

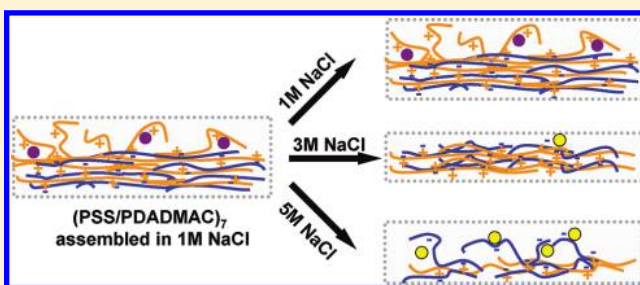
Modulating the Structure and Properties of Poly(sodium 4-styrenesulfonate)/Poly(diallyldimethylammonium chloride) Multilayers with Concentrated Salt Solutions

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S Supporting Information

ABSTRACT: Poly(sodium 4-styrenesulfonate) (PSS)/poly-(diallyldimethylammonium chloride) (PDADMAC) multilayers were treated with 1–5 M NaCl solutions, resulting in continuous changes in the physicochemical properties of the multilayers. Significant mass loss was observed when the salt concentration was higher than 2 M and reached as high as 72% in a 5 M NaCl solution. The disassembly occurred initially in the superficial layers and then developed in the bulk multilayers. For the multilayers with PDADMAC as the outmost layer, the molar ratio of PSS/PDADMAC was increased and the surface chemistry was changed from PDADMAC domination below 2 M NaCl to PSS domination above 3 M NaCl. Owing to the higher concentrations of uncompensated for polyelectrolytes at both lower and higher salt concentrations, the swelling ratio of the multilayers was decreased until reaching 3 M NaCl and then was increased significantly again. The salt-treated PSS/PDADMAC thin films are expected to show different behaviors in terms of the physical adsorption of various functional substances, cell adhesion and proliferation, and chemical reaction activity.



Layer-by-layer (LbL) assembly is a versatile method of building up thin polymer films on various substrates.^{1–5} In particular, the polyelectrolyte multilayers (PEMs) are assembled by the alternative adsorption of polycations and polyanions via electrostatic attraction.^{6,7} Their well-defined nanostructures and properties, including compositions, thicknesses, surface functional groups, and internal linkages between layers, can be governed by many parameters during the building process and post-treatment, for example, the types of polyelectrolytes and salts, salt concentration, temperature, and pH.^{8–15} Therefore, PEMs have attracted much interest with respect to their applications in chemical and biological sensors,^{16–18} drug-delivery carriers,^{19–21} microelectronics,^{22,23} nano-optics,^{24,25} biomimetics,²⁶ and tissue engineering.^{27–30}

Many previous studies have reported that the PEMs can be regarded as insoluble polyelectrolyte complexes (PECs) bound to a surface, and the phase behavior of PECs can be controlled by the salt strength and the stoichiometry of polycations and polyanions.^{31–37} Generally, the charge interaction between polyelectrolytes is more strongly screened at a higher salt strength, leading to a lower solubility of PECs. However, post-treatment of the multilayers in a salt solution with a critical high ionic strength will redistribute the charge and multilayer structure and soften, swell, and even dissolve the PEMs.^{12,38–44} However, the decomposition behaviors of the multilayers are also dependent on the building blocks. For weak polyelectrolyte multilayers such as

poly(acrylic acid) (PAA)/(allylamine hydrochloride) (PAH), their thickness is decreased progressively in 1–5 M NaCl solutions. The degree of etching is also tuned by the molecular weight of the building blocks and the pH value during assembly that influences the ionic cross-linking density of the PEMs. In this process, the chemical composition and properties of PAA/PAH are not changed after salt treatment, and thereby the swelling ratio of the multilayers is kept constant in water.⁴⁵ In contrast, the mass loss of poly(sodium 4-styrenesulfonate) (PSS)/PAH multilayers occurs only in NaCl solution above 3 M, and the multilayer swelling in salt solution is shown.³⁸

The strong polyelectrolyte multilayers assembled from PSS and poly(diallyldimethylammonium chloride) (PDADMAC) are stable in salt solutions that are less concentrated than 2 M.³⁹ The distribution of charges and the intrinsic persistence length of the PDADMAC chain mismatch that of PSS,⁴⁶ leading to the strong responses of the multilayers to the salt solution. For example, both the thickness and hydration of the PDADMAC/PSS multilayers are greater and more sensitive than those of the PAH/PSS system built up or post-treated at a relatively high salt concentration such as 1 M NaCl, with a more obvious odd–even effect.^{11,12,47} More recently, the salt-induced fusion of PSS/PDADMAC multilayer

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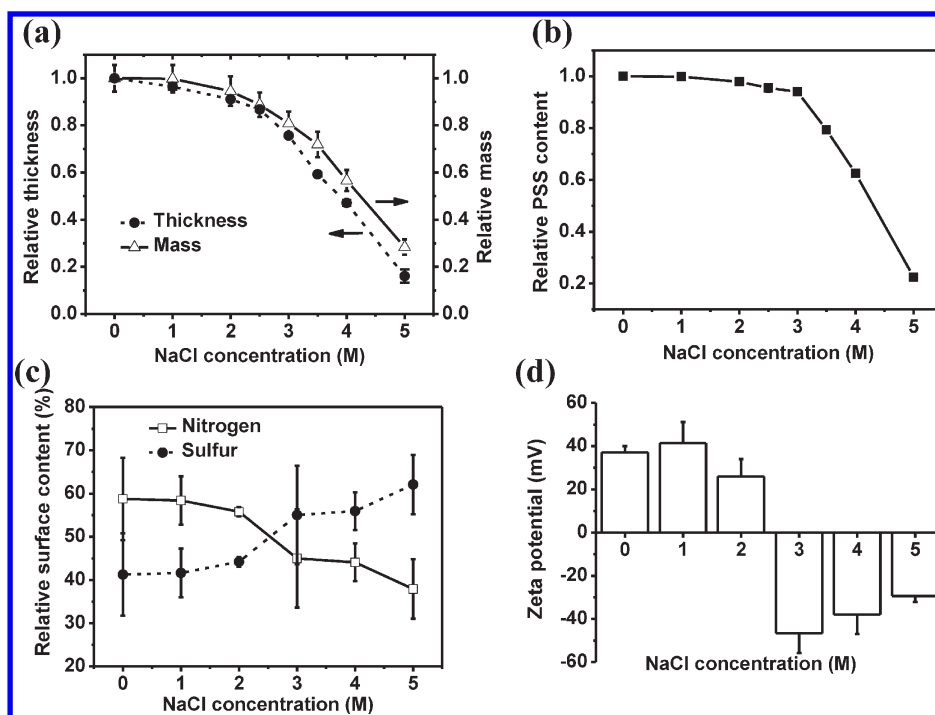


Figure 1. Mass and surface properties of (PSS/PDADMAC)₇ multilayers post-treated with different concentrations of NaCl solutions. (a) Alteration of mass and thickness as a function of NaCl concentration as determined by QCM-D and ellipsometry. The mass and thickness are normalized to those of the pristine multilayers, which are 38.5 $\mu\text{g}/\text{cm}^2$ and 190 nm, respectively. (b) Integrated value over 215–240 nm in the UV–vis absorption spectra of the multilayers after incubation in different concentrations of NaCl solutions. The value is proportional to the PSS content in the multilayers. (c) Relative surface contents of nitrogen and sulfur as determined by XPS, which denote the relative PDADMAC and PSS surface contents, respectively. (d) Surface zeta potential of the multilayers post-treated with different concentrations of NaCl solutions. The measurement was conducted in a 10 mM NaCl solution.

microcapsules at increasing salt concentration above 3 M has been reported.⁴⁸ However, less attention is paid to alterations in the chemical composition and physicochemical properties of PSS/PDADMAC multilayers after post-treatment in higher concentrations of salt solutions.

In this study, we shall make use of the well-acknowledged salt treatment method to post-treat the PSS/PDADMAC multilayers in 0–5 M NaCl solutions. The changes in mass, thickness, chemical composition, surface charge, counterions, and viscoelastic properties are investigated by means of ellipsometry, UV–vis and X-ray photoelectron spectroscopy, the zeta potential, and the quartz crystal microbalance. Some interesting phenomena (until now, only in these PE pairs) are found, and the underlying mechanism is elucidated. The resulting ultrathin films with unique features are expected to find diverse applications in surface engineering and biological fields.

MATERIALS AND METHODS

Materials. Polyethyleneimine (PEI, $M_w = 25$ kDa), poly(diallyldimethylammonium chloride) (PDADMAC, $M_w = 200$ –350 kDa), and poly(sodium 4-styrenesulfonate) (PSS, $M_w = 70$ kDa) were obtained from Sigma-Aldrich. The water used in the experiments was purified by a Milli-Q water system (Millipore, U.S.A.). The polyelectrolytes were prepared as 1 mg/L aqueous solutions. PEI was dissolved in water, and PSS and PDADMAC were supplemented with 1 M NaCl. Quartz, glass, and silicon wafers were cleaned in piranha solution (7:3 v/v% $\text{H}_2\text{SO}_4/\text{H}_2\text{O}_2$). (*Caution! Piranha is a strong oxidizer and should not be stored in a closed container.*) After being copiously rinsed with water, they were dried under a smooth stream of N_2 .

Multilayer Assembly. To ensure successful adsorption, a precursory layer of PEI was deposited onto the silicon wafers. PSS and PDADMAC in a 1 M NaCl solution were then alternately assembled by autodipping at 20 °C. Between alternate exposures to the two kinds of polymer solutions for 20 min, there were three rinses with 0.1 M NaCl solution for 3 min. In the last step, the films were immersed in water for at least 5 min to eliminate the adsorbed salt. In total, seven bilayers were assembled, and the multilayers are expressed as (PSS/PDADMAC)₇ if not otherwise stated.

Post-treatment of the Multilayers. The (PSS/PDADMAC)₇ multilayers were incubated in NaCl solutions of different concentrations at room temperature for 2 h and were then rinsed with water and dried under a smooth stream of N_2 .

Spectroscopic Ellipsometry. The thickness and refractive index of the multilayers were determined in air from a spectroscopic ellipsometer (model M2000D, J. A. Woollam Inc., Lincoln, NE) at an incident angle of 75° within a wavelength range of 300–1700 nm. The thickness was calculated from the ellipsometric parameters, Δ and ψ , using a Cauchy model. The measurement in water was carried out in a liquid cell within a wavelength range of 300–1100 nm.

UV–Vis Spectroscopy. Quartz slides were used as the substrates to assemble the multilayers. UV–vis spectra were obtained from a UV–vis spectrophotometer (Shimadzu, UV2550) within a wavelength range of 200–360 nm. The absorbance between 215 and 240 nm, which is assigned to the benzene ring of PSS, was integrated for quantitative comparison.

X-ray Photoelectron Spectroscopy (XPS). The compositions of the multilayers after salt treatment were detected by an Axis Ultra spectrometer (Kratos Analytical, U.K.) with a monochromated Al K α source at pass energies of 160 eV for survey spectra and 80 eV for core-level spectra.

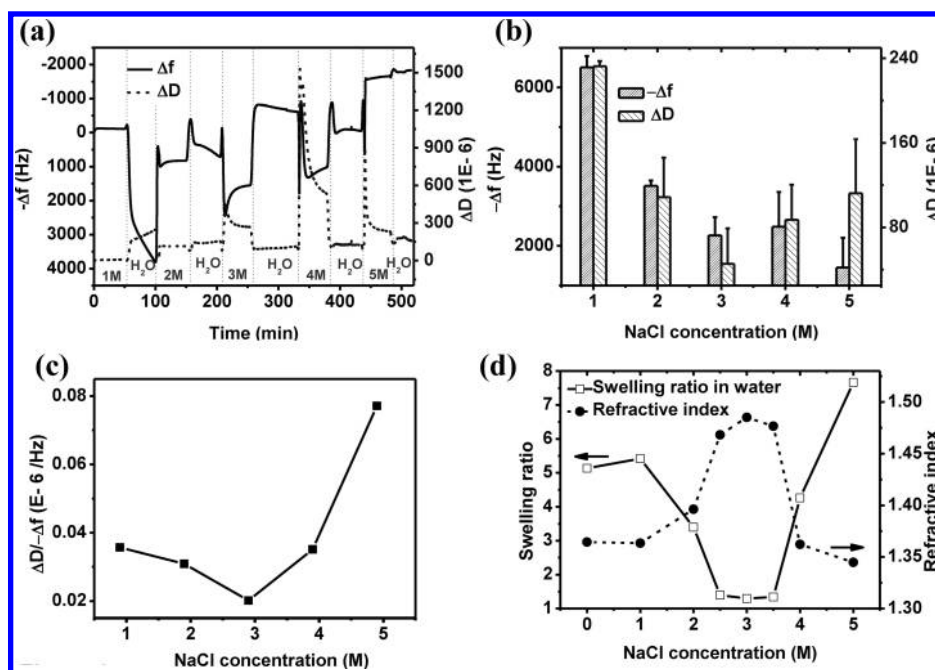


Figure 2. Viscoelastic properties of the multilayers post-treated with different concentrations of NaCl solutions. (a) The alteration of (PSS/PDADMAC)₇ multilayers was monitored stepwise in situ in 1, 2, 3, 4, and 5 M NaCl solutions by QCM-D. After each exposure of the salt solution, the sample was rinsed with ultrapure water. (b) Values of $-\Delta f$ and ΔD of the multilayers in water as a function of NaCl concentration. The data represent the differences between the values of the multilayers in water after each salt treatment and the blank substrate (gold-coated quartz crystal). (c) Viscoelastic parameters $\Delta D/-\Delta f$ of the multilayers in water as a function of salt concentration. (d) Swelling ratio and refractive index of the salt-treated multilayers in water as measured by ellipsometry.

The binding energy was corrected for static charging of the C 1s peak at 284.8 eV. Data analysis was performed with Kratos Vision Processing.

Zeta Potential. The surface zeta potentials of the multilayers were measured in 10 mM NaCl using a Delsa Nano Series zeta potential/sub-micrometer particle size analyzers (Beckman Coulter, U.S.A.) via electrophoresis technology.

Quartz Crystal Microbalance with Dissipation (QCM-D). Changes in both the dissipation (D) and resonance frequency (f) of the quartz crystal assembled with multilayers after salt treatment were monitored by QCM-D (model Q-SENSE E4, Sweden) using gold-coated quartz crystals (5 MHz) as the substrates. In situ ΔD and Δf (Figure 2a) were expressed as the directly measured values, and others were calculated from the differences between the values of measured samples and blank substrates. The mass change in air was calculated by using the Sauerbrey relation with QTools software.

RESULTS

Changes in Mass and Surface Properties. After the (PSS/PDADMAC)₇ multilayers (PDADMAC as the outmost layer) were post-treated in different concentrations of NaCl solutions, their mass and thickness were measured by QCM and ellipsometry in a dry state. Figure 1a shows that they were both gradually decreased along with the increase in salt concentration from 1 to 5 M and became more serious above 2 M NaCl. Only 28% mass and 16% thickness were retained after 5 M NaCl treatment. The mass loss is known to be caused by the disassembly of the multilayers as a result of the electrostatic screening by NaCl solution of the charge interaction.⁴⁹

To identify the loss of each component, UV-vis absorption spectra were recorded and the value in the range from 215 to 240 nm was integrated (Figure 1b). This value is solely attributed

to PSS, which was largely retained at a lower salt concentration. For example, at 3 M, 94% PSS remained (Figure 1b), which was much larger than the retained total mass of 81% (Figure 1a). Therefore, the mass loss at lower concentrations of salt solutions (≤ 3 M) is mainly contributed by PDADMAC. When the salt concentration was greater than 3 M, PSS was dissolved significantly as well. For example, at 5 M NaCl only 25% PSS was retained (Figure 1b), which conveys that both PSS and PDADMAC are dissolved simultaneously, compared with the 28% remaining mass.

The loss of the polyelectrolytes shall inevitably cause a change in the surface chemistry, which was verified by XPS measurement (Figure 1c). The S/N molar ratio, which is proportional to the PSS and PDADMAC contents on the surface, was found to be 41:59 in the pristine multilayers. This is consistent with the PDADMAC-terminated surface of the multilayers. The S/N ratio remained almost unchanged after 1 M treatment (42:58), which is in good agreement with the constant mass and thickness. After 2 M NaCl treatment, the S/N ratio was improved slightly to 44:56 and then increased substantially to 55:45, 56:44, and 62:38 after 3, 4, and 5 M NaCl treatments, respectively, indicating that PDADMAC molecules are released more significantly from the multilayers at critical high salt concentrations.

Along with the alteration of the PSS/PDADMAC ratio, small balanced ions (e.g., Cl^- and Na^+) must be changed correspondingly to compensate for the extra charge in the multilayers.⁵⁰ XPS characterization indeed found that the Cl/N ratios were 10:59, 9:58, and 6:56 for the pristine multilayers and the multilayers treated with 1 and 2 M NaCl solutions, respectively. No Na^+ was found in these multilayers. By contrast, no Cl^- was found in the multilayers treated with ≥ 3 M NaCl solutions. In the multilayers treated with 3, 4, and 5 M NaCl solutions, the S/Na ratios were

55:3, 56:22, and 62:34, respectively. If we assume that the counterions ($\text{SO}_3^-/\text{Cl}^-$, or $\text{N(R)}_4^+/\text{Na}^+$) shall compensate for each other regardless of their types, then the overall ratios between the anions and cations are roughly equal, except in the 4 M NaCl-treated multilayers (multilayers 4 and 5 M) in which about 17% of the cations were present in excess. The reason is not known but is likely caused by the stronger interaction between sulfonic and sodium ions, which surpasses that of ammonium chloride and sulfonic ammonium ion pairs.⁵¹

The change in the surface zeta potential is in good agreement with the above results. Figure 1d shows that the surfaces of the pristine and 1 M NaCl-treated multilayers were positively charged with a zeta potential of +40 mV, which is consistent with the multilayer structure of the PDADMAC-dominated surface. This value was decreased to +25 mV after the partial release of PDADMAC in 2 M NaCl. Along with the increase in salt concentration, the surface charge was reversed to negative with values of -47 ± 9 , -39 ± 7 , and -29 ± 3 mV for multilayers 3, 4, and 5 M, respectively.

It is worth mentioning that the QCM measured 81 and 28% remaining mass at 3 and 5M, respectively, which were smaller and almost equal to the PSS mass (94 and 25% at 3 and 5M, respectively) as measured by UV-vis. This result implies that the increase in the ionic strength from 0 to 3 M results in the depletion of PDADMAC and the enrichment of PSS in the multilayers. Further increases in the salt concentration from 3 to 5 M should shift the balance back. However, XPS data demonstrated statistically significant increases in the PSS/PDADMAC ratio only upon changing the salt concentration from 2 to 3M. Further increases in the salt concentration to 5 M never changed this ratio back. The reason for such a discrepancy could be the fact that QCM and UV-vis spectroscopy analyze the bulk but XPS is a true surface analytical method that shows just the top few nanometers of the surface. Zeta potential measurements show that the surface charge changed from positive to negative when the salt concentration increased from 2 to 3M, conveying that the terminal layer changes from PDADMAC to PSS. These results suggest the possible different properties of the bulk and the outmost surface of the multilayers after salt etching.

Changes in Viscoelasticity. As a result of the change in chemical composition, the physical properties should be reasonably altered, especially their viscoelasticity. In this regard, QCM-D was used to record the resonance frequency (Δf) and dissipation factor (ΔD) of each treated multilayer, which can provide information about the internal structure and viscoelastic properties of the thin films. It is known that $-\Delta f$ is proportional to the mass increase and a dense/rigid (e.g., dehydrated) or swollen/flexible (e.g., highly hydrated) film has a small or large ΔD value, respectively. When the pristine (PSS/PDADMAC)₇ multilayers were incubated in pure water, no meaningful data could be collected by QCM-D. It is likely that the larger film thickness (190 nm) and high swelling nature (Figure 2d) surpass the measuring limit. Therefore, the measurement started from 1 M NaCl solution and thereby the $-\Delta f$ and ΔD values were normalized to those measured in 1 M NaCl solution (Figure 2a). When the medium was changed to water, the $-\Delta f$ increased sharply within the first few minutes and then increased slowly. Equilibrium was not achieved within the 1 h measuring time. Correspondingly, ΔD was improved. This result reveals that a large amount of water diffuses into the multilayers and the process lasts for a very long time. After the medium was changed to the 2 M NaCl solution, both $-\Delta f$ and ΔD were decreased, implying the loss of

the infiltrated water. No large change was found after the multilayers were rinsed with water again. However, when the medium was changed to a 3 M NaCl solution, $-\Delta f$ increased immediately and then decreased slowly to a new balanced state, thus confirming the greater amount of swelling of the multilayers and the gradual mass loss in 3 M NaCl solution. Unlike their counterparts of multilayers 1 and 2 M, the $-\Delta f$ and ΔD values of multilayer 3 M decreased substantially in water, implying a huge loss of infiltrated water. A similar alteration regime was found in a 4 M NaCl solution, whereas in a 5 M NaCl solution water rinsing did not bring about changes in terms of the $-\Delta f$ and ΔD values.

To quantify the real $-\Delta f$ and ΔD values in water, the data of the substrate (gold-coated quartz crystal) were subtracted by the measured data in Figure 2a. Figure 2b shows that $-\Delta f$ decreased monotonously along with the increase in salt concentration whereas ΔD decreased initially until 3 M NaCl and increased again above 3 M NaCl. It is known that $\Delta D/(-\Delta f)$ is proportional to the water content per mass unit in the multilayer films.⁵² Figure 2c confirms that the water content in the multilayers was decreased until 3 M NaCl and then was increased. Therefore, multilayer 3 M possesses the lowest swelling structure. By contrast, multilayer 5 M is highly hydrated.

The difference in swelling of the salt-treated multilayers was further confirmed by ellipsometry. For each multilayer film, its thickness in both the dry and wet states was independently measured. The ratio of wet thickness to dry thickness thus directly reflects the swelling ratio, which showed a V shape with a minimum value at 3 M NaCl in water (Figure 2d). Again, the maximum swelling appeared at 5 M NaCl. By contrast, the refractive index, which is an average of the polymer matrix (~ 1.52) and water (1.33) values and thereby proportional to the polymer content, showed perfect reverse alteration regimes to those of the swelling ratios.

Surface Morphology. Figure S1 shows the surface morphology of the salt-treated multilayers detected by AFM in PBS. (In water, no images could be recorded except for multilayer 3 M because of the very hydrated, soft structure.) Compared to the pristine layers and multilayers treated with lower concentrations of salt solutions (Figure S1a,b), fewer vermiculate structures existed on the multilayers treated with higher concentrations of the NaCl solution (Figure S1c-f). Nonetheless, the overall roughness (rms) in PBS was varied within a small range (i.e., 12.1 ± 2.8 , 11.0 ± 1.7 , 4.1 ± 1.3 , 3.6 ± 2.2 , 6.4 ± 0.1 , and 4.6 ± 0.4 nm for the multilayers treated in 0, 1, 2, 3, 4, and 5 M NaCl solutions, respectively).

DISCUSSION

Many previous studies reported that the ionic strength plays a significant role in the multilayer structures and that post-treatment in salt solution can soften, swell, and even dissolve the PEMs because salt can screen the charge interaction between polyelectrolytes.^{12,38-42} The decomposition behaviors of the multilayers are strongly dependent on the building blocks. According to the schematic stability diagram for polyelectrolyte multilayers proposed by Kovacevic et al.,³¹ the polyelectrolyte chains become sufficiently mobile and multilayer dissolution occurs at a certain salt concentration (c_{cr}). The c_{cr} of polyelectrolyte pairs is low for the weak interactions (for example, 0.45 M for poly(*N*-ethyl-4-vinylpyridinium bromide)/poly(methacrylic acid) (PVP/PMAA) multilayers), and the polyelectrolyte multilayers can be formed only in a narrow range of the polycation/polycation ratio

($\sim 1:1$).^{32,50,53} PSS is one of the strongest binders to polycations because of its abundant SO_3^- groups, and those polyamines containing primary amino groups have the strongest interactions with polyanions. Therefore, PSS/poly(allylamine hydrochloride) (PAH) multilayers can resist decomposition in highly concentrated NaCl solution (3 M).³³ By contrast, the dissolution of both types of PSS/PDADMAC and poly(acrylic acid) (PAA)/PAH multilayers occurs in a salt solution at around 2 M.⁴⁵ Nonetheless, the chemical composition of the PAA/PAH multilayers remained constant as a result of a similar extent of PAA and PAH release. Compared to those PAH/PAA and PSS/PAH polyelectrolyte pairs, the interaction between PSS/PDADMAC polyelectrolyte pairs is weaker,^{46,54} leading to the change in the chemical compositions and thereby the physicochemical properties as demonstrated in this study.

Herein, we found that for the pristine layers and multilayers treated with 1 and 2 M NaCl solutions, the original structure and properties of the multilayers are mostly retained because of little electrostatic repulsion, with a PDADMAC-dominated positively charged surface and a larger swelling ratio in water. The extra charge on PDADMAC is balanced by Cl^- ions. The hardly swollen multilayer 3 M film, by contrast, has roughly equal amounts of PDADMAC and PSS and a PSS-dominated negatively charged surface as a result of the larger loss of PDADMAC. For the multilayer 4 and 5 M films, as a result of the substantial mass loss, PSS becomes abundant and the swelling ratio is very high, especially for the multilayer 5 M film, which has the highest hydration in water. The extra charge of PSS is balanced by Na^+ ions in these multilayers.

According to previous results, the basic structure of a multilayer film can be subdivided into three zones: a few layers deposited onto the substrate (zone I), a “bulk” film (polyelectrolyte complexes, zone II), and an outer region (uncompensated for polyion, zone III).⁵⁵ The XPS result (Figure 1c) shows that N is present in excess on the assembled (PSS/PDADMAC)₇ multilayers. Hence, it is reasonable to assume that the less-fixed PDADMAC is easier to dissociate than the internal polyelectrolytes. In addition, the swelling behaviors between the outer region and the bulk film are different: zone II swells in salt solutions owing to the broken ionic bonds between polyanions and polycations but collapses in water; zone III, however, is more similar to that of the classic polyions and shows a reverse alteration in response to salt solution and water.^{55,56} Therefore, the larger swelling behaviors (namely, the large ΔD values) in water after treatment in 1 and 2 M NaCl (Figure 2a) convey that zone III should exist and dominate the swelling behavior. Compared to that of multilayers 1M, the ΔD value in water is increased only slightly for multilayers 2 M, implying that the effect of zone III is largely reduced. This result is consistent with the fact that the electrostatic screening length of PDADMAC is slightly larger (~ 1 nm) than the average distance between the effective charge (~ 0.7 nm), causing little electrostatic repulsion of the polyelectrolyte in 2 M NaCl solution, which is not enough to dissociate the bulk.^{44,57} After a substantial loss of mass along with the increase in the salt concentration, the regular multilayer structure of three zones is reasonably destroyed and therefore zone III no longer remains. The larger swelling of multilayers 4 and 5 M in water should result from the uncompensated for PSS molecules, which possess the same physicochemical behavior as that of free polyions.

To confirm this explanation, we compared the mass loss per layer. The mass of the terminal PDADMAC layer and the last PSS/PDADMAC bilayers contributed 15 and 33% of the total

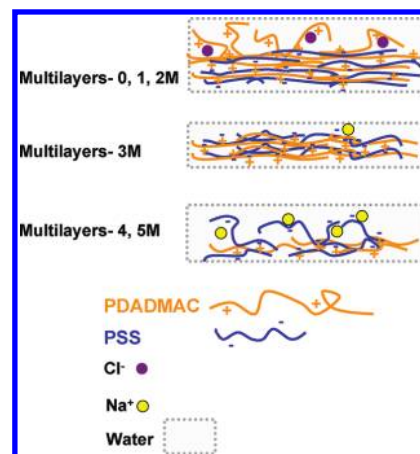


Figure 3. Schematic illustrations showing the typical physicochemical properties of the (PSS/PDADMAC)₇ multilayers treated with different concentrations of NaCl solutions.

mass of the multilayers as measured by QCM, respectively. The 6% mass loss of multilayer 2 M (Figure 1a) is smaller than the mass of the terminal PDADMAC layer, confirming that the outside PDADMAC is only partially removed from the surface. After the treatment in 3 M NaCl solution, a 19% mass loss was found on the multilayers, which is larger than the mass of terminal PDADMAC but smaller than that of the last bilayers. The results thus reflect that the last PDADMAC layer is completely etched off but part of the last PSS layer remains on the surface. All of the results are in good agreement with the fact that the outmost layer is first removed, resulting in the increasing S/N ratio, and then the bulk of the multilayers is exposed and broken sharply along with the increase in salt concentration, leading to 43 and 72% mass losses in multilayers 4 and 5 M, respectively. This huge mass loss ($>70\%$) is much larger than that of the PAA/PAH ($\sim 50\%$) and PSS/PAH multilayers ($\sim 15\%$) treated in the same 5 M salt solution⁴⁵ because of the weaker interaction.^{46,54}

By applying the salt treatment to PSS-terminated multilayers (i.e., (PSS/PDADMAC)₇-PSS), we obtained a similar result. The film surface was dominated by PSS, with an S/N ratio of 61:39, which was decreased to 53:67 and 47:53 after treatment with 1 and 2 M NaCl solutions, respectively. This result further proves that the uncompensated for polyions on the superficial layers are more easily etched off. After the (PSS/PDADMAC)₇-PSS multilayers were treated in 3, 4, and 5 M NaCl solutions, however, the S/N ratios on the surfaces (55:45, 60:40, and 65:35) were almost the same as those of the salted, treated PDADMAC-dominated multilayers (i.e., multilayers 3, 4, and 5 M (55:45, 56:44 and 62:38), respectively). Therefore, when the dissolution occurs, the remaining film structure is controlled thermodynamically by the chemical nature of the building blocks but is not influenced by the chemical structure of the last layer. The larger loss of PDADMAC on the surface in concentrated NaCl solution (>3 M) can be explained by the fact that the distances between monomer units of PSS and PDADMAC are 2.6 and 5.2 Å,⁵⁸ respectively, which implies that PDADMAC has a smaller charge density than PSS and therefore is more sensitive to salt screening.⁵⁷

CONCLUSIONS

The salt treatment can easily change the structure and physicochemical properties of the PSS/PDADMAC multilayers, resulting

in thin films with various features. Because the polyanion/poly-cation stoichiometry in bulk multilayers is observed to be 1:1 or at least close to this value,⁵⁵ multilayer 3 M can be regarded as the bulk film because of the roughly equal amounts of PSS and PDADMAC. As a result of the better compensation (5% counterions), the largest cross-linking density is expected among others, leading to the smallest swelling behavior in water (Figure 3). For the thin films with larger numbers of uncompensated for polyions such as multilayers 1 and 5 M, a swollen, hydrated structure is formed. Moreover, because the slight mass loss does not obviously change the multilayer structure, multilayers 0, 1, and 2 M can basically maintain their initial physicochemical structure (a PDADMAC-dominated surface). By contrast, the massive loss of polyelectrolytes completely destroys the layered structure of multilayers 4 and 5 M, leading to a surface chemistry reversal. In such a case, the structure is not composed of multilayers any longer. The obtained polymer thin films with various structures and properties are expected to find diverse applications in the fields of biomaterials, medicine, and nanotechnology.

■ ASSOCIATED CONTENT

S Supporting Information. Atomic force microscopy. Morphology of the (PSS/PDADMAC)₇ multilayers in PBS. Relative thickness of (PSS/PPDADMAC)₇ multilayers treated in 3 and 5 M NaCl solutions as a function of time. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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