the refractive index increments,  $dn/dc$ , provided in Table 1.

$$\Gamma = \frac{d_f(n_f - n_{\text{buffer}})}{dn/dc} \quad (2)$$

A 100  $\mu\text{m}$  thick silicon mask with two slits is placed on top of the waveguide chip. As the chip is mounted in the instrument, these two slits create two separate flow channels, 1 mm wide and 17 mm long, which constitute the actual 1.7  $\mu\text{L}$  measurement chambers. Solution is continuously flowed through the channels by use of a syringe pump (model PHD200, Harvard Apparatus, Holliston, MA), and samples are injected through an HPLC valve and can be directed to flow through both or just one of the two channels. Before the adsorption is started, the instrument and the waveguide are calibrated by injecting two solutions of known index of refraction, in this case 5 mM NaCl aqueous solution and ethanol (80%).

**X-ray Photoelectron Spectroscopy.** The chemical composition of the adsorbed PEC layer was analyzed using X-ray photoelectron spectroscopy. The XPS spectra were recorded using a Kratos AXIS Ultra X-ray photoelectron spectrometer (Kratos Analytical, Manchester, UK). The samples were analyzed using a monochromatic Al X-ray source, illuminating a sample area of less than 1  $\text{mm}^2$ . First, a wide spectrum was recorded in order to detect the elements present in the surface layer. Next, high-resolution spectra were recorded for each element, and the surface composition was determined from such spectra, using peak areas and sensitivity factors provided by Kratos Analytical.

**Experimental Procedures.** Stock solutions of the polycations with a concentration of 5000 ppm were prepared in 5 mM sodium chloride. NaPSS stock solutions were prepared in 5 mM NaCl in such a manner that the concentrations of the anionic charges from PSS were equal to the concentrations of cationic charges from the bottle-brush polyelectrolytes in their stock solutions. The polyelectrolyte stock solutions were vigorously stirred for  $\sim 24$  h and thereafter filtered employing a 0.1  $\mu\text{m}$  inorganic membrane filters (Whatman, Anotop 25). All dilutions were made using 5 mM NaCl, and all samples were prepared at room temperature ( $\sim 25^\circ\text{C}$ ).

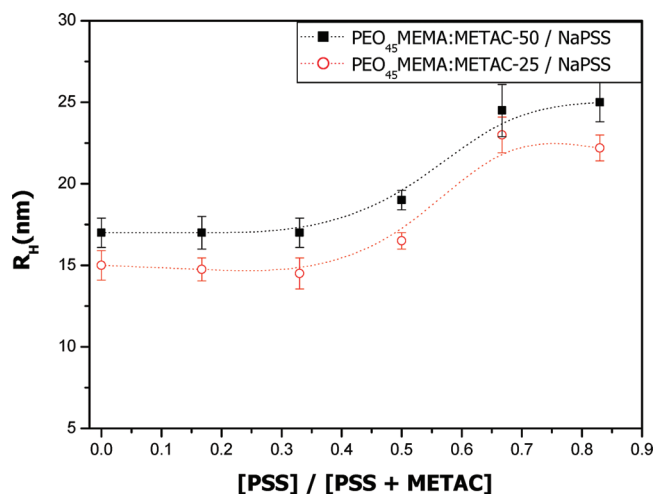
The PECs were formed by means of an automatic mixing process, using a programmable infusion pump (model PHD200, Harvard Apparatus, Holliston, MA). Mixing is achieved by simultaneous

(43) Schmitz, K. S. *An Introduction to Dynamic Light Scattering by Macromolecules*; Academic Press Limited: London, 1990.

(44) Krivocheeva, O.; Dedinaite, A.; Claesson, P. M. Manuscript in preparation.

(45) Cross, G. H.; Reeves, A.; Brand, S.; Swann, M. J.; Peel, L. L.; Freeman, N. J.; Lu, J. R. *J. Phys. D: Appl. Phys.* **2004**, *37*, 74.





**Figure 2.** Hydrodynamic radius ( $R_H$ ) of complexes containing PEO<sub>45</sub>MEMA:METAC-50 (squares) and PEO<sub>45</sub>MEMA:METAC-25 (circles) as a function of the charge fraction of NaPSS. The solution contained 5 mM NaCl and 50 ppm of PEO<sub>45</sub>MEMA:METAC-25(50). Each data point represents measurements performed on separately prepared PEC samples.

injection of the two polyelectrolyte solutions (2.5 cm<sup>3</sup> from each) via small diameter tubes ( $d = 1$  mm) into 5 cm<sup>3</sup> of continuously stirred 5 mM NaCl solution. The applied infusion rate was 1 cm<sup>3</sup>/min. The final volume of the PEC containing solution was 10 cm<sup>3</sup>. Complexes of the following stoichiometrical ratios 5:1, 2:1, 1:1, 1:2, and 1:5 between cationic groups from PEO<sub>45</sub>MEMA:METAC- $X$  and anionic groups from NaPSS were investigated. We note that the ratio 1:1 corresponds to electroneutral stoichiometric PECs, 5:1 and 2:1 represent positively charged complexes, and 1:2 and 1:5 correspond to negatively charged PECs.

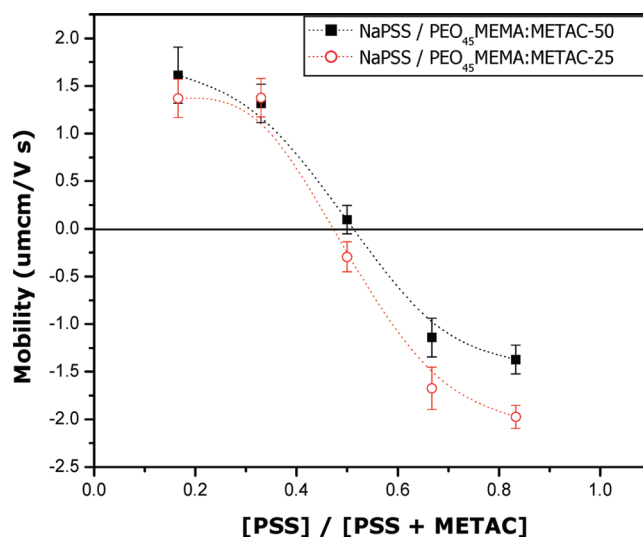
The DPI chip surface was cleaned by using the following steps: (i) dipping in a 1:1 mixture of HCl (37%) and CH<sub>3</sub>OH(abs) for 15 min, (ii) rinsing with water, (iii) dipping in a 2% surfactant-free Deconex 20 NS (Fisher Scientific) for 15 min, (iv) rinsing with water, and finally it was kept in water for 12 h. The chip surface was prior to measurements additionally cleaned by injection of a surfactant-free solution of Deconex 20 NS (2%) for 20 min and then rinsing with water until stable DPI signals were achieved (30 min). We found that this cleaning procedure provided hydrophilic surfaces and results with good reproducibility. For DPI measurements, solutions of PECs were freshly prepared to contain a concentration of cationic bottle brush polymer of 100 ppm. The concentrations were then adjusted to 10, 20, and 50 ppm by using aqueous 5 mM NaCl solution. The PEC solutions were injected into the measurement cell, and the adsorption process was followed in real time. The rinsing buffer was aqueous 5 mM NaCl solution. The flow rate used in our experiments was 50  $\mu$ L/min, and all measurements were carried out at 20 °C.

Silicon oxynitride wafers for XPS measurements were cut into square-shaped pieces (1  $\times$  1 cm<sup>2</sup>) and cleaned by using the same protocol as for DPI measurements. They were immersed in freshly prepared PEC solutions (50 ppm with respect to the cationic component) in aqueous 5 mM NaCl solution for 24 h. Finally, the samples were rinsed with water and dried in a nitrogen stream just prior to XPS analysis.

## Results

**Dynamic Light Scattering.** The hydrodynamic radii,  $R_H$ , of the brush polyelectrolytes as well as of the PECs were determined by DLS measurements in aqueous 5 mM NaCl solution. The  $R_H$  values determined for PEO<sub>45</sub>MEMA:METAC-25 and PEO<sub>45</sub>MEMA:METAC-50 were 15 and 17 nm, respectively.

The hydrodynamic radius, plotted as a function of the charge fraction of NaPSS in the PECs, is reported in Figure 2. The data



**Figure 3.** Electrophoretic mobility vs PSS content for (■) PEO<sub>45</sub>MEMA:METAC-50/NaPSS and (○) PEO<sub>45</sub>MEMA:METAC-25/NaPSS. The concentration of the cationic polymer was fixed to 50 ppm. The horizontal line represents zero value. Each data point represents measurements performed on separately prepared PEC samples.

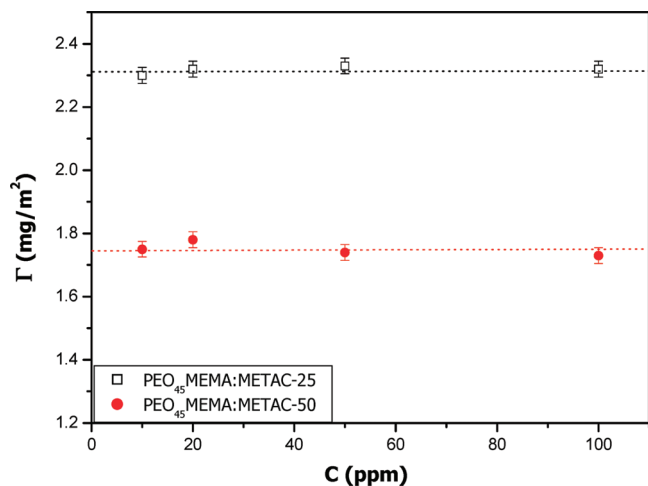
sets obtained with the two different bottle-brush polyelectrolytes show the same trend. An increase in NaPSS content, expressed by the ratio  $[PSS]/([PSS] + [METAC])$ , from 0 to 0.35 hardly affects the hydrodynamic size of the PECs. A further increase in PSS content results in a clear increase in the hydrodynamic radius to a value of 23 nm for complexes with PEO<sub>45</sub>MEMA:METAC-25 and to 25 nm for complexes with PEO<sub>45</sub>MEMA:METAC-50.

Complex formation was supported by the fact that the scattered light intensity increased for cationic PEC samples compared to the scattered intensity measured for the pure bottle-brush polyelectrolytes and additionally by measurements of the electrophoretic mobility (see Figure 3). Hence, we conclude that the hydrodynamic size for both types of complexes PEO<sub>45</sub>MEMA:METAC-25/NaPSS and PEO<sub>45</sub>MEMA:METAC-50/NaPSS increases in the order 1:0  $\approx$  5:1  $\approx$  2:1 < 1:1 < 1:2  $\approx$  1:5. The size of the NaPSS by itself was too small to be determined even when a high concentration was used (5000 ppm).

Since the hydrodynamic radius is unaffected when a small amount of PSS is incorporated in the complex, we conclude that the short and linear NaPSS present in cationic and uncharged PECs are located close to the backbone of the larger brush polyelectrolyte. In contrast, the hydrodynamic radius increases as the PECs become negatively charged, suggesting that the NaPSS chains are extended away from the backbone.

**Dual Polarization Interferometry. Adsorption of Bottle-Brush Polyelectrolytes: Effect of Polyelectrolyte Concentration.** Adsorption of the bottle-brush polyelectrolytes PEO<sub>45</sub>MEMA:METAC-25 and PEO<sub>45</sub>MEMA:METAC-50 on silicon oxynitride surfaces was performed from aqueous 5 mM NaCl. For a concentration of the polyelectrolytes of 10 ppm at 20 °C, adsorption equilibrium was reached within 10 min. The adsorbed amount for PEO<sub>45</sub>MEMA:METAC-25 was determined to be 2.3 mg/m<sup>2</sup>, larger than the 1.7 mg/m<sup>2</sup> obtained for PEO<sub>45</sub>MEMA:METAC-50. Both values are slightly lower than reported for the adsorption of these brush polyelectrolytes from water, revealed by DPI.<sup>46</sup> A further subsequent increase in polyelectrolyte concentration to 20, 50, and

(46) Bijelic, G.; Shovsky, A.; Varga, I.; Makuska, R.; Claesson, P. M. *J. Colloid Interface Sci.* **2010**, *348*, 189.



**Figure 4.** Adsorbed mass vs polyelectrolyte concentration for PEO<sub>45</sub>MEMA:METAC-25 (open squares) and PEO<sub>45</sub>MEMA:METAC-50 (closed circles) on silicon oxynitride in contact with aqueous 5 mM NaCl. The adsorption isotherms were obtained by increasing the polymer concentration stepwise.

100 ppm did not affect the adsorbed mass as illustrated in Figure 4. Hence, full coverage of the surface was reached when both polyelectrolytes were adsorbed from 10 ppm solution, indicating a high affinity to the surface. The thickness of the layers, 11.0 nm for PEO<sub>45</sub>MEMA:METAC-25 and 7.3 nm for PEO<sub>45</sub>MEMA:METAC-50, was also not affected by the polyelectrolyte concentration in the investigated concentration range and slightly lower than observed in salt-free water.<sup>46</sup>

**Electrophoretic Mobility.** The PECs were also characterized by electrophoretic mobility measurements, as shown in Figure 3. The data for both types of PEC show the same trend. The mobility decreases as the PSS content in the solution is increased. Positive values were observed for PECs prepared in solution with excess cationic bottle-brush polymer, a close to zero mobility was found for PECs formed from stoichiometric solutions, and significant negative mobility values were detected for PECs prepared from solution with excess NaPSS. These electrophoretic mobility data suggest strong complexation and formation of stoichiometric PECs when the polycation and polyanion are in equal (charge) quantities.

**Adsorption of PECs: Effect of PEC Concentration.** Adsorption of PEO<sub>45</sub>MEMA:METAC-25/NaPSS and PEO<sub>45</sub>MEMA:METAC-50/NaPSS complexes with stoichiometric and nonstoichiometric compositions on silicon oxynitride surfaces was performed under identical experimental conditions as used in the adsorption experiments for the bottle-brush polyelectrolytes. As illustrated in Figure 5, the concentration of the PECs has no significant effect on the final adsorbed mass for any PEC composition.

**Adsorption of PECs: Effect of PEC Composition.** As illustrated in Figure 5, the composition of the PECs has a pronounced effect on the adsorbed mass with cationic PECs adsorbing more than uncharged ones, and even less adsorption is achieved by the anionic PECs. This suggests that electrostatic forces are of major importance for the adsorption of these PECs to silicon oxynitride, and this will be elaborated further in the Discussion section. For both stoichiometric and nonstoichiometric compositions the adsorbed amounts of the PEO<sub>45</sub>MEMA:METAC-50/NaPSS complexes were found to be lower than those obtained by the PEO<sub>45</sub>MEMA:METAC-25/NaPSS complexes.

The adsorbed amount and layer thickness as a function of the ratio  $[\text{PSS}]/([\text{PSS}] + [\text{METAC}])$  are illustrated in Figure 6. For both bottle-brush polyelectrolytes we note that the adsorbed mass and the

layer thickness reach a maximum at a ratio of about 0.3, corresponding to 2:1 complexes.

The adsorbed mass of PEO<sub>45</sub>MEMA:METAC-25 in the absence of NaPSS was 2.3 mg/m<sup>2</sup> in 5 mM NaCl, while the thickness was found to be 7.1 nm. The presence of a small amount of NaPSS (5:1) in the PECs increased the adsorbed mass to 2.7 mg/m<sup>2</sup> and the thickness to 10 nm. Maximum adsorption was obtained for positively charged complexes with composition 2:1, the numerical value was found to be 2.9 mg/m<sup>2</sup>, and the corresponding film thickness was 11.1 nm. A further increase in PSS content resulted in decreasing adsorbed mass, to about 0.2–0.3 mg/m<sup>2</sup> for anionic complexes, and layer thickness. Thus, we note that anionic complexes adsorb to some extent on the negatively charged surface. In contrast, no adsorption was detected for pure NaPSS.

The effect of the PSS content on the adsorption of PEO<sub>45</sub>MEMA:METAC-50/NaPSS complexes show the same general pattern as observed for the complexes formed with PEO<sub>45</sub>MEMA:METAC-25 as the cationic component. However, both the adsorbed mass and thickness are significantly lower when PEO<sub>45</sub>MEMA:METAC-50 is used as the cationic component as compared to when PEO<sub>45</sub>MEMA:METAC-25 is employed.

**X-ray Photoelectron Spectroscopy: Composition of Adsorbed Layers.** In order to determine the composition of the adsorbed complexes, the surface layers formed by cationic and uncharged complexes were examined by XPS spectroscopy. A quantitative analysis is complicated by the fact that nitrogen is present in both the polyelectrolyte and the substrate surface. However, the chemical shifts are quite different, with the nitride peak being located at a binding energy of 398 eV and that of charged ammonium at 402 eV, and therefore the nitrogen arising from the polyelectrolyte can be identified. The substrate has no interfering photoelectron peaks in the sulfur region, and thus the presence of PSS would be easily detected. However, in all cases the sulfur peak was very small or even below the detection limit (about 0.1 atom %). Thus, in most cases the ratio between the cationic polyelectrolyte and PSS cannot be determined, but we can only provide a lower limit to this ratio. Nevertheless, it is clear that the adsorbed layer contains less PSS than the complexes formed in bulk solution as seen by the data reported in Table 2.

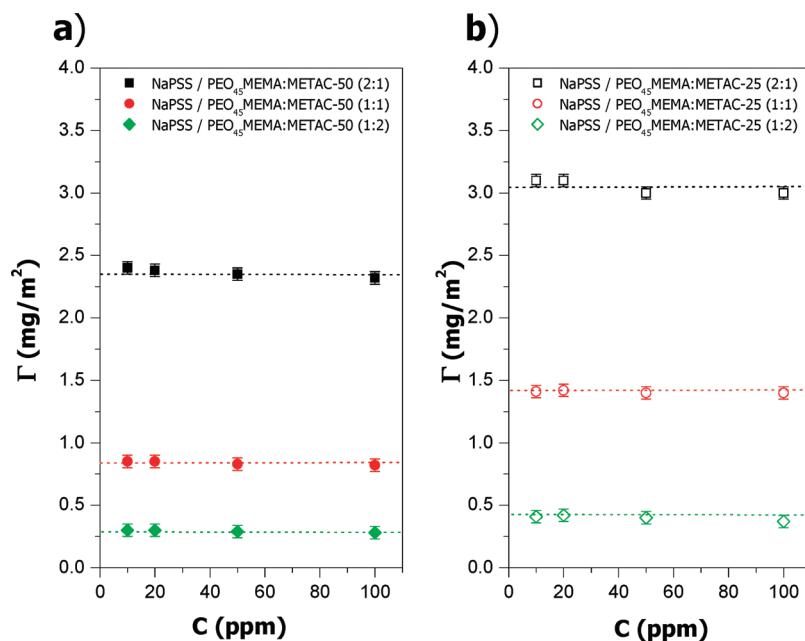
## Discussion

**PEO<sub>45</sub>MEMA:METAC-X Adsorption to Silicon Oxynitride.** The adsorption of PEO<sub>45</sub>MEMA:METAC-X bottle-brush polyelectrolytes to silicon oxynitride from water has previously been investigated with DPI<sup>46</sup> and shown to be driven by both electrostatic interactions and attractive interactions between the PEO side chains and the surface. Similar conclusions have been reached for the adsorption of these polymers onto silica<sup>32</sup> and by lattice mean-field calculations.<sup>47,48</sup> On silicon oxynitride the maximum adsorbed amount was obtained for PEO<sub>45</sub>MEMA:METAC-25, whereas on silica it was obtained for PEO<sub>45</sub>MEMA:METAC-10 with somewhat lower charge. The uncharged bottle-brush poly(PEO<sub>45</sub>MEMA) also adsorbs to silicon oxynitride, but to a rather small amount, 0.8 mg/m<sup>2</sup>, forming a 2 nm thick adsorption layer.<sup>46</sup>

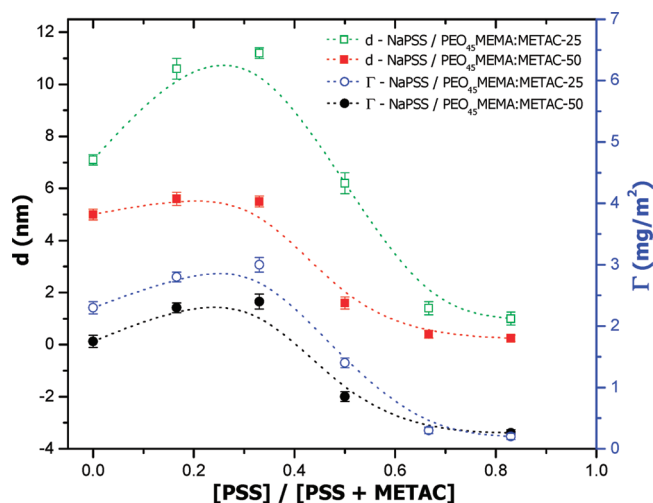
**Adsorption of Cationic PEO<sub>45</sub>MEMA:METAC-X/NaPSS Complexes.** The cationic complexes formed between NaPSS and the cationic bottle-brush polyelectrolytes have an electrostatic affinity for the surface. Further, the conformation of the large bottle-brush polyelectrolyte is not significantly disturbed by association with the small PSS as demonstrated by dynamic light scattering measurements. Thus, for these complexes we

(47) Linse, P.; Claesson, P. M. *Macromolecules* **2009**, *42*, 6310.

(48) Linse, P.; Claesson, P. M. *Macromolecules* **2010**, *43*, 2076.



**Figure 5.** Adsorbed mass as a function of (a) PEO<sub>45</sub>MEMA:METAC-50 concentration in solutions containing NaPSS/PEO<sub>45</sub>MEMA:METAC-50 complexes (closed symbols) and (b) PEO<sub>45</sub>MEMA:METAC-25 concentration in solution containing NaPSS/PEO<sub>45</sub>MEMA:METAC-25 complexes (open symbols). The adsorption isotherms were obtained by increasing the PEC concentration stepwise.



**Figure 6.** Adsorbed mass and layer thickness as a function of PSS content in NaPSS/PEO<sub>45</sub>MEMA:METAC-25 and NaPSS/PEO<sub>45</sub>MEMA:METAC-50 complexes adsorbed on silicon oxynitride. Squares correspond to layer thickness, and circles to adsorbed amount. Each data point was obtained from a separately prepared sample. The error bars show the standard deviation from four separate measurements. The concentration of the cationic polyelectrolyte was in each case 50 ppm.

expect the adsorption to be driven by both electrostatic forces and the side chain–surface affinity. Thus, one reason why the adsorption increases due to addition of a small amount of NaPSS is suggested to be that larger amount of polymer is needed in order to neutralize the surface charge density. Furthermore, the brush polymer is expected to retain some of the PSS polyions even in its surface bound state, which further increases the adsorbed amount. The fact that the XPS analysis of the surface layer demonstrates that the complex composition changes in the direction toward less PSS in the adsorbed complexes does not invalidate this explanation.

**Table 2. Chemical Composition of Adsorbed PECs**

	bulk composition N/S	surface composition N/S
PEO <sub>45</sub> MEMA:METAC-25/NaPSS	5:1	> 8:1
PEO <sub>45</sub> MEMA:METAC-25/NaPSS	2:1	> 6:1
PEO <sub>45</sub> MEMA:METAC-25/NaPSS	1:1	3.6:1
PEO <sub>45</sub> MEMA:METAC-50/NaPSS	5:1	> 7:1
PEO <sub>45</sub> MEMA:METAC-50/NaPSS	2:1	> 5:1
PEO <sub>45</sub> MEMA:METAC-50/NaPSS	1:1	> 3:1

The bulk composition expressed as ratio of nitrogen (from PEO<sub>45</sub>MEMA:METAC-X) to sulfur (from PSS) compared with the same ratio in the adsorbed layer.

**Adsorption of Uncharged Complexes.** The uncharged poly-(PEO<sub>45</sub>MEMA) adsorbs significantly less than PEO<sub>45</sub>MEMA:METAC-25 to silicon oxynitride.<sup>46</sup> The uncharged complex formed between PEO<sub>45</sub>MEMA:METAC-X and NaPSS is similar to poly(PEO<sub>45</sub>MEMA) in that it is a close to uncharged entity (see mobility data in Figure 3) with a typical bottle-brush conformation in bulk solution. Provided all PSS remained in the complex during adsorption, the complex would anyway be able to adsorb due to the affinity between the side chains and the surface. Indeed, this seems reasonable considering that the adsorbed mass of the stoichiometric complexes, about 1 mg/m<sup>2</sup>, is comparable to that of poly(PEO<sub>45</sub>MEMA). However, the XPS results must also be considered, and they demonstrate a considerable loss of PSS from the complexes during the adsorption. Thus, the adsorption cannot be rationalized by only considering adsorption via the uncharged side chains. Rather, the XPS data suggest that the adsorption process should be considered as being due to an ion exchange reaction, where negative surface sites and negative sites on PSS compete for binding to the positive charges on the bottle-brush polymer. Thus, the reduced adsorption for the stoichiometric



complexes is primarily due to the competing binding possibility to PSS.

**Adsorption of Negatively Charged Complexes.** Our data illustrate that adsorption also occurs in the presence of negatively charged complexes, but to a significantly smaller extent than observed for the stoichiometric complexes. This is a consequence of the increased competition from the negative charges in PSS that counteracts binding to the negative surface sites. It has been shown that the surface–side chain affinity is of importance during the initial adsorption of PEO<sub>45</sub>MEMA:METAC-X on silicon oxynitride, and it is suggested that this is the case also for both stoichiometric and nonstoichiometric complexes. It is conceivable that the side-chain affinity to the surface allows anionic complexes to reside next to the surface, despite the electrostatic repulsion. When this occurs, a fraction of the small PSS molecules desorb from the complex, and this facilitates some adsorption. Because of the low adsorbed amount achieved from solutions of anionic complexes, XPS data become unreliable, and thus our suggestion of desorption of PSS from anionic complexes should be viewed as a logical extrapolation of the data obtained for cationic and uncharged complexes.

**Comparison with Other Adsorption Studies of Complexes.** Adsorption of negatively charged complexes to anionic surfaces has previously been demonstrated. For instance, adsorption of negatively charged complexes formed by the association of oppositely charged linear acrylamides on silica surfaces has been demonstrated by QCM-D measurements.<sup>39</sup> The authors suggested that decomplexation of negatively charged PECs occurs, and only the positively charged component of the PEC adsorbs to the silica surface. The data presented in this work support the hypothesis that the PEC component having the same charge as the surface is able to, at least partly, desorb from the complex during the PEC adsorption event.

Adsorption properties of cationic polyelectrolyte–anionic surfactant complexes on negatively charged mica surface have previously been studied using the surface force apparatus and XPS.<sup>49</sup> It was found that these complexes adsorb on negatively charged mica surfaces regardless of the sign of their own charge. Thick layers were formed for close to uncharged complexes, whereas highly negatively charged aggregates adsorbed in rather thin layers. The adsorbed layers were characterized by XPS measurements, and a small amount of surfactant was detected in the thin layers formed by the negatively charged complexes, whereas large amount of SDS was revealed in the thicker layers built by the close to uncharged complexes. However, in all cases the amount of SDS within the adsorbed layer was found to be less than in the complexes formed in bulk solution, suggesting, just as in our case, that the low molecular weight anionic component is able to leave the complex to facilitate adsorption to the negatively charged surface.

Wågberg et al. studied adsorption of positively and negatively charged PECs composed of weak polyelectrolytes poly(allylamine) and poly(acrylic acid) on kraft lignin films.<sup>50</sup> Positively charged PECs adsorbed in high amounts and electrostatic interactions between the negatively charged lignin model surfaces and cationic PECs were dominant. Anionic PECs adsorbed in lower amount compared to cationic PECs. The authors concluded that nonelectrostatic interactions contributed to the adsorption process, despite the electrostatic repulsion.

The nonelectrostatic interactions between the PEC and the surface could assist the PEC to overcome the repulsive barrier and adsorb to the surface. The strength of the nonionic interaction is

generally system specific and thus dependent on both the characteristics of the polyelectrolyte and the chemistry of the substrate. The data presented in this article suggest that compositional changes in the PECs occurring during adsorption also should be considered then discussing polymer adsorption.

## Conclusions

The adsorption behavior of water-soluble stoichiometric and nonstoichiometric polyelectrolyte complexes was investigated by DPI and XPS. Two large bottle-brush polyelectrolytes with different charge densities were used as polycations, and a short chain linear NaPSS was employed as polyanion. It was shown that PECs of PEO<sub>45</sub>MEMA:METAC-25/NaPSS adsorbed in greater amounts and formed thicker layers on silicon oxynitride compared to PECs of PEO<sub>45</sub>MEMA:METAC-50/NaPSS, independently of the stoichiometric composition. This is suggested to be a consequence of the higher electrostatic affinity to the surface for PEO<sub>45</sub>MEMA:METAC-50.

Cationic, uncharged, and negatively charged complexes adsorb to the negatively charged silicon oxynitride surface, and the adsorbed amount is highest for cationic complexes with moderate NaPSS content. Thus, PEC formation can under optimal conditions increase the adsorption over that of any of the individual polyelectrolytes alone. This has been noted previously for large PEC aggregates and is true also for the molecular PECs utilized in the present investigation. The adsorption achieved for the stoichiometric PECs is considerably less than obtained for cationic PECs. We argue that this is due to competition between anionic surface sites and anionic sulfate groups in PSS for association with the cationic charges present in the bottle-brush polyelectrolyte. This competition leads to removal of a fraction of the PSS in the PECs during the adsorption process. In the anionic PECs this competition is shifted in favor of PSS, and as a consequence the adsorbed amount becomes low—but not zero. Our data demonstrate that the composition of adsorbed PECs can be significantly different to that of the PECs formed in bulk solution.

The adsorption characteristics of the PECs are strongly affected by their stoichiometric composition in bulk solution. The adsorbed mass and layer thickness decrease in the order 5:1  $\approx$  2:1 > 1:0 > 1:1 > 1:2  $\approx$  1:5 > 0:1. In contrast, the adsorbed amount is insensitive to the PEC concentration. The hydrodynamic size for both PEO<sub>45</sub>MEMA:METAC-25/NaPSS and PEO<sub>45</sub>MEMA:METAC-50/NaPSS PECs increases in the order 1:0  $\approx$  5:1  $\approx$  2:1 < 1:1 < 1:2  $\approx$  1:5. This demonstrates that PSS in the cationic complexes are residing close to the backbone, and only in the negatively charged complexes do these chains extend sufficiently to increase the hydrodynamic radius of the complex to values above that of the cationic bottle-brush polymer alone.

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(49) Dedinaite, A.; Claesson, P. M. *Langmuir* **1999**, *16*, 1951.

(50) Norgren, M.; Gärdlund, L.; Notley, S. M.; Htun, M.; Wågberg, L. *Langmuir* **2007**, *23*, 3737.