Layer-by-Layer Assembly between Poly(vinylamine hydrochloride-*co*-*N*-vinylformamide) with Variable Primary Amine Content and Poly(sodium styrenesulfonate)

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ABSTRACT: Layer-by-layer (LbL) assemblies between poly(vinylamine hydrochloride-*co*-*N*-vinylformamide) [poly(VAm-*co*-NVF)] with various amounts of VAm and poly(sodium styrenesulfonate) (PSS) from their aqueous solutions were analyzed by the quartz crystal microbalance (QCM) technique, attenuated total reflection (ATR) spectra, and atomic force microscopic (AFM) observations. QCM analyses revealed that the assembly amount was strongly affected by the VAm content. At a VAm content of less than 30% in total units of poly(VAm-*co*-NVF), the LbL assembly did not proceed, and the frequency shift zigzagged with the step number. The total frequency shift, however, increased with an increasing step number and with an increasing VAm content. At 30% VAm, the frequency shifted exponentially with an increasing number of assembly steps, and the shift achieved a maximum value, indicating that the greatest amount was assembled with this VAm content. The total shift decreased with a VAm content of 50%. Above 50%, however, the frequency increased linearly with an increasing number of steps, and the total shift after a 40-step assembly was almost the same as that observed with 50% VAm. An assembly mechanism dependent on the VAm content was proposed to explain these observations. AFM observations revealed that the surfaces of the assemblies were smooth at the nanometer level. The VAm content significantly affected the density of the assembly. The density of the assemblies was similar in air and ranged from 1.22 to 1.28 g cm^{-3}, even though the VAm content differed. On the other hand, the density of the film prepared by using poly(VAm-*co*-NVF) with a VAm content of 30% decreased to 0.86 g cm^{-3} in water, while the density of the film prepared using poly(VAm) was not changed.

Introduction

The fabrication of ultrathin polymer films on material surfaces is attractive not only as a method to improve or modify surface characteristics without changing the mechanical properties of materials but also as a method to study specific properties of polymers in ultrathin films or on film surfaces. Layer-by-layer (LbL) assembly is a simple method for fabricating layered ultrathin polymer films by alternate immersion of materials into aqueous solutions of oppositely charged polyelectrolytes, based on the driving force of polyion complex formation.[1] Not only linear polyelectrolytes but also dyes, biomacromolecules, and organic or inorganic colloids can be applied in LbL assembly. Since the LbL assembly is in principle realized by combining various interactive polymers, the driving forces in LbL assembly include hydrogen bonding,[2] charge transfer,[3] and stereocomplex formation.[4] We have developed a novel methodology based on the LbL assembly process, involving repetitive physical adsorption/drying processes in the preparation of ultrathin films composed of strongly self-interactive polymers.[5] The processes involved in LbL assembly, in addition to the deconstruction and desorption processes which are dependent on preparation conditions and media environments, have been recently discussed.[2b,6] Although considerable knowledge regarding LbL assembly has been revealed, further investigation of the latter is required.

In mechanistic analyses of LbL assembly, the effect of the charge densities of corresponding polymers on the assembly is one important area of investigation. A decrease in charge may affect the assembly process and/or physical properties of resulting films, possibly dependent on interactive forces between polymers and conformational changes of polymers in solutions. Rubner et al. analyzed LbL assembly using weak polyelectrolytes under suitable pHs and revealed that layer thickness, level of layer interpenetration, and surface characteristics were sensitive to the pH of polymer solutions.[7] Although these considerations are very important in regulated LbL assembly, delicate changes in charge densities are difficult to manipulate, as the density of weak polyelectrolytes is nonlinearly changed by pH. Stuart et al. performed LbL assembly between partially quaternized poly(vinylimidazole) and fully charged poly(acrylic acid) at an ionic strength of 0.01 M.[8] They demonstrated that stable multilayers were formed above the quaternization of 18%, although the hydrodynamic layer thickness was maximal at approximately 8%. Klitzing et al. investigated the LbL assembly between copolymers of diallyldimethylammonium chloride (DADMAC) and *N*-methyl-*N*-vinylacetamide (NMVA) with different cationic charge densities and poly(sodium styrenesulfonate) (PSS) in the presence of 0.1 M NaCl.[9] They revealed that film thickness after a 10-cycle assembly was steeply increased when the cationic unit fraction was increased from 50 to 75% and was decreased slightly when the cationic fraction exceeded 75%. This observation indicated that an increased amount of cationic charge effectively facilitated LbL assembly on surfaces, although details of this assembly process were not analyzed. More recently, Jonas et al. analyzed the LbL assembly between copolymers of DADMAC and *N*-methyl-*N*-vinylformamide (NMVF) with different cationic charge densities and PSS at low ionic strength.[10] On the basis of the resulting variations

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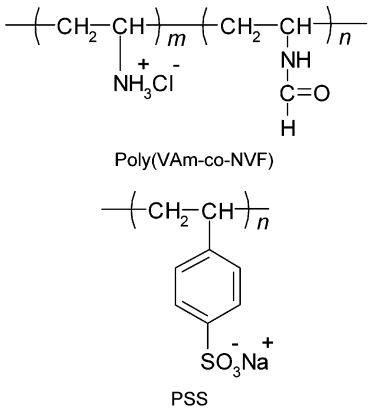

Figure 1. Chemical structures of poly(VAm-*co*-NVF) and PSS used in the present study.

in thickness vs the cationic unit of the copolymer, three different assembly zones could be differentiated: below 9% DADMAC, the change in thickness was zero; between 10 and 30%, the increment strongly decreased with increasing DADMAC content; above 30%, the increment reached a constant value. Caruso et al. also used copolymers of DADMAC and NMVA assembled with PSS at a higher ionic strength and revealed that LbL assembly preferentially occurred at 75% DADMAC.[11] Although these studies discussed the influence of the charge density of the polyelectrolytes on the LbL assembly, further analysis is necessary using other combinations of polymers.

Our research group has investigated novel monomers, *N*-vinylalkylamides and their water-soluble polymers, which were prepared by free radical polymerization of the corresponding monomers in the presence of azo-type initiators in water or water-soluble organic solvents.[12] Since amide linkages of the polymers were hydrolyzed under acidic and alkaline conditions, the simplest polyamine having primary amines, poly(vinylamine) (polyVAm), was successfully prepared.[12c,d] The VAm content in polymers could be easily controlled by regulating the reaction times and the pH of the media. The hydrolysis rate was dependent on the hydrophilicity of the lateral groups and basically increased with decreasing hydrocarbon chain length. For instance, when copolymers of *N*-vinylformamide (NVF) and *N*-vinylisobutyramide (NVIBA) were treated under suitable conditions, the NVF unit was selectively hydrolyzed to obtain poly(VAm-*co*-NVIBA).[12d] Accordingly, we were able to prepare water-soluble polymers with an adjustable primary amino content based on two methods: controlled hydrolysis of homopolymers of *N*-vinylalkylamides and selective hydrolysis of suitable copolymer combinations.

In the present study, LbL assembly was performed between poly(VAm-*co*-NVF)s with variable amounts of VAm, which were prepared by partial hydrolysis of NVF units of polyNVF, and PSS on surfaces, and the effect of VAm content on the LbL assembly was analyzed in detail. The chemical structures of the polymers used are shown in Figure 1.

Experimental Section

Materials. PolyNVF was prepared by free radical polymerization of NVF (M_n 15 000, M_w/M_n 3.2) as described in our previous paper.[12c,d] PolyNVF was partially hydrolyzed in aqueous 2 N NaOH solution at 60 °C for an adequate amount of time. The reaction media were neutralized at approximately pH 7 by 2 N HCl. The VAm content was regulated by varying the reaction time. A plot of VAm content against reaction time gave a saturation curve which could be fitted to the equation of a pseudo-first-order rate profile with a coefficient of variation of 0.996. For instance, the reactions for 11 and 50 min yielded copolymers with VAm unit fractions of 30% and 69%, respectively, which were analyzed by ^{1}H NMR. PSS (M_w ca. 70 000) was purchased from Aldrich and used without further purification.

QCM. An AT-cut quartz crystal with a parent frequency of 9 MHz (9 mm in diameter) was coated on both sides with polished gold electrodes (4.5 mm in diameter). An Iwatsu frequency counter (model SC7201) monitored the frequency. The leads of the QCM were sealed and protected by rubber gel. The amount of polymers assembled, Δm, was measured by the frequency shift of the QCM, ΔF, using Sauerbrey's equation as follows:[13]

$$-\Delta F = \frac{2F_0^2}{A\sqrt{\rho_q \mu_q}} \Delta m$$

where F_0 is the parent frequency of QCM (9×10^6 Hz), A is the area of the electrode (0.159 cm^2), ρ_q is the density of the quartz (2.65 g cm^{-3}), and μ_q is the shear modulus (2.95×10^{11} dyn cm^{-2}). Before LbL assembly, the QCM electrodes were treated three times with a piranha solution [concentrated H_2SO_4/H_2O_2 (30 wt % in water) = 3/1, v/v] for 1 min each time, followed by rinsing with pure water and drying with N_2 gas to clean the electrode surface.

Assembly. The QCM was immersed in an aqueous poly(VAm-*co*-NVF) solution (0.02 M) for 20 min at 25 °C, taken out, washed with pure water, and dried with N_2 gas. The frequency shift was then measured in air. The QCM was immersed again in an aqueous PSS solution (0.02 M) for 20 min at 25 °C, and the same procedure was repeated. This alternating cycle was repeated for the LbL assembly. Although assembly could be achieved when starting with the PSS step, all assemblies in the present study were performed with the copolymers as the starting polymer. Accordingly, odd and even steps indicate copolymer and PSS immersion, respectively. In all assembly experiments, salts were not added into the solutions to simplify interpretation of the results.

Characterization. Attenuated total reflection (ATR) spectra were obtained with a Perkin-Elmer Spectrum One in air at ambient temperature. One side of a poly(ethylene terephthalate) film was coated with gold to obtain a reflective surface. The polymers were then assembled for 40 steps similar to the method used in QCM measurements. The interferograms were co-added 32 times and Fourier transformed at a resolution of 4 cm^{-1}. Atomic force microscopic (AFM) images were obtained with a Digital Instruments NanoScope III that was operated in noncontact mode in air or water at ambient temperature. We did not perform any image processing other than flat leveling. The mean roughness (Ra) in a given observed area was estimated from the following equation:

$$Ra = \frac{1}{LxLy}\int_0^{Ly}\int_0^{Lx}|F(x,y)|\,dx\,dy$$

where $F(x,y)$ is the surface relative to the center plane, which is a flat plane parallel to the mean plane, and Lx and Ly are the dimensions of the surface. Scratching of assembled polymers for thickness measurements using the AFM tip was performed under conditions when did not scratch the gold QCM substrate.

Results and Discussion

Quantitative analyses of the LbL assembly using a QCM substrate provide significant information regarding the process, since the amount assembled at each step can be successfully monitored to the nanogram level on the basis of its frequency shift. This technique facilitates analysis of the effect of the charge density of

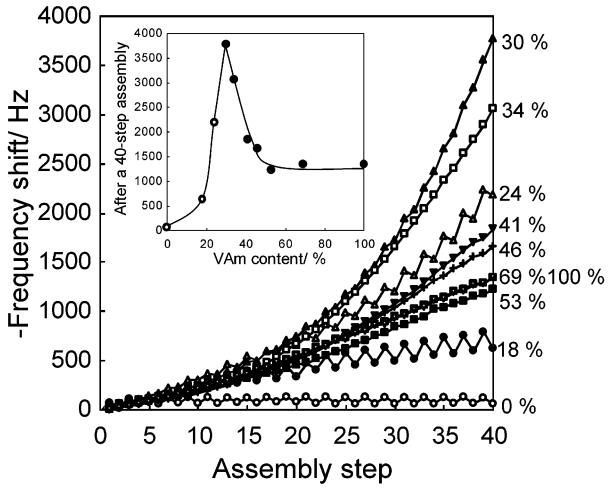

Figure 2. Frequency shifts against assembly step. Poly(VAm-*co*-NVF) with variable VAm content and PSS were assembled at odd and even steps, respectively. The inset shows the frequency shifts after a 40-step assembly against the VAm content of poly(VAm-*co*-NVF).

water-soluble polymers on LbL assembly, as shown in previous papers.[4,5,11] Figure 2 shows the dependence of frequency shifts on the assembly step when a QCM was alternately immersed in poly(VAm-*co*-NVF) with variable VAm contents and PSS at 0.02 M for 20 min at 25 °C. The decrease in the frequency indicates the increase in the assembly amount. Ten types of copolymers were synthesized with the VAm content ranging from 0 to 100%. The shifts were reproducible in all cases, and the experimental errors were within 10% deviation. Ideally, the shifts should be represented in terms of the thickness of the assemblies. However, since the density of the assembly seemed to be dependent on the VAm content (see AFM analysis), the assembly is discussed only in terms of the frequency shift. LbL assembly could not be achieved using polyNVF without VAm, but assembly was observed with poly(VAm-*co*-NVF) and all of the various VAm contents analyzed. The frequency shift was zigzag in form in the case of poly(VAm-*co*-NVF) with a VAm content of less than 30%, indicating the partial desorption of poly(VAm-*co*-NVF) already assembled at the even PSS steps, although the frequency shifted through a 40-step assembly. The frequency continuously shifted above a VAm content of 30%, indicating successful stepwise assembly between poly(VAm-*co*-NVF) and PSS. This difference is typically due to the effect of charge densities. Since the electrostatic interaction between poly(VAm-*co*-NVF) with less than 30% VAm and PSS is very weak for sequential assembly on surfaces, the poly(VAm-*co*-NVF) already deposited was forced to be desorbed by PSS in the aqueous phase. On the other hand, sufficient interaction between poly(VAm-*co*-NVF) with more than 30% VAm and PSS leads to LbL assembly without any desorption of the polymers already deposited.

The inset of Figure 2 shows the frequency shift after a 40-step assembly plotted against the VAm content of poly(VAm-*co*-NVF). The shift increased steeply from 0 to 30% and reached a maximum at 30%. The shift was subsequently decreased until approximately 50% VAm and then became constant at a VAm content above 50%. The maximum shift indicates the threshold VAm content for zigzag and stepwise assembly. We also found that a decrease in the charge densities of one polymer leads to a steep increase in the assembly amount.

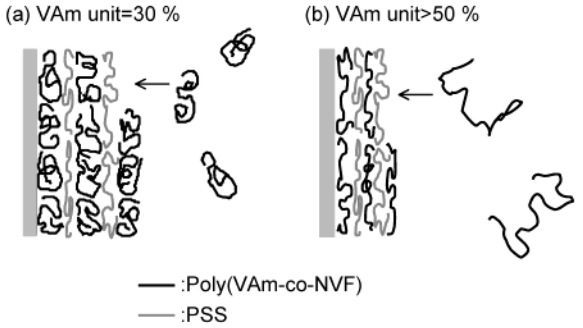

Figure 3. Schematic representation of the assembly mechanism of the assemblies involving (a) poly(VAm-*co*-NVF) with a VAm content of 30% and (b) poly(VAm-*co*-NVF) with a VAm content of approximately 50%.

Although this decrease in the charge densities of the polymers used in LbL assembly may result in a simple decrease in the assembly amount, our polymer system indicates the increase in assembly is related to suitable charge density. A possible mechanism for the increase at 30% VAm is schematically represented in Figure 3 and can be described as follows. The decrease in the charge density of poly(VAm-*co*-NVF) possibly leads to a polymeric conformation in the aqueous phase that is more coiled due to the relaxation of electrostatic repulsions between the amines. This coiled polymer with a VAm content of 30% was adsorbed onto the PSS surface for the LbL assembly, resulting in an apparent increase in the amount adsorbed, as shown in Figure 3a. For more than 50% VAm, the poly(VAm-*co*-NVF) extended due to electrostatic repulsions was adsorbed onto PSS on surfaces through sufficient electrostatic interactions, resulting in a similar frequency shift above 50%, as shown in Figure 3b. Klitzing et al. demonstrated that the thickness of films, which were prepared by the LbL assembly between copolymers of DADMAC and NMVA with different cationic charge densities, and PSS, was small and constant with the amine content ranging from 0 to 50% but increased steeply at 75% amine content and then decreased slightly above 75%.[9] The present study analyzed the combination of poly(VAm-*co*-NVF) and PSS, and completely different results were observed, although Klitzing et al. added 0.1 M NaCl into both polymer solutions. The differences in chemical structure between both amine polymers may explain the present results and may be attributable to differences in the efficiency of cationic charges in forming electrostatic interactions and/or to differences in the conformations of polymers in solutions or on surfaces. In fact, Stuart et al. revealed that the hydrodynamic layer thickness of the LbL assembly between partially quaternized poly(vinylimidazole) and fully charged poly(acrylic acid) at a ionic strength of 0.01 M was maximal at the quaternization value of approximately 8%.[8] Jonas et al. also demonstrated a similar profile for the LbL assembly between copolymers of DADMAC and NMVF, and PSS, in which the thickness increment was maximal at a DADMAC content of approximately 10% at low ionic strength.[10] Other types of amine-containing water-soluble polymers of *N*-vinylalkylamides[12] can similarly be prepared, and detailed analyses of these polymers will reveal further insights into assembly profiles.

The presence of both polymers in the LbL assembly was analyzed by ATR spectra. A typical example of an ATR spectrum of the LbL assembly between poly(VAm-

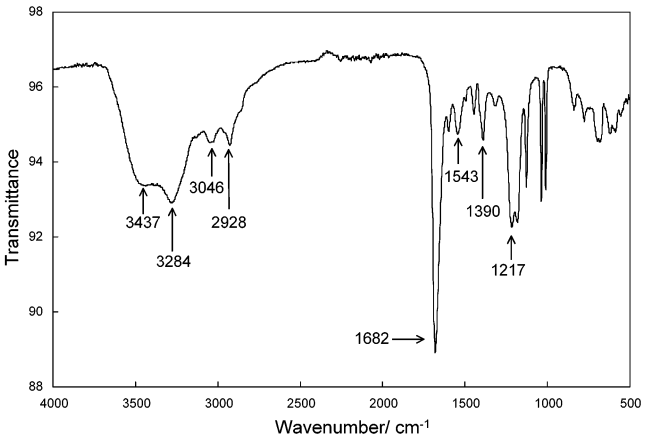

Figure 4. ATR spectrum of a 40-step assembly between poly(VAm-*co*-NVF) with a VAm content of 30% and PSS.

co-NVF) with a VAm content of 30% and PSS is shown in Figure 4. N−H stretching (ν_{N-H}) for amides, amide I ($\nu_{C=O}$), amide II (δ_{N-H}), and protonated primary amine bands assigned to NVF and VAm units were observed at 3437, 1682, 1543, and 3284 cm^{-1}, respectively, indicating the presence of poly(VAm-*co*-NVF). Antisymmetric and symmetric vibration bands of sulfonic acids were observed at 1390 and around 1217 cm^{-1}, respectively, indicating the presence of PSS. Antisymmetric and symmetric vibration bands of methylene in the main chains were also observed at 3046 and 2928 cm^{-1}, respectively. These observations show that both polymers were assembled by alternate immersion of substrates in both aqueous solutions.

To analyze the QCM results in detail, the frequency shifts at each step are presented as a bar graph against the assembly step for all polymer combinations as shown in Figure 5. This graph indicates that the LbL assembly between poly(VAm-*co*-NVF) and PSS can be divided into three different assembly patterns. The first pattern was observed with a VAm content ranging from 0 to 24% and consists of deposition at the poly(VAm-*co*-NVF) step and subsequent desorption of polymers at the PSS step, as already discussed. The second pattern was observed from 30% to 46% VAm content and consists of an exponential increase in the assembled amounts of both polymers with an increasing number of assembly steps. This is possibly due to an increase in the apparent surface area of the assemblies with increasing steps (see AFM analysis). Picart et al. suggested, on the basis of a mechanistic analysis of the LbL assembly between poly(L-lysine) and hyaluronic acid, that the exponential increase in the apparent thickness derived from the diffusion of free poly(L-lysine) chains, which was the starting polymer for the LbL assembly, into the interior of the films with the expulsion of water after the formation of continuous films on surfaces.[14] In our case, poly(VAm-*co*-NVF) might also diffuse into the films after approximately 15 steps. In fact, with exponential growth, the film swelled with water molecules, possibly forming a hydrogel structure on the surface (see AFM analysis). The third pattern was observed with a VAm content exceeding 53% and the conventional LbL process, in which the assembled amount of both polymers was approximately constant after an adequate step number. In all three patterns, the LbL assemblies from 24% and 46% VAm content maintained boundary characteristics. At 24% the amine charge is used for the assembly of coiled poly(VAm-*co*-NVF). However, PSS caused slight peeling of the poly(VAm-*co*-NVF) weakly deposited on surfaces. Furthermore, at 46% the profile had the intermediate features of both exponential increase and constant assembly.

On the basis of the results shown in Figure 5 which indicate the assembly amounts at each step and which can be derived from the frequency shifts, it is difficult to determine whether the cationic and anionic charges compensated for each other in LbL assembly. It is useful to estimate the number of amines relative to sulfonyl groups in the assemblies, although both charges are not necessary for interactions. Figure 6 shows the number of VAm units relative to PSS units in the LbL assemblies plotted against the VAm content of poly(VAm-*co*-NVF) after the 40-step assembly. The number of amino groups in the 40-step assembly was estimated from both the mean unit molecular weight of each poly(VAm-*co*-NVF) and the VAm content, and then those were divided by the number of sulfonyl groups of PSS totally assembled, assuming that amino and sulfonyl groups have counterions (sodium and chloride for PSS and VAm units, respectively). The profile was not affected by the presence or absence of counterions. The number was approximately 1 for poly(VAm), indicating that almost all cationic charges were compensated for by anionic charges. On the other hand, the number of amines increased with decreasing VAm content. This observation suggests that some VAm units did not interact electrostatically with the sulfonyl groups in the LbL assemblies, and the quantity was dependent on the VAm content. The number of amines reached a maximum at 30% VAm content, at which the assembly amount was also maximal, indicating fewer ionic pairs between poly(VAm-*co*-NVF) and PSS. This observation strongly supports the assembly mechanism shown in Figure 3a. Since the interaction between the polymers at 30% seemed to be very weak, one might suppose the assembly to be unstable in an aqueous phase. However, the polymers did not peel off in water at any VAm content, indicating stability similar to that of conventional LbL assemblies.

AFM observation facilitates visualization of the surface topographic features of the LbL assemblies and provides information regarding the assembly mechanism. Figure 7 shows the AFM images of surfaces of a bare QCM, a 40-step assembly between poly(VAm-*co*-NVF) with a VAm content of 30% and PSS, and a 40-step assembly between poly(VAm) (corresponding to a VAm content of 100%) and PSS in air. The surfaces were smooth at the nanometer level, and the *Ra* values estimated from the given area were 1.5, 2.6, and 3.1 nm. Although the apparent film thickness of a 40-step assembly using poly(VAm-*co*-NVF) with a VAm content of 30% was much larger than that of a similar assembly using poly(VAm), the former *Ra* was smaller that that of the latter, indicating a smoother surface. The *Ra* of the assemblies using poly(VAm-*co*-NVF) with a VAm content of 30% in air increased with an increasing number of steps; the values were 0.8, 1.3, 1.5, and 2.6 nm at 10, 20, 26, and 40 steps, respectively. This increase in the *Ra*, which leads to an increase in the apparent surface area, might be one of the reasons why the assembly amount exponentially increased at each step, as shown previously. However, this should not be a major reason for the exponential increase in the amount. Further research on this topic is necessary. The *Ra* values of the assembly using poly(VAm) were 3.2

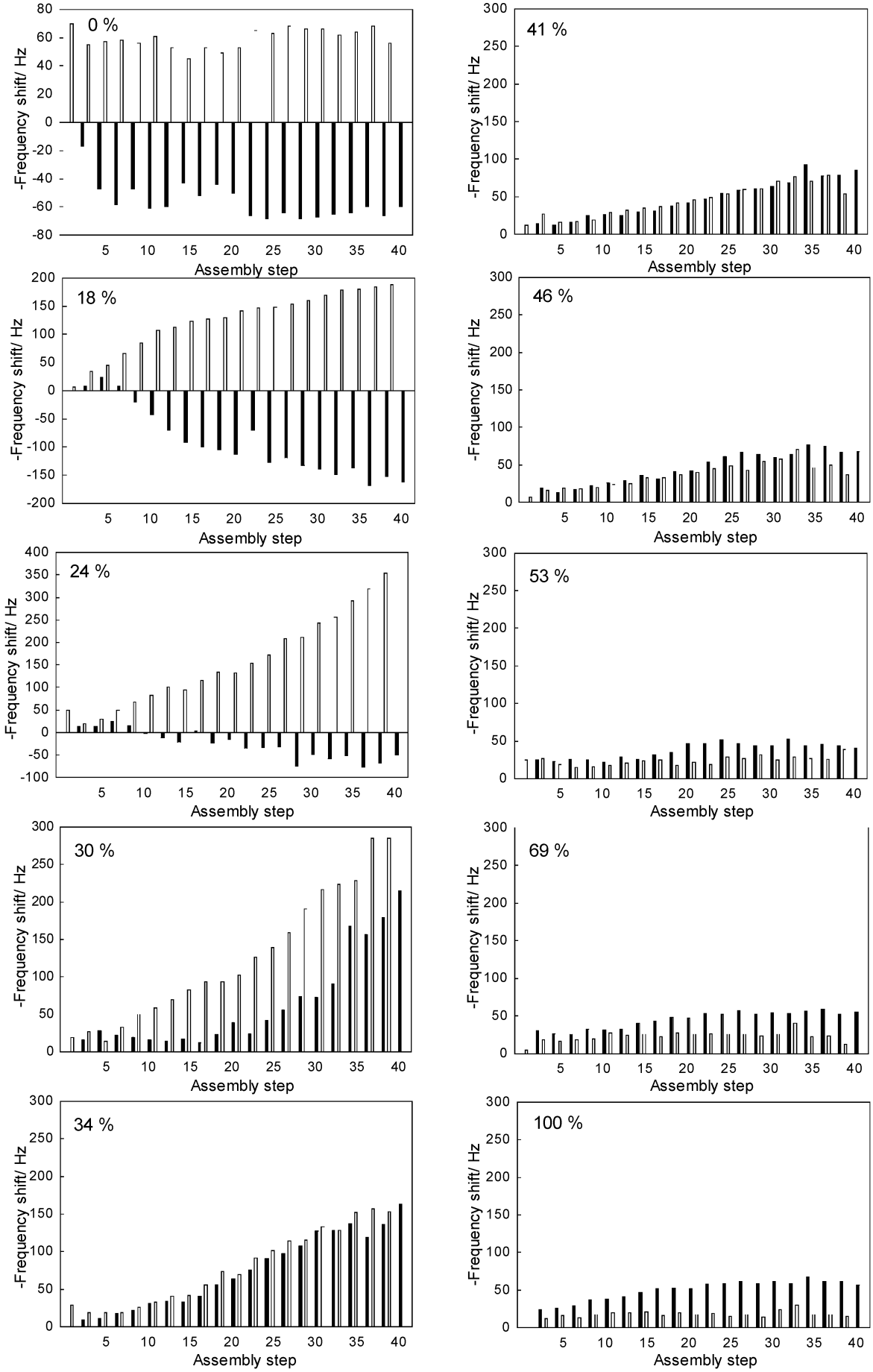

Figure 5. Frequency shifts at each step against assembly step. Open and closed bars indicate the poly(VAm-*co*-NVF) and PSS steps, respectively.

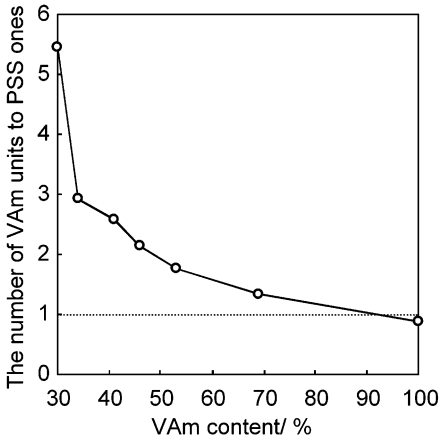

Figure 6. Number of VAm units of poly(VAm-*co*-NVF) relative to sulfonyl groups of PSS against the VAm content in the 40-step assemblies.

and 3.2 nm at 20 and 40 steps, respectively, and were the same even though the step number was changed. This observation was also consistent with the previous result, in which the assembly amount at each step was constant. Note that the *Ra* of a 40-step assembly between poly(VAm) and PSS was greater than that of a 26-step assembly between poly(VAm-*co*-NVF) with a VAm content of 30%, while the assembly amounts were almost the same. This is possibly due to the strong interactions between poly(VAm) and PSS, resulting in an aggregated structure on the assembly surface.

To reveal the thickness and the apparent density of the assemblies in air and water, the tip of the AFM apparatus was used to scratch the films, and cross-sectional images were obtained. Figure 8 shows the resulting AFM images as well as the cross-sectional images. The thickness of a 40-step assembly using poly(VAm-*co*-NVF) with a VAm content of 30% in air and water was 80 and 120 nm, respectively. The densities estimated by considering the assembly amount and the electrode area of the QCM were 1.28 and 0.86 g cm^{-3}, respectively. The density in air was similar to that of conventional polyion complexes (1.2 ± 0.1 g cm^{-3}).[15] However, the density in water was much smaller. This observation indicates that the film swelled with water molecules in aqueous phases possibly due to the presence of hydrophilic NVF and VAm units that did not participate in the electrostatic interactions, forming an ultrathin hydrogel structure (see the analysis of charge compensation in the LbL assembly described above). Since we have already demonstrated the preparation of ultrathin hydrogels by sequential chemical reactions involving water-soluble polymers on surfaces,[12e] it will be interesting to compare the physicochemical properties of both ultrathin hydrogels in the near future. On the other hand, the thickness of the assembly using poly(VAm) was 30 nm, the same in air and water. The density was estimated to be 1.22 g cm^{-3}, which was the same as the conventional value. This observation indicates that this film does not absorb water molecules in aqueous phases, as no hydrophilic lateral groups remained in the film.

Conclusions

The LbL assemblies between cationic poly(VAm-*co*-NVF)s with variable VAm content and anionic PSS on the surface were investigated. The fabrication process was quantitatively analyzed by frequency shifts of a QCM which was used as the assembly substrate. The presence of both polymers in the assembly was confirmed by ATR spectra. The assembly was strongly affected by the VAm content. The amount assembled increased steeply with decreasing VAm content and decreased below a certain content. Plots of assembly amount against step number revealed three distinct assembly patterns (zigzag, exponential, and linear increases), depending on the VAm content. The apparent charge compensation between amino and sulfonyl groups in the assembly was analyzed and was related to the assembly profiles. AFM observations revealed that the surfaces of the assemblies were molecularly smooth and that the films swelled with water molecules, depending on the content, to form ultrathin hydrogels.

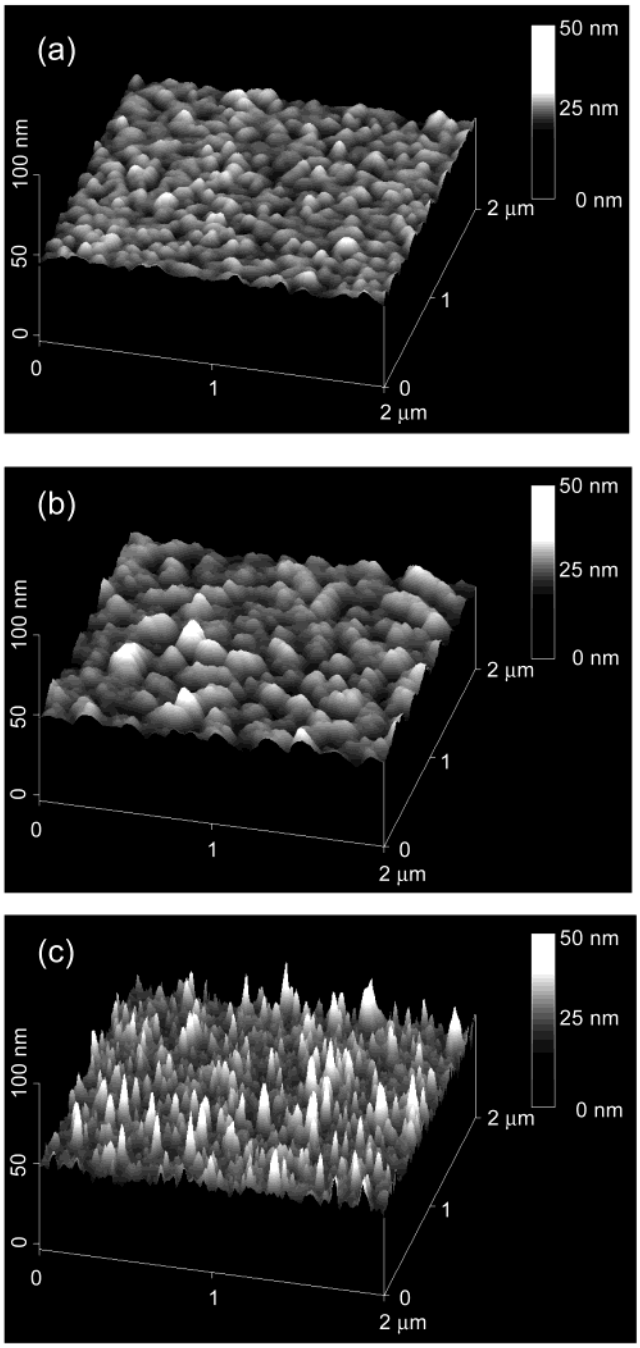

Figure 7. AFM images of (a) a bare QCM, (b) a 40-step assembly between poly(VAm-*co*-NVF) with a VAm content of 30% and PSS, and (c) a 40-step assembly between poly(VAm) and PSS in air.

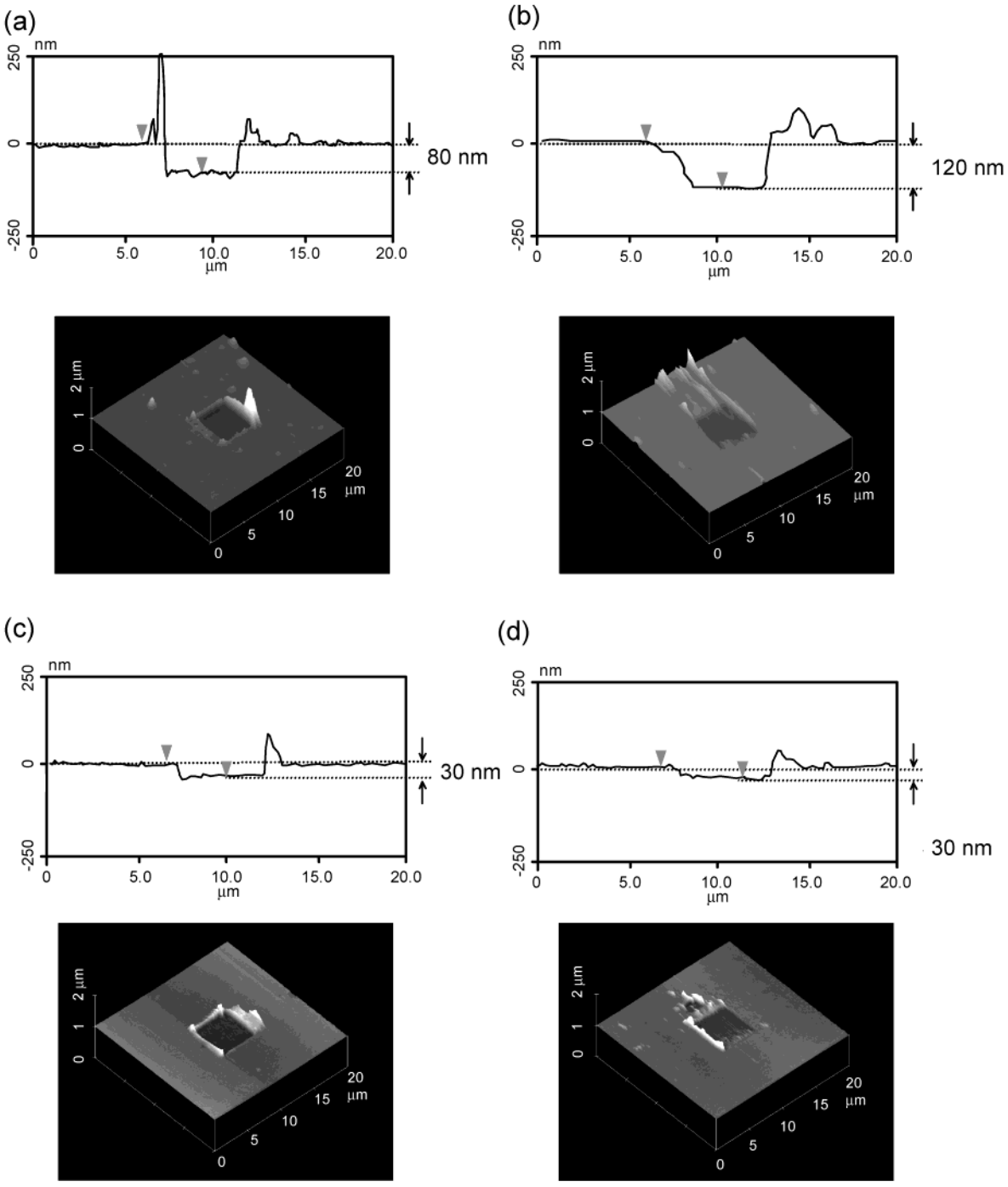

Figure 8. Scratching AFM images of a 40-step assembly between poly(VAm-*co*-NVF) with a VAm content of 30% and PSS (a) in air and (b) in water and of a 40-step assembly between poly(VAm) and PSS (c) in air and (d) in water.

Polymers of *N*-vinylalkylamides have simple chemical structures and have primary amines after hydrolysis suitable for electrostatic interactions. Accordingly, the polymers can also be applied to LbL assemblies for the systematic investigation of the effect of charge density as well as chemical structure in LbL assemblies.

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