Thermoresponsive Ultrathin Hydrogels Prepared by Sequential Chemical Reactions

Takeshi Serizawa, Kazuhisa Nanameki, Kazuya Yamamoto, and Mitsuru Akashi*

Department of Applied Chemistry and Chemical Engineering, Faculty of Engineering, Kagoshima University, 1-21-40 Korimoto, Kagoshima 890-0065, Japan

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ABSTRACT: Thermoresponsive ultrathin hydrogels were prepared by the sequential chemical reaction of poly(vinylamine-*co*-*N*-vinylisobutyramide) [poly(VAm-*co*-NVIBA)] and poly(acrylic acid) (polyAAc) on a gold surface. The carboxyl group of polyAAc was activated by 1-ethyl-3-(3-(dimethylamino)propyl)-carbodiimide hydrochloride (EDC) for the reaction with the amino group of poly(VAm-*co*-NVIBA) to yield the amide linkage. This stepwise assembly was analyzed quantitatively by a quartz crystal microbalance (QCM), which revealed that the 39 mol % VAm content of poly(VAm-*co*-NVIBA) was suitable for the preparation of ultrathin hydrogels. A detailed analysis was performed by the assembly of poly(VAm-*co*-NVIBA), with a 39 mol % VAm content and polyAAc. The reflection−absorption spectra (RAS) showed the presence of both polymers in the assembly. Atomic force microscopic (AFM) observations confirmed the hydrogel structure of the assembly; the thickness of the hydrogel in an aqueous medium (around 320 nm) was 2 times greater than that in air (around 150 nm). The dynamic process probably proceeded by water swelling into the assembly when immersed in an aqueous phase from air. This was also observed by AFM analysis, in which the surface roughness increased from 14 nm in air to 35 nm until 10 min postimmersion, subsequently decreased to 19 nm, and then saturated after 30 min. The thermoresponsive properties were analyzed by the static contact angle measurement in water by using an air bubble. The assembly became more hydrophobic above 30−40 °C, suggesting that the phase transition was derived from the polyNVIBA unit. The phase transition was affected by the pH of the water in the present system, and no phase transition was observed from 20 to 60 °C at a pH of 2 and 12. Layer-by-layer assembly using chemical reactions will open a new field of research on the suitable selection of functional polymers.

Introduction

The formation of ultrathin polymer films on material surfaces by suitable methods promises the modification or improvement of the surface characteristics for applications in the chemical and technological fields. Layer-by-layer (LbL) assembly is a significant technique that fabricates ultrathin polymer films by the alternate immersion of materials into interactive polymer solutions, resulting in a layered nanostructure.[1] Polyion,[1] charge-transfer,[2] hydrogen-bonding,[3] and van der Waals[4] interactions between the polymers have all been used for the sequential assembly. Since LbL assembly includes the simple immersion of substrates into polymer solutions, various materials of assorted shapes that are insoluble in the solvent of the polymers can be used. In addition, LbL assembly is very simple, and no specific apparatus is necessary.

Although LbL assembly normally includes noncovalent interactions between polymers, the technique can be used for the formation of covalent bonds between polymers using sequential chemical reactions. For the assembly with covalent bonds, the formation of covalent bonds by heat treatment after polymer assembly,[5] the assembly of polymers with activated functional groups,[6] and assembly based on metal coordination[6d,7] have been demonstrated. These assemblies should become more stable under certain atmospheres as compared to conventional assembly, and their applications will expand even more. On the other hand, when an adequate amount of covalent bonds can be formed in the assembly of water-soluble polymers by suppressing the unnecessary interactions between the polymers, then ultrathin hydrogels can be generally prepared on the surfaces. It is well-known that hydrogels have significant properties that may be useful for applications in various fields. Accordingly, novel surface modification will be achieved by the preparation of ultrathin hydrogels on material surfaces. To realize this system, structurally regulated polymers with an adequate amount of functional groups are necessary.

In our research group, functional polymers with various alkyl side chains were prepared by the free radical polymerization of a novel monomer, *N*-vinylalkylamide.[8] The side chains linked with an amide linkage could be hydrolyzed, resulting in poly(vinylamine) (polyVAm) with a primary amine.[8b,n] Monomers with different alkyl side chains were readily copolymerized with similar reactivity to form highly random copolymers.[8f,n,o] In the case of the copolymer [poly(NVF-*co*-NVIBA)] of *N*-vinylformamide (NVF) and *N*-vinylisobutyramide (NVIBA), the NVF unit was selectively hydrolyzed under suitable conditions to prepare poly(VAm-*co*-NVIBA).[8n,o] These observations suggest that the primary amine in poly(VAm-*co*-NVIBA) can be readily controlled for applications in the LbL assembly with covalent bonds. On the other hand, since polyNVIBA has a reversed amide linkage to a thermoresponsive polymer poly(*N*-isopropylacrylamide) and showed a lower critical solution temperature (LCST) at around 39 °C,[8d] poly(VAm-*co*-NVIBA) is also a thermoresponsive polymer although its LCST is dependent on the solution pH and the VAm content.[8n,o] Thus, it may be a possible to prepare a thermoresponsive assembly.

In the present study, the preparation of thermoresponsive ultrathin hydrogels composed of poly(VAm-*co*-NVIBA) with different VAm contents and poly(acrylic acid) (polyAAc) were analyzed by the sequential chemical reaction of the amino and carboxyl groups by the

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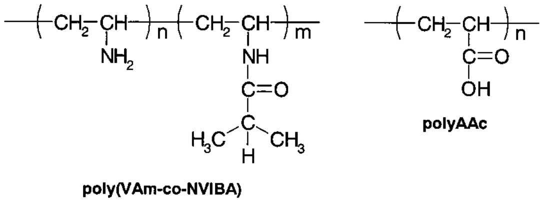
Scheme 1. Chemical Structures of Polymer and Activating Reagent Used for the Preparation of Ultrathin Hydrogels



amide linkages on the surface, respectively. The carboxyl group was activated by 1-ethyl-3-(3-(dimethylamino)propyl)carbodiimide hydrochloride (EDC) and was sequentially reacted with the amino group. The assembly was analyzed quantitatively by a quartz crystal microbalance (QCM) and was characterized by its reflection−absorption spectra (RAS), atomic force microscopy (AFM), and static contact angle measurements. Although it is difficult to control the covalent bonds and electrostatic interactions in the assembly between polyVAm and polyAAc, it may become easier by using the combination of poly(VAm-*co*-NVIBA) and polyAAc. The chemical structures of the polymers are shown in Scheme 1.

Experimental Section

Materials. Poly(VAm-*co*-NVIBA)s with VAm contents of 10, 25, and 39 mol % were synthesized from the starting polymer poly(NVF-*co*-NVIBA) (M_n 31 000, M_w/M_n 2.5), according to our previous study.[8n,o] PolyAAc (M_w 2000) was purchased from Aldrich and was used without further purification. EDC (>98.0%) and acetic acid anhydride were purchased from Wako (Japan) and used without further purification. Ultrapure distilled water (17.8 ΩM cm^{-1}) was provided by the Milli-Q labo system.

QCM. The assembly was analyzed quantitatively by a 9 MHz QCM, essentially as reported in our previous studies.[4] The crystal (9 mm in diameter) was coated on both sides with gold electrodes 4.5 mm in diameter, of which the roughness was 1.8 nm. The frequency was then monitored by an Iwatsu frequency counter (model SC7201). The leads of the QCM were sealed and protected with a silicone rubber gel in order to prevent degradation during immersion in the aqueous solutions. The amount of polymer assembled, Δm, was calculated by measuring the frequency shift of the QCM, ΔF, using Sauerbrey's equation[9] as follows:

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

where F_0 is the parent frequency of the QCM (9 × 10^6 Hz), A is the electrode area (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}). This equation was reliable when the measurements were performed in air as described in the present study. The mass of the solvents was never detected as a frequency shift, and thus the effects of the viscosity of the absorbent could be ignored. Before the 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, followed by rinsing with pure water and drying with N_2 gas to clean the electrode surface.

Assembly. The assembly was started with polyAAc. Although the polyAAc at the first step was physically adsorbed without any chemical reaction onto the QCM electrode, that did not affect the stepwise assembly. The cleaned QCM was immersed in an aqueous polyAAc solution (0.05 unitM) containing EDC (5 mol % to the total units of polyAAc), in which the carboxyl group had been already activated for 5 min before the immersion. The QCM was immersed for 15 min, rinsed thoroughly with pure water, and then dried under N_2 gas. The frequency decrease was then measured. The QCM was immersed again into an aqueous poly(VAm-*co*-NVIBA) solution (0.05 unitM), and the same procedure was repeated. This sequential cycle was repeated for the appropriate number of steps in the assembly. The assembly was performed at 4 °C in order to maintain the activity of EDC.

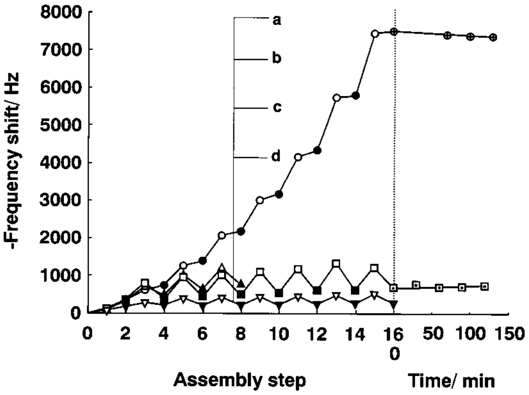


Figure 1. QCM analysis of the stepwise assembly of poly(VAm-*co*-NVIBA) with VAm contents of (a) 39, (b) 25, and (c) 10 mol %, plus polyAAc in the presence of EDC, and (d) the assembly of poly(VAm-*co*-NVIBA) with a 39 mol % VAm content plus polyAAc in the absence of EDC. The open and closed symbols show the polyAAc and poly(VAm-*co*-NVIBA) steps, respectively. The right side of the figure shows the stability of the assembly in water.

Characterization. RAS were obtained with a Jasco Herschel FT/IR-610 (Japan) under a nitrogen atmosphere at ambient temperature. One side of a poly(ethylene terephthalate) film was coated with gold in order to obtain a reflective surface. The polymers were then assembled for 16 steps similarly to the QCM analysis. The interferograms were coadded 50 times and Fourier transformed at a resolution of 8 cm^{-1}. The static contact angle of the assembly was measured with a Kyowa Interface Science CA-X (Japan) using an air bubble in an aqueous phase. The AFM images were obtained with a Digital Instruments NanoScope III that was operated in tapping mode in both air and aqueous phases at ambient temperature. We did not perform any image processing other than flat leveling. The roughness (R_a) in a given observed area was estimated from the following equation:

$$R_a = \frac{1}{L_x L_y}\int_0^{L_y}\int_0^{L_x} |F(x,y)|\, dx\, dy$$

where $F(x,y)$ is the surface relative to the center plane that is a flat plane parallel to the mean plane, and L_x and L_y are the dimensions of the surface.

Results and Discussion

Preparation of Ultrathin Hydrogel. Ultrathin hydrogels were prepared from poly(VAm-*co*-NVIBA) at different VAm contents plus polyAAc, on the QCM surface, by sequential chemical reactions between the amino and activated carboxyl groups. A total of 5 mol % of water-soluble carbodiimide EDC to the total amount of carboxyl groups was added to the aqueous polyAAc solution for activation in order to suppress unnecessary cross-linking, thus resulting in ultrathin hydrogels with a suitable amount of cross-linking. In fact, 5 mol % was the maximum solubility in the polyAAc solution due to precipitation. Poly(VAm-*co*-NVIBA) at a maximum VAm content of 39 mol % was used, since the polymer has shown thermoresponsive properties around that content.[8o]

Figure 1 shows the dependence of the frequency shift against the assembly step when the QCM was alter-

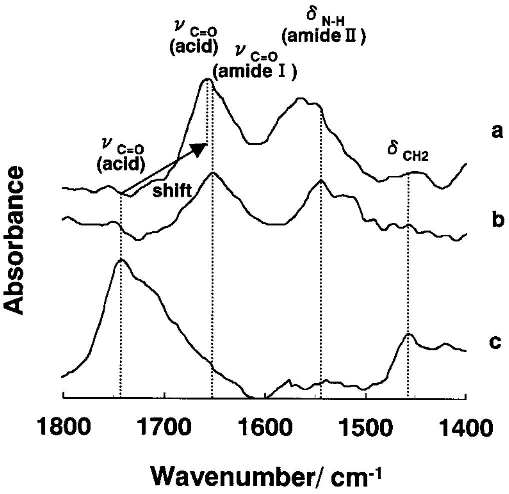


Figure 2. RAS data from a 16-step assembly (a) and from cast films of poly(VAm-*co*-NVIBA) with a 39 mol % VAm content (b) and polyAAc (c).

nately immersed into aqueous poly(VAm-*co*-NVIBA) at VAm contents of 10, 25, and 39 mol % and polyAAc solutions, in the presence or absence of EDC. The stepwise assembly was not observed for poly(VAm-*co*-NVIBA) at VAm contents of 10 and 25 mol %, resulting in a zigzag shape for the frequency shift. On the other hand, the assembly was achieved with poly(VAm-*co*-NVIBA) at a 39 mol % VAm content, and the amount assembled was drastically increased. The amino group seemed to react effectively with the activated carboxyl group upon increasing the VAm content of poly(VAm-*co*-NVIBA). The stepwise assembly was not observed, and the amount assembled was much less in the absence of EDC, indicating that the sequential chemical reaction proceeded in the presence of EDC. In addition, the assembly obtained was quite stable in an aqueous phase, also supporting the formation of chemical bonds. From the QCM analysis, we found that poly(VAm-*co*-NVIBA) with a 39 mol % VAm content and polyAAc could be sequentially assembled by chemical reactions between the amino and carboxyl groups, respectively. The subsequent detailed analyses were performed using this assembly system.

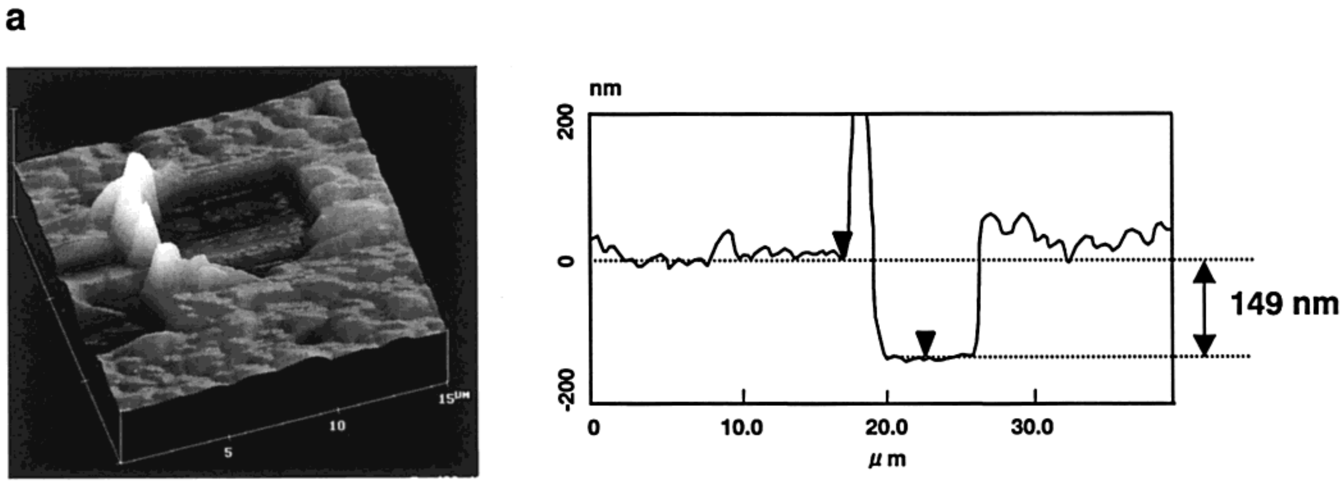
Figure 2 shows the RAS data for the assembly as well as for cast films of poly(VAm-*co*-NVIBA) with a 39 mol % VAm content and polyAAc. The amide II band (δ_{N-H}) was clearly observed at around 1545 cm^{-1} for the assembly, indicating the presence of poly(VAm-*co*-NVIBA) in the assembly. The carbonyl vibration band ($\upsilon_{C=O}$) for the carboxyl group in polyAAc seemed to shift from 1740 cm^{-1} (cast film) to around 1660 cm^{-1} (assembly) and overlapped to the amide I band ($\upsilon_{C=O}$) at 1650 cm^{-1}. This shift is possibly due to the presence of carboxylate anions of polyAAc that formed ionic complexes with protonated amino groups of poly(VAm-*co*-NVIBA). From these observations, we concluded that the assembly included both polymer components. On the other hand, an increase in the amide peak as compared to the peak of the carboxyl group should be observed for the assembly due to amide bond formation caused by the sequential chemical reaction. However, since this increase should be quite small compared to the amide group already present in poly(VAm-*co*-NVIBA), we could not detect a new amide formation corresponding to the cross-linking for the ultrathin hydrogel. Compared to conventional hydrogels, characterization of the amount of cross-linking is quite difficult. Researchers generally only discuss the amount of cross-linking for the hydrogel preparation. We did not investigate the actual degree of cross-linking in the assembly, although this might correspond to the amount of EDC. However, the stepwise assembly in the presence of EDC and the stability of the assembly in an aqueous phase on the QCM experiments strongly suggest the formation of ultrathin hydrogels on the surfaces.

AFM Analysis. To characterize the formation of ultrathin hydrogels on the QCM, we analyzed the 16-step assembly of poly(VAm-*co*-NVIBA) with a 39 mol % VAm content and polyAAc by AFM in tapping mode. Figure 3 shows the AFM images generated by scratching the assembly and the cross-sectional views in air and water at ambient temperature. The thickness of the assembly in air was estimated to be around 150 nm. On the basis of the QCM result, the mean density of the assembly was estimated to be 0.74 g cm^{-3}, which is lower than that of polyion complex films (1.2 g cm^{-3}).[10] This is reasonable since both polymers in the assembly were bound only by a small amount of cross-linking, although there might be weak electrostatic interactions between the amino and carboxyl groups remaining in the present polymers (see pH effect). On the other hand, the thickness in water was estimated to be around 320 nm, which is more than twice that in air. This strongly suggests swelling of the assembly in water, indicating the formation of an ultrathin hydrogel. To characterize its thickness in water, other methods will have to be used. When the assembly was immersed in water after scratching in air, the furrows caused by the scratching disappeared. This is due to the entropy-driven movement of the hydrogel assembly in water, as shown in a previous study.[11] Note that in the present study the scratching of the assembly after immersion in water was performed for the cross-sectional data.

Figure 4 shows the time dependence of the surface topology when the assembly was immersed in an aqueous phase from air at ambient temperature. Interestingly, the topology changed with time. The surface became rougher for up to 10 min and subsequently became smooth. We believe that this represents the dynamic process of water swelling the ultrathin hydrogel. We could not see any changes after 30 min, suggesting that equilibrium has been attained.

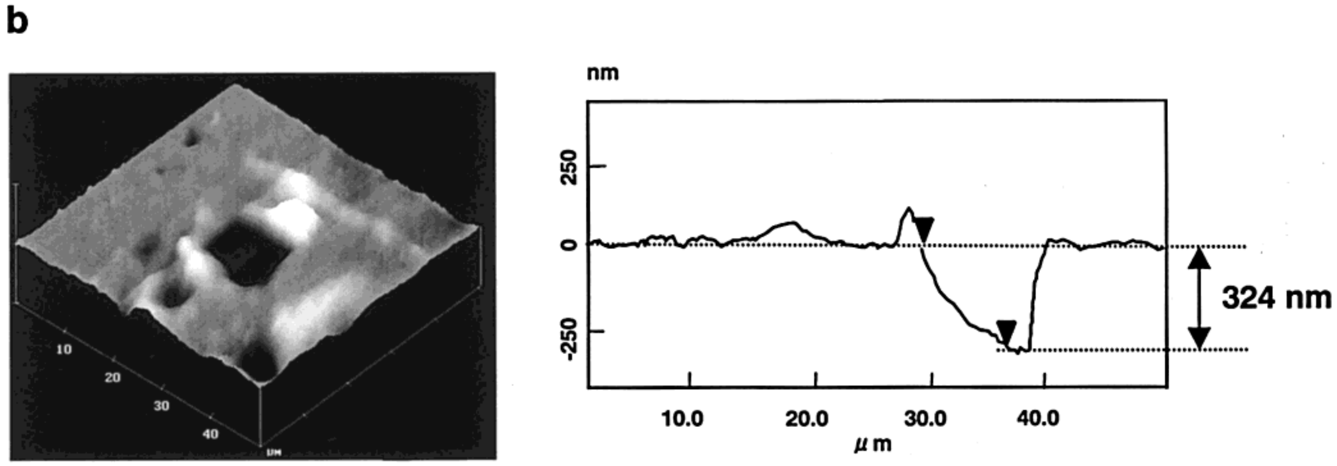
Thermoresponsive Properties of Ultrathin Hydrogels. The ultrathin hydrogels prepared should show thermoresponsiveness derived from its poly(VAm-*co*-NVIBA) component with a 39 mol % VAm content, which has a LCST around 65 °C under alkaline conditions.[8o] The static contact angle measurement using an air bubble was utilized to analyze these properties. We were not sure whether this measurement was the best method to quantify the thermoresponsiveness in the present case. Differential scanning calorimetry or volume phase transition analysis would normally be applied. However, it seemed difficult to apply these methods to “ultrathin” hydrogels. Since a polymer should be more hydrophobic above its LCST, we used the surface property as a measure of the bulk property of the hydrogel.

Figure 5 shows the temperature dependence of the static contact angle of the air bubble for a 16-step assembly of poly(VAm-*co*-NVIBA) with a 39 mol % VAm content and polyAAc. The assembly became hydrophobic at around 30−40 °C, indicating that the assembly has



Scratching in air

Cross section in air



Scratching in water

Cross section in water

Figure 3. AFM images of the 16-step assembly in air (a) and water (b).

a phase transition derived from the thermoresponsive polymer. This profile was reversible and was quite similar to that for the volume phase transition of conventional hydrogels analyzed by weighing the hydrogels or by estimating the diameter of the hydrogels.[8g,o] This also supports the formation of a hydrogel structure for the assembly. On the other hand, the LCST of the poly(VAm-*co*-NVIBA) used was 65 °C under alkaline conditions,[8o] which is much higher than the transition temperature of the assembly. It is well-known that the introduction of hydrophobic components into thermoresponsive polymers leads to a lower LCST. In the present system, since the polymer is present in the ultrathin hydrogel, its LCST might be changed by the electrostatic interactions of poly(VAm-*co*-NVIBA) with polyAAc (see IR and next sections). As a consequence, we found that the assembly showed thermoresponsive properties.

pH Effect on Thermoresponsive Properties. Considering the amount of EDC added, the amino group in poly(VAm-*co*-NVIBA) and the carboxyl group in polyAAc should have remained intact in the assembly. Accordingly, it is important to analyze the effects of pH on the thermoresponsive properties of the assembly. To represent acidic and alkaline conditions, aqueous 0.01 N HCl and 0.01 N NaOH solutions were used, since these were below the pK_a (4.3) of the carboxyl group of polyAAc[12] and above the pK_a (10.0) of the amino group of polyVAm,[13] respectively. The thermoresponsive properties were also analyzed by the static contact angle measurement using an air bubble, as shown in the previous section. The angle was analyzed at 20 and 60 °C, since thermoresponsiveness was clearly demonstrated in Figure 5.

Table 1 shows the angle for a 16-step assembly at the two temperatures. In an aqueous phase, the angle decreased by 8° upon increasing the temperature, suggesting a thermoresponsive property, as shown in the previous section. However, under acidic and alkaline conditions, the thermoresponsiveness was not observed during the temperature change. It is difficult to reasonably explain these results, and a possible mechanism is discussed as follows.

In an aqueous phase (pH $\approx$ 5.8), the amine and carboxyl groups might form an ionic complex in the assembly, as already discussed in Figure 2, resulting in the hydrophobic atmosphere in the assembly. This will facilitate the thermoresponsible properties of polyN-VIBA units in the assembly. Note that the hydrophilic unit in the poly(VAm-*co*-NVIBA) should increase its LCST.[8f,n,o] On the other hand, under the acidic and alkaline conditions, one component still has a charge in the assembly due to the lack of electrostatic interaction, resulting in a more hydrophilic atmosphere in the

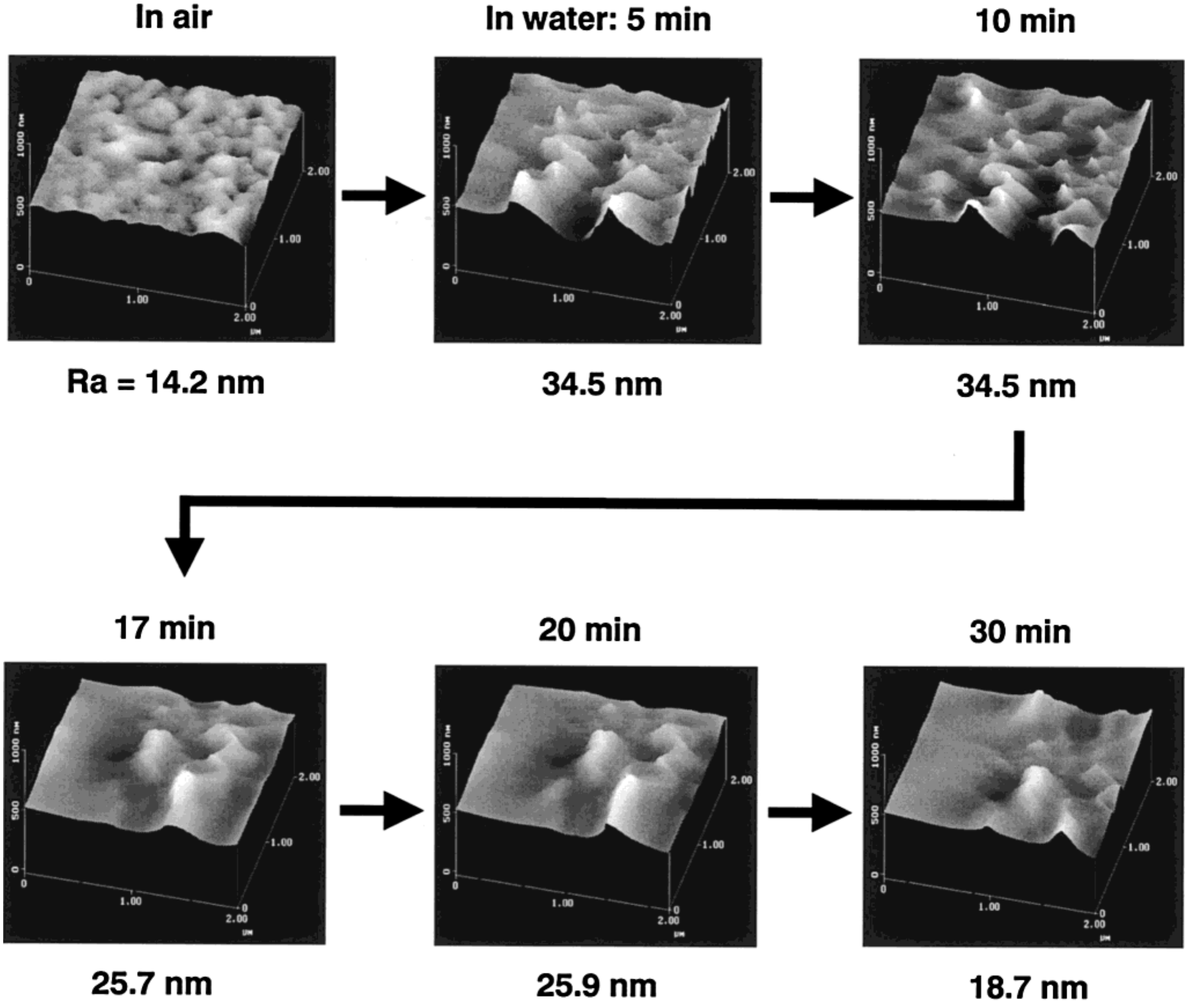


Figure 4. Time dependence of the AFM images of the 16-step assembly when immersed in water.

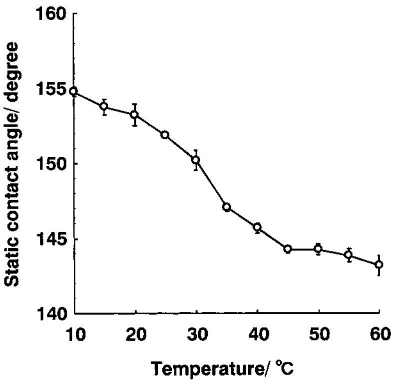


Figure 5. Temperature dependence of the static contact angle of the 16-step assembly in water.

Table 1. Static Contact Angles (deg) of the 16-Step Assembly at Different pH

solvent	at 20 °C	at 60 °C
water	155.4 ± 0.1	147.8 ± 1.3
0.01 N HCl	154.8 ± 0.4	155.4 ± 0.6
0.01 N NaOH	150.2 ± 1.2	150.2 ± 0.2

assembly. This leads to an increase in the apparent LCST of the assembly. In other words, under the acidic and alkaline conditions, there is a possibility that the assembly shows the thermoresponsiveness above the 60 °C used in this study. Further analysis of this pH dependence, as well as control of the thermoresponsiveness, is now in progress.

In the present study, the thermoresponsive properties were analyzed only by the static contact angle measurement. There is a possibility that the change in the angle may be due to the phase transition of the surface component poly(VAm-*co*-NVIBA) for the 16-step assembly. Considering the angles at 20 °C in Table 1, they seem to be strongly affected by the surface components; under the alkaline conditions, the surface became hydrophobic due to the deprotonation of the amino group. However, we could not observe any thermoresponsiveness under acidic and alkaline conditions. In addition, when the assembly was stopped at a 15-step as a polyAAc surface, the angles at 20 and 60 °C were 151.6 ± 0.1° and 146.0 ± 1.8°, thus showing thermoresponsiveness. These results indicate that the change in the angle was not related to the surface component of the assembly, although polyAAc also affected the angle at 20 °C. Furthermore, when the 16-step assembly was reacted with acetic acid anhydride in order to block the amino group, the surface became more hydrophobic (angle at 20 °C: 151.5 ± 0.5°), but the assembly was still thermoresponsive (angle at 60 °C: 140.5 ± 0.5°).

On the basis of these observations, we concluded that the change in the static contact angle for the ultrathin hydrogel was due to the phase transition in its bulk phase.

Conclusion

An ultrathin hydrogel was successfully prepared by the sequential chemical reaction of amine-containing, thermoresponsive poly(VAm-*co*-NVIBA) and polyAAc. Quantitative QCM analysis showed a stepwise deposition of the polymers by immersing it into aqueous poly(VAm-*co*-NVIBA) and activated polyAAc solutions. There was an adequate VAm content in the poly(VAm-*co*-NVIBA) for the assembly. The assembly was quite stable in an aqueous phase. The presence of both polymers in the assembly was confirmed by RAS measurements. AFM images revealed the ultrathin hydrogel structure of the assembly. The static contact angle of the assembly decreased with increasing temperature, indicating its thermoresponsive properties. The present system can be applied to a wide variety of stimuli-responsive polymers with various functional groups for the assembly. A detailed analysis of the pH effect and the control of the phase transition temperature, as well as other combinations of polymers, are now in progress.

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