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## Specific Ion versus Electrostatic Effects on the Construction of Polyelectrolyte Multilayers<sup>†</sup>

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Self-assembled multilayers of a strong polyanion, poly(sodium 4-styrenesulfonate) (PSS), and a strong polycation, poly[(diallyl-dimethyl-ammonium chloride)-*stat*-(*N*-methyl-*N*-vinyl acetamide)] (P(DADMAC-*stat*-NMVA)), are fabricated on silicon substrates. This article addresses the effect of electrostatics versus ion specificity. Therefore, multilayer formation and growth are investigated as a function of the charge density of the polycation, the type of salt in the polyelectrolyte dipping solution, and its ionic strength. This study focuses on monovalent ions (Li<sup>+</sup>, Na<sup>+</sup>, K<sup>+</sup>, Cs<sup>+</sup>, Rb<sup>+</sup>, F<sup>-</sup>, Cl<sup>-</sup>, Br<sup>-</sup>, and ClO<sub>3</sub><sup>-</sup>). Ellipsometry and X-ray reflectometry data indicate that anions have a significantly larger effect on the thickness of the multilayer, but contrary to other studies on ion-specific effects, the influence of the type of cation is *not* negligible at higher salt concentrations. Larger ions, with smaller hydration shells, are highly polarizable and consequently interact strongly with charged polyelectrolytes, resulting in thicker and rougher multilayers. AFM studies confirm a higher roughness of the multilayer prepared from larger anions. The substrate can mask ion-specific effects over a distance of about 10 nm. Ion-specific effects become important above an ionic strength of 0.1 M in the case of anions and above an ionic strength of 0.25 M for cations. At lower ionic strengths, electrostatic interactions between and within the polyelectrolyte chains are dominating. Reducing the degree of polymer charge down to 75% does not shift this threshold of ionic strength. It is shown that a combination of ionic strength, polymer charge, and type of ion is a suitable tool for tuning the mobility and stability of polyelectrolyte multilayers.

### Introduction

In the early 1990s, Decher et al.<sup>1,2</sup> developed the layer-by-layer (LbL) technique whereby polyelectrolyte multilayers are deposited by the alternate adsorption of polyanions and polycations, from aqueous solutions, onto a charged substrate surface. This type of coating has many advantages such as easy thickness control, functionalization, and no limitation with respect to the shape or size of the template.<sup>3–5</sup> This makes the LbL technique a versatile and interesting tool for many technical applications such as sensor coatings. The properties are summarized in many review articles<sup>6–9</sup>

and books or book chapters.<sup>10–12</sup> Current issues such as the permeability (or porosity)<sup>13,14</sup> of these multilayers and their response to external stimuli<sup>8,9,15</sup> are of great interests, and therefore a control and understanding of the internal structure is required. The internal structure of the deposited polyelectrolyte multilayer is determined by the conformation of the polyelectrolyte chains in solution, which in turn is governed by parameters such as the degree of charge of the polyelectrolyte,<sup>16–21</sup> the pair of polyelectrolytes,<sup>16–28</sup> the ionic

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**Table 1. Compilation of Some Relevant Properties of Ions, Extracted from Reference 42**

	ionic radii/pm			polarizability, $\alpha/10^{-6} \text{ m}^3/\text{mol}$			volume of solvated ions/ $\text{cm}^3\text{mol}^{-1}$	
	Gold Schmidt	Pauling	Marcus	Heyd- Weller	Fajans-35	Pauling	Millero	Akitt
$\text{Li}^+$	78	60	71	0.12	0.12	0.07	−6.40	−6.40
$\text{Na}^+$	98	95	97	0.65	0.64	0.46	−6.70	−6.70
$\text{K}^+$	133	133	141	2.71	2.70	2.12	3.50	3.50
$\text{Rb}^+$	149	148	150	4.10	4.23	3.57	8.60	8.50
$\text{Cs}^+$	165	169	173	6.71	6.98	6.15	15.80	15.80
$\text{F}^-$	133	136	124	2.27	2.17	2.65	4.30	4.30
$\text{Cl}^-$	181	181	180	8.57	8.62	9.30	23.30	23.30
$\text{Br}^-$	196	195	198	12.22	12.23	12.14	30.20	30.20
$\text{I}^-$	220	216	225	18.68	18.78	18.07	41.70	41.70
$\text{SCN}^-$				17.33			41.20	41.20
$\text{ClO}_3^-$	200	200		12.40			42.20	42.20
$\text{IO}_3^-$				18.71	19.01		30.80	31.60
$\text{ClO}_4^-$			241	12.89	12.80		49.60	49.50
$\text{BrO}_3^-$				15.58			40.80	40.80

strength, the type of salts,<sup>26–31</sup> and the pH of the solution.<sup>32,33</sup> With decreasing degree of polymer charge or increasing ionic strength, the polyelectrolyte chains become more coiled as a result of the reduction in electrostatic repulsion along the polyelectrolyte chains, leading to thicker and rougher multilayers. Below a certain charge threshold no multilayer is formed, which might give a hint as to the electrostatic driving forces. This is supported by surface potential measurements that show mostly charge overcompensation after each adsorption step.

However, from an energetic point of view the charge overcompensation is not favorable.<sup>8,34</sup> In the last few years, much effort has been devoted to ionic effects in different systems, which also hints that electrostatic interaction is not the only factor that governs LbL deposition.<sup>35–39</sup> During multilayer buildup, polyelectrolytes are in solution (and thus hydrated) and then are transported to a charged surface where they anchor via complexation. Polyion pairing is known to be athermal and is facilitated by an entropy gain due to the release of counterions originally neutralizing the polyelectrolytes in solution. In addition, multilayers can still be built up at high ionic strengths, where the electrostatic attraction between the surface and the adsorbing oppositely charged polyelectrolytes should be screened.

It is well known that the addition of salt induces changes in the water structure,<sup>40,41</sup> and it is likely to be different depending not only on the ionic charge and the ion size but also on the type of ions in the salt solution; see Table 1.<sup>42,43</sup> Ions have been ranked in the Hofmeister series<sup>44</sup> according to their ability to precipitate a

given protein. Lewith<sup>45</sup> and Hofmeister<sup>44,46</sup> published accounts of great differences between the minimum concentrations of various salts required to precipitate a given protein from solution, even among those with identical charge characteristics. Because of these variations, the relative positions of the ions in the series should be thought of merely as indicative because they depend on the properties being investigated to establish that order.<sup>47,48</sup> For example, the relative order of cations may reverse with different anions under some circumstances as a result of ion pair effects.<sup>49</sup> Ions that have weaker interactions with water than water itself are known as structure breakers or chaotropes, whereas ions having the opposite effect, that is, exhibiting stronger interactions with water molecules, are known as structure makers or kosmotropes.<sup>50</sup> Femtosecond spectroscopy showed that for all ions the dynamics of water is reduced only within the hydration shell and that the structure of the bulk water is not affected.<sup>51</sup> These results mean that no long-range structure-making or structure-breaking effects exist and that the ion-specific effects are caused by short-range (direct) contact between, for example, the polyelectrolyte and the small ion. Many experiments can be explained by the size, charge density, and related polarizability of the small ions, but there are some experiments that show reverse effects of the same ion series in the presence of different macromolecules, micelles, or vesicles. That shows clearly that the respective small ions cannot be considered independently but that the specific interactions between the small ion and the respective macromolecule or aggregate have to be taken into account.<sup>40,52,53</sup>

There exists a very intricate interplay of different contributions from ion–water, surface–water, surface–ion, polyelectrolyte–water, polyelectrolyte–ion, and surface–polyelectrolyte<sup>54,55</sup> interactions; these determine the conformation of the polyelectrolyte in solution. This in turn dictates the conformation in which it is adsorbed, thereby controlling the amount and thickness of the

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adsorbed polyelectrolyte layer.<sup>29–31</sup> It has been shown that at high ionic strength (above 0.1 M), where the electrostatic interactions are partially screened, the interion interactions are controlled by dispersion forces that depend on the polarizability of the ionic species.<sup>56</sup> Because of such a wide spectrum of experimental observations of ion-specific effects, the modern approach is not to study the ion alone but instead models are being developed that depend upon direct ion–macromolecule interactions as well as interactions with water molecules in the first hydration shell of the macromolecule.<sup>56–64</sup>

Often the problem of interactions between ions and macromolecules or aggregates is broken down to the adsorption of ions at a nonpolar surface. Recent simulations of the adsorption of ions at nonpolar interfaces show that polarizable force fields and nonpolarizable force fields give very similar results. This might indicate that the ion hydrophobicity rather than the polarizability is the decisive parameter.<sup>64</sup> Experimentally, the effects of ion size, polarizability, and hydrophobicity are not distinguished because all of these parameters are highly correlated. As for polyelectrolyte multilayers, most studies have been done on systems prepared from NaCl solutions, and very few systematic investigations of ions on both sides of Na<sup>+</sup> and Cl<sup>−</sup> ions have been done.<sup>29–31</sup> Beside these studies, the effect of the nature of salts on polyelectrolyte multilayer formation and growth is not well documented, and it is still not yet fully understood. Recent studies showed that the mobility of polyelectrolyte chains within the multilayer increases when Br<sup>−</sup> ions instead of Cl<sup>−</sup> ions are used during multilayer preparation.<sup>65</sup> Such an observation is clearly indicative that the choice of counterions might give new opportunities to control the mobility and therefore the sensitivity to external parameters. Therefore, more effort should be spent on studying these parameters.

In an attempt to understand multilayer growth and formation, one needs to take into account the previously neglected importance of ions. Herein, the following salts have been chosen to study the effects of cations and anions on the formation and growth of polyelectrolyte multilayers: LiCl, NaCl, KCl, RbCl, CsCl, NaF, NaBr, NaI, NaClO<sub>3</sub>, NaSCN, and NaClO<sub>4</sub>. To obtain information on the effect of electrostatics versus ion specificity on the formation and growth of polyelectrolyte multilayers, the present article focuses on three factors that determine the chain conformation and the complex architectural density within the deposited multilayers: the charge density of the polymer, the ionic strength of the polyelectrolyte dipping solutions, and the type of salt.

## Experimental Section

**Materials.** A strong polycation, poly[(diallyl-dimethyl-ammonium chloride)-*stat*-(*N*-methyl-*N*-vinyl acetamide)], was employed in the self-assembly of multilayers studied in the present work. P(DADMAC-*stat*-NMVA) is a linear statistical copolymer consisting of positively charged diallyl-dimethylammoniumchloride

(DADMAC) monomers and neutral *N*-methyl-*N*-vinylacetamide (NMVA) monomers. Details about the synthesis and characterization of P(DADMAC-*stat*-NMVA) are described elsewhere.<sup>66,67</sup> As well as the homopolymer, poly(diallyl-dimethyl-ammonium chloride) or PDADMAC(100%), copolymers with linear charge densities of 89, 75, and 50%, noted as PDADMAC(89%), PDADMAC(75%), and PDADMAC(50%), respectively, were also studied. The molecular weight ( $M_w$ ) is about 100 000 g/mol. Branched polyethylenimine ( $M_w$  = 750 000 g/mol) (PEI) and poly(styrene sulfonate) sodium salt ( $M_w$  = 70 000 g/mol) (PSS) were purchased from Aldrich (Steinheim, Germany). The polyelectrolyte dipping solutions of 10<sup>−2</sup> M (based on the monomer unit) were freshly prepared from 0.1, 0.25, and 0.5 M LiBr, NaCl, KCl, RbCl, CsCl, LiBr, NaBr, KBr, NaClO<sub>3</sub>, and NaF in 18 MΩ cm Millipore water. NaI, NaSCN, and NaClO<sub>4</sub> precipitate the polycation in the solution; therefore, the study of anions will be limited to F<sup>−</sup>, Br<sup>−</sup>, Cl<sup>−</sup>, and ClO<sub>3</sub><sup>−</sup>. For the colloid coating, 550 nm silica particles (Giltech Inc.) were immersed in 10<sup>−2</sup> M polyelectrolyte dipping solutions (based on the monomer unit) freshly prepared from the respective 0.5 M salt. All salts purchased from Aldrich were of analytical grade quality and were used without further purification.

**Multilayer Preparation.** For planar assembly, the substrates for multilayer deposition were silicon wafers provided by Wacker Siltronic AG, Burghausen, Germany. Substrates were cleaned for 30 min in a 1:1 mixture of H<sub>2</sub>O<sub>2</sub>/H<sub>2</sub>SO<sub>4</sub> and then rinsed thoroughly with deionized water and finally with Millipore water. The LbL deposition technique was used to build polyelectrolyte multilayers. The first layer was a PEI layer; thereafter, PSS and P(DADMAC-*stat*-NMVA) were deposited. The silicon wafers were alternatively immersed in aqueous solutions of 10<sup>−2</sup> monomol/L (concentration of monomer units) of the respective polyelectrolyte. Between instances of manual dipping into the polyelectrolyte solutions, the silicon wafers were rinsed three times in fresh Millipore water to remove any loosely bound polyelectrolyte. Only after the completion of the multilayer assembly with the desired number of layers was the system dried in a gentle air stream filtered by an active carbon filter.

Most of the experiments were carried out at planar interfaces, but for ζ-potential measurements, colloidal particles were used. For the colloidal assembly, the sequential adsorption steps of the polycation and polyanion to the particles are identical to those for planar substrates, with the rinsing steps replaced by three centrifugation/washing cycles with water to remove any excess or loosely bound polyelectrolyte after each adsorption step. The dipping time in each polyelectrolyte solution was 30 min, and centrifugation was performed at 5000 rpm for 30 min.

**Apparatus and Measurement Procedure.** Ellipsometry measurements were determined under ambient conditions using a null ellipsometer from Optrel (Berlin, Germany) with a Nd–Yt laser at 532.0 nm at a 70° angle of incidence. The complex refractive indices are  $n = 4.150 - i0.044$  at 532 nm for bulk silicon and  $n = 1.46$  for silicon oxide, respectively. The native oxide layer is about 15 Å. The average error associated with the ellipsometry measurements was determined to be approximately ±3%. Because the multilayers were too thin (i.e., the contrast was too low) to change the angle Ψ that is related to the polarizer angle, only Δ changed (related to the analyzer angle); therefore, only one parameter (thickness  $d$  or refractive index  $n$ ) could be fit. In the present case, the refractive index of thick multilayers was taken, where  $n$  and  $d$  could be fit, and it was assumed that  $n$  is the same for thin multilayers. There was no systematic difference in  $n$  among multilayers prepared under different conditions (type of salt, ionic strength, polymer charge), and the average value was 1.54.

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The surface potentials of coated particles in various 0.5 M salts were obtained from a Malvern Zetasizer 4. For each point, an average of 10 successive, consistent measurements was taken.

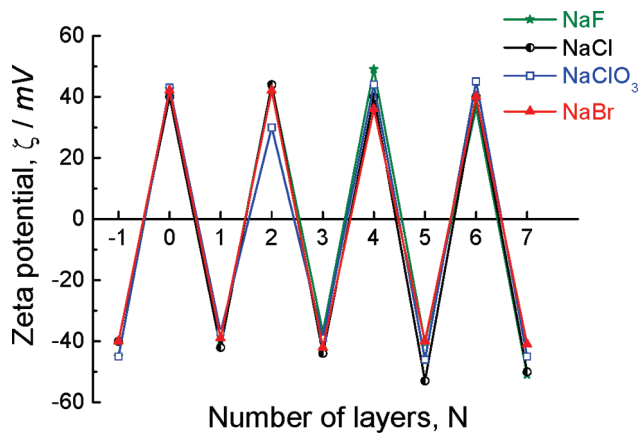
X-ray reflectivity measurements were carried out on a Bruker D5000, with a conventional  $\theta/2\theta$  instrument [ $U = 40$  kV,  $I = 50$  mA, and  $\lambda = 1.54$  Å (Cu K $\alpha$ )].

Atomic force microscopy (AFM) images were obtained with a Digital Instruments multimode nanoscope operating in tapping mode under ambient conditions. Silicon nitride cantilevers with spring constants of 38–66 N m $^{-1}$  were used as purchased. The resonance frequency of the cantilever was in the range of 130–150 kHz. Topographical height mode and phase contrast images were recorded simultaneously over scan areas of 30  $\mu\text{m}^2$  at a scanning rate of 1 Hz. The images were processed using Nano-scope software. Quantitative measurements of the local rms surface roughness, which defines the height fluctuations in a given area, were determined from a 1.0  $\mu\text{m}^2$  area. The length of 1.0  $\mu\text{m}$  corresponds to the correlation length of X-rays and enables a direct comparison between the values of roughness obtained from both techniques.

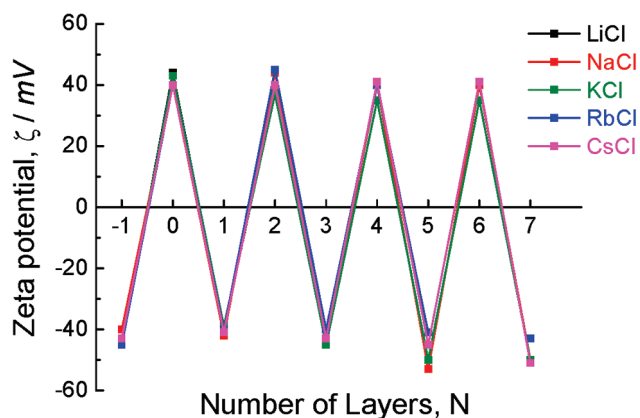
## Results and Discussion

**Effect of Type of Salts.** The successful deposition of polyelectrolyte multilayers onto colloids was monitored by electrokinetic measurements.<sup>68</sup> Figure 1 shows the  $\zeta$  potential as a function of the number of layers of PSS/PDADMAC(100%) deposited onto PEI-coated silica particles ( $N=0$  being PEI) from dipping solutions of 0.5 mol/L NaF, NaCl, NaBr, NaClO<sub>3</sub>, LiCl, KCl, RbCl, and CsCl. The particles bear an initial negative potential due to the charge stabilization. On adsorption of the polycation, the potential becomes positive and reverses to negative upon adsorption of the polyanion. The  $\zeta$  potential oscillates between +40 mV after PEI or PDADMAC adsorption and −40 mV after PSS adsorption. Surface potentials recorded on other polycation/polyanion systems (e.g., PAH/PSS) showed that the  $\zeta$  potential oscillates between similar values.<sup>69</sup> It is intriguing to note that the  $\zeta$  potential oscillates between the same values, irrespective of the size of the counterions in the medium (the medium being the same as that of the dipping solution, i.e., 0.5 M respective ions). The  $\zeta$  potential is the overall charge that a particle acquires in a specific medium. One reason for this potential is the dissociation of ionogenic groups at the particle surface and the differential adsorption of solution ions into the surface region. To the best of our knowledge, no  $\zeta$  potential has ever been recorded for various salts in the PDADMAC/PSS system. The insensitivity of the  $\zeta$  potential to the type of ion means that the shear plane is beyond the length scale, which is important for differences in dispersion forces. Even if there were local differences in the surface charges of the coated particles, they would be compensated for by counterions on length scales shorter than the distance of the shear plane from the surface of the particle. To summarize,  $\zeta$  potential measurements are insensitive to ion-specific effects. From now on, all discussions will be related to multilayers on planar surfaces.

Figure 2 shows the thickness of multilayers obtained by ellipsometry for the PSS/PDADMAC(100%) system as a function of the number of deposited single layers using different sodium salts (NaF, NaCl, NaBr, and NaClO<sub>3</sub>) at an ionic strength of 0.25 M. The thickness increases in the order of  $\text{F}^- < \text{Cl}^- < \text{ClO}_3^- < \text{Br}^-$ . This result is in good agreement with that obtained by Salomäki et al.<sup>29,30</sup> According to the Hofmeister



(a)



(b)

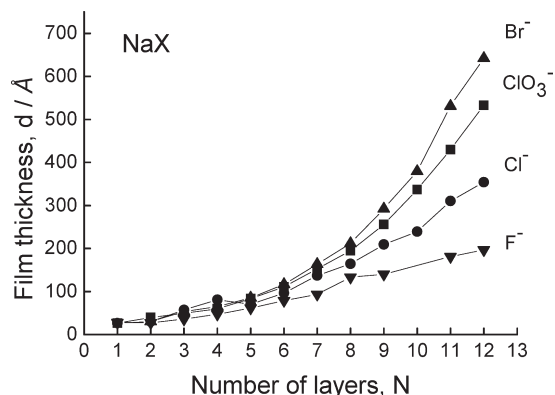
**Figure 1.** Dependence of the  $\zeta$  potential on the number of layers deposited onto PEI-coated silica colloidal particles of 550 nm obtained from various 0.5 M (a) sodium and (b) chloride salts. To be consistent with the later nomenclature,  $N = -1$  corresponds to the bare silicon,  $N = 0$  corresponds to the PEI layer, and further multilayer buildup consists of alternating outermost layers of PSS ( $N = 1, 3, 5$ , and  $7$ ) and PDADMAC ( $N = 2, 4$ , and  $6$ ).

series,  $\text{F}^-$  is a water structure maker and  $\text{Br}^-$  is a water structure breaker. In Table 1, the properties of the ions are shown. In the following text, the effect of the two extreme ions,  $\text{F}^-$  and  $\text{Br}^-$ , is discussed.  $\text{F}^-$  is a small ion ( $\sim 130$  pm) with a low polarizability ( $\sim 2.3 \times 10^{-6}$  m $^3$ /mol) and tends to have a well-ordered thick hydration shell whereas  $\text{Br}^-$  has a much larger radius ( $\sim 196$  pm) and a larger polarizability ( $\sim 12.2 \times 10^{-6}$  m $^3$ /mol) and is surrounded by a thin, less-ordered hydration shell and adapts more easily to the environment. Because of the thin, loosely packed hydration shell, the adjustment of  $\text{Br}^-$  to the environment is easier. Therefore, the polycation (PDADMAC) can interact more strongly with  $\text{Br}^-$  than with  $\text{F}^-$ , perhaps via a kind of “bridging” and/or overlap of hydration shells of counterions and polycation. Consequently, the charges along the polycation chain are more effectively screened in the case of  $\text{Br}^-$ , which results in stronger coiling of the chains and therefore yields thicker and rougher multilayers. An increase in attraction between polycations and anions with increasing anion size was proven by conductivity measurements in solution.<sup>70</sup> This in turn results in

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(69) Sukhorukov, G. B.; Donath, E.; Davis, S.; Lichtenfeld, H.; Caruso, F.; Popov, V. I.; Möhwald, H. *Polym. Adv. Technol.* **1998**, *9*, 759–767.

(70) Ghimici, L.; Dragan, S. *Colloid Polym. Sci.* **2002**, *280*, 130–134.



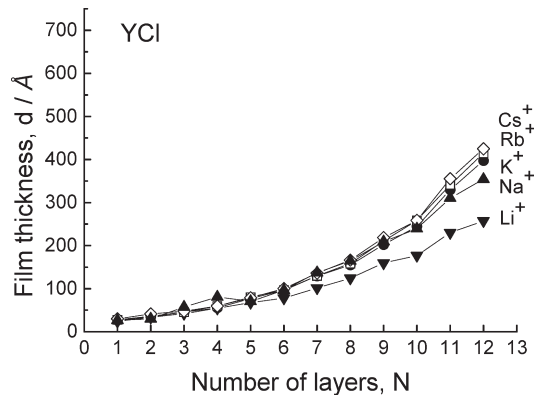
**Figure 2.** Ellipsometric thickness obtained for the formation and growth of PSS/PDADMAC(100%) multilayers deposited from various 0.25 M sodium salts on PEI-coated silicon substrates. Odd and even numbers of layers are indicative of PSS- and PDADMAC-terminated layers, respectively.  $X = F^-$ ,  $Cl^-$ ,  $ClO_3^-$ , and  $Br^-$ .

stronger chain coiling in solution as a result of the reduction in intrachain repulsion, confirmed by a reduction in solution viscosity.<sup>70</sup>

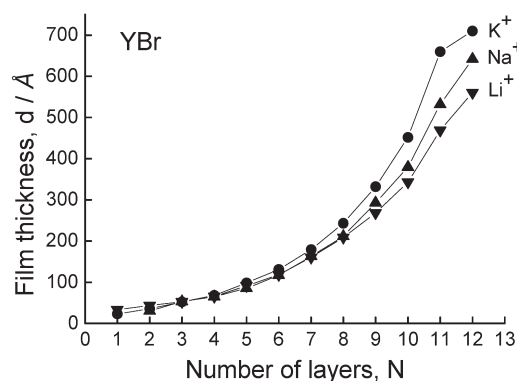
According to the concept of matching water affinities by Collins<sup>40</sup> and others, this result indicates that the cationic monomer (DADMAC) does not attract very much water and prefers to bind the larger  $Br^-$ . Indeed, this result confirms MD simulations.<sup>71</sup>  $ClO_3^-$  and  $Br^-$  have the same radius and polarizability (Table 1), but multilayers prepared from solutions containing  $ClO_3^-$  ions are thinner, which has also been observed by Salomäki et al.<sup>29</sup> The reason for this could be a different charge distribution in both ions, which leads to different coupling to the charged groups of PDADMAC and therefore to a difference in coiling of the PDADMAC chains.

Figure 3a shows the thickness of multilayers obtained by ellipsometry for the PSS/PDADMAC(100%) system as a function of the number of deposited single layers using different chloride salts (LiCl, NaCl, KCl, RbCl, and CsCl) at 0.25 M. By analogy to different anions, a variation of the type of cations, from small and strongly hydrated  $Li^+$  to larger and less strongly hydrated ions such as  $K^+$ ,  $Rb^+$ , and  $Cs^+$ , results in an increase in multilayer thickness.<sup>22</sup> However, the effect of cations (at least at this concentration of 0.25 M) is not as pronounced as that of the anions simply because cations are generally smaller than anions. For instance, the radius of the smallest studied cation,  $Li^+$ , is about 70 pm, and the polarizability is about  $0.1 \times 10^{-6} \text{ m}^3/\text{mol}$ ; the radius of the largest studied cation,  $Cs^+$ , is about 170 pm, and the polarizability is about  $6.6 \times 10^{-6} \text{ m}^3/\text{mol}$  (Table 1). That means that the effect of the  $Cl^-$  (radius  $\sim 180$  pm, polarizability  $\sim 8.8 \times 10^{-6} \text{ m}^3/\text{mol}$ ) on the conformation of the polycation could be larger and dominate the smaller effect of the cations on the conformation of polyanions. In addition, the polarizability of the charged groups of the polyion has to be taken into account for the overlap between the hydration shells of the polyion and the oppositely charged ions. This is much more difficult to quantify because the adjacent groups along the polyelectrolyte chain affect each other, but a difference in polarizability between the charged groups of the polyanion and polycation is very likely.

Figure 3b shows multilayer growth as prepared from different bromide salts (LiBr, NaBr, and KBr) for the PSS/PDADMAC-(100%) system at 0.25 M. The trend in the order in thickness



(a)



(b)

**Figure 3.** Ellipsometric thickness obtained for the formation and growth of PSS/PDADMAC(100%) multilayers deposited from various 0.25 M (a) chloride and (b) bromide salts on PEI-coated silicon substrates. Odd and even numbers of layers are indicative of PSS- and PDADMAC-terminated layers, respectively.  $Y = Li^+$ ,  $Na^+$ ,  $K^+$ ,  $Rb^+$ , and  $Cs^+$ .

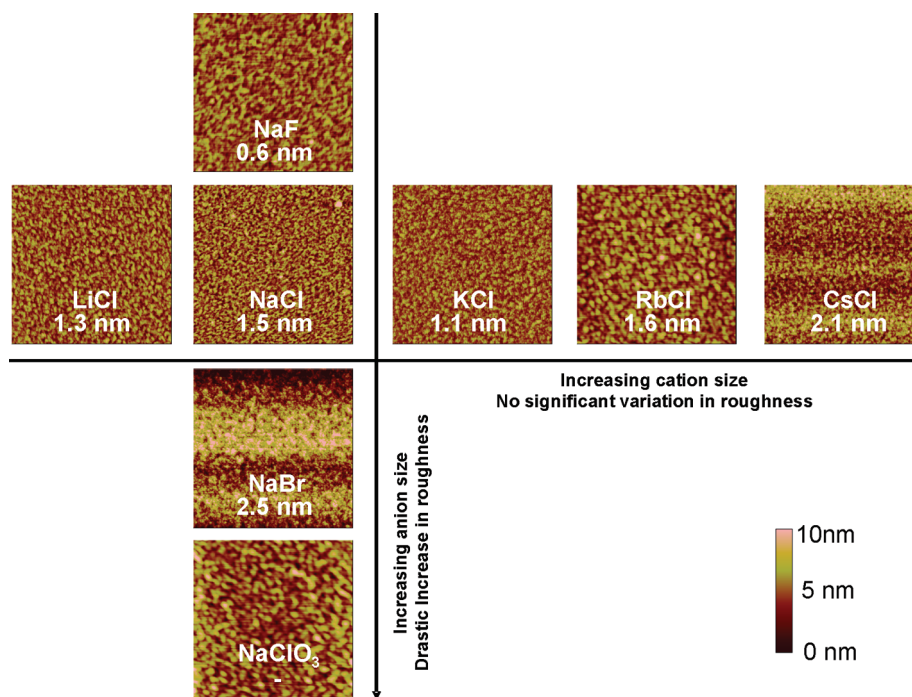
with respect to the type of cation is similar to that for  $Cl^-$  salts. At 0.25 M, replacing  $Cl^-$  ions by  $Br^-$  ions has the effect of increasing the multilayer thickness as expected and explained above. The absolute effect of cations on the thickness is similar in multilayers prepared with  $Cl^-$  or  $Br^-$ , but the relative effect is smaller for  $Br^-$ . This could be explained by the fact that the higher polarizability of  $Br^-$  leads to rather thick multilayers and masks the small effect of cations.

With increasing size of anions and cations, a nonlinear (so-called “exponential”) growth was observed for most of the multilayers shown in Figures 2 and 3. Linear growth means that the new layer adsorbs on top of the multilayer, probably with a certain trend toward interdigitation with underlying layers, but the increment per deposition cycle (i.e., polyanion/polycation layer deposition) remains constant. In the case of “exponential” growth, it is assumed that at least one type of polyelectrolyte can diffuse into the multilayer system.<sup>72,73</sup> In the next deposition step, charge reversal occurs at the multilayer surface, and the polyelectrolyte diffuses from the inner regime of the multilayer system to the surface in order to form additional complexes with the “new” adsorbing polyelectrolyte. With increasing thickness, the amount of diffusing polyelectrolyte increases because more polyelectrolyte can be reabsorbed by the multilayer. This leads to an

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**Figure 4.** Tapping-mode AFM images of 12-layer PSS/PDADMAC(100%). All images cover a  $2.5 \times 2.5 \mu\text{m}^2$  scan area, and the rms surface roughness quoted was determined from a  $1.0 \times 1.0 \mu\text{m}^2$  area.

increasing thickness increment per deposition cycle. In the present work for thinner systems, it is difficult to distinguish between linear and slight exponential growth (e.g., systems that are prepared from NaF (Figure 2)).

Because stronger coiling leads to a thicker multilayer, the amount of diffusing polymer increases with increasing polarizability of the ions. Therefore, the exponential growth is most pronounced for large ions with a thin hydration shell. Another reason could be that the polyelectrolyte chains within the multilayer become more mobile in the presence of larger ions.<sup>65</sup> Such an observation strongly suggests that polyions can diffuse easily into and out of the multilayer. The lateral diffusion coefficient increases by about 1 order of magnitude from about  $10^{-14}$  to  $10^{-13} \text{ cm}^2/\text{s}$  by replacing  $\text{Cl}^-$  with  $\text{Br}^-$ .<sup>65</sup> In the presence of  $\text{F}^-$  in Figure 2, rather linear growth is observed, which would support the assumption of almost immobile nondiffusing chains. However, also from the type of growth, one can recognize the dominating effect of the anions. For instance, in Figure 3b even  $\text{Li}^+$  results in pronounced exponential growth although  $\text{Li}^+$  has a smaller radius than  $\text{F}^-$ , which shows almost linear growth in Figure 2. Such growth clearly suggests that  $\text{Br}^-$  is the dominating ion type in Figure 3b. The stronger attraction of  $\text{Cs}^+$  by PSS in comparison to  $\text{Li}^+$  was predicted by MD simulations.<sup>74</sup>

To obtain structural information about multilayers prepared from various salts, tapping-mode AFM images of 12-layer PSS/PDADMAC(100%) on PEI precoated silicon substrates were recorded. Results of the measurements for different salts (0.1 M) are shown in Figure 4. Topographical height mode and phase contrast images were recorded simultaneously at scan areas of  $30 \mu\text{m}^2$  down to  $2.5 \mu\text{m}^2$ , but for ease of comparison, only images of  $2.5 \mu\text{m}^2$  scans are shown. Images are presented with a simple first-order flattening. Figure 4 shows clear differences in the surface morphology as influenced by the size of the ions present in the dipping solutions. The surface roughness increases as the ionic radius of the ions increases and has values ranging from

0.6 nm in the presence of  $\text{F}^-$  ions to 2.5 nm in the case of  $\text{Br}^-$  ions (no reliable mean roughness could be measured for  $\text{ClO}_3^-$ ). As explained above, with increasing radius of the anions, the interaction between polyion and counterions becomes stronger; therefore, the chains are more coiled. For multilayers prepared from various chloride salts, the rms value varies between 1.2 and 1.6 nm without any systematic change, except for systems prepared with CsCl where an rms value of 2.1 nm was obtained. This confirms that the effect of cations on the structure is much smaller than that of anions.

It is noteworthy to point out that in this study on multilayer formation of the PSS/PDADMAC(100%) system the growth for the first few layers (up to layer 6) is clearly independent of the nature of the ions (Figures 2 and 3). Similar observations have been reported whereby the initial growth (up to the first four bilayers) in the same multilayer system seems to be independent of temperature.<sup>31</sup> The authors explained the temperature independence originating from the fact that the multilayer has to have a certain compactness in order to act as a separate phase with characteristic properties. According to this consideration, in the present system, from layer 6 onward, a noticeable effect of the ions becomes evident in the growth behavior of the multilayers equivalent to a separate phase with its own characteristics. Another argument might be that the first layers are within the decay of the surface potential of the silicon substrate. During the deposition of these first few layers, co-ions cannot be in the vicinity of the charged silicon surface because of the repulsive interactions, equivalent to a depletion zone.<sup>75</sup> This would mean that the counterion distribution is dominated by the electrostatic potential in front of the substrate surface and that ion-specific effects are masked by the substrate influence. Although the  $\zeta$  potential of the bare silicon substrate is not different from that of multilayers with PSS as an outermost layer in the present study (Figure 1), the ion distribution might be different close to the surface. One can speculate about at least two regimes of

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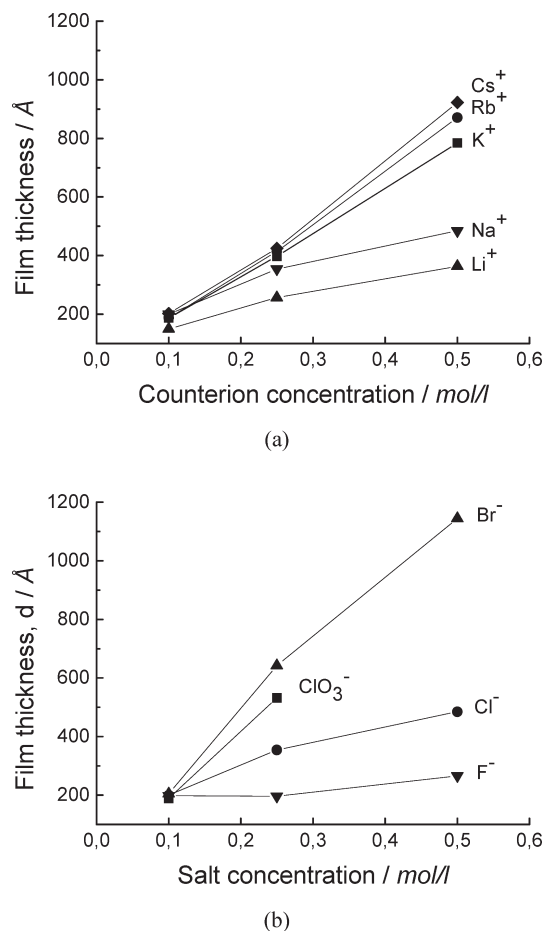
(75) Castelnovo, M.; Joanny, J. F. *Langmuir* **2000**, *16*, 7524–7532.



multilayer stacking. In the first regime, which involved the anchoring of the first few layers of polyelectrolyte onto the PEI-coated substrate (up to five layers, i.e., about 10 nm), the growth seems to be identical in all cases, irrespective of the nature of the ions. The first few layers are most probably thin precursor layers that act as an adhesive between the substrate and the bulk of the multilayer (effect of substrate is dominating). In the second regime, after the first few layers have been well-established and served as a cushion for the additional layers (layer 6 onward), the nature of the ions seems to play a significant role in the increment of the thickness after each deposition, with the ion with the largest ionic radius giving rise to the thickest increment, therefore resulting in the thickest multilayer. It is certainly not the first time that it has been demonstrated that a different layering regime is observed in polyelectrolyte multilayers. Ladam et al. proposed a three-regime model from streaming potential measurements, distinguishing between inner (closest to the substrate), middle, and outer layers (in contact with air).<sup>76</sup> For the hydration of PAH/PSS multilayers, a two-regime model from the ellipsometric studies was reported, distinguishing between the inner and outer layers in thin ( $N < 6$ ) and thick ( $N > 6$ ) systems.<sup>15</sup> However, this is the first time that it has been demonstrated that the inner layers (closer to the substrate) of the PDADMAC(100%)/PSS system, surprisingly, adsorbed in the same way irrespective of the nature (size or polarizability) of the counterions.

**Effect of Ionic Strength.** Figure 5a,b shows the ellipsometric multilayer thickness of 12 layers as a function of the salt concentration for different cations ( $\text{Li}^+$ ,  $\text{Na}^+$ ,  $\text{K}^+$ ,  $\text{Rb}^+$ , and  $\text{Cs}^+$ ) and anions ( $\text{F}^-$ ,  $\text{Cl}^-$ ,  $\text{Br}^-$ , and  $\text{ClO}_3^-$ ). With increasing ionic strength, the thickness increases because of screening of the intrapolymer and the interpolymer electrostatic repulsion. A new insight is the dependence on the ionic strength as a function of different types of salts. At 0.1 M, the ion-specific effects on the multilayer thickness are rather minor. At 0.25 M, apart from a relatively significant increment in the thickness of a multilayer prepared from NaCl as compared to LiCl, systems prepared from KCl, RbCl, and CsCl all have similar thicknesses. However, at 0.25 M, the more pronounced influence of anions is already noticeable. Twelve-layer systems prepared from NaF, NaCl, NaClO<sub>3</sub>, and NaBr are about 200, 300, 500, and 600 Å thick, respectively. At 0.5 M, the influence of the cations is no longer negligible. With larger cations, the increment in thickness is significantly important. A 12-layer system prepared from 0.5 M LiCl has a thickness of about 300 Å whereas that prepared from CsCl is about 3 times thicker. At 0.5 M, the influence of anions is even greater, with multilayers prepared from NaBr being about 5 to 6 times thicker than those prepared from NaF. It was not possible to measure the thickness of the multilayer prepared from NaClO<sub>3</sub> at 0.5 M as a result of the strong scattering of the laser beam in ellipsometry measurements, which indicates high surface roughness.

McAloney et al. has shown that the system PSS/PDADMAC at high ionic strength induces exponential initial buildup.<sup>24</sup> Large anions seem to have the same effect. Both increasing ionic strength and increasing diameter of anions lead to an increase in the lateral diffusion coefficient.<sup>65</sup> A softening of the polyelectrolyte multilayer can also be observed with increasing temperature.<sup>65</sup> Salomäki et al. has shown that the growth of the PSS/PDADMAC multilayer buildup at different temperatures using 0.1 M NaBr changes from a predominantly linear buildup (when  $T = 15$  and  $25^\circ\text{C}$ ) to a clearly exponential buildup (when  $T = 45$  or  $55^\circ\text{C}$ ).<sup>31</sup> They even found that, at high temperature, there is a difference in



**Figure 5.** Ellipsometric thickness obtained for a 12-layer PSS/PDADMAC(100%) system prepared from various salt concentrations of different (a) chloride and (b) sodium salts.

the buildup of polycations and polyanions, with PDADMAC gaining more temperature-induced mass growth than PSS.<sup>31,77</sup> They also found that PSS/PDADMAC from 0.1 M NaF yields a much thinner multilayer with different internal structure, which they described as much softer than that deposited from NaBr.<sup>30,31</sup> Actually, it has been proposed that the effect of increasing the temperature is somehow equivalent to adding more salt to the polyelectrolyte solutions with respect to the coiling and mobility of the polyelectrolyte chains within the multilayers.<sup>65,77</sup> Indeed, similar tendencies were observed as illustrated in Figure 5.

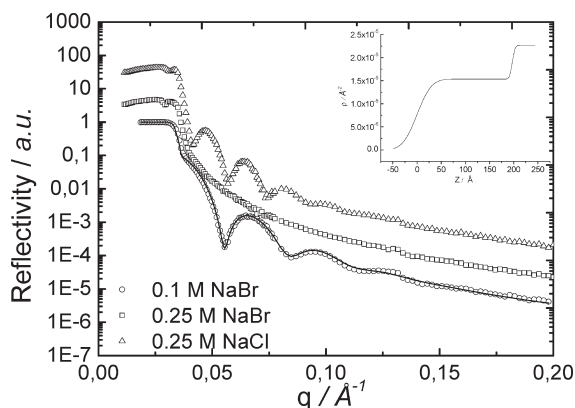
The fact that the ion-specific effects are detectable only above an ionic strength of 0.1 M can be explained by the competition between electrostatic and dispersion forces. Below this ionic strength, electrostatics is important and masks the ion-specific effects. At higher ionic strength, electrostatic interactions are screened, and dispersion forces become important. Indeed, Ghimici et al. found a correlation between the hydration states of salt counterions and the strength of their interaction with polyelectrolytes in solution.<sup>70</sup> Dispersion forces depend not merely on the charge but on the ionic polarizabilities and electron affinities, which in turn depend on the electronic structure of the ions. Anions are more polarizable than typical cations and are therefore expected to lead to stronger dispersion forces.<sup>56–58</sup>

X-ray reflectivity curves were obtained for 12-layer systems from various 0.1, 0.25, and 0.5 M salts. Figure 6 shows the X-ray

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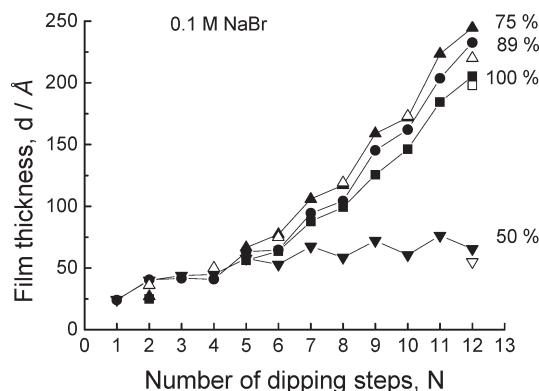




**Figure 6.** X-ray reflectivity curves obtained for a 12-layer PSS/PDADMAC(100%) system prepared from 0.1 and 0.25 M NaBr. The curve obtained from 0.25 M NaCl is included for comparison. The inset shows the density profile for the fitted reflectivity curve for 0.1 M NaBr.

reflectivity curves as a function of the momentum-transfer vector,  $q = 4\pi/\lambda \sin(\theta)$  (where  $\lambda$  is the radiation wavelength (1.54 Å) and  $\theta$  is the scattering angle), collected on 12-layer PSS/PDADMAC(100%) systems prepared from NaCl and NaBr. From the positions of the minima, the thicknesses were calculated (the ellipsometry data are in brackets): For 0.5 M NaCl, the multilayer has a thickness of 500 Å (484 Å); for 0.25 M, 370 Å (354 Å); and for 0.1 M, 180 Å (200 Å). For 0.1 M NaBr, the thickness was 197 Å (205 Å). The thicknesses obtained by both techniques are in the same order. The differences might occur as a result of the fixed refractive index used for analyzing the ellipsometry data. At 0.1 M, multilayers prepared from NaBr have roughly the same thickness as those prepared from NaCl. At 0.25 M NaCl (Figure 6), there are more Kiessig fringes appearing that are shifted to lower  $q$  values, indicating that the systems prepared from higher  $\text{Cl}^-$  concentrations are thicker, which is in good agreement with the results presented in Figure 5. At higher concentrations of NaBr (0.25 and 0.5 M), multilayers are not only much thicker but also much rougher, as can be seen from the flat, oscillation-free X-ray curve for multilayers prepared from 0.25 M NaBr (Figure 6). This renders it impossible to fit the data and to determine the thickness from this technique as a result of the absence of any Kiessig fringes. Note that systems prepared from the same ionic strength but from NaCl still show Kiessig fringes. Multilayers from 0.1 M NaCl and NaBr were fitted,<sup>78</sup> and roughnesses of 1.8 and 2.3 nm were obtained, respectively. To summarize, increasing salt concentration leads to an increase in surface roughness as already mentioned elsewhere, but at higher ionic strengths (0.25 and 0.5 M), the comparison of the NaCl and NaBr data shows a clear ion-specific effect.

**Effect of Degree of Charge.** The results show that both the ionic strength and the type of ions have a strong effect on the structure (i.e., roughness and thickness of the multilayers). However, it was shown that a pronounced effect of the type of ions occurs above 0.1 M for anions and above 0.25 M for cations. One explanation is that the dispersion forces overcome the effect of electrostatic forces at those concentrations. Besides the ionic strength, the degree of polymer charge influences the electrostatic interactions and plays a dominant role in the formation of polyelectrolyte multilayers. It has been previously shown by X-ray reflectometry<sup>17</sup> and ellipsometry<sup>18</sup> that a minimum charge of about 70% is necessary for the formation of



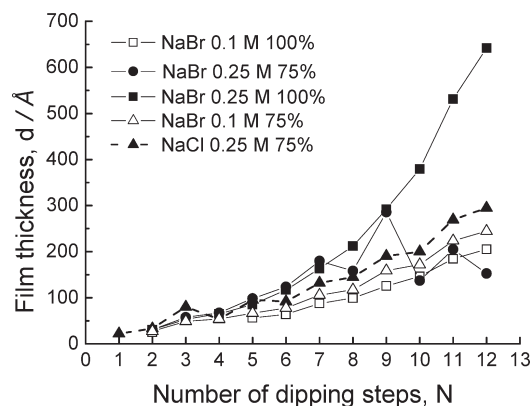
**Figure 7.** Ellipsometric thickness obtained for the formation and growth of multilayers deposited from 0.1 M NaBr for different charge densities of P(DADMAC-*stat*-MNVA). The open symbols represent the respective thicknesses of the multilayers prepared from 0.1 M NaCl (data taken from ref 20).

a stable multilayer obtained from NaCl solution.<sup>17–21</sup> The question arises as to whether a reduction in the degree of polymer charge might reduce the electrostatic interactions in such a way that the effect of the type of ion becomes more visible even at low ionic strengths. Because the ion-specific effect is more pronounced for anions than for cations, the influence of charge density was studied for two different anions:  $\text{Cl}^-$  and  $\text{Br}^-$ . The multilayers were built from 0.1 M NaBr solution of PSS and P(DADMAC-*stat*-NMVA) of four different degrees of charge (50, 75, 89, and 100%). For comparison, the thicknesses for two systems (50 and 75%) prepared from 0.1 M NaCl solutions (taken from ref 20) are indicated with open symbols in Figure 7. The largest difference between multilayers prepared from NaCl and NaBr was expected for the 75% charged polycation because the electrostatic effects should be the lowest among the stable multilayers. Nevertheless, at all three degrees of charge (75, 89, and 100%) no significant difference between the types of salt was detectable.<sup>17,18,20</sup>

Multilayers obtained for a 100% charged polyelectrolyte, PDADMAC(100%), are thinner than those obtained for lower-charge-density (e.g., 75 and 89%) polyelectrolytes. The amount of polyelectrolyte adsorbed at the surface is critically dependent on the conformation of the polyelectrolyte in solution. In the case of a 100% charged polyelectrolyte, PDADMAC(100%), the electrostatic interactions between the charges along the polyelectrolyte backbone tend to repel each other strongly, thereby forcing the polymer to adopt an extended, stiff conformation in solution and consequently to be deposited in a rather flat (and thin) conformation. In the case of lower-charge-density polyelectrolytes (PDADMAC(75%) and PDADMAC(89%)), the electrostatic repulsion along the polymer backbone is weaker and they adsorb in a more coiled conformation, resulting in an increase in the adsorbed amount and, hence, a thicker multilayer. However, when the charge density of the polyelectrolyte falls below a critical charge density, no stable multilayer can be formed, as at a charge density of PDADMAC of 50%. Figure 7 shows that one can build up to only four layers. Additional buildup of layers results in a sequence of alternate adsorption and subsequent stripping. There is a minimum threshold of charges necessary for the LbL assembly to take place, and this threshold depends on the type of combined polyelectrolytes as stated elsewhere.<sup>20</sup>

In multilayers composed of a 75% charged polycation from 0.1 M salt, electrostatic interaction dominates so much that it

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**Figure 8.** Ellipsometry data for the build up of PDAMAC/PSS multilayers containing 75 and 100% charged PDAMAC adsorbed from 0.1 and 0.25 M NaBr. For comparison, data on multilayers containing 75% charged PDAMAC prepared from 0.25 M NaCl are also shown.

renders any ion-specific effects undetectable. However, for lower-charge-density polyelectrolytes (about 70%) the multilayer becomes unstable, which makes it impossible to test the electrostatic versus ion-specific interactions at lower polymer charge densities.

In the following text, higher salt concentrations at which ion-specific effects should be detectable were taken into account. Indeed, Figure 8 shows that the polyelectrolyte charge density, the ionic strength, and the type of salt have an obvious effect on multilayer formation. Figure 8 shows the buildup of multilayers of 75 and 100% PDAMAC with PSS from 0.1 and 0.25 M NaBr. The result for 0.25 M NaCl with PDAMAC(75%) is also shown as a reference. Preparation from 0.1 M NaBr results in the formation of multilayers that could be described by linear or slightly “exponential” growth, with the thickest film obtained for the 75% charged polycation. At an ionic strength of 0.25 M NaBr, the order is now reversed. The fully charged PDAMAC(100%) now gives much thicker multilayers and shows a strong “exponential” increase. However, the build up of PDAMAC(75%) gives a zigzag kind of growth that is indicative of an unstable formation with alternating adsorption and stripping off (as mentioned above for PDAMAC(50%) prepared from 0.1 M NaBr, Figure 7). The multilayer with PDAMAC(75%) but prepared from 0.25 M NaCl shows exponential growth during formation, as shown in Figure 8. Multilayers formed from NaCl solutions are thicker for PDAMAC(75%) than for PDAMAC(100%) even at an ionic strength of 0.3 M.<sup>20</sup> However, for NaCl an unstable formation was observed with PDAMAC(75%) and PSS from an ionic strength of 0.5 M, related to a gel-like film.

From this study, decreasing polymer charge density, increasing ionic strength, and preparation from solutions with larger anions support the transition from linear to exponential growth and even further to unstable multilayers. Recent studies showed that this change in the type of growth is related to an increase in the mobility of the polyelectrolyte chains.<sup>65</sup> Obviously, in the case of PSS/PDAMAC multilayers with 75% charged PDAMAC the ion-specific effect can tune the stability of the multilayers dramatically.

The ionic strength and the type of ion (size, polarity, and polarizability) determine the conformation of the polyelectrolyte chains in the solution, through to their transport to the surface and ultimately their deposition. As to whether the ions are still present in the internal polyelectrolyte multilayer is debatable. For overall neutrality, one can assume that each

charge is compensated for either intrinsically or extrinsically. In the latter case, excess charges are balanced by salt counterions derived from the dipping solutions, whereas in the former case the two oppositely charged polyelectrolytes neutralize each other, assuming 1:1 complex formation. During rinsing, most of the ions are washed away, and if there are any that are trapped, it is legitimate to think that they are minor and compensating for nonbound sites on the polymeric chains. So far, it was not possible to detect counterions in the polyelectrolyte multilayers.<sup>79</sup>

## Conclusions

The influence of cations and anions and their concentrations in the dipping solutions have been investigated with respect to the formation and growth of multilayers deposited from a strong polyanion, poly(sodium 4-styrenesulfonate) (PSS), and a strong polycation of variable degrees of charge, poly[(diallyldimethyl-ammonium chloride)-*stat*-(*N*-methyl-*N*-vinyl acetamide)] (P(DADMAC-*stat*-NMVA)). This study has focused on monovalent ions ( $\text{Li}^+$ ,  $\text{Na}^+$ ,  $\text{K}^+$ ,  $\text{Cs}^+$ ,  $\text{Rb}^+$ ,  $\text{F}^-$ ,  $\text{Cl}^-$ ,  $\text{Br}^-$ , and  $\text{ClO}_3^-$ ) and shows that the influence of anions is indeed more significant than that of cations, but contrary to other studies on ion-specific effects, the influence of the type of cations is *not* negligible. It has been demonstrated that large, highly polarized ions with smaller hydration shells interact strongly with charged polyelectrolytes, resulting in thicker and rougher multilayers. The thicknesses obtained for different sizes of ions are in agreement with their positions in the Hofmeister series, as revealed by ellipsometry, AFM, and X-ray data. It has also been demonstrated that the nature or size of the ions has no influence on the formation and growth of thin layers (up to five, i.e., 10 nm), where the multilayer properties are mainly dominated by the substrate.

Ion-specific effects become more pronounced in case of higher ionic strength (above 0.1 M), where the electrostatic interpolyion interactions are strongly screened and the dispersion forces between the ions and polyions dominate the interactions.

With decreasing hydration shell, the type of multilayer growth switches from linear to exponential. The same effect is observed with increasing ionic strength and decreasing polymer charge density and is related to an increase in the mobility of the polymer chains. This means that at least one type of polyelectrolyte (polycation or polyanion) becomes more mobile by changing the type of salt, increasing the ionic strength, or decreasing the degree of polymer charge. The effect of the degree of charge is not significantly different for multilayers built up with NaCl or NaBr at an ionic strength of 0.1 M. A maximum thickness is observed for 75%, and the minimum charge density required for multilayer formation is between 50 and 75%. That means that even for a lower polymer charge such as 75% the electrostatics is not reduced enough that ion-specific effects become important at an ionic strength of 0.1 M, but at higher ionic strength, ion-specific effects can play a significant role in the stability of multilayers, especially at a lower degree of polymer charge (75%).

Hence, with the proper choice and balance of the type of ions, ionic strength, and degree of polymer charge, one can fine tune the thickness, the mobility, and even the stability of the multilayers. This article supports the assumption suggested in ref 8 of three states of the multilayers from (1) unmobile (glassy) multilayers, which show linear growth to (2) more mobile,

(79) Schollmeyer, H.; Guenoun, P.; Daillant, J.; Novikov, D. V.; von Klitzing, R. *J. Phys. Chem. B* **2007**, *111*, 4036–4042.

exponentially growing, thicker multilayers to (3) unstable systems.

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