Hydrogen-Bonding-Directed Layer-by-Layer Multilayer Assembly: Reconformation Yielding Microporous Films

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ABSTRACT: The influence of a basic aqueous solution on a hydrogen-bonding-directed layer-by-layer (LbL) self-assembled film, based on poly(acrylic acid) (PAA) and poly(4-vinylpyridine) (PVP), was investigated. The composition change of a multilayer film in a NaOH solution was monitored by X-ray photoelectron spectroscopy, Fourier transform infrared spectroscopy, and UV−vis spectroscopy. The morphology variation was observed by atomic force microscopy. A two-step variation was observed: the first step is the dissolution of PAA from the film into the basic solution; the second is the gradual reconformation of PVP polymer chains remaining on the substrate, which produces a microporous film. The evidence for the reconformation of the polymer chains was further provided by single molecule force spectroscopy. Both the release of PAA and the formation of the microporous film are attributed to the properties of the LbL film based on hydrogen bonding. This interesting and novel way to fabricate microporous films is envisaged to have potential applications in areas ranging from pharmaceutics to materials science.

Introduction

Since its first report by Decher et al., the layer-by-layer (LbL) self-assembly technique has attracted increasingly more attention as an effective method to fabricate ultrathin films in both theoretical and experimental fields.[1−3] The popularity of this method is due to its simplicity, versatility, and systematical control over the structure and the thickness of the resulting film.[4] In addition to charged synthetic polymers, a variety of materials, such as dyes, nanoparticles, clay particles, proteins, and DNA, are suitable for the LbL assembly.[1] The LbL method is not only applied to modify the surface of materials but also used to fabricate capsules.[5,6] The latter has received much attention in recent years. The potential applications of the LbL multilayer film have been explored in very diverse areas, such as (bio)sensors, light-emitting diodes, optical storage devices, separation membranes, and so on.[4]

Although the LbL film was commonly constructed based on electrostatic attraction between two neighboring polymers, other weak interactions, such as hydrogen bonding, were also employed as the driving force for the LbL assembly.[3,7] For example, in 1997, almost at the same time, Rubner et al. and Zhang et al. reported a new concept of assembling a LbL film using hydrogen bonding.[8,9] Recently, depending on the ionization of carboxylic acid groups in the hydrogen-bonding-directed LbL film, Granick et al. prepared layered, erasable multilayers.[10,11] Furthermore, combined with light-initiated chemical reaction or the dip-pen technique, this kind of erasable multilayer was developed by Rubner et al. to fabricate a patterned surface.[12] In addition, on the basis of the hydrogen-bonded erasable system, Schlenoff's group has successfully produced multiple strata of membranes.[13]

In this article, we investigated the structure variation of the hydrogen-bonding-directed poly(acrylic acid) (PAA)/poly(4-vinylpyridine) (PVP) LbL film in a basic aqueous solution. At the beginning of the immersion, PAA from the multilayer film dissolves in the basic solution because of the destruction of hydrogen bonding. However, the release of PAA does not destroy the whole film; the other component of the film, PVP, remains on the substrate due to its poor solubility in the basic aqueous solution. Prolonged immersion of the PVP film in the basic aqueous solution yields a microporous film. As we suggest, this is a consequence of the reconformation of the PVP chains induced by the basic solution. Both the release of PAA and the formation of the microporous film result from the nature of the hydrogen-bonding-directed LbL film in contact with basic aqueous solution. Potential applications of this phenomenon in pharmaceutics and materials science are greatly anticipated.

Experimental Section

Materials. Poly(acrylic acid) (PAA) ($M_w = 2.3 \times 10^4$) and poly(4-vinylpyridine) (PVP) ($M_w = 1.8 \times 10^5$) were synthesized as previously described.[14] Their molecular weights were determined by the viscosity method. PAA: $[\eta] = 11.5$ (in 1,4-dioxane at 30 °C), $\alpha = 0.50$, and $K = 0.076$. PVP: $[\eta] = 92.4$ (in ethanol 25 °C), $\alpha = 0.68$, and $K = 0.025$.

Methods. The X-ray photoelectron spectroscopy (XPS) spectra were acquired on an ESCALAB Mark II (VG company, UK) photoelectron spectrometer using a monochromatic Mg Kα X-ray source. Fourier transform infrared (FT-IR) spectra were recorded on a Bruker IFS 66V instrument. X-ray diffraction (XRD) was carried out on a Rigaku X-ray diffractometer (D/max 2500V PC, using Cu Kα radiation of a wavelength of 1.542 Å). UV−vis spectra were carried out on a Shimadzu 3100 UV−vis−near-IR recording spectrometer. Atomic force microscopy (AFM) images were taken with a multimode Nanoscope IIIA (Digital Instrument, Santa Barbara, CA) under ambient conditions. AFM was operated in the tapping mode with an optical readout using Si cantilevers.

Preparation of the Samples. The LbL films were assembled on substrates of quartz or CaF_2 plates. The quartz

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substrate was used for UV−vis, X-ray, XPS, and AFM measurements and the CaF_2 substrate for FT-IR. The quartz slides and CaF_2 plates need to be modified before LbL deposition. In the case of quartz, the surface was modified with (4-aminobutyl)dimethylmethoxysilane, yielding a NH_2-tailored surface,[15] and the CaF_2 surface was modified with a monolayer of poly(ethylenimine) (PEI). As mentioned in detail previously,[14] the LbL film was fabricated by alternating immersion of the NH_2 modified substrate in PVP (1 mg/mL) and PAA (1 mg/mL) solutions in methanol for 10 min each with rinsing in methanol three times (1 min each) after each step. To investigate the influence of basic aqueous solution on the hydrogen-bonding multilayer film, the resulting LbL film was immersed into NaOH aqueous solution. After rinsing in water and drying by N_2 gas, the samples were stored under ambient conditions prior to measurement. For comparison, two types of spin-coated films were fabricated on the NH_2-modified quartz slide. One is prepared by directly spin-coating (1000 rpm) the mixture of PVP (1 mg/mL) and PAA (1 mg/mL) solution in methanol (PVP/PAA(mol/mol) = 1/1), and the other is prepared by alternate spin-coating (1000 rpm) of PVP (1 mg/mL) and PAA (1 mg/mL) solutions in methanol.

Single Molecule Force Spectroscopy (SMFS) Measurements. The sample for SMFS was prepared by immersing a NH_2-modified substrate into 1×10^{-3} mg/mL PVP methanol solution for 10 min. To remove the nonadsorbed polymers, the slide was rinsed with pure methanol three times.

All of the single molecule force measurements were carried on a home-built AFM. Silicon nitride cantilevers from Digital Instruments (DI, Santa Barbara, CA) and Park Scientific Instruments (PARK, Sunnyvale, CA) were used as received from the manufacturer. The cantilevers with the spring constants of 0.03−0.15 N/m were used. The spring constants were determined from their thermal excitation.[16,17] The experimental details of SMFS have been described elsewhere.[18] Briefly, a drop of liquid, acting as a buffer, was deposited onto the substrate, and then the cantilever was lower into the buffer solution. In this study, for comparison of the conformation of PVP chains in methanol and basic aqueous solution, two kinds of liquid were employed as the buffer: (1) pure methanol, (2) NaOH aqueous solution (pH = 12.5). In the case of the basic aqueous solution, the sample was immersed in the buffer for more than 100 min before measurement to achieve the conformation equilibrium of the PVP chains. By the movement of the piezotube, the sample was brought into contact with an AFM tip, and some molecules adsorbed onto the tip due to nonspecific interactions between the polymer and the tip, thus producing a bridge. When the distance between the tip and the sample was increased, the polymer chain stretched and the cantilever deflected. At the same time, the deflection−extension curve was recorded and converted into a force−extension curve (in brief, force curve). As a test of the reliability of the experimental setup, we measured the characteristic transition of heparin according to the work of Li et al.[19] The resulting transition force was approximately 690 pN, which agrees with the reference.

Results and Discussion

Fabrication of the PAA/PVP LbL Film. As described previously,[14] the LbL film of PAA and PVP can be fabricated in methanol solutions based on hydrogen bonding between carboxylic acid and pyridine groups. The thickness of the film can be adjusted by changing the concentrations and the molecular weights of the polymers. Herein the concentrations of both polymers were 1 mg/mL, and the molecular weights (M_w) were 2.3×10^4 and 1.8×10^5 for PAA and PVP, respectively. The assembly process was followed by UV−vis spectroscopy and X-ray diffraction. As shown in Figure 1, both the UV−vis absorbance at 256 nm and the thickness of the film increase linearly with the number of layer pairs, which indicates that the LbL assembly process under the present conditions is uniform. Moreover, X-ray diffraction measurements can also be used to explore the film roughness. As shown in Figure 2A, well-resolved Kiessig fringes, in the X-ray diffraction pattern, suggest that the film surface is smooth with a constant thickness. Meanwhile, the homogeneous coverage and low roughness of the surface were observed with AFM (Figure 2B). This further indicates that the PAA/PVP LbL film formed was of high quality.

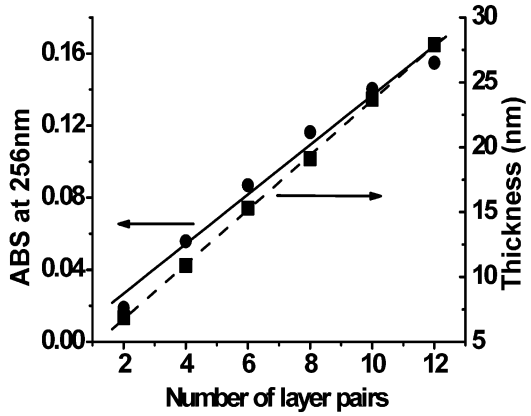


Figure 1. Growth of the UV−vis absorbance at 256 nm (donated by circle, fitted by solid line) and the thickness calculated from X-ray patterns (donated by square, fitted by dash line) of PAA/PVP LbL films as a function of the number of layer pairs.

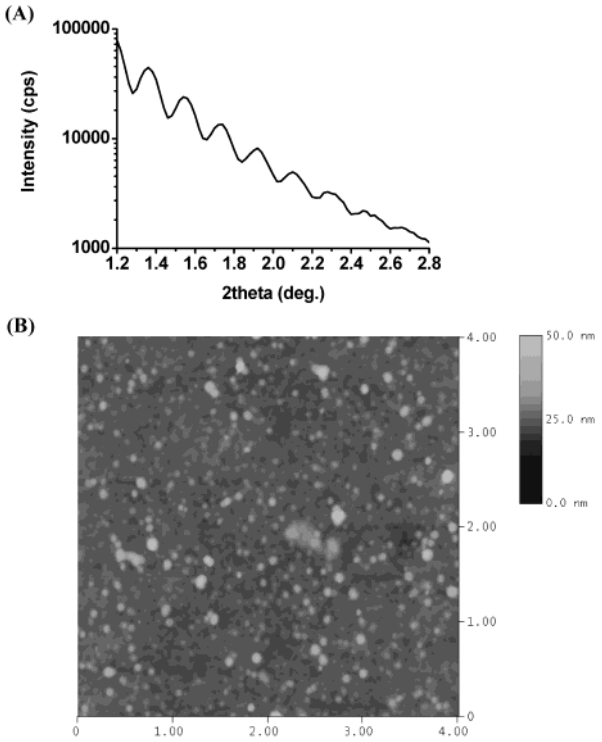


Figure 2. (A) X-ray diffraction pattern of 24-layer PAA/PVP LbL film. (B) AFM height image (4 μm × 4 μm) of 25-layer PAA/PVP LbL film.

The interaction between the neighboring polymers in the film was identified as hydrogen bonding by FT-IR. Figure 3 shows the second-derivative plots of FT-IR spectra of PAA, PVP, and a 25-layer LbL film in the region from 1525 to 1810 cm^{-1}, where there are two bands characteristic of the hydrogen bonding. The bands of PAA appearing at 1705 and 1741 cm^{-1} are assigned to the stretching modes of carbonyl groups of carboxylic acids in the cyclic dimer and free state, respectively.[20]

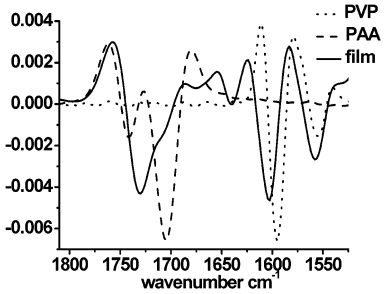


Figure 3. Second-derivative plots of the FT-IR spectra of PAA (denoted by dash line), PVP (denoted by dot line), and 25-layer PAA/PVP LbL film (denoted by solid line) in the region from 1525 to 1810 cm^{-1}.

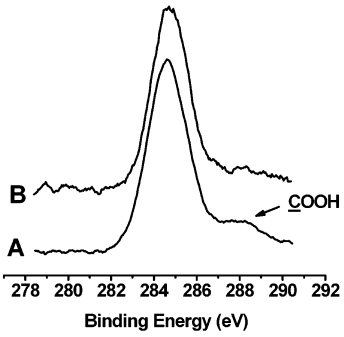


Figure 4. C 1s XPS spectra of 13-layer PAA/PVP LbL films before (A) and after (B) immersion in pH = 12.5 NaOH aqueous solution at 25 °C for 1 min.

The band of PVP at 1595 cm^{-1} is assigned to the ring vibration of pyridine groups. In the case of the LbL film, the stretching bands of carbonyl groups appearing at 1730 and 1708 cm^{-1} are assigned to the carboxylic acid groups associated with pyridine nitrogen atom and in the cyclic dimer state, respectively. Moreover, optical densities suggest that the carboxylic acid groups associated with pyridine groups are dominant. Meanwhile, it is noticed that the band of pyridine groups is shifted from 1595 to 1603 cm^{-1}, which is another piece of evidence for the hydrogen-bonding formation between carboxylic acid and pyridine groups.[21] Therefore, hydrogen bonding is identified as the driving force of the PAA/PVP LbL film growth. In our previous article,[14] the vibration of the carbonyl groups in the LbL film appearing at 1718 cm^{-1} was simply assigned to the acid groups associated with pyridine. According to the above discussion, this band is a combination of the bands at 1725 and 1708 cm^{-1}.

Release of PAA from the PAA/PVP LbL Film. To study the influence of a basic aqueous solution on the PAA/PVP LbL film, XPS was used to detect the composition variation of the LbL film in a NaOH solution. First, the XPS survey spectra of 5-, 9-, and 13-layer LbL films on a quartz slide were acquired to find out the penetration depth of XPS into the film. In the spectra, there are two C 1s photopeaks at approximately 280 and 284 eV as shown in Figure 4A, which are assigned to the carbon of carboxylic acid in PAA and the remaining carbons of the two polymers, respectively.[22] The N 1s photopeak attributed to the pyridine nitrogen of PVP appears at 390 eV. The C 1s and N 1s photopeaks of all these films are similar, whereas the Si 2p photopeak at 103 eV (Si−O) ascribed to the quartz slide appears only in the spectrum of the five-layer film. Therefore, from the film thickness the penetration depth of XPS into the film is estimated as approximately 10 nm. Next, the

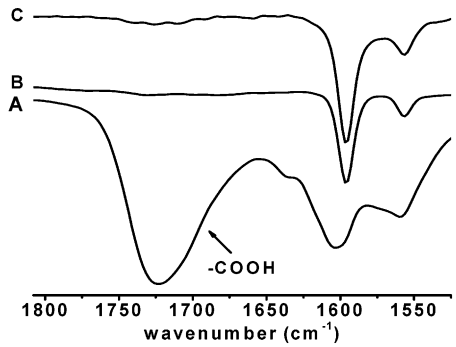


Figure 5. FT-IR spectra in the region from 1525 to 1810 $cm^{-1}$of 25-layer PAA/PVP LbL films before (A) and after immersion in pH = 13 (B) and pH = 12.5 (C) NaOH aqueous solution for 1 min at 25 °C.

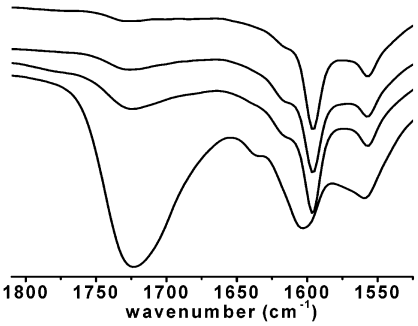


Figure 6. FT-IR spectra in the region from 1525 to 1810 $cm^{-1}$of 25-layer PAA/PVP LbL films after immersion in pH = 11 NaOH aqueous solution at 25 °C for 0, 1, 5, and 15 min (from bottom to top).

XPS spectra of 13-layer LbL films before and after immersion in a pH = 12.5 NaOH aqueous solution for 1 min were compared. The distinct photopeak at 288.5 eV corresponding to the carbon of carboxylic acid in PAA disappears in the spectrum of the film after immersion as shown in Figure 4. This change suggests that PAA was removed from the LbL film by the basic aqueous solution, at least in the upper five layers. In N 1s spectra, no obvious difference between the films before and after immersion is observed, which implies that the PVP still remains on the surface. From the above discussion, we suggest that when the PAA/PVP LbL film is immersed into a basic aqueous solution, one of the film components, PAA, dissolves away and the other component, PVP, remains on the substrate.

As the penetration depth of XPS is limited, the variation of the LbL film in the basic aqueous solution was further monitored by FT-IR. As shown in Figure 5, the spectra of the films after immersion in the basic aqueous solution are significantly different from that of the original LbL film. The characteristic band around 1718 cm^{-1} attributed to carbonyl groups of PAA vanishes, which confirms the result of XPS that PAA can be removed from the LbL film by the basic aqueous solution. Concomitantly, the band at 1603 cm^{-1} shifts to 1595 cm^{-1} and becomes narrower, which could be explained by the "liberation" of pyridine groups from the association with carboxylic acids.[21] According to the disappearance of the characteristic band of carbonyl groups, we can estimate that nearly all of PAA is removed after immersion in pH = 12.5 or pH = 13 NaOH solution for only 1 min. Moreover, even if the immersion time in pH = 13 solution is reduced to 5 s, the band of the carbonyl groups is still too weak to be seen. Thus, the release rate of PAA is very fast in the

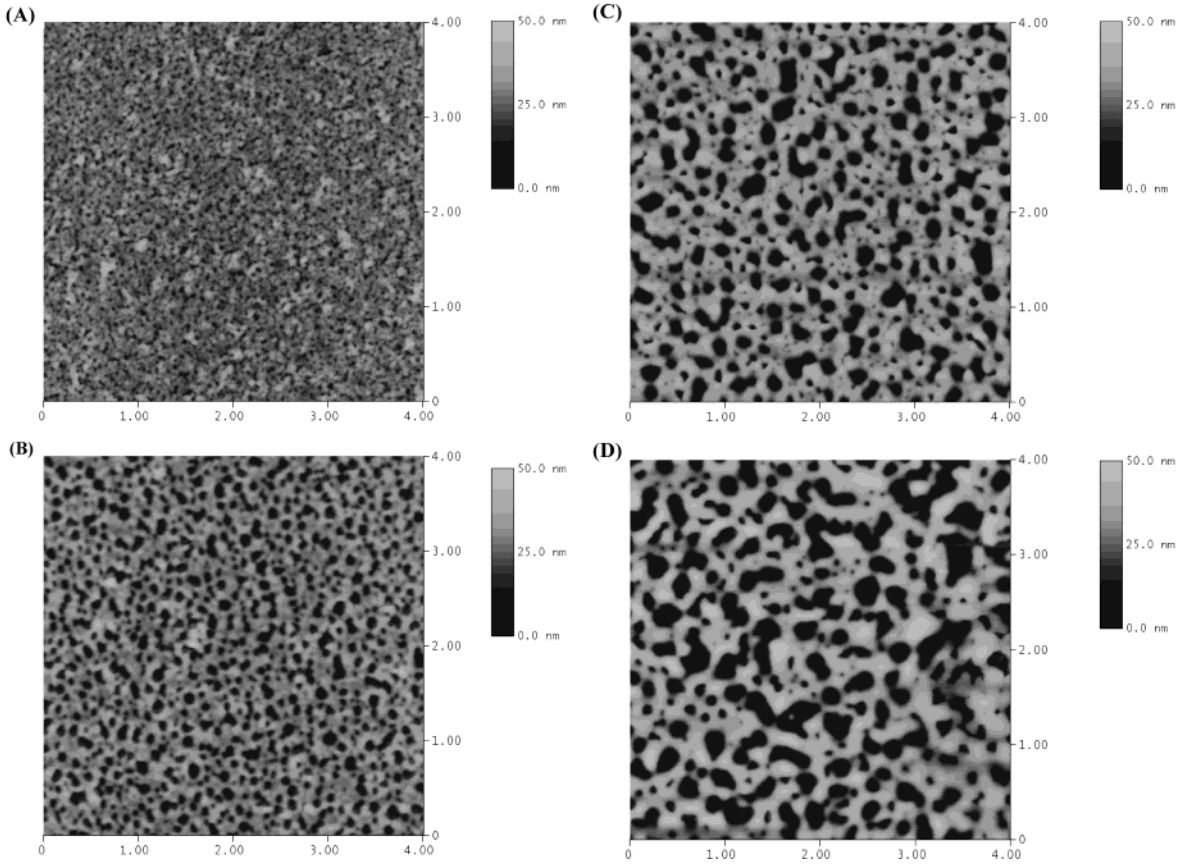


Figure 7. AFM height images (4 μm × 4 μm) of 25-layer PAA/PVP LbL films after immersion in pH = 13 NaOH aqueous solution at 25 °C for 10 (A), 40 (B), 100 (C), and 180 min (D).

solution with high pH value. Figure 6 shows the FT-IR spectra of the films after immersion in a pH = 11 solution for different periods of time. The shift from 1718 to 1725 cm^{-1} is due to the decrease of the amount of carboxylic acid groups in the dimer state. After 1 min immersion, the intensity of the carbonyl group band drops greatly. Afterward, it decreases gradually. The release of PAA slows down with decreasing pH of the solution. Unlike pH, temperature has little effect on the release process of PAA. At 18 °C, still almost all of PAA is removed after 1 min immersion in pH = 13 solution. (This observation is useful in the forthcoming discussion.) In addition, the UV−vis spectra of the films before and after immersion in a pH = 13 NaOH solution for 1 min were compared. Except for the decrease in the intensity induced by the dissolution of PAA, the position of the absorption band at 256 nm assigned to PVP is unchanged. Moreover, the absorbance at 256 nm of the film after the immersion is approximately equal to the accumulated PVP absorbance in the LbL film. The two measurements combined with the XPS analysis reveal that when the LbL film is immersed into a basic aqueous solution, PAA leaves away from the film, yet PVP remains on the substrate.

This interesting and unique phenomenon, in which one component of a multilayer film is removed and the other remains, could be attributed to the destruction of hydrogen bonds. Immersing a multilayer film into the basic aqueous solution, the carboxylic acid groups of PAA are ionized by the solution, which leads to the destruction of hydrogen bonding between the two polymers. After the hydrogen bonds are destroyed, PAA leaves the film because of its solubility in the basic solution, while PVP remains due to its poor solubility in the basic solution. This hypothesis is further supported by the fact that PAA in the LbL film cannot be removed by a acid solution(pH = 1.8), since the carboxylic acid groups cannot be ionized in the environment.

Reconformation of the Remaining PVP Film. The variation of the PAA/PVP LbL film in the basic aqueous solution was also explored using AFM. The AFM images of the 25-layer LbL films after immersion in pH = 13 NaOH aqueous solutions at 25 °C for different periods of time are shown in Figure 7. The images feature a series of microporous films with different surface coverage, depth, and shape of the holes. The spinodal holes, several hundred nanometers in diameter, grow with time. During immersion from 10 to 180 min, the coverage and depth of the holes increase from 10 to 30% and from approximately 12 to 35 nm, respectively. The above study indicates that a microporous film can be produced by prolonged immersion of the LbL film in a basic solution.

The pH value of the basic solution is an important factor in determining the surface morphology and its change with time. Figure 8 shows morphology variation of the 25-layer LbL film in pH = 12.5 solution, which is visibly different from that in pH = 13 solutions (Figure 7). For pH = 12.5, separate round holes, not the spinodal holes, form, and for the same immersion time, the surface hole coverage is significantly lower than that for pH = 13 solutions. For example, after 180 min immersion, the coverage is only 20%, about one-third lower than that in pH = 13 solutions. In addition to pH, temperature is of great importance to the morphology variation, although it has little effect on the release of

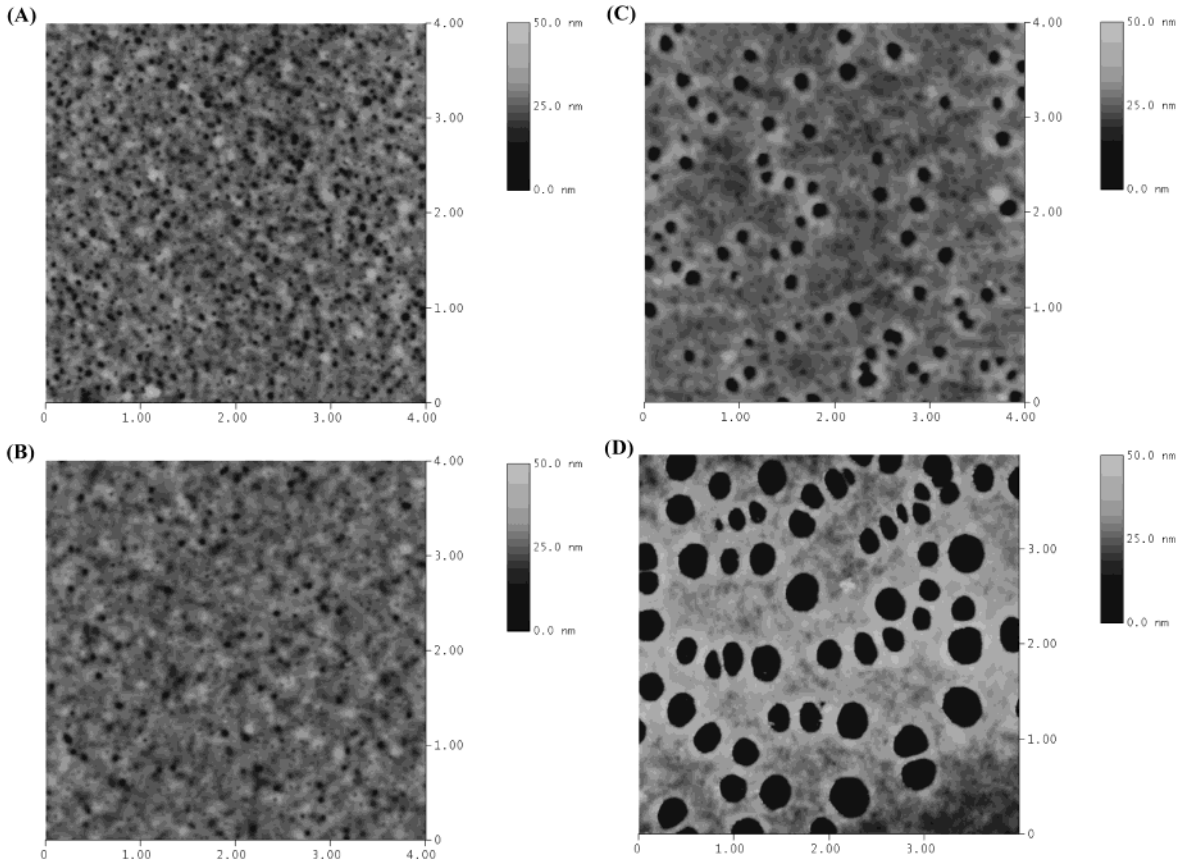


Figure 8. AFM height images (4 μm × 4 μm) of 25-layer PAA/PVP LbL films after immersion in pH = 12.5 NaOH aqueous solution at 25 °C for 10 (A), 40 (B), 140 (C), and 180 min (D).

PAA. Figure 9 shows the AFM images of the films after immersion in pH = 13 solutions at 30 °C for different periods of time. Compared with that at 25 °C, the variation at 30 °C is much faster. For example, after 180 min immersion, the coverage and depth of the holes reach 40% and 50 nm, respectively, much higher than 30% and 35 nm at 25 °C. When the immersion temperature is decreased to 18 °C, after 180 min immersion no visible morphology variation is found. The layer number of the PAA/PVP film is also an important factor. By comparing the microporous films fabricated through the LbL films with different layer numbers, we find that they do not differ in the surface hole coverage and shape, but in the depth. For example, after immersion of a 13-layer LbL film into a pH = 13 solution for 180 min, the depth of the holes is about 25 nm, which is 10 nm lower than that of the 25-layer film. It offers a possibility to adjust the depth of the holes without a major change to the surface morphology.

So far we have discussed a microporous film, produced by immersion of a PAA/PVP LbL film into a basic aqueous solution, as well as the influence of the immersion time, pH, temperature, and the layer number on the coverage, depth, and shape of the resulting holes in the film. This kind of porous film is very stable under the room conditions. After exposure to atmosphere for more than 2 months, the morphology of the microporous film showed little change. Then what caused the formation of the microporous film? Since the microporous film was formed after PAA was released from the LbL film, it is reasonable to assume that the holes are caused by PAA leaving the film. However, this assumption is inconsistent with the following experimental results. First, the morphology of the film varies gradually with time, yet PAA is released very rapidly. Second, although PAA can be removed by immersion in a pH = 13 solution at 18 °C, the microporous film observed elsewhere is not produced. Then, we prepared a PAA-removed LbL film by immersing a 25-layer PAA/PVP film in a pH = 13 solution for 1 min, followed by immersion in water or a 0.1 M NaCl solution instead of the basic solution. In contrast, the microporous film was not produced, which indicates that the basic solution plays a much more critical role in the formation of the microporous film than the release of PAA. At last, for comparison, we prepared two kinds of spin-coated films of PAA and PVP as described in the Experimental Section. The FT-IR measurements indicate that PAA in the two kinds of spin-coated films can also be removed by a basic solution. However, analogous microporous morphology cannot be found. All the experiments suggest that the release of PAA should not be directly responsible for the formation of the microporous film, whereas it should be some features of the LbL film absent in the spin-coated film. Therefore, we propose that the morphology variation is a result of the reconformation of PVP induced by the basic solution. In the process of PVP assembly onto the LbL film, the extended conformation is preferred to the folded conformation for the contact with PAA.[23] After PAA is removed by the basic solution, at the beginning the remaining PVP should retains the extended state. With increasing immersion time the extended PVP chains gradually fold due to their high surface tension in the basic solution. As a result, in the lateral direction the film coverage decreases and in the vertical direction the thickness increases, bringing out the above-mentioned morphology variation. Unlike in the basic aqueous solution, at

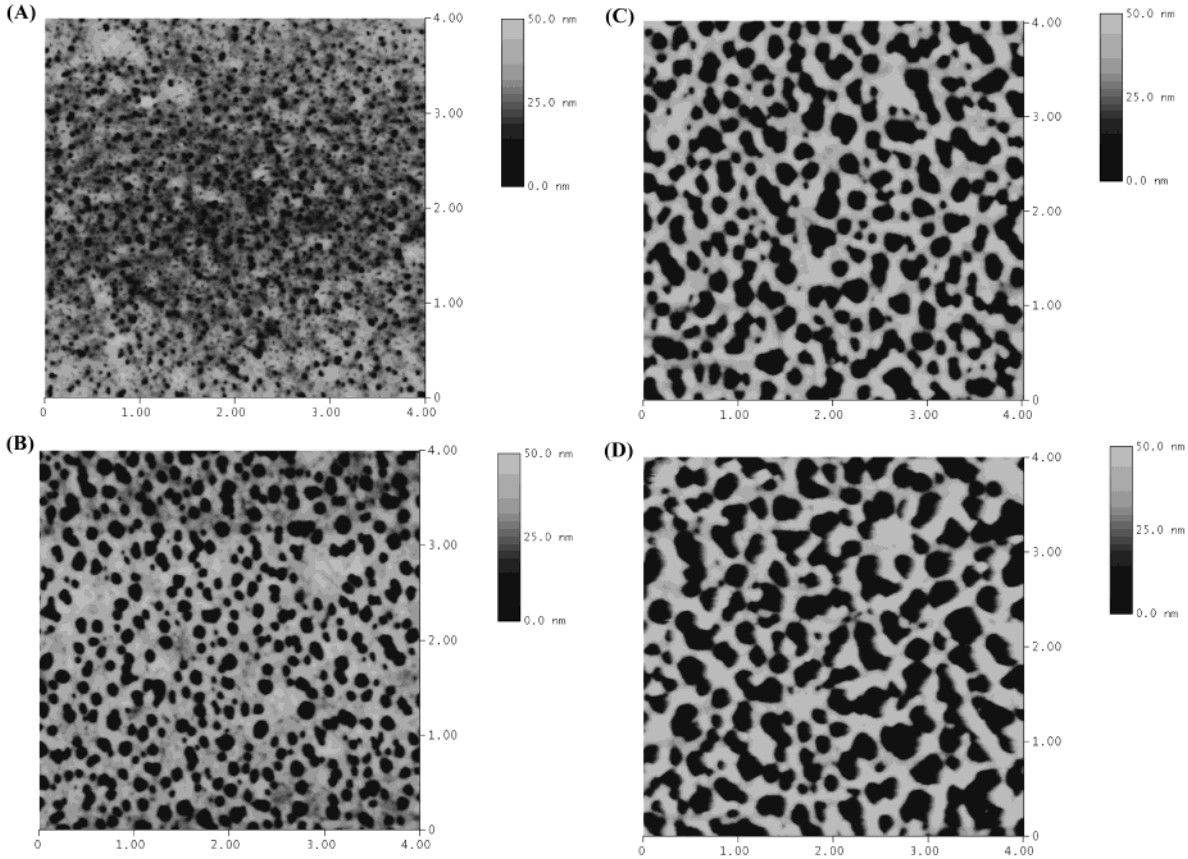


Figure 9. AFM height images (4 μm × 4 μm) of 25-layer PAA/PVP LbL films after immersion in pH = 13 NaOH aqueous solution at 30 °C for 10 (A), 40 (B), 100 (C), and 180 min (D).

neutral pH, the remaining PVP becomes partially charged due to the protonation of pyridine groups and slightly less hydrophobic. This would have consequences for the surface tension; therefore, the films after immersion in water and an aqueous solution of salt do not form microporous morphology.

The above hypothesis was further supported by single molecule force spectroscopy (SMFS). Since it was introduced by Gaub et al., SMFS has been an effective method to investigate the conformation change of polymer chains and intermolecular interactions.[24] As reported elsewhere,[23] when the desorption of PVP chains assembled on the NH_2-modified substrate in a methanol solution was measured by SMFS, the saw-tooth-like force profiles were obtained (see Figure 10). This is indicative of the detachment of polymer loops from the substrate. According to the present study, if PVP chains are folded in a basic solution as proposed, the number of PVP attached points per unit length in a basic solution would be less than that in methanol; i.e., the average length of loops in the basic solution is greater as shown in Figure 10. SMFS measurements of PVP were carried on separately in a methanol buffer and in a pH = 12.5 NaOH aqueous solution buffer. The samples were prepared analogously to the first layer assembly of the LbL method. It is worth to emphasize that, in the case of the NaOH aqueous solution, the sample was immersed in the basic solution for more than 100 min before measurement to equilibrate the PVP chains. The average length of the loops was estimated by dividing the curve length by the number of peaks. As shown in Figure 11, based on the statistical analysis of over 70 force curves in each case, the average lengths of loops in methanol and in the basic solution

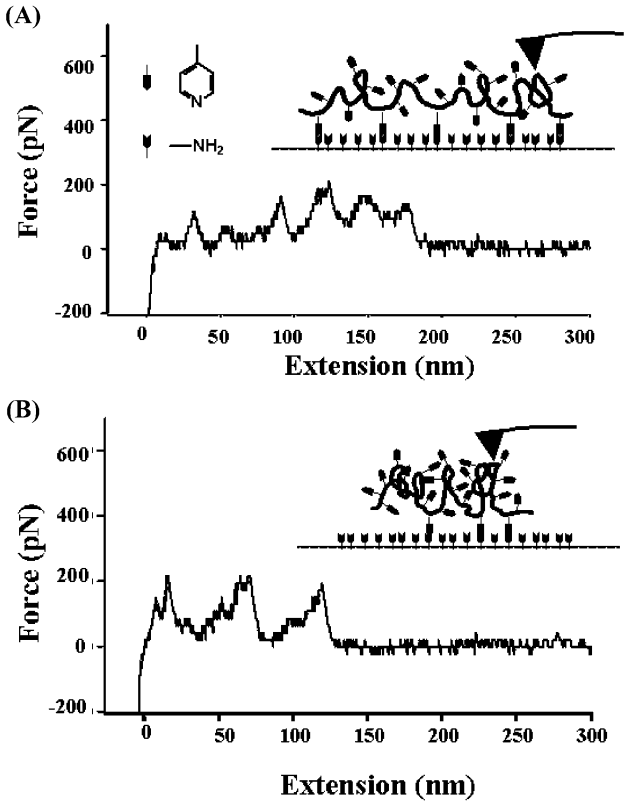
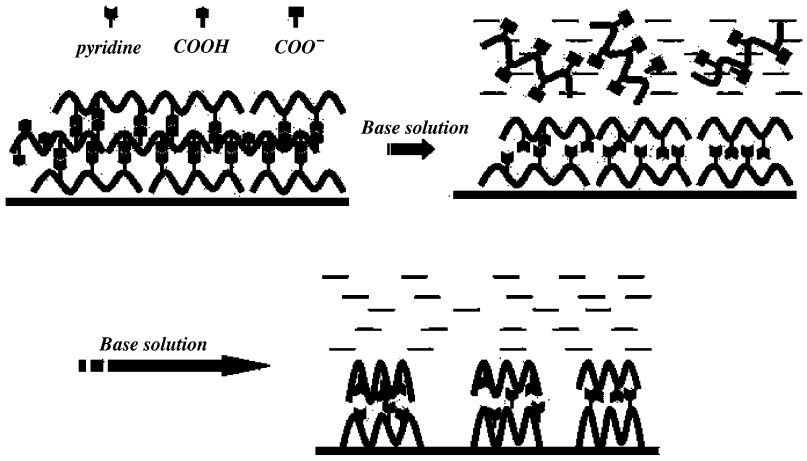


Figure 10. Typical force−extension curves of PVP in methanol (A) and in pH = 12.5 NaOH aqueous solution (B). The insets are the corresponding schematic drawings of SMFS.

are 27.9 and 35.8 nm, respectively. The average length of loops in the basic solution is greater than that in

Scheme 1



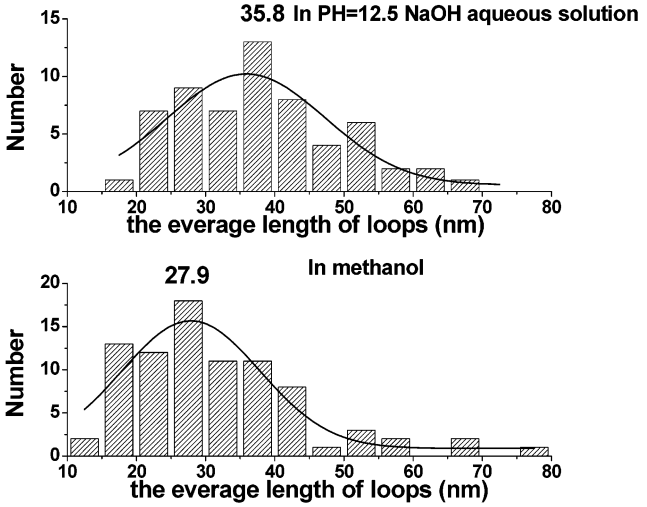


Figure 11. Histogram of the average length of PVP loops in pH = 12.5 NaOH aqueous solution (top) and in methanol (bottom).

methanol, which is in agreement with our hypothesis. Herein the SMFS data are used as an auxiliary evidence to support our hypothesis that the basic aqueous solution can induce a conformation change of PVP polymer chains at interface. Although SMFS reveals the conformation change of only a single polymer chain, we may argue that the conformation change of many polymer chains should be connected with the morphology change. In a word, prolonged immersion of the remaining PVP film in the basic aqueous solution induces the reconformation of the PVP chains, resulting in the formation of a microporous ultrathin film.

Conclusion

In this article, the variation of a hydrogen-bonding-directed LbL film based on PAA and PVP in a basic solution was investigated, and a two-step process was proposed (Scheme 1). At the onset of the immersion, one component of the multilayer, PAA, dissolves into the basic solution, while the other component, PVP, remains on the substrate. The extended PVP chains on the substrate are gradually folded, and a microporous ultrathin film is produced. This interesting and unique process is a consequence of the features of the hydrogen-bonding-directed LbL film, such as the ionization of PAA, the poor water solubility of PVP, and the extended PVP chains.

Recently, many studies have focused on the variation of properties of a LbL film in a solution with specific pH or a aqueous solution of a salt. They have shown that the variation of properties is related to the reorganization of the polymers in the immersion solution.[25,26] Our study, combined with these investigations, implies that the extended conformation of the polymer chains is a key feature of the LbL film for future application and deserves undoubtedly further investigation from both the experimental and theoretical point of view. The applications of the release of PAA and the resulting microporous film in pharmaceutics and materials science are greatly anticipated.

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