

# Influence of salt on assembly and compression of PDADMAC/PSSMA polyelectrolyte multilayers

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Influence of NaCl and NaBr and their concentration on assembly of polyelectrolyte multilayers and their compression behavior was studied using poly(diallyldimethylammonium chloride) (PDADMAC) and poly(4-styrenesulfonic acid-co-maleic acid, 1 : 1 SS:MA) sodium salt (PSSMA 1 : 1) as the building blocks. Stepwise growth of the PSSMA/PDADMAC multilayers was characterized by a quartz crystal microbalance with dissipation (QCM-D), revealing faster and slower growth of the layer thickness in higher concentration of NaCl and NaBr solutions, respectively. Moreover, QCM-D, ellipsometry and scanning force microscopy (SFM) measurements demonstrated that the multilayers were highly hydrated with a factor of  $3 \sim 9$  in a wet state depending on the type and concentration of the salts used during the assembly. The type and concentration of the salts used during the assembly also influenced greatly the compression ratio of the polyelectrolyte multilayers, *i.e.* the compression ratio increased along with the increase of NaCl concentration, whereas it was constant when NaBr was used. The friction force of the PEI(PSSMA/PDADMAC)<sub>7</sub> multilayers measured by SFM showed that the force peaks gradually shifted from low to high scanning frequency along with the increase of NaCl concentration, illustrating the gradual softening of the multilayers. By contrast, the peak positions in the friction force curves for all the multilayers assembled in NaBr solution kept unchanged regardless of the NaBr concentration. Contrast experiments further revealed that the compression ratios, masses in wet and wet thicknesses of the multilayers alternately treated in Cl<sup>−</sup> and in Br<sup>−</sup> solutions were all reversible.†

## Introduction

The layer-by-layer (LbL) technique, first introduced by Iler<sup>1</sup> in 1966 and re-established and refined by Decher<sup>2</sup> in the 1990s, has shown great success in fabricating polymer thin films with controllable compositions, structures and properties.<sup>3</sup> In 2002, CIBA-Vision has announced the first commercially available product that is equipped with a multilayer coating.<sup>4</sup> The ultrathin films are also expected to be used as chemical and biological sensors,<sup>5–7</sup> drug delivery carriers,<sup>8–10</sup> micro-electronics,<sup>11,12</sup> and nano-optics<sup>13,14</sup> *etc.* In this context, the creation of physical and chemical patterns on the multilayers is of practical importance.

Several techniques have been developed for obtaining the chemical and/or physical patterns on polyelectrolyte multilayer films.<sup>15–18</sup> For example, Hammond and co-workers fabricated complex multilevel microstructures by patterning

an initial set of multilayer films using a microcontact printing ( $\mu$ CP) technique, and then patterning atop the surface of the subsequently assembled multilayers.<sup>19</sup> Rubner and co-workers used a water-based subtractive patterning technique to micropattern multilayers such as poly(acrylic acid) (PAA)/polyacrylamide (PAAm) and poly(methacrylic acid) (PMA)/PAAm constructed by hydrogen-bonding to create more complex cell-resistant/-adhesive surfaces.<sup>20</sup> Besides the frequently used poly(dimethylsiloxane) (PDMS) stamp, other polymeric molds such as polyurethane acrylate mold, UV-cured hard mold and hydrophilic composite mold have also been used for the polyelectrolyte multilayer patterning.<sup>21–23</sup>

In 2004, we found an important phenomenon of the multilayer compression, which can yield geometric patterns on the multilayers without an alteration of their surface chemistry.<sup>24</sup> The overall compression degree of poly(styrene sulfonate) (PSS)/PDADMAC multilayers is as high as 70–90% depending on the film thickness, and thereby the absolute height of the formed patterns increases along with the layer number and concentration of NaCl used during the assembly. The multilayer compression depends on several factors such as the multilayer compositions and drying conditions. At the experimental conditions, the multilayers assembled with PDADMAC as one component and dried at 40–70% relative humidity (RH) for 12 h can be compressed by pressing a PDMS stamp against the multilayers. The formed patterns are not varied even

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incubated in 2 M NaCl solution. The enhanced stability is also observed in PAA/PDADMAC multilayers assembled at pH 11. Pores with a diameter of microns appeared in the uncompressed PAA/PDADMAC multilayers as a result of pH variation, but are completely inhibited after compression.<sup>25</sup> It is understandable that after compression a more densely packed microstructure is formed in the multilayer films, namely, the compression leads to shrinkage of the vacancies in the multilayer films.<sup>26</sup> Moreover, the compressed films become more hydrophobic because of the exposure of the hydrophobic groups.<sup>27</sup>

Besides the humidity during drying, the drying time is another important factor controlling the pattern formation.<sup>28</sup> After the poly(4-styrenesulfonic acid-co-maleic acid) sodium salt (PSSMA)/PDADMAC multilayers were dried at 70% relative humidity and room temperature for 2, 6 and 12 h, compression of the multilayers by the PDMS stamp with linear patterns obtained double strips, high ridges and linear patterns on the multilayers, respectively. The stability of these patterns is very different. While the compression created patterns (12 h drying) are still very stable, the strips and high ridges formed by the lateral flow of the multilayers (2 or 6 h drying) can be erased by incubation in water.

It is known that the structures and properties of the polyelectrolyte multilayers are influenced by many factors during the assembly and/or post-fabrication such as types of the polyelectrolytes and salts, salt concentration, temperature, pH, *etc.*<sup>29–34</sup> Therefore, it can be expected that these factors will in turn influence the compression performance as well. In this work, we shall focus on the effect of salt on the multilayer compression, which influences the charging degree and physical entanglement of the polyelectrolytes during assembly and the binding strength of the multilayers.

In the assembly procedure, it has been diversely demonstrated that the concentration of NaCl, which is the most frequently used salt, can significantly control the deposited amount of a layer. For the strong polycation/polyanion pair, the film thickness is approximately proportional to the salt concentration, and reaches to 27 nm/bilayer for the PSS/PDADMAC multilayers assembled in 1 M NaCl.<sup>35</sup> For the multilayers made from a combination of a weak polyacid and a strongly dissociated polycation, the film thickness will reach a maximum and then decrease quickly along with the increase of salt concentration.<sup>36</sup> However, Klitzing and co-workers have found that below a charge density of 50% of the building block the film thickness is independent of NaCl concentration, whereas it increases along with  $c\text{NaCl}^{1/2}$  above a charging degree of 75%.<sup>37</sup> Kovačević *et al.* have found that regular buildup of multilayers is independent of the types of salts used at a very low ionic strength. However, at a higher ionic strength, multilayer dissolution will take place, and the critical “glass-transition ionic strength” needed for the multilayers to be dissolved depends on both the polycation/polyanion pair and the salt used.<sup>38</sup>

On the other hand, post-treatment of the multilayers in salt solution shall also bring significant variation of the multilayer structure. For example, the morphology of the films can be annealed when they are immersed in salt solutions of various concentrations.<sup>39</sup> The stability of the multilayers composed of

a weak polycarboxylic acid and one of several polycations each having different charging density can be increased dramatically in salt solutions when the pH value is below a critical point.<sup>40</sup> On the other hand, the polyelectrolyte multilayers are swollen on exposure to salt solutions, the degree of which strongly depends on the polyelectrolyte pairs constituting the multilayers.<sup>41</sup> Using the polyelectrolytes of PAA and poly(allylamine) (PAH), Fery *et al.* fabricated nanometer-sized porous film by exposing the film assembled in salt solution to pure water for a period of time.<sup>42</sup>

Previously we have found that the compression degree of PSS/PDADMAC multilayers assembled below 1 M NaCl is between 70–90%, and shows no regular correlation with the salt concentration.<sup>24</sup> Probably the softness and the defects of these multilayers have no significant difference. As the salt can significantly influence the multilayer structures and properties, in this work we shall study the multilayer compression mediated by the type of salts and salt concentration, using PSSMA/PDADMAC multilayers as typical examples. It is expected, the weakly charged MA segments are more sensitive to the salt type and concentration. The results indeed show that the compression ratio increases along with the increase of NaCl concentration used during the assembly, whereas keeps constant when NaBr is used. Further studies show that the compression ratio of the multilayers treated in NaCl and NaBr solutions is reversible. The results not only disclose some basic properties of the multilayers at different ionic strengths or types of salt, but also augment the compression technique for facile fabrication of patterns on the multilayers. Particularly, the present work is useful for understanding the influence of counter anions on film mechanical properties, which might be neglected by many others in their work. To our best knowledge, although the influence of salt on the polyelectrolyte multilayer films has been extensively studied, neither the effect of NaBr on this PSSMA/PDADMAC pair containing both weak and strong charge interactions nor the influence of salt on the multilayer compression has been studied.

## Materials and methods

### Materials

Polyethyleneimine (PEI, Mn 60 kDa, Mw 750 kDa), poly(diallyldimethylammonium chloride) (PDADMAC, very low molecular weight), poly(4-styrenesulfonic acid-co-maleic acid) sodium salt (PSSMA, SS:MA 1:1, Mw 20 kDa) and poly(styrene sulfonate) sodium salt (PSS, Mw 70 kDa) were obtained from Aldrich and used as received to prepare 1 mg mL<sup>-1</sup>/0.3–1 M NaCl or NaBr solutions. Poly(dimethylsiloxane) (PDMS) prepolymers, Sylgard 184, were obtained from Dow Corning and were used to fabricate the PDMS stamps with desired pattern structures.

### Substrate preparation

Silicon wafers were firstly cleaned with piranha solution (70:30 v/v% sulfuric acid/hydrogen peroxide) (*Caution: piranha is a strong oxidizer and should not be stored in a closed container*), and then were sonicated in a 1:1 mixture of water and 2-propanol for 15 min. They were further treated in a

5:1:1 mixture of water, hydrogen peroxide (30%) and ammonia solution (29%) at 60 °C for 15 min. After the wafers were rinsed in a copious amount of water, they were blow-dried in a nitrogen stream.

### Assembly of polyelectrolyte multilayers

To establish a highly charged precursor layer on the surface, a layer of PEI was firstly deposited on the silicon substrates. Sequential adsorption of polyelectrolytes on the silicon substrates was then performed by manual dipping to obtain the multilayers for scanning force microscopy (SFM) and ellipsometry studies. Between alternate exposures to two kinds of polymer solutions for 15 min, there were 3 rinses with triple-distilled water containing 0.1 M NaCl or NaBr for 3 min. The NaCl or NaBr concentration of the polyelectrolyte solutions was varied from 0.3 to 1 M. After the desired layer numbers were deposited, the PSSMA/PDAMMAC multilayers were rinsed with triple-distilled water for at least 5 min to eliminate the adsorbed salt (salt crystals on the film surface greatly interfere the accurate measurement of morphology, surface roughness, frictional force and pattern height). The multilayers were then dried in 70% relative humidity (RH) at room temperature (20 °C) for 12 h before compression.

### Creation of the patterns under pressure

The PDMS stamps with strips were molded from lithographically prepared masters.<sup>43,44</sup> The PDMS stamps had a physical pattern structure of strips (6 × 6 μm in width and space with a depth of 2 μm). The soft PDMS stamps were put onto the polyelectrolyte multilayers obtained in the previous section with the patterned surfaces towards the multilayers under a normalized pressure of 200 g cm<sup>-2</sup>. 2 h later, the stamps were carefully peeled off to obtain the patterned multilayers.

### Post-treatment of the multilayers

The PEI(PSSMA/PDADMAC)<sub>7</sub> multilayers were incubated in 1 M salt solution at room temperature for 8 h, and compressed according to the above process. The pattern heights of the compressed multilayers treated with different salts were then checked by scanning force microscopy (SFM).

### SFM

Topographic images were collected using SPI3800N Probe Station and SPA400 SPM Unit (Seiko Instruments Inc.) in a dynamic force mode in air. Silicon tips with a resonance frequency  $f_0$  of 150 kHz and a spring constant of 20 N m<sup>-1</sup> were utilized. The scanning frequency was 0.5 Hz. The contact force between the tip and the samples was kept as low as possible (<2.5 nN). To measure the film thickness, part of the films was scratched off by a thin needle of syringe. Then the height difference between the exposed silicon substrate and the multilayers was measured.

### Lateral force measurements

To investigate the relaxation behavior of the multilayer surface, frictional forces were measured by SFM at 20 °C in a closed chamber with certain humidity. The lateral force

curve was obtained in a contact force mode under a repulsive force of 25 nN. A triangle 100 μm cantilever with a force constant of 0.09 Nm<sup>-1</sup> and an integrated silicon nitride (Si<sub>3</sub>N<sub>4</sub>) tip were applied. The magnitude of the lateral force was evaluated with the line scan mode. The scan rate was equal to 2 × (scan length) × (scan frequency). Six friction loop cycles were averaged for every measurement to improve the signal-to-noise ratio.<sup>45</sup>

### Ellipsometry

The thicknesses of the multilayers (30–60% relative humidity) were also measured by ellipsometry. The measurement was carried out on a variable-angle spectroscopic ellipsometer (model VASE; J. A. Woollam Inc., Lincoln, NE) at incident angles of 65, 70 and 75° within a wavelength range of 600–1700 nm. The thickness was calculated from the ellipsometric parameters,  $\Delta$  and  $\psi$ , by which the film thickness and refractive index was automatically fitted using a Cauchy model. Data were obtained on a different place of the film and reported as mean ± standard deviation.

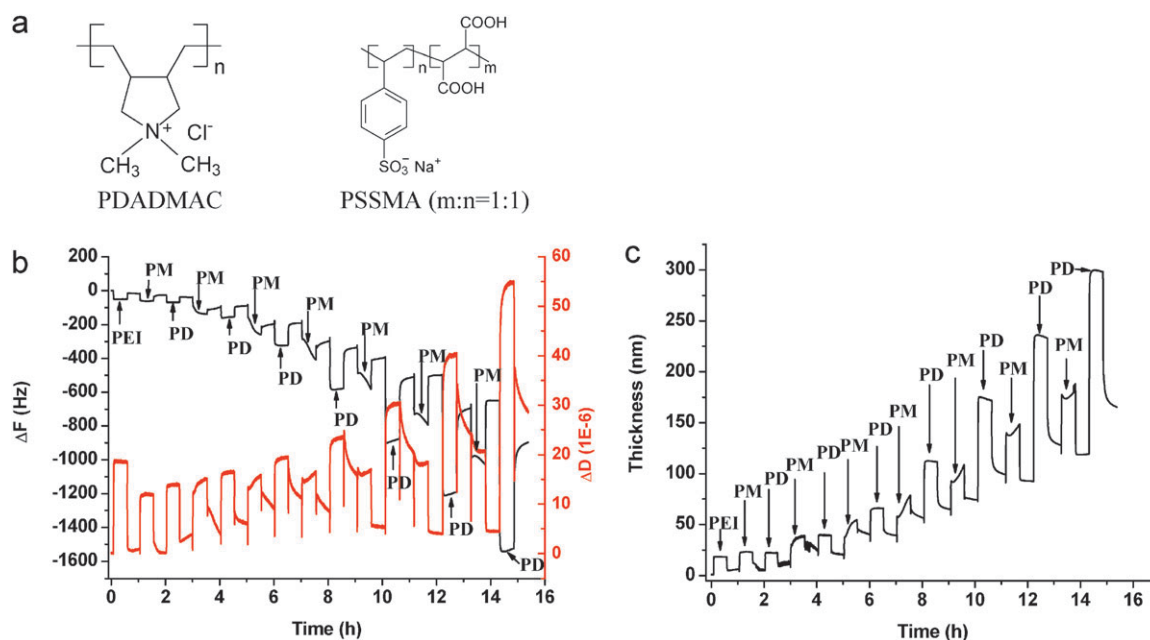
### Quartz crystal microbalance with dissipation

The changes of frequency and dissipation of the multilayers were monitored by a quartz crystal microbalance with dissipation (QCM-D) (model Q-SENSE E4) during the multilayer assembly. Gold coated quartz crystals (5 MHz) initially covered by PEI were used as substrates. PSSMA and PDADMAC layers were alternately deposited. The incubation time was 30 min for each layer, followed by washing with 0.1 M NaCl or NaBr for 30 min. In total up to 7 bilayers of PSSMA/PDADMAC were assembled on the crystals. The wet thickness was fitted based on a Voigt model with the Q-tools graphing and modeling software from Q-SENSE E4 by assuming a density of 1.1 g cm<sup>-3</sup> for the multilayers.

## Results and discussion

It is known that the influence of anions on the multilayer properties is much larger than that of cations because the anions have much larger difference in polarizability due to their larger variety of diameters.<sup>46</sup> Therefore, in this work we compared the effect of NaCl and NaBr on both multilayer assembly and compression.

First, the deposition process of PSSMA and PDADMAC (molecular structures shown in Fig. 1a) was monitored by QCM-D. The temperature of the deposition solution was kept between 4–10 °C to avoid the potential influence of temperature on the assembly as reported before for PSS/PDADMAC pair.<sup>47</sup> Within this temperature range, the influence of temperature alteration on the thickness of the PSSMA/PDADMAC multilayers was very trivial and thus could be neglected. Fig. 1b shows that, in 1 M NaBr solution, the frequency decreased regularly along with the increase of the layer number, whereas dissipation oscillated with an enhanced amplitude at the larger layer number. Generally, the frequency was decreased after each adsorption of the polyelectrolyte, and increased to some extent after rinsing. The overall decrease tendency confirms the successful assembly of the PSSMA/PDADMAC multilayers. According to the frequency and



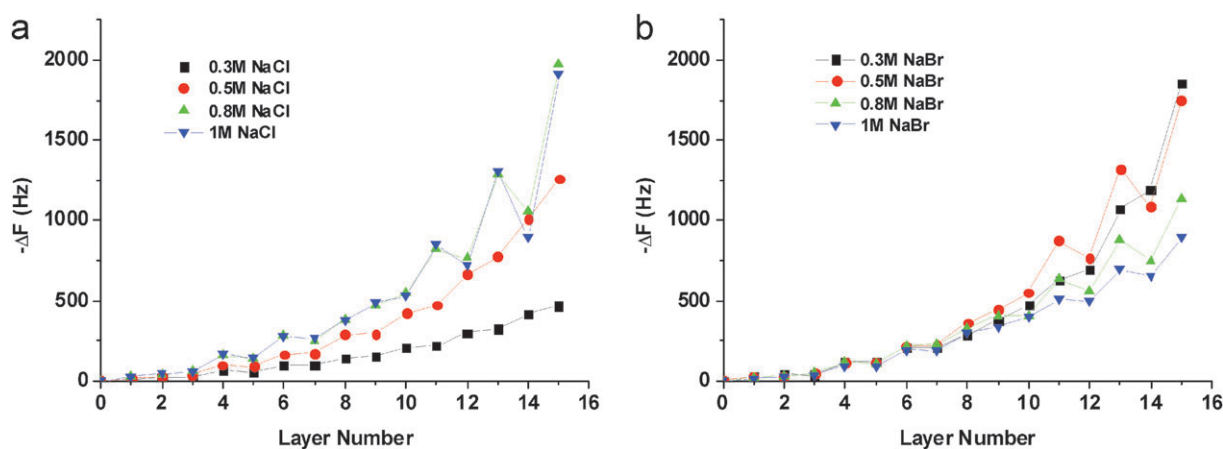
**Fig. 1** (a) Chemical structures of the polyelectrolytes used. (b) Changes in frequency ( $\Delta F$ ) and dissipation ( $\Delta D$ ) during assembly of PSSMA/PDADMAC multilayers in 1 M NaBr solution, where the overtone number  $n$  was 3. (c) Corresponding wet thickness as a function of the layer number. PM and PD represents PSSMA and PDADMAC in this figure, respectively.

dissipation changes, the film thickness in the wet state was obtained (Fig. 1c). It shows that after 12 layers (here PEI as the first layer), adsorption of PSSMA resulted in the overall decrease of the film thickness in comparison with the precursory layer.

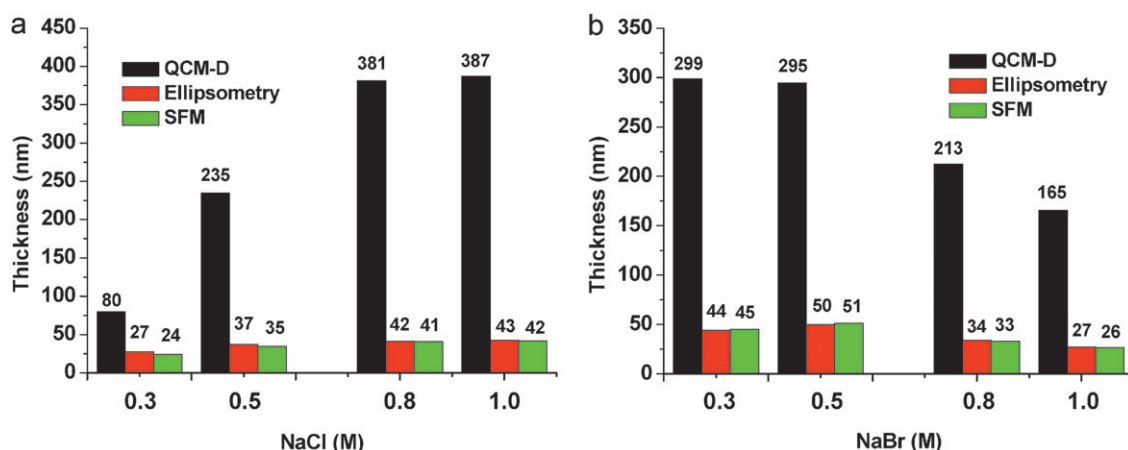
Using the QCM-D, growth (here a change of the frequency is used so that the mass can be unambiguously identified) of the PSSMA/PDADMAC multilayers in NaCl or NaBr solution with various concentrations was similarly monitored (Fig. 2), showing a significant influence of salt in particular at higher concentration. In all salt solutions regardless of the salt type and concentration, all the  $-\Delta F$  increased along with the layer number with a sharper rate at a higher layer number, demonstrating that the PSSMA/PDADMAC multilayers can be successfully assembled in these conditions. Again, the

zigzag alterations of the  $-\Delta F$  were observed after 12 layers for all multilayers assembled in NaBr solutions and in NaCl solutions with a concentration higher than 0.8 M, revealing the overall desorption of the multilayer mass after PSSMA deposition. On the other hand, the difference between the multilayers assembled in a different salt solution is also distinctive. In the NaCl solution, the adsorbed mass at a higher layer number was generally increased along with the salt concentration until 0.8 M (Fig. 2a). However a reverse alteration of the adsorbed mass along with the NaBr concentration was observed (Fig. 2b).

The intrinsic reason for the zigzag growth behavior shown in Fig. 2 should most possibly attribute to the overall adsorption and weak bonding of the polyelectrolyte in the superficial layer because the same phenomenon has been observed by



**Fig. 2** Changes in frequency ( $\Delta F$ ) of PSSMA/PDADMAC multilayers as a function of the layer number. The multilayers were assembled in (a) NaCl solution and (b) NaBr solution with concentrations of 0.3, 0.5, 0.8, and 1 M.



**Fig. 3** Thicknesses of the PEI(PSSMA/PDADMAC)<sub>7</sub> multilayers assembled in (a) NaCl solution and (b) NaBr solution with different concentrations. The wet thickness was measured in 0.1 M NaCl (a) and 0.1 M NaBr (b) solution (by QCM-D), respectively, while the dry thickness was measured (using ellipsometry and SFM) after the multilayers were rinsed with water. The data in the figure represent the film thickness in nm.

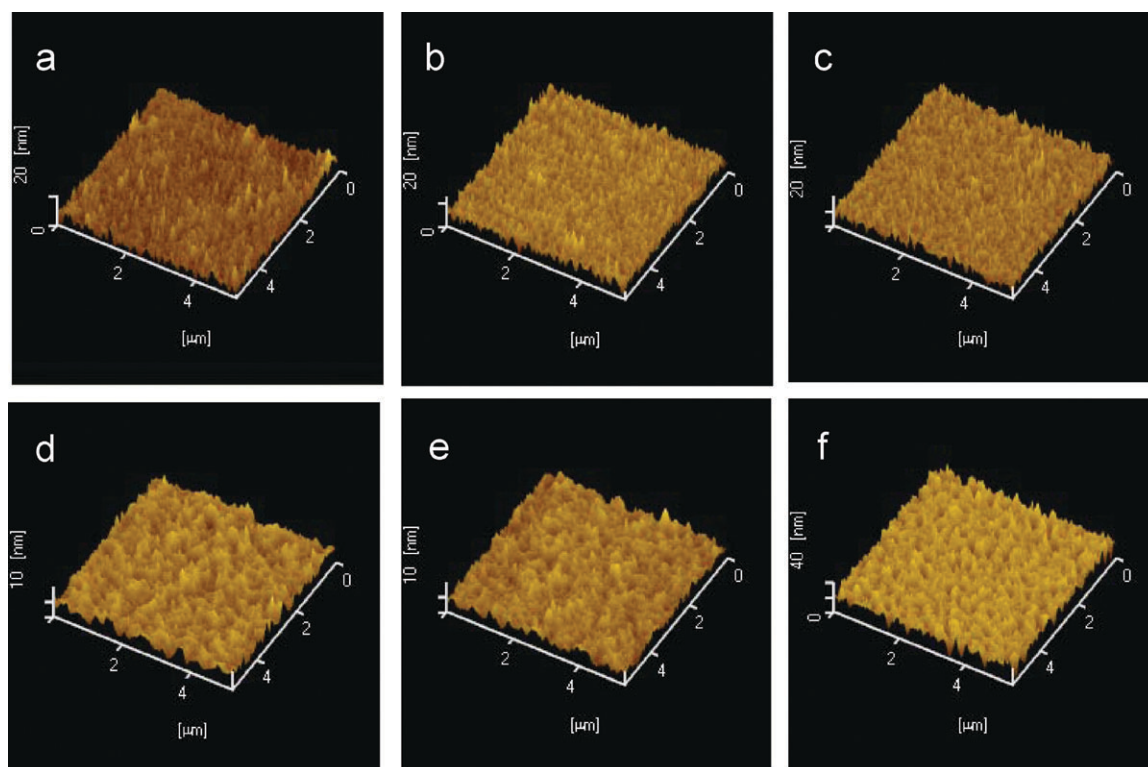
ellipsometry and absorbance spectroscopy in a dry state,<sup>48–50</sup> though the changes in the viscoelasticity on the measured mass may also have influence.<sup>51</sup> Here when the multilayers ending with PDADMAC are further brought into contact with a PSSMA solution, some of the loosely attached PDADMAC molecules on the super-surface will interact with PSSMA in the solution to form PSSMA/PDADMAC complex, leading to partial release of PDADMAC. This will result in the overall decrease of the deposited mass but building block and charge reversal.

Fig. 3 compares the thicknesses of PEI(PSSMA/PDADMAC)<sub>7</sub> multilayers assembled in NaCl (Fig. 3a) and NaBr solutions (Fig. 3b) with variable salt concentrations. Here the wet thickness was obtained from QCM-D, and the dry thicknesses were measured by SFM and ellipsometry. It shows that along with the increase of salt concentration, the film thickness has an overall reverse alteration tendency. At a higher salt concentration such as 1 M, in NaCl solution both the wet and dry thicknesses of the PEI(PSSMA/PDADMAC)<sub>7</sub> multilayers were increased, whereas in NaBr solution thinner films were obtained. While the dry thickness of the films measured using AFM and ellipsometry is very consistent for the PEI(PSSMA/PDADMAC)<sub>7</sub> multilayers assembled in a definite salt solution, the wet thickness measured by QCM-D is quite different and is several times the one measured in a dry state. Moreover, the ratio between the wet and dry thickness increases and decreases for the multilayers assembled in NaCl and NaBr solution, respectively. These results reveal the fact of the highly hydrated nature of the multilayers in the wet state, and the variable hydration degree mediated by the types and concentration of the salts used during assembly. This is quite normal since the ionic strength can significantly affect the conformation and charge density of the polyelectrolytes, and thereby the growth and properties of the multilayers.<sup>33,40,52–54</sup> With increasing salt concentration, the polyelectrolyte molecules become more entangled because of screening of the charge repulsion of the polyelectrolytes, therefore a thicker film is produced.<sup>55</sup> This is exactly the case for the multilayers assembled in NaCl solution. However, when NaBr is used as

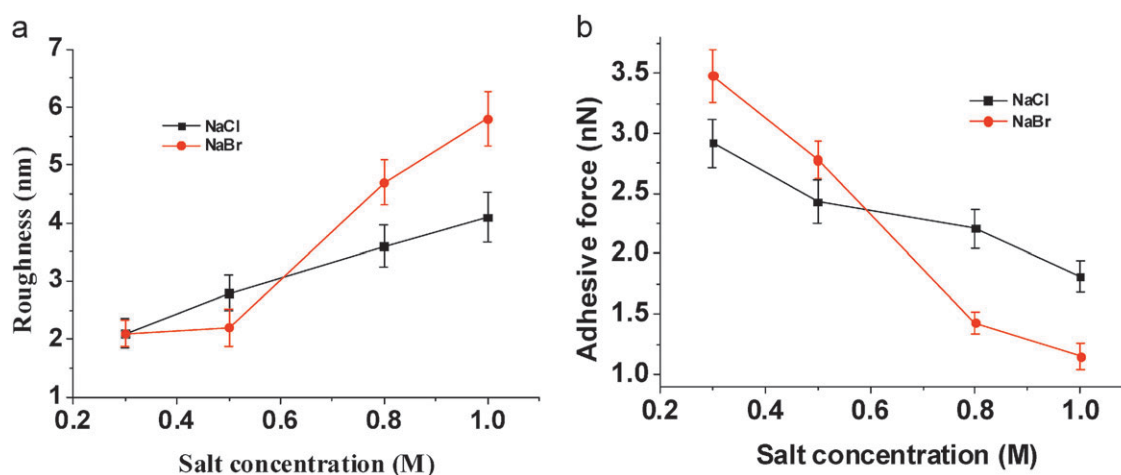
the salt and its concentration reaches a certain point during assembly, the polyelectrolytes become more difficult to adsorb onto the substrate due to the stronger interaction between Br<sup>−</sup> and the polycation.<sup>55</sup> Consequently, thinner multilayers are obtained at higher NaBr concentration.

To some extent, the roughness can reflect the influence of solution quality on the film properties, and may correlate with the compactness of the multilayer film, as observed before for the PSS/PDADMAC films assembled from solutions having different anions.<sup>56</sup> In this context, the surface morphology of PEI(PSSMA/PDADMAC)<sub>7</sub> multilayers assembled in a series of NaCl and NaBr solutions was measured using SFM (Fig. 4). It shows that all the surfaces of the multilayers are very homogenous with regular tiny protrusions. Fig. 5a quantitatively compares the surface roughness (RMS roughness), revealing an increase tendency along with the salt concentration. This is quite normal since in a concentrated salt solution the polyelectrolytes are deposited in a more coiled format. The multilayers assembled in NaBr solution with a higher concentration have greater surface roughness because those of the Br<sup>−</sup> ions have a stronger interaction with the polyelectrolytes. Moreover, the mobility of the polyelectrolyte chains in Br<sup>−</sup> solution is larger than that in Cl<sup>−</sup> solution because the Br<sup>−</sup> ion has a smaller hydration shell than that of Cl<sup>−</sup>.<sup>57</sup> Consequently, a stronger chain coiling occurs, resulting in an increase in surface roughness.<sup>46</sup>

Compared to the surface roughness, the adhesive force between the multilayer films and the tip of AFM cantilever shows a reverse alteration tendency, *i.e.* along with the increase of salt concentration, the adhesive force was monotonously decreased (Fig. 5b). It should be pointed out that in this measurement the tip moved towards the multilayer surface at a constant velocity until a predetermined distance was reached, and then the direction of movement was reversed until the tip departed from the multilayer surface. During the departing process, there is a sticking force between the tip and the sample surface, which is defined as adhesive force.<sup>58</sup> The adhesive force can result from capillary, electrostatic, van der Waals interactions *etc.* Unfortunately, at present we can not



**Fig. 4** SFM images of PEI(PSSMA/PDADMAC)<sub>7</sub> multilayers assembled in (a) 0.3 M NaCl, (b) 0.5 M NaCl, (c) 1 M NaCl, (d) 0.3 M NaBr, (e) 0.5 M NaBr, and (f) 1 M NaBr solutions.



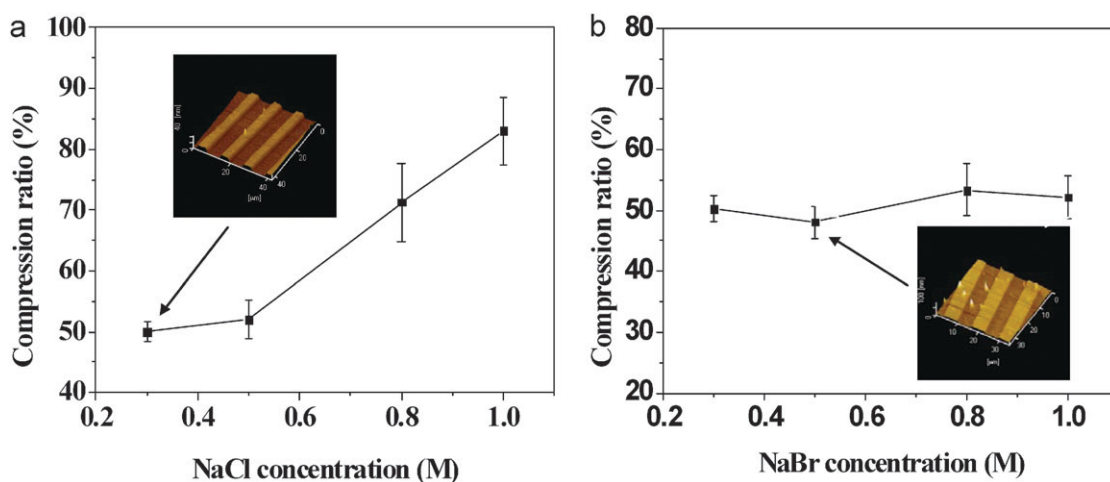
**Fig. 5** (a) Surface roughness and (b) adhesive force of PEI(PSSMA/PDADMAC)<sub>7</sub> multilayers as a function of concentration of the salt used during the assembly.

distinguish the degree of each contribution. Nonetheless, the results indicate that the overall number of polyelectrolyte molecules which interact with the tip should be decreased along with the increase of salt concentration, namely the structure of the multilayer changes from denser to sparser. This is consistent with the layer growth regimes (Fig. 2 and 3) and surface morphology (Fig. 4 and 5a) and could be similarly explained.

In the following, the series of the PEI(PSSMA/PDADMAC)<sub>7</sub> multilayers were subjected to a compression study in typical conditions explored before (for details, see Experimental

section). Linear physical discontinuities can be clearly observed on the multilayers regardless of the salt type and concentration, as is typically shown in the insets of Fig. 6, illustrating that the PEI(PSSMA/PDADMAC)<sub>7</sub> multilayers assembled in all conditions can be pattern compressed. However, the compression ratio (the ratio of the pattern height to the original dry thickness of the multilayers) of the multilayers was increased from ~50 to ~83% when the NaCl concentration was increased from 0.3 to 1.0 M (Fig. 6a), respectively. In contrast, the compression ratio was around 50% and kept almost unchanged when the multilayers were assembled in NaBr





**Fig. 6** Compression ratio of PEI(PSSMA/PDADMAC)<sub>7</sub> multilayers as a function of salt concentration. The multilayers were assembled in (a) NaCl solution and (b) NaBr solution.

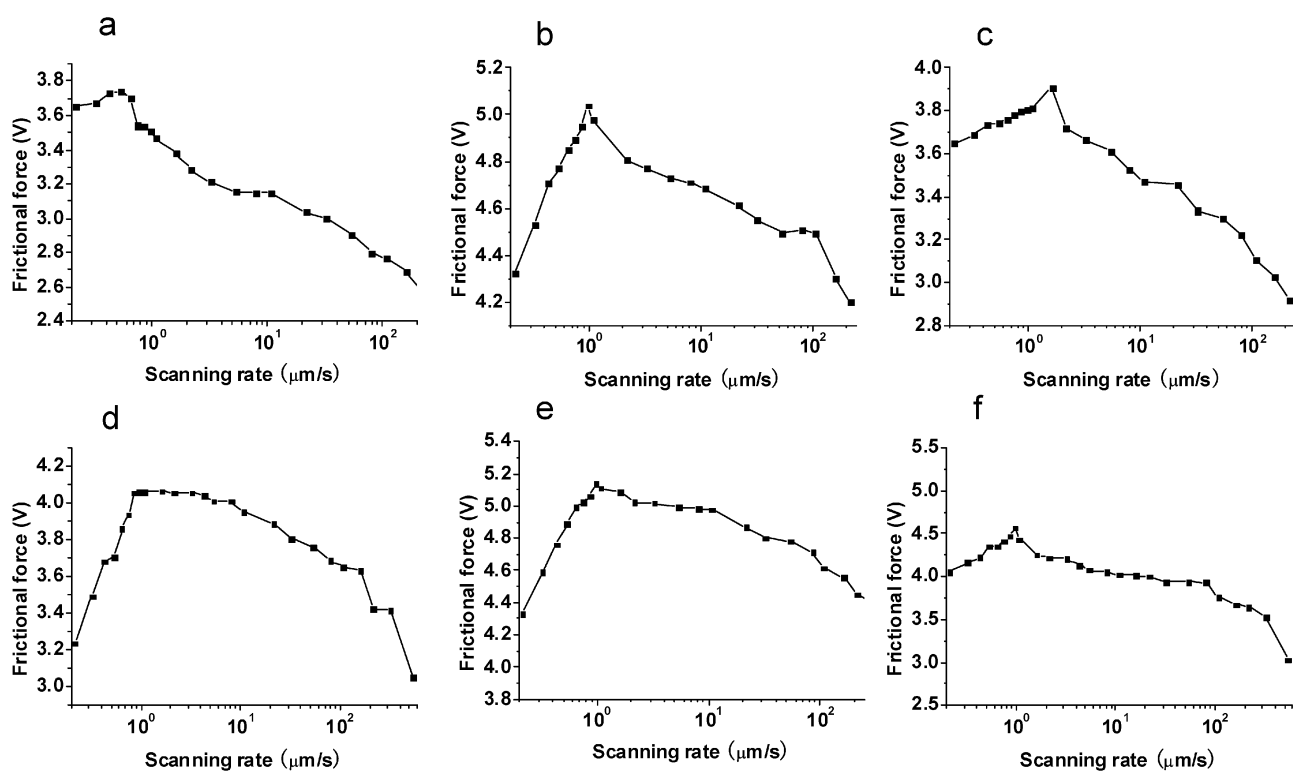
solution with a concentration ranging from 0.3 to 1 M (Fig. 6b). As explored above and recognized before, the multilayers assembled at a higher salt concentration are thicker with a higher ratio of defects,<sup>59,60</sup> which can be corrected to some extent by the compression. Therefore, a higher compression ratio is achieved on these multilayers. This is the case for the PEI(PSSMA/PDADMAC)<sub>7</sub> multilayers assembled in NaCl solution. The constant compression ratio for the PEI(PSSMA/PDADMAC)<sub>7</sub> multilayers assembled in NaBr solution, however, reveals that there should be other contributions affecting the multilayer structure, which are exclusively derived from the Br<sup>−</sup> ions. As aforementioned, the Br<sup>−</sup> ion has a higher polarizability and a smaller hydration shell than that of the Cl<sup>−</sup> ion, and thereby the interaction between the anions and the polyelectrolytes is enhanced.<sup>55</sup> As a result, the multilayers assembled in NaBr solution contain fewer hydration water molecules. It is known that the hydration water molecules inside the multilayers can improve the mobility of the polyelectrolyte segments in the multilayers, leading to easier adjustment of the film structure in response to the applied press. The interplay between the increase of defects and decrease of chain mobility results in a constant compression ratio of 50% for the PEI(PSSMA/PDADMAC)<sub>7</sub> multilayers assembled in NaBr with a concentration ranging from 0.3 to 1 M, which is a rather small value comparable to that of PEI(PSSMA/PDADMAC)<sub>7</sub> multilayers assembled in 0.3 M NaCl solution but far smaller than that in 1 M NaCl (83%).

Indeed, the influence of the anions on the mechanical properties of polyelectrolyte multilayers has been reported previously, although there is discrepancy between the results by different researchers. For example, Klitzing reported that the multilayers assembled in Br<sup>−</sup> ions are softer than those assembled in F<sup>−</sup> ions because of the increasing internal mobility.<sup>46</sup> However, using QCM Salomäki and co-workers<sup>29</sup> observed that the polyelectrolyte multilayers assembled in F<sup>−</sup> ions were rather “rubber-like”, while the films with Br<sup>−</sup> ions were rather glassy.

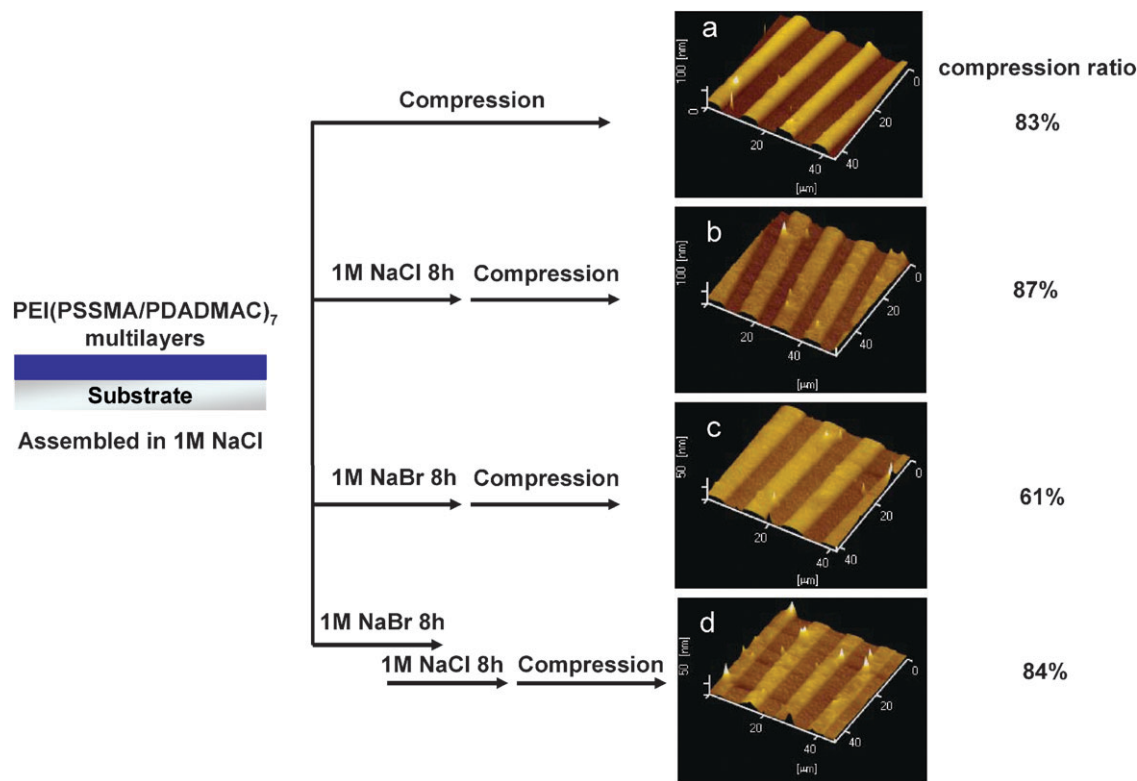
To explore the stiffness of our multilayers and further confirm our above explanation, lateral force microscopy was

used to measure the friction forces of the series of PEI(PSSMA/PDADMAC)<sub>7</sub> multilayers, using the method described previously.<sup>45</sup> Fig. 7a–c show that the peaks in the friction force curves gradually shifted from a low to a high scanning rate along with the increase of NaCl concentration. By contrast, the positions of the peaks in the friction force curves for all PEI(PSSMA/PDADMAC)<sub>7</sub> multilayers assembled in NaBr solution kept unchanged regardless of the NaBr concentration (Fig. 7d–f). In this measurement, the peak appearing at a higher scanning rate implies that the materials are relatively softer.<sup>25</sup> Therefore, along with the increase of salt concentration during the assembly, the multilayers assembled in NaCl solution gradually become softer, while the multilayers assembled in NaBr solution keep unchanged in terms of their stiffness. Moreover, Fig. 7 shows that the PEI(PSSMA/PDADMAC)<sub>7</sub> multilayers assembled in 1 M NaCl solution are obviously softer than that assembled in 1 M NaBr solution. This is consistent with our above explanation on the different compression performance, and confirms again the different microstructures of the multilayers assembled in different conditions.

To further explore the salt effect on the compression performance of the multilayers, we carried out the following contrast experiments. The freshly prepared PEI(PSSMA/PDADMAC)<sub>7</sub> multilayers assembled in 1 M NaCl were exposed either to 1 M NaCl or to 1 M NaBr solution for 8 h, and then pattern compressed. By incubation in 1 M NaCl, the compression ratio kept almost unchanged, *i.e.* from ~83% (Fig. 8a) to 87% (Fig. 8b). However, by incubation in 1 M NaBr solution, the ratio significantly decreased to ~61% (Fig. 8c). If the freshly prepared multilayers assembled in 1 M NaCl was first exposed to 1 M NaBr solution for 8 h, then to 1 M NaCl solution for 8 h, and then pattern compressed, the compression ratio was back to ~84% again (Fig. 8d). To testify if this is a universal phenomenon, PEI(PSS/PDADMAC)<sub>7</sub> multilayers were assembled in 1 M NaCl and similarly treated following the process shown in Fig. 8. Exactly the same alterations were obtained (ESI, Fig. S1) although the absolute compression ratio was different. Similar

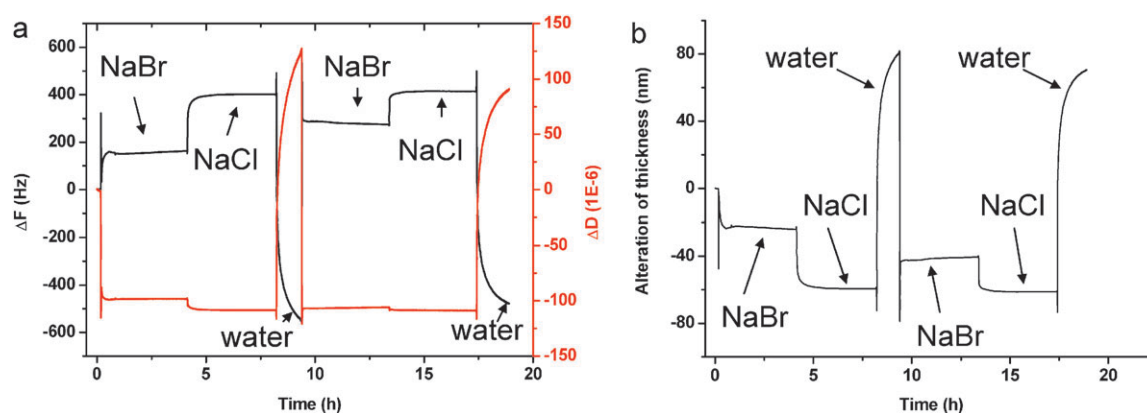


**Fig. 7** Friction force curves of PEI(PSSMA/PDADMAC)<sub>7</sub> multilayers assembled in (a) 0.3 M NaCl, (b) 0.5 M NaCl, (c) 1 M NaCl, (d) 0.3 M NaBr, (e) 0.5 M NaBr, and (f) 1 M NaBr solutions.



**Fig. 8** SFM images of the pattern-compressed PEI(PSSMA/PDADMAC)<sub>7</sub> multilayers. (a) The multilayers were assembled in 1 M NaCl. The multilayers were further treated by 1 M NaCl (b) or by 1 M NaBr (c) for 8 h before compression. (d) The multilayers were first treated by 1 M NaBr for 8 h and then by 1 M NaCl for 8 h before compression. The left of the figure illustrates the treating conditions.





**Fig. 9** (a) Changes in frequency ( $\Delta F$ ) and dissipation ( $\Delta D$ ) of PEI(PSSMA/PDADMAC)<sub>7</sub> multilayers assembled in 1 M NaCl solution as a function of post-treatment time. The salt concentrations were all 1 M. The overtone number  $n$  was 3. (b) Wet thickness of the multilayers derived from (a).

contrast experiments for the PEI(PSSMA/PDADMAC)<sub>7</sub> multilayers assembled in 1 M NaBr obtained the following results (ESI, Fig. S2): higher and lower compression ratios were obtained for the NaCl and NaBr treated multilayers, respectively. These results further reveal that the compression ratio of the multilayers treated in Cl<sup>-</sup> and in Br<sup>-</sup> solution is almost reversible, illustrating that the multilayer structure can be reversibly tuned by this simple incubation.

Lastly, the mass alteration during the process of salt treatment and ringing in water was monitored by QCM-D, which further confirms the difference of multilayer structures in different salt solutions. Fig. 9 shows that when the PEI(PSSMA/PDADMAC)<sub>7</sub> multilayers assembled in 1 M NaCl was rinsed with water (the 0 point) and then incubated in 1 M NaBr solution, the relative mass and wet thickness were decreased to some extent, indicating the dehydration effect of the NaBr salt. After further incubation of the multilayers in 1 M NaCl solution, further dehydration occurred leading to the decrease of mass and wet thickness again, indicating NaCl solution has a stronger dehydration effect on the multilayers. The next incubation of the multilayers in pure water resulted in highly hydrated multilayers (notice here the incubation time was much longer than the 0 point). Repeating the experiment for another cycle of treatment confirmed that the alteration process was completely reversible. A reverse treating cycle (ESI, Fig. S3), namely incubation of the PEI(PSSMA/PDADMAC)<sub>7</sub> multilayers (assembled in 1 M NaBr) in 1 M NaCl, then in 1 M NaBr and finally in pure water, gave the same conclusions, *i.e.* the process is completely reversible and NaCl has a stronger dehydration effect. These results and conclusions are consistent with the compression results (Fig. 8). It is worth mentioning that the smaller water content and thereby the relative thinner thickness of the multilayers in 1 M NaCl solution are not contradictory with the result of the higher compression ratio (Fig. 6a), because compression was conducted in the conditions without salt.

## Conclusions

We explore in this work the effects of salt on the properties, stiffness and compression ratio of the PSSMA/PDADMAC

multilayers. The thickness of the multilayers assembled in NaCl and NaBr increased and decreased along with the salt concentration, respectively. The compression performance of the multilayers was significantly influenced by the salts, too, *i.e.* the compression ratio increased along with the increase of NaCl concentration used during the assembly, whereas it kept constant when NaBr was used. Friction force measurements revealed that along with the increase of salt concentration during the assembly, the multilayers assembled in NaCl solution gradually became softer, while the multilayers assembled in NaBr solution kept unchanged in terms of their stiffness. QCM-D and SFM measurements confirmed that the compression ratios, masses in wet and wet thicknesses of the multilayers alternately treated in Cl<sup>-</sup> and in Br<sup>-</sup> solutions were all reversible. These results reveal the difference in the structures of the PSSMA/PDADMAC multilayers brought about by the anions and thereby in their response to the applied force, which is mainly attributed to the smaller hydration shell of the Br<sup>-</sup> and stronger interaction between Br<sup>-</sup> and the polycation.

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