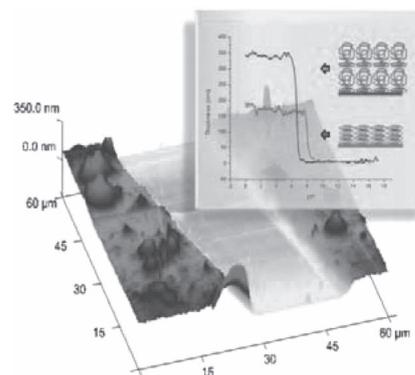


Responsive Polyelectrolyte Multilayers Assembled at High Ionic Strength with an Unusual Collapse at Low Ionic Strength

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Responsive polyelectrolyte multilayers (PEMs) of poly(diallyl dimethyl ammonium chloride) (PDADMAC) and poly(styrene sodium sulfonate) (PSS) with thicknesses between 350 and 400 nm for 11 deposited polyelectrolyte layers were fabricated assembling the polyelectrolytes at 3 M NaCl. When the 3 M NaCl bulk solution is replaced by water, the PEMs release water, approximately a 46% of the total mass, and experience a thickness reduction of more than 200 nm. Changes in thickness and water content are fully reversible. The film recovers its original thickness and water content when it is exposed again to a 3 M NaCl solution. A responsive polymer film is achieved with the capability of swelling at high ionic strength and collapsing in water with variations in thickness of hundred of nanometers.



1. Introduction

Polyelectrolyte multilayers (PEMs) fabricated by the layer-by-layer (LbL) alternative assembly of polycations and polyanions on charged surfaces have gained a lot of attention in recent years as a tool for noncovalent surface modification and device fabrication.^[1–4]

LbL is easy and robust. PEM assembly is principally driven by electrostatic interactions between oppositely charged polyelectrolytes, favored by the increase in entropy due to the release of counterions during

polyelectrolyte deposition. From a practical point of view, LbL assembly only requires the dipping of a charged substrate in a solution of a polyelectrolyte with a charge opposite to that of the substrate. The procedure is repeated a number of times alternating between polycations and polyanions, including water or salt washings in between layers, until a film of the desired thickness is obtained.^[5–7] Alternatively, if working with colloids, these are suspended in a polyelectrolyte solution, centrifuged, washed a number of times alternating between polycations and polyanions until a film of the desired thickness is obtained. The practical procedure applied by the different groups working in LbL assembly varies, regarding the number of washings between the deposition of layers, the use of NaCl or water for the washings, assembly time, pH, and the ionic strength of the polyelectrolyte solution.^[8–11] For some of these parameters, variations in the conditions of assembly can indeed have a strong impact on the quality of the assembled PEMs.

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For instance, although polyelectrolyte conformation is determined by the ionic strength in bulk solution, the thickness of an LbL film will be notably influenced by the ionic strength at which the assembly has been performed. If polyelectrolyte assembly takes place at low ionic strength, the polymer chains are normally extended, resulting in a thin film. Increasing the ionic strength results in the coiling of the chains, which become less extended but increase in volume.^[11] This, in turn, results in an increase in layer thickness. Standard values of ionic strength for PEM fabrication range between 0.1 and 1 M NaCl due to considerations of layer thickness and packing of polyelectrolyte chains.^[7,12,13]

Polyelectrolyte assembly can, nevertheless, be performed at higher ionic strengths even though the electrostatic interaction between subsequent layers is reduced because of charge screening. There are examples in literature of PEMs assembly and studies of PEM stability at salt concentrations higher than 1 M NaCl. Although electrostatic interactions become weaker, the assembly at high ionic strengths is still favored by the release of counterions during layer assembly. It has been reported that poly(diallyl dimethyl ammonium chloride) (PDADMAC)/poly(styrene sodium sulfonate) (PSS) remains stable at 3 M NaCl but post-treatment of these multilayers with 4 and 5 M NaCl leads to the destruction of the layered structure.^[14] Also fusion of PSS/PDADMAC microcapsules at increasing salt concentration above 3 M has been shown.^[15]

In general, PEMs do not show significant changes in thickness with the ionic strength. It has been reported that an increase in the ionic strength makes PEM swell since the interaction between oppositely charged polyelectrolytes is weakened and the film has the possibility to swell.^[7] On the contrary, we have shown that for thick films of PDADMAC/PSS assembled at 0.5 M NaCl, an increase in the ionic strength causes the PEM to reduce thickness and water content in a reversible way.^[16] The PEM employed had a thickness over 157 nm built after 17 layers. A reversible decrease in thickness between 70 and 100 nm was observed when the PEMs were exposed to 0.5 M or 1 M NaCl solutions, respectively. This behavior was explained as the result of conformational changes in the top layer of PDADMAC and it is largely absent when PSS is the top layer.

In this study, we explore the LbL assembly and responsiveness of PDADMAC and PSS at 3 M NaCl. Working at this salt concentration, polyelectrolyte assembly takes place and results in highly hydrated thick PEMs. These films release water and experience a reduction in thickness of more than 200 nm when they are exposed to pure water as we will show by the quartz microbalance with dissipation (QCM-D) and atomic force microscopy (AFM). Changes in thickness and water content are fully reversible and comparable with those observed

in polyelectrolyte brushes following changes in the ionic strength. But contrary to polyelectrolyte brushes or to PDADMAC/PSS PEMs prepared at 0.5 M NaCl, PDADMAC/PSS PEMs assembled at 3 M remain in a collapsed state at low ionic strength and are extended at 3 M NaCl.^[17,18] The observed phenomena can be interpreted as a consequence of the high water uptake during the assembly at 3 M NaCl and a reversible conformational change in the polyelectrolytes in the PEM. At 3 M NaCl, the interaction between PSS and PDADMAC is weak and probably there is a high concentration of free amine and sulfonate groups in the layer. This excess of ionic groups can generate a strong osmotic difference that makes the PEM swell. At low ionic strength the interaction between PDADMAC and PSS layer becomes stronger and there is an overcompensation of charges resulting in the deswelling of the PEM.

A responsive polyelectrolyte film that increases thickness close to a 50% with increasing ionic strength has not been reported before. PDADMAC/PSS PEMs combining ease of preparation with the capability of reversible changes in thickness of more than 200 nm can have interesting applications in the fabrication of smart surfaces and nanoactuators.

2. Experimental Section

2.1. Chemicals

Poly(sodium 4-styrene sulfonate) [$\bar{M}_w \approx 70,000$], poly(diallyldimethyl ammonium chloride) 20% in water [$\bar{M}_w = 2 \times 10^5 - 3.5 \times 10^5$], and Sodium chloride were purchased from Sigma-Aldrich. All reagents were used without further purification.

2.2. Methods

QCM-D PEMs formation was monitored with an E4 quartz crystal microbalance with dissipation (QCM-D) from Q-Sense, Goteborg, Sweden. QSX 303 SiO₂ (50 nm)-coated quartz crystals (5 MHz) from Q-Sense, previously treated using a UV-Ozone cleaning protocol, were used as substrates to be coated in situ in the chamber with PDADMAC/PSS films.

The quartz crystals are blown with a N₂ gun, placed during 20 minutes inside a UV-Ozone procleaner chamber from Bioforce nanoscience, removed and blown again with N₂ gun prior to use them for the LbL deposition. Inside the chamber, a mercury vapor lamp generates 254 nm light, which cleaves organic molecules deposited on the surface. The atmospheric oxygen is converted into reactive ozone, which degrades small molecular fragments creating volatile organics.

The LbL technique was performed in situ in the QCM-D chamber by passing, with a peristaltic pump, a 1 mg mL⁻¹ polyelectrolyte solution in 3 M NaCl through the water-filled QCM-D chamber. The fundamental frequencies of the system were found in water to establish a reference zero value. Polyelectrolyte deposition was followed by the decrease of the resonance frequency of

the quartz crystal. When the frequency levels stabilized, the polyelectrolyte solution was replaced by a 3 M NaCl solution until a plateau in the frequency response was reached. This procedure was repeated until the deposition of the desired number of layers was achieved. QCM-D data were acquired for the third overtone (15 MHz) with subsecond time resolution.

2.3. Atomic Force Microscopy

Cross-sectional analysis of the PEMs was measured with a Veeco Multimode atomic force microscope (AFM) connected to a Nanoscope V controller, the PEMs films previously deposited by QCM-D were manually, softly cut with a razor blade, making stripes, and imaged in Tapping mode in a closed fluid cell allowing the “in situ” exchange of salt to water. The particular silicon nitride cantilever used was a DNP available from Bruker with a $K = 0.32 \text{ N m}^{-1}$.

3. Results

PDADMAC/PSS PEMs were grown at 3 M NaCl in the QCM-D chamber. Changes in frequency response and dissipation were measured for each layer deposited (Figure 1). The initial three polyelectrolyte layers were assembled in 0.5 M NaCl to facilitate the polyelectrolyte deposition on top of the silica surface. After the third layer, polyelectrolytes were assembled at a salt concentration of 3 M NaCl. At this salt concentration the interaction of the first PDADMAC layer and the silica is too weak and the assembly proceeds with difficulty and for that reason it was decided to start first with 0.5 M NaCl. After the third layer, the assembly was performed at 3 M NaCl. A total change in the frequency response of 2600 Hz was measured after the 11th polyelectrolyte layer was deposited. This frequency variation is

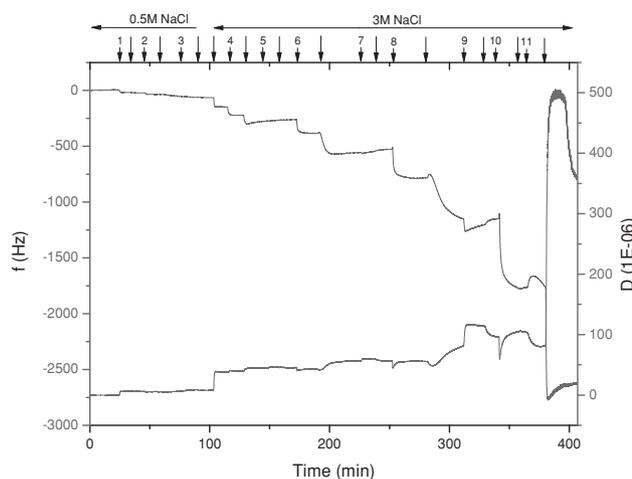


Figure 1. Frequency response and dissipation curves measured with QCM-D showing the variation of the third overtone during the assembly of 11th layers PDADMAC/PSS PEM in 3 M NaCl.

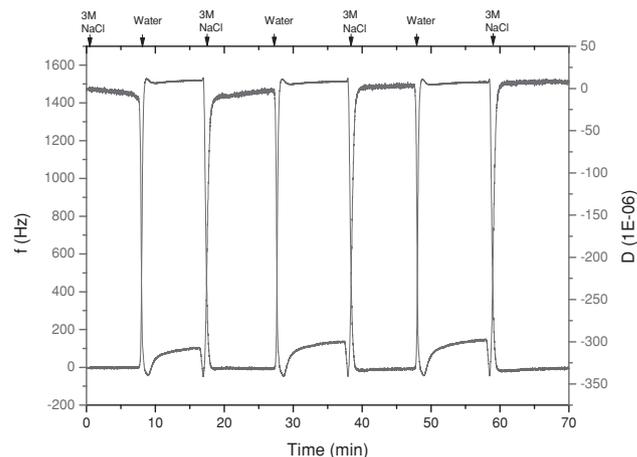


Figure 2. Frequency response and dissipation curves measured with QCM-D (third overtone) for the alternating rinsing of 11 layers of PDADMAC/PSS with water and 3 M NaCl.

significantly higher than for the same polyelectrolyte combination assembled at 0.5 M NaCl, around 300 Hz after 11 layers and 800 Hz after 17 layer deposition.^[17]

A total mass of $47.28 \mu\text{g cm}^{-2}$ can be calculated according to the Sauerbrey equation (Equation 1), where $C = 18.06 \pm 0.15 \text{ ng cm}^{-2} \text{ Hz}^{-1}$.

$$m_{\text{QCM}} = -C \left(\frac{\Delta f_i}{i} \right) \quad (1)$$

When the film is exposed back to the 3 M NaCl solution, the frequency goes back to their original values before the treatment with water. In Figure 2, we can appreciate the changes in frequency and dissipation as a film is alternatively exposed to water and 3 M NaCl.

In Figure 2, a PEM is subsequently exposed to water and 3 M NaCl up to 6 times. The changes are fully reversible. The exchange of the 3 M NaCl bulk solution with water results in a change of frequency of approximately 1500 Hz and a reduction in dissipation of 300 e^{-6} . The frequency change corresponds to a mass variation of $27.30 \mu\text{g cm}^{-2}$ approximately 42% of the total mass. This change in frequency would mean, in terms of acoustic thickness, a variation of approximately 273 nm of the total thickness of the film. A reversible decrease in the frequency response of the PEM can only be explained as the system losing water when exposed to water and regaining the lost water when exposed to 3 M NaCl. The change in dissipation is also indicative of a system becoming more rigid when the ionic strength is reduced. Such behavior resembles more that of a polyelectrolyte brush than a PEM but with an opposite trend. Brushes are extended in water and reduce thickness, losing water and become more rigid as the ionic strength increases. Recently, we have shown that thick PDADMAC/PSS multilayers (17 layers) assembled at

0.5 M NaCl display similar behavior to a polyelectrolyte brush and also show pronounced thickness variations with reversible loss of water when exposed to water and solutions of higher ionic strengths.^[16] Assembling PEMs at 3 M NaCl, results in thicker PEMs at 11 layers with a mass significantly larger than that obtained after assembling 17 layers at 0.5 M NaCl. The opposite behavior in response to the ionic strength variation highlights a different arrangement of the polymer chains in the PEM and hints that the chains have different conformational freedom within the PEM.

When PSS is the last layer the film initially shows a decrease frequency when passing from 3 M NaCl to the aqueous solution but the changes lose their reversible character after a couple of washings and the frequency starts to increase in water at certain point. In Figure S1 (Supporting Information), the frequency and dissipation are shown for the alternating rinsing of 10 layers of PDADMAC/PSS with water and 3 M NaCl. The first rinsing with water causes the frequency to increase and the washing back with a 3 M NaCl solution returns frequency to original values. In the next washing with water frequency increases but less than in the first washing. In the third washing, however, the frequency starts increasing instead decreasing, becoming more negative in the fourth washing. In all cases, the frequency returns to its original values at 3 M NaCl. The same tendency is observed for the dissipation, which always turns more positive in water and returns to original values in 3 M NaCl but it does not follow a clear trend. A decrease in frequency as shown by in Figure S1 (Supporting Information) after three washings with water could be meaning that the PEM at a certain point starts taking up more water instead of releasing. The increase in dissipation with the water washings speaks of a film becoming more viscoelastic and it is opposite to the trend shown by the films with PDADMAC as top layer. The behavior of the PEMs with PSS as top layer requires a deeper structural study that is underway. In any case, the results from QCM-D show a different trend and responsiveness of the PEMs according to the top layer and hint that the observed water release and thickness changes are due to processes taking place at the top layer.

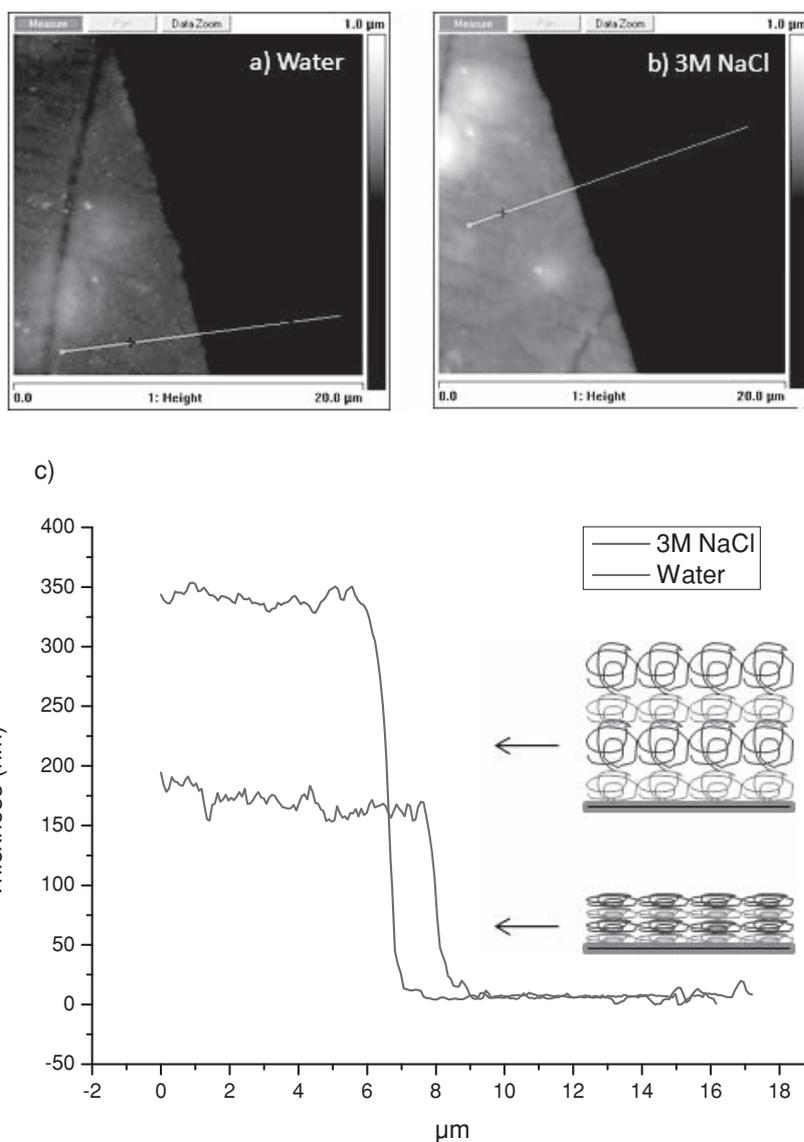


Figure 3. AFM images of an 11 layer PDADMAC/PSS PEMs in a) water and in b) 3 M NaCl, and c) cross-sectional analysis.

We employed AFM to verify the changes in the PDADMAC/PSS PEMs observed by QCM-D measurements. AFM helps to visualize thickness variations in the film. A stripe of PEM was removed from the film as explained in “Section 2.” By doing this, a profile of the film was created that allows changes in film thickness to be measured from the naked substrate to the top of film.

AFM images in Figure 3a and b have been taken in water and at 3 M NaCl respectively. The thickness profile of the PEM, from the removed area to the top of the PEM, is shown in Figure 3c for both water and 3 M NaCl. The profiles clearly illustrate that there is a decrease in thickness of the film of approximately 185 nm, approximately 46% of the total thickness, when going from 3 M NaCl to water. The AFM measurements confirmed that the change was

reversible and the multilayer regained its original thickness when going back to 3 M NaCl.

However, the roughness of the films increased as the ionic strength decreased. An average roughness (R_a) of 1.03 was calculated in 3 M NaCl, while in water the values of R_a increased to 18.03. This can be understood as the chains grow laterally; the packing of the grains is altered creating defects between grains.

Both QCM-D and AFM measurements prove the reversible collapse of the PDADMAC/PSS PEMs with PDADMAC as top layer when decreasing the ionic strength by water loss and thickness reduction. The changes in thickness correspond to approximately 200 nm, and the water loss represents approximately 42%–46% of the total mass. Such variations in thickness and water content are more significant than the usually observed with polyelectrolyte brushes.^[17] Taking brushes as a reference for responsive polyelectrolyte films with varying ionic strength, PDADMAC/PSS PEM prepared at 3 M NaCl shows an opposite behavior to the expected ionic strength response. Due to a decrease in the ionic strength, the thickness of the film decreases. This can be explained by the change in conformation of the polyelectrolyte molecules that results in a thickness reduction and a lateral growth of the chains that, in turn causes the water entrapped in the layers to be expelled. The collapse of brushes can be explained by the screening of the charges of the chains, which diminishes the internal repulsion of the charged monomers, allowing the chains to acquire a more coiled conformation. Also at 3 M NaCl, the interaction between PSS and PDADMAC must be weak and this may lead to uncompensated monomers, not interacting with the previously assembly polyelectrolyte layer, and the presence of more counter ions than the normal assembly conditions at 0.5 M. The presence of these uncompensated monomers and their counter ions could generate an osmotic difference that makes the layer swell and gain water. When the ionic strength is decreased and the 3 M NaCl solution replaced by water, the interactions between the polyelectrolytes layers may increase and the number of uncompensated monomers and free ions may also decrease as well as the osmotic difference with bulk. The film should then release water. The interaction between the layers in water may indeed trigger a lateral displacement of the chains in a layer trying to maximize the contact with the layers below and above. This would also cause a reduction in water content. In any case, there is a reorganization of the polyelectrolyte layers when changing the ionic strength that causes the release of water entrapped in the film. For PDADMAC, the change in water content is reversible but not for PSS. This means that the intrinsic arrangements of the polymer chains in the layer for PDADMAC and PSS are different. More structural studies on the structure of the polyelectrolyte layers assembled at 3 M NaCl in the film at

different ionic strengths are on going to fully understand their changes with the ionic strength.

4. Conclusions

PEMs with the ability to collapse, displaying a variation in thickness of 200 nm, approximately a 46% reduction in its thickness, has been fabricated by assembling PDADMAC/PSS at 3 M NaCl. PEM assembly at 3 M NaCl with the chains highly coiled results in a high content of water entrapped between polyelectrolyte chains. When reducing the ionic strength to that of pure water the chains expand and flatten, thus occupying lateral space and removing the water between chains. As a consequence, the thickness of the PEM is reduced. An increase in the ionic strength to 3 M reverses the process and the film stands up and regains the water lost. Such a PEM film could have interesting applications, such as nanoactuators or controllable barrier. Applications that are normally regarded for polyelectrolyte brushes, with the advantage that the response of the PEMs to varying ionic strength would be opposite to that observed by a brush, collapsing at low ionic strength and increasing thickness at 3 M NaCl. Additionally, the thickness of the film can be easily varied over a few hundred nanometers by simply controlling the number of polyelectrolyte layers assembled.

Supporting Information

Supporting Information is available from the Wiley Online Library or from the author.

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