Specific Ionic Effects on Weak Polyelectrolyte Multilayer Formation[†]

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The layer-by-layer deposition method to prepare multilayers of polyelectrolytes of alternating charge has been followed in situ by means of optical reflectometry. It has been shown previously that in solutions containing both weak polyelectrolytes and appropriate salt the buildup of multilayers is modified and becomes an adsorption/dissolution process. The influence of different salts (phosphates, chlorides, and nitrates) and polyelectrolyte molecular weight on formation and erosion of multilayers on silica surfaces was investigated. In all experiments, the anionic polyelectrolyte was poly(acrylic acid). As the cationic polyelectrolyte, poly-(dimethylaminoethyl methacrylate), poly(allylamine hydrochloride), and poly(2-vinyl-*N*-methylpyridinium iodide) were used. It has been shown that at very low ionic strength (1 mM) regular buildup of multilayers is observed independent of the salt used. However, at higher ionic strength, dissolution also takes place, and the critical "glass-transition ionic strength" needed for the multilayer to be dissolved depends on the salt used, as well as on the polycation/polyanion pair studied.

Introduction

The layer-by-layer method of constructing polyelectrolyte multilayers on surfaces has been intensively studied[1−5] over the past 10 years. With the increasing interest in such processes, the importance of understanding the mechanisms of multilayer formation is permanently growing. The reasons for such interests lay both in fundamental and applied aspects. Different efforts were made, both from experimental and theoretical points of view, to get better insight into the process. To form stable multilayers, not only polyelectrolytes themselves are used; multilayers containing other charged components (e.g., proteins,[6,7] dendrimers,[8] and different inorganic particles[9]) are also subjects of numerous investigations.

Until recently, studies in the field of polyelectrolyte multilayers were almost completely devoted to the behavior of highly charged strong polyelectrolytes. However, in several studies,[10−15] it was shown that introduction of a weak polyelectrolyte in the system leads to a significant difference in the behavior in comparison with highly charged, strong polyelectrolyte systems. It has been shown that, in the case of weak polyelectrolytes, the variation of pH,[11,12] ionic strength,[13−15] or charge density significantly (sometimes even dramatically) influences various parameters such as surface charge, layer thickness, and interpenetration between layers. Even the very formation of the multilayer may be prohibited, that is, the deposition process may become an adsorption/dissolution process.

In most of the studies,[1,2] the multilayers are prepared by alternatingly dipping the substrate into solutions containing negative and positive polyelectrolyte. As shown recently,[13] additional useful information about the process of multilayer formation can be obtained by in situ monitoring of the deposition process using optical reflectometry, combined with an "impinging jet" flow cell.

It is known from well-investigated properties of the inter-polyelectrolyte complexes in solution that electrostatic interactions between oppositely charged chains are mainly responsible for the formation of such complexes.[16−19] There are several factors that influence the structure and properties of such systems, for example, the characteristics of polyelectrolytes (p*K* and nature of ionic groups, charge density, degree of polymerization), the ratio of polyelectrolyte charges, and the method of complex preparation. Regarding the characteristics of the medium (pH, temperature, etc.), the type of salt used and the ionic strength play a crucial role.[20−24] In our previous paper,[13] we showed that, for a system containing two weakly charged components, poly(dimethylaminoethyl)methacrylate and poly-(acrylic acid), and in the presence of phosphate buffer, there is a typical "glass-transition ionic strength". Above this ionic strength, the preformed multilayer loses its glasslike properties and starts to erode. To further explore the conditions leading to such a transition, we have carried out a more detailed study of the specific effect of low-molecular-weight salts on formation and erosion of multilayers of weak polyelectrolytes.

Experimental Section

The formation of multilayers of weak polyelectrolytes of alternating charge has been followed in situ by means of optical, fixed angle reflectometry. This method enables the continuous monitoring of the amount of polymer per unit area on the substrate during exposure to various solutions. Silica in the form of silicon wafers (Aurel GmbH, Germany) carrying an oxide layer of about 70 nm was used as the solid substrate. Because the pH in all experiments was kept above the isoelectric point, the silica surface was always negatively charged. Accordingly, the first polyelectrolyte injected into the cell was always the polycation. As the cationic polyelectrolyte, poly(dimethylami-noethyl methacrylate)[25] (PAMA, M_w = 20 000 g/mol), poly-

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(allylamine hydrochloride) (M_w = 70 000 g/mol), and poly(2-vinyl-N-methylpyridinium iodide) (M_w = 61 000 g/mol, quaternization > 80%) were used. As the anionic polyelectrolyte, poly(acrylic acid) (PAA, Polymer Source) was used with M_w = 12 500 g/mol unless specified otherwise. The mass concentrations of all used polymers were 10 mg/dm^3.

The supply of polymer was controlled by an impinging jet flow cell mounted on a reflectometer, as described by Dijt et al.[26,27] It is important to note here that the flow field set up by the impinging jet allows accurate control over the transport of molecules toward the substrate and effectively shields the observed part of the surface from other molecules or particles than those carried by the jet. During all experiments, the solution injected into the cell was switched every 20 min from polycation to polyanion and vice versa, unless otherwise stated. Rinsing the flow cell during 20 min with solvent was found to have a negligible effect on the signal and the multilayer buildup and was omitted in most experiments. The reflectometry signal, ΔS, is (almost) linear with the mass of polymer per unit area and can be converted when the refractive index increment, dn/dc, of the polymer is known. Because of somewhat different refractive indices of the used polymers and because of the unknown composition of the multilayer, this conversion cannot be done very precisely. However, the trends found for ΔS are expected to represent, at least semiquantitatively, the changes in adsorbed amount; one unit of ΔS corresponds to roughly 2.2 mg/m^2. Therefore, only the raw $\Delta S(t)$ data are presented. Sodium nitrate, potassium chloride, and calcium chloride were of pro analysis quality. In the experiments in which phosphate buffer was used, solutions were made up to a predetermined pH of 6.8 (at which both polyelectrolytes are charged to a large extent) and varying ionic strength by using appropriate amounts of Na$_2$HPO$_4$ and NaH$_2$PO$_4$. In all other experiments, an appropriate amount of salt (KCl, NaNO$_3$, or CaCl$_2$) was added in the presence of small amounts of phosphate buffer (I_c = 1 mM) to keep pH constant at pH = 6.8.

Results

PAMA−PAA System. In a previous paper,[13] we extensively discussed experiments for a poly(dimethylaminoethyl methacrylate)−poly(acrylic acid) (PAMA−PAA) system performed in the presence of phosphate buffer. In that system, a "glass-transition ionic strength" was observed; that is, the ionic strength at which the buildup of layers ceases because a dissolution process starts. In the case of the PAMA−PAA multilayers formed in the presence of phosphate buffer, the glass-transition region was observed to be between I_c = 1 mM and I_c = 5 mM; that is, at 1 mM, the typical layer-by-layer multilayer buildup was observed, whereas at 5 mM, during polycation deposition overshoots were noticed, which were ascribed to dissolution of complexes.

It may be expected that the value of that glass-transition ionic strength will depend on the type of counterions and the chemical composition of the polyelectrolyte groups. To examine in more detail the influence of the type of ions and ionic strength on the formation and, possibly, destruction of PAMA−PAA multilayers, additional experiments were performed in the presence of other salts.

In Figure 1, the multilayer buildup in the presence of NaNO$_3$ at I_c = 5 mM is shown, together with results obtained in the presence of a phosphate buffer at the same ionic strength. In the presence of 5 mM NaNO$_3$, each switch between PAMA and PAA produces a simple stepwise increase in the signal; a certain amount of polymer is adsorbed, and the multilayer is
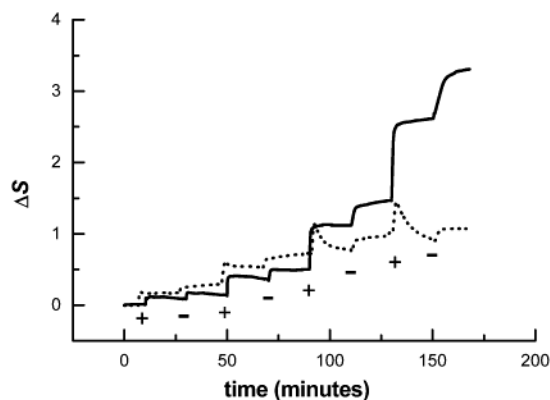

Figure 1. Multilayer formation on silica by sequential addition of PAMA and PAA at I_c = 5 mM in the presence of NaNO$_3$ (solid curve) and phosphate buffer (dotted curve). PAMA additions are indicated with + sign and PAA additions with − sign. Experimental parameters were pH = 6.8 and polyelectrolyte concentration = 10 mg/dm^3.
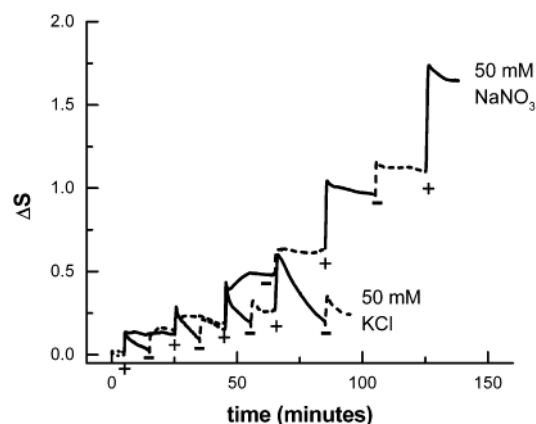

Figure 2. Multilayer formation on silica by sequential addition of PAMA (solid curve) and PAA (dashed curve) at I_c = 50 mM in the presence of NaNO$_3$ and KCl. When KCl was used, the solution injected into the cell was switched every 10 min. PAMA additions are indicated with + sign and PAA additions with − sign. Experimental parameters were pH = 6.8 and polyelectrolyte concentration = 10 mg/dm^3.

built up layer-by-layer. In contrast, in the presence of phosphate buffer, accumulation of added polymer (at least for PAMA addition) ceases after the first four layers (four switches).

The multilayer buildup in the PAMA−PAA system was also conducted at somewhat higher ionic strength, namely, at I_c = 50 mM, for both NaNO$_3$ and KCl solution. The results are shown in Figure 2.

When we increased the ionic strength up to 50 mM, the behavior of the system containing NaNO$_3$ was qualitatively identical to the 5 mM case; the stepwise formation of layers was still observed. For 50 mM NaNO$_3$, small overshoots seem to develop after four layers are formed. On the other hand, when we tried to form layers in the presence of 50 mM KCl, significant overshoots were observed. The overshoots were more pronounced when PAMA was added than when PAA was injected into the cell.

PAH−PAA System. The second investigated system was poly(allylamine hydrochloride)−poly(acrylic acid) (PAH−PAA). In the literature, many studies on multilayers containing poly(allylamine) as polycation can be found, very often in alternation with poly(styrene sulfonate).[23,28−31] Recently, the PAH−PAA system has been used by several authors as a model system for multilayers containing (at least) one weak polyelectrolyte. Rubner and co-workers[11,12] showed that variation of the pH can significantly alter the net charge of these multilayers,
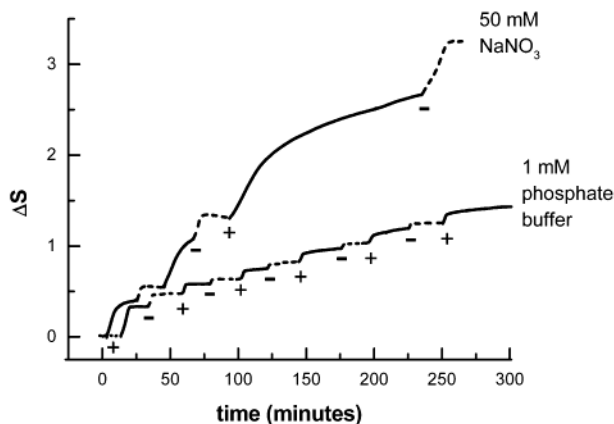
Figure 3. Multilayer formation on silica by sequential addition of PAH (solid curve) and PAA (dashed curve) at $I_c = 1$ mM in the presence of phosphate buffer and at $I_c = 50$ mM in the presence of NaNO$_3$. PAH additions are indicated with + sign and PAA additions with − sign. Experimental parameters were pH = 6.8 and polyelectrolyte concentration = 10 mg/dm^3.

Figure 4. Multilayer formation on silica by sequential addition of PVP and PAA 12 500 at $I_c = 50$ mM in the presence of NaNO$_3$ (solid curve), KCl (dashed curve), and phosphate buffer (dotted curve). PVP additions are indicated with + sign and PAA additions with − sign. Experimental parameters were pH = 6.8 and polyelectrolyte concentration = 10 mg/dm^3.

Figure 5. Multilayer formation on silica by sequential addition of PVP and PAA at $I_c = 1$ mM in the presence of phosphate buffer. Two different PAA molecular weights were used: 12 500 (dashed curve) and 164 000 (solid curve). PVP additions are indicated with + sign and PAA additions with − sign. Experimental parameters were pH = 6.8 and polyelectrolyte concentration = 10 mg/dm^3.

interpenetration between the layers, and the layer thickness. Fery[15] et al. prepared PAH−PAA multilayers with and without added NaCl and concluded that there is a salt effect on the formation of multilayers and that the surface roughness increases when multilayers are formed by the dipping method from a salt-containing solution.

We initially performed the experiments in the presence of phosphate buffer; later, NaNO$_3$ and KCl were also investigated. The formation of PAH−PAA multilayers in the presence of phosphate buffer was performed at three different ionic strengths. At $I_c = 1$ mM (Figure 3) and at $I_c = 5$ mM (not shown here), the PAH adsorption was very slow (20 min and in some layers even several hours were not enough to reach the plateau value). At 50 mM, no adsorption of PAH occurred, that is, no increase in the signal after injection of PAH was observed.

When NaNO$_3$ was used as the electrolyte, a very different behavior was observed. At $I_c = 50$ mM, at which in the phosphate case no adsorption was observed, multilayers were formed, but the PAH adsorption steps were extremely slow, as shown in Figure 3. In contrast, in the presence of KCl even at significantly higher ionic strength ($I_c = 200$ mM), both PAH and PAA steps were rather steep and did not show any tendency for overshoots; the same type of behavior as shown in Figure 1, solid curve. From these results, it seems that the binding between PAH and phosphate and (to a lesser extent) between PAH and nitrate inhibits the formation of multilayers. This is in accordance with findings of Kioussis et al.[32,33] These authors showed that poly(allylamine hydrochloride) hydrogels efficiently remove phosphate and, to a lesser extent, nitrate ions from wastewater. It may be noted that the effects of nitrate and chloride on the PAMA−PAA and PAH−PAA systems are just opposite.

PVP−PAA System. The effect of salt type and ionic strength was also investigated in the system poly(2-vinyl-*N*-methylpyridinium iodide)−poly(acrylic acid) (PVP−PAA). In Figure 4, the formation of multilayers at $I_c = 50$ mM in the presence of different salts is presented. Again, two types of behavior are observed. In the presence of NaNO$_3$ and KCl, regular multilayer formation is observed; no significant difference between these experiments is noticed. However, in the presence of phosphate buffer, after six layers typical overshoots appeared.

In the experiments above, the PAA had a relatively short chain. However, it is likely that erosion of a multilayer by the
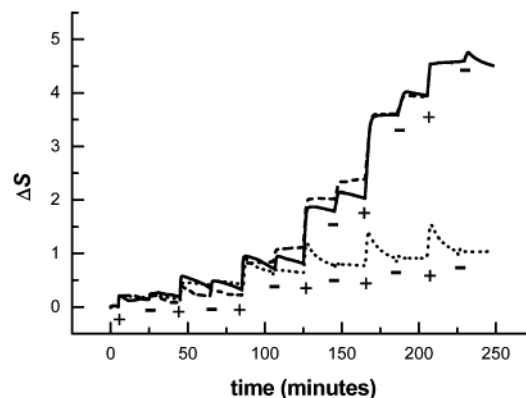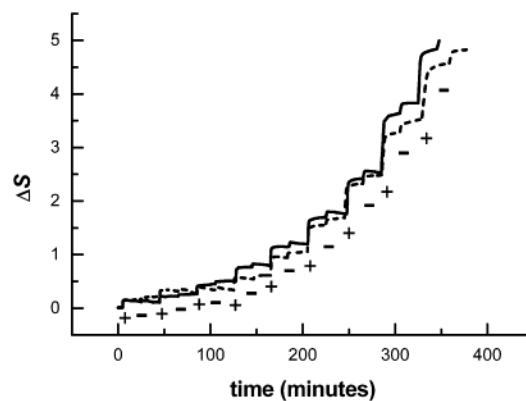
anionic polyelectrolyte will be more pronounced with increasing molecular weight. To investigate that, we performed experiments with two different molecular weights of PAA (12 500 and 164 000). At low ionic strength (1 mM), the multilayer was in a "glassy state" and no significant difference in behavior was observed, as shown in Figure 5. However at $I_c = 50$ mM phosphate buffer, the multilayer with 12 500 PAA is in a "liquid state" (Figure 4) and shows the overshoots such as those observed in Figures 1 and 2. With the longer PAA (164 000), very dramatic adsorption/dissolution effects are observed, see Figure 6, solid curve.

Discussion

In all systems investigated, specific ion effects on polyelectrolyte multilayer formation were observed. Both the polycation/polyanion pair and the type of salt used influence significantly the existence and the value of the critical glass-transition ionic strength, that is, the ionic strength at which the dissolution of the multilayer starts. It seems that the presence of phosphate induces the erosion of the multilayer already at rather low ionic strength (e.g., $I_c \leq 5$ mM for PAMA−PAA system). Chloride or nitrate can also induce the same dissolution process, but much higher amounts are needed. All of these effects were observed during the flow of polyelectrolyte in the presence of salt; as
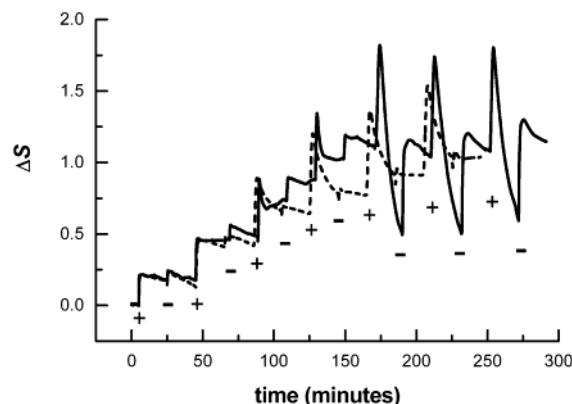
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Figure 6. Multilayer formation on silica by sequential addition of PVP and PAA at $I_c = 50$ mM in the presence of phosphate buffer. Two different PAA molecular weights were used: 12 500 (dashed curve) and 164 000 (solid curve). PVP additions are indicated with + sign and PAA additions with − sign. Experimental parameters were pH = 6.8 and polyelectrolyte concentration = 10 mg/dm^3.

shown before,[13] the addition of salt itself is not enough (at least at the ionic strengths used here) to destroy the multilayers.

These findings are in agreement with findings of Dubas and Schlenoff[14] who observed that the thickness of poly(diallylammonium chloride)−poly(acrylic acid) (PDADMA−PAA) multilayers, when exposed to NaCl solution, reaches a maximum at around 0.3 M and then decreases quickly. They showed that an ionic strength of 0.6 M was required to fully dissolve the PDADMA−PAA multilayer. The importance of salt for the multilayer formation process was also discussed by Fery et al.[15] They examined, by means of scanning force microscopy, the salt influence on the PAH−PAA multilayer structure and noticed an increase in surface roughness for multilayers deposited from salt-containing polyelectrolyte solutions in comparison with multilayers prepared from salt-free solutions.

The specificity of the effects of different ions on multilayer formation resembles electrolyte effects noticed repeatedly[34−37] during formation of polyelectrolyte complexes in the solution. Even more, we showed that for the same pair of polyelectrolytes similar effects of appropriate low-molecular-weight salts are noticed. This confirms that the behavior of polyelectrolyte multilayers is governed by the same physics as that of corresponding polyelectrolyte complexes in solution. Clearly, multilayer formation and solution complex formation are very similar processes, which depend on exactly the same interactions. This is in accordance with findings of Boulmedais et al.[38] who claim that, for the poly(L-glutamic acid)−poly(L-lysine) system, complexes are formed both in multilayer architectures and in solution and, moreover, their secondary structures are similar. Similar conclusions were drawn by Arys et al.[39] who compared the structures of a multilayer and a bulk complex for a system containing a lyotropic ionene and a strong polyelectrolyte. These authors state that "depending on whether the polyelectrolytes are capable of forming structural complexes or not, the self-assembled films will present different levels of internal organization". Moreover, they suggest that multilayers should be better designated as "electrostatic self-assemblies".

Another very intriguing point in the evaluation of reflectometry data is the fact that the size of the steps increases with step number (e.g., Figure 5). There are several reports in the literature[22,24,40−42] showing that the amount of polyelectrolyte on the surface can increase more than linearly with the number of deposited layers. Ellipsometric measurements performed by Ruths et al.[24] for the PSS−PAH system showed that the

thickness of individual layers grows proportionally with the number of layers. McAloney et al.[22] followed the buildup process of poly(diallyldimethylammonium chloride)−poly-(styrene sulfonate) multilayers by means of AFM and also observed a change from a linear to a so-called superlinear regime. Additional evidence about the presence of superlinear regimes and their association with buildup processes involving the diffusion of at least one of the polyelectrolytes through the whole film at each bilayer deposition step were shown by Schaaf and co-workers[40−42] for hyaluronic acid−poly(L-lysine) and poly(L-glutamic acid)−poly(L-lysine) systems using AFM, waveguide light mode spectroscopy, and confocal laser microscopy. It is tempting to conclude that the superlinear regime is due to weakness of the complexes. Such weak complexes will have a low surface tension and a very diffuse interface with the dilute solution, and the gradual development of this diffuse interface may well cause the nonlinear growth.

Conclusions

Results obtained by "in situ" reflectometry investigations of polyelectrolyte multilayers containing different polycation/polyanion pairs in the presence of different salts confirmed the importance of low-molecular-weight salts on multilayer formation and its properties. It was also shown that ion effects are very sensitive to the chemical nature of the ionic groups of the polyelectrolytes. The buildup of multilayers can, in the presence of a weak polyelectrolyte and appropriate salt, become an adsorption/dissolution process. Although a certain systematic trend in multilayer behavior for a series of inorganic cations for every used polycation could be expected, our results do not show such a trend. The specific combination of a polycation and a polyanion seems to determine the buildup mechanism.

Additionally, it was shown that optical reflectometry can be a powerful tool for investigation and characterization of multilayers. The experimental data reported here provide evidence that the stability of the polyelectrolyte multilayers (especially in the case of weak polyelectrolytes) can be controlled by variation of salt and ionic strength in the surrounding medium and therefore contribute to different potential polyelectrolyte multilayer applications.

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