Influence of assembly pH on compression and Ag nanoparticle synthesis of polyelectrolyte multilayers

Xiao Gong a,b, Lulu Han a, Yanan Yue a, Jianrong Gao b, Changyou Gao a,*

a MOE Key Laboratory of Macromolecular Synthesis and Functionalization, Department of Polymer Science and Engineering, Zhejiang University, Hangzhou 310027, China
b College of Chemical Engineering, Zhejiang University of Technology, Hangzhou 310014, China

Abstract

Influence of assembly pH on compression and Ag nanoparticle synthesis of polyelectrolyte multilayers was studied using poly(diallyldimethylammonium chloride) (PDADMAC) and poly(4-styrenesulfonic acid-co-maleic acid, 1:1SS:MA) sodium salt (PSSMA 1:1) as the building blocks. The thickest multilayers turned out at pH 4. A homogeneous compression by a silicone rubber stamp increased significantly the water contact angle to a same value which was independent on the original assembly pH anymore. The multilayers assembled at pH 4 could be maximumly compressed to a ratio of 70% by a silicone rubber stamp with linear patterns, which was considerably larger than those assembled at other pHs (the compression ratio ~50%). The Ag nanoparticles were then synthesized inside the multilayers either flat compressed or not. The results showed that the compression reduced significantly the amount of Ag nanoparticles for the multilayers assembled at pH 2 and pH 4. The particle amount was also decreased significantly when the multilayers were assembled at higher pH, pH 6, for example, regardless of the compression. Substantial alteration of the multilayers in terms of the surface morphology, thickness and refractive index was found during the reduction of Ag+ containing multilayers by NaBH4 solution.

1. Introduction

Recently, creation of the physical and chemical patterns on the multilayers has been well demonstrated by methods of micro-contact printing, nano-imprint and compression [1–6]. The multilayer compression does not bring changes in the surface chemistry while the geometric patterns are prepared at very mild conditions. The compression degree can be modulated by multilayer compositions, environmental humidity, drying time and salt treatment [6–10]. As an important consequence of the compression, the multilayers become harder with improved glass transition temperature and enhanced stability against post treatments. For example, compression of the poly(acrylic acid) (PAA)/poly(diallyldimethylammonium chloride) (PDADMAC) multilayers assembled at pH 11 completely inhibits the formation of pores at pH 5, a phenomenon known as mass loss [7]. It is understandable that the compression makes the multilayers becomes more densely packed and creates more binding sites per unit volume, leading to a better stability. More recently, poly(4-styrenesulfonic acid-co-maleic acid) sodium salt (PSSMA), which contains both strong (sulfonate) and weak (carboxylate) charging units, is used to prepare the multilayers with PDADMAC which exhibit a drying time and salts dependent compression behavior [10,11].

PSSMA has both weak and strong charge groups, in which the strong charge groups can enhance the stability of the multilayers and the weak charge groups can be adjusted by pH value [12,13]. Therefore, one would expect that the multilayers assembled from this polymer may show unique performance in terms of pH controlled compression. Since the compression of the multilayers can form more temporary ionic bonds and adjust the degree of ionization of carboxyl to some extent [7], difference in synthesis of metal nanoparticles inside the compressed and uncompressed multilayers is expectable too. The results not only disclose some basic properties of the multilayers at different pH values, but also augment the technique for facile fabrication of the patterned functional multilayers. To our best knowledge, although the influence of pH on the polyelectrolyte multilayers assembly has been extensively studied, neither effect of pH on this PSSMA/PDADMAC multilayers compression nor influence of the compression on synthesis of Ag nanoparticles within the multilayer has been reported.

2. Materials and methods

2.1. Materials

Polyethyleneimine (PEI, Mn 60 kDa, Mw 750 kDa), poly(diallyldimethylammonium chloride) (PDADMAC, very low molecular weight), and poly(4-styrenesulfonic acid-co-maleic acid) sodium salt (PSSMA, SS:MA 1:1, Mw 20 kDa,) were obtained from Aldrich...
and used as received to prepare 1 mg/mL/0.5 M NaCl solutions. AgNO3 (Mw 169.87) and NaBH4 (Mw 37.85) were obtained from Aldrich. Poly(dimethylsiloxane) (PDMS) prepolymer, Sylgard 184, were obtained from Dow Corning and were used to fabricate the PDMS stamps with desired pattern structures.

2.2. Substrate preparation

Silicon wafers and quartz slides were firstly cleaned with Piranha solution (70:30 v/v sulfuric acid/hydrogen peroxide) (Caution: piranha is a strong oxidizer and should not be stored in a closed container), and then were sonicated in a 1:1 mixture of water and 2-propanol for 15 min. They were further treated in a 5:1:1 mixture of water, hydrogen peroxide (30%) and ammonia solution (29%) at 60 °C for 15 min. After the wafers were rinsed in a copious amount of water, they were blown-dried in a nitrogen stream.

2.3. Assembly of polyelectrolyte multilayers

To establish a highly charged precursory layer on the surface, the silicon substrates were firstly incubated in PEI solution. The polyelectrolytes of PSSMA and PDADMAC were all prepared as 1 mg/mL solutions with 0.5 M sodium chloride, which were then adjusted to a certain pH value. Sequential adsorption of the polyelectrolytes on the silicon substrates was then performed by manually dipping. Between alternate exposures to the two solutions for 15 min, there were three rinses with triple-distilled water having a same pH value as the polyelectrolyte solutions for 3 min. After the desired layer numbers were deposited, the PSSMA/PDAMMAC multilayers were rinsed with triple-distilled water having a same pH value as the polyelectrolyte solutions for at least 5 min to eliminate the adsorbed salt. The multilayers were then dried in 70% relative humidity (RH) at room temperature (20 °C) for 12 h.

2.4. Creation of the patterns under pressure

The PDMS stamps with strips were molded from lithographically prepared masters [14,15]. The soft PDMS stamps were put onto the polyelectrolyte multilayers with the patterned surfaces toward the multilayers under a normalized pressure of 200 g cm

2.5. Synthesis of Ag nanoparticles

After the multilayers were immersed in 1 mM AgNO3 solution for 12 h at a neutral pH, and followed by rinsing in pure water, they were incubated in 10 mM NaBH4 solution at neutral pH for 1 h to reduce the silver ions to Ag nanoparticles.

2.6. SFM

Topographical images were collected using SPI3800N Probe Station and SPA400 SPM Unit (Seiko Instruments Inc.) in a dynamic force mode. Silicon tips with a resonance frequency f0 of 150 kHz and a spring constant of 20 N/m were utilized. The scanning frequency was 0.5 Hz. The contact force between the tip and the samples was kept as low as possible (<2.5 nN). To measure the film thickness, part of the films was scratched off by a thin needle of syringe. Then the height difference between the exposed silicon substrate and the multilayers was measured.

2.7. Ellipsometry

The thicknesses of the multilayers (30–60% relative humidity) were also measured by ellipsometry. The measurement was carried on a variable-angle spectroscopic ellipsometer (model M2000D; J.A. Woollam Inc., Lincoln, NE) at incident angles of 65°, 70° and 75° within a wavelength range of 600–1700 nm. The thickness was calculated from the ellipsometric parameters, α and ψ, using a Cauchy model. Data were obtained on different place of the film and reported as mean ± standard deviation.

2.8. UV–vis spectroscopy

The UV–vis spectra of the multilayers prepared on quartz substrates were obtained by a UV–vis spectrophotometer, UV-2450, Shimadzu.

2.9. Water contact angle

The static water contact angles of the multilayers were measured at saturated humidity by a sessile-drop method on a DSA 100 water contact angle measuring system (Krüss, Germany). The apparatus was equipped with a microscope and illumination system to visualize the water droplets sitting on the substrates. The samples were placed into a chamber mounted to the apparatus. The water droplets were put onto the samples. Each value was averaged from five parallel measurements and reported as mean ± standard deviation.

2.10. Scanning electron microscopy (SEM) and transmission electron microscopy (TEM)

The multilayers were assembled on carbon-coated copper grids. Then Ag nanoparticles were in situ synthesized within the multilayers. SEM and TEM images were obtained on a SIRION 100 field emission scanning electron microscope and a JEM-1230 microscope at an acceleration voltage of 120 kV, respectively. Only the uncompressed multilayers could be checked by this method.

2.11. X-ray diffraction (XRD)

XRD patterns of the compressed and uncompressed PEI/PSSMA/ PDADMAC multilayers after in situ synthesis of Ag nanoparticles were obtained with D/max-rA X-ray diffraction equipment.

3. Results and discussion

3.1. Influences of pH on compression of PSSMA/PDADMAC multilayers

It is known that the charging degree of the maleic acid (MA) segment is significantly influenced by pH, while the charging degree of the styrene sulfonate (SS) segment and PDADMAC could be regarded constant within medium pH range. Thus the influences of pH on the PSSMA/PDADMAC multilayers might be complicated, which in turn brings uncertainty to their structures and performance such as compression. As shown in Fig. 1a, both SFM and ellipsometry recorded the consistent values of film thicknesses, which increased initially and then decreased along with the pH increase. The thickest value appeared at pH 4, resulting in a loosed multilayers (refractive index 1.49 vs. 1.51–1.53 for others). As reported previously, the pK values of PSSMA 1:1 are about 2.9 and 8.8 due to the two step dissociation of the AA group [12]. This would mean that at pH 10 the AA groups are almost fully deprotonated, resulting in a highly charged PSSMA molecule which adopts a flat molecular confirmation and thereby renders a thin film [12,13]. At pH 2 most of the AA groups are protonated and thereby can not form the electrostatic cross-linkages with PDADMAC. In this case the PSSMA can be regarded as a pure strong polyelectrolyte except of a lower charging density than PSS. However, due to
the diminished intramolecular repulsive force the molecule becomes more coiled and adsorbs thicker [12]. Moreover, larger amount of PSSMA of lower charging density is required to make the surface charge reversal. These differences can then explain the thicker film obtained at pH 2. When the assembly pH values were set between 4 and 8, the AA groups are partially dissociated, making the PSSMA molecules behave the characteristics of weak polyelectrolytes to some extent. Consequently, thicker multilayers were obtained as a result of interdiffusion of the polyelectrolytes within the multilayers [16–18]. In this case, the PSSMA has a certain charge density which offers better mobility and diffusivity for the polyelectrolyte chains within the multilayers. However, different from other traditional exponential growth multilayers, the thickness is not so thick except at pH 4 (Fig. 1a). Along with the pH increase from 4 to 8, the deprotonation degree of AA groups is steadily enlarged, leading to the decrease of diffusivity for the polyelectrolyte chains within the multilayers. This can explain the phenomenon of thickest film obtained at pH 4.

All the PEI(PSSMA/PDADMAC)_7 multilayers could be compressed regardless of the assembly pH (Fig. 1b). The compression ratios (the ratio of the pattern height to the original dry thickness of the multilayers) were generally about 50%, except of that assembled at pH 4, which was up to 70%. This is consistent with the multilayer structures (Fig. 1a). The loose structure should thus have a larger ratio of voids and smaller strength, leading to a higher compression ratio. As found previously, the patterns on the multilayers dried in 70% relative humidity (RH) at room temperature (20 °C) for 12 h were formed by vertical compression, while the lateral flow of the multilayers under the normal force was neglectable [6]. The present results showed that the assembly pH is another factor mediating the compression degree of the PSSMA/PDADMAC multilayers.

Fig. 2 compares the static contact angle of uncompressed PEI(PSSMA/PDADMAC)_7/PSSMA multilayers and flat compressed PEI(PSSMA/PDADMAC)_7/PSSMA multilayers assembled at different pH value. The water contact angle is usually tied with the surface chemistry, roughness, and wettability of the material [19]. In the present case, both the ionization degree of the PSSMA molecules and surface roughness were altered, the interplay of which should be then responsible for the alteration tendency of the water contact angle [20]. The static contact angle first increased then decreased fast with the assembly pH increase, revealing that the overall hydrophilicity of the multilayers became worse before pH 6. When the PEI(PSSMA/PDADMAC)_7/PSSMA multilayers assembled at different pH values were flat compressed by PDMS stamp without pattern, the contact angle was largely improved and all reached almost the same value (−90°). Especially at pH 10, the contact angle greatly improved from 23° to 88°. This is mainly because the hydrophilic groups can be embedded within the multilayers after compression [9].

### 3.2 Influences of compression on in situ synthesis of Ag nanoparticles

Synthesis of metal nanoparticles in polyelectrolyte multilayers is greatly affected by the content of carboxyl groups in the multilayers [21,22]. Since the compression of the multilayers can form more temporary ionic bonds and adjust the degree of ionization of carboxyl to some extent [7], difference in synthesis of the nanoparticles inside the compressed and uncompressed multilayers is expected. In this study, the biggest compression ratio was achieved at pH 4, thus the PEI(PSSMA/PDADMAC)_7 multilayers assembled at this pH and either compressed or not were firstly subject to the in situ synthesis of Ag nanoparticles. Here the flat compressed instead of the pattern-compressed multilayers were used in order to simplify the study and easily control the conditions. Experiments showed that both the flat and pattern compression achieved a similar compression ratio. Fig. 3a shows that the absorbance of SS at 225 nm after in situ Ag synthesis almost kept unchanged regardless of the compression, revealing no mass loss of the multilayers occurred during the synthesis process. Compared with the pristine multilayers, new absorbance at 400–500 nm with maxima of 430 nm appeared after the synthesis, confirming the existence of Ag nanoparticles [21]. Quantitative analysis found that the increase of the absorbance at 430 nm was 0.022 and 0.004 for the uncompressed and the compressed multilayers, respectively, revealing...
that the content of the Ag nanoparticles in the former was 5–6 times higher than that in the latter. The XRD characterization further provided solid proof for the success synthesis of the Ag nanoparticles (Fig. 3b), by which more content of Ag nanoparticles in the uncompressed multilayers can be safely concluded.

Compression of the multilayers can not close the channels for the Ag$^+$ ions to penetrate due to the very small diameter of the ions. However, the compression makes the polycations and polyanions more closer, thus more physical entanglement of the polymers and electrovalent bonds are formed, leading to a denser structure of the multilayers [7]. On the other hand, in the PEI(PSSMA/PDADMAC)$_7$ multilayers the Ag$^+$ can only complex with the protonated carboxyl groups to form COO$^-$Ag$^+$ conjugates [23], which are then reduced to the Ag nanoparticles in the NaBH$_4$ solution. These facts explain the results that fewer Ag nanoparticles are formed in the compressed multilayers.

To identify the Ag nanoparticles by TEM, the multilayers were assembled on the copper grids and used for the similar synthesis. Due to the difficulty of experimental operation, compression of the multilayers on the copper grids was not possible thus only the uncompressed PEI(PSSMA/PDADMAC)$_7$ multilayers were used for this investigation (Fig. 3c). The Ag nanoparticles showed from near-spherical to polygonal morphologies, and evenly distributed within/on the multilayers. Basically, the particles could be categorized into two types according to their size: the smaller one (about 5 nm) and the bigger one (50–100 nm). Using the Scheller equation [24], the average Ag particle size in the uncompressed PEI(PSSMA/PDADMAC)$_7$ multilayers was calculated to be 19.9 nm according to the XRD broadening Ag (1 1 1) reflection peaks (Fig. 2b). This value is roughly consistent with the TEM observation. Since the multilayers thickness was only about 50 nm (Table 1), the bigger nanoparticles extruded from the multilayers as shown in Fig. 3d. The size of the smaller one is comparable with that reported previously [21,22]. In this study, the bigger one could be possibly formed by the physically adsorbed Ag ions, especially on the multilayer surface. Growth of the Ag nanoparticles becomes then possible during the reduction process.

Alteration of the multilayer thickness and morphology during the Ag nanoparticles synthesis was further investigated by AFM and ellipsometry as shown in Fig. 4 and Table 1. Incubation in the AgNO$_3$ solution did not bring significant change on the

Table 1
Thickess, RMS, and refractive index of the PEI(PSSMA/PDADMAC)$_7$ multilayers assembled at pH 4, and treated in AgNO$_3$ solution, then treated in NaBH$_4$ solution, respectively.

<table>
<thead>
<tr>
<th></th>
<th>Before in situ synthesis</th>
<th>After treatment in AgNO$_3$ solution</th>
<th>After treatment in NaBH$_4$ solution</th>
</tr>
</thead>
<tbody>
<tr>
<td>Thickness (nm) (ellipsometry)</td>
<td>49.6</td>
<td>45.5</td>
<td>34.3</td>
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<td>Thickness (nm) (AFM)</td>
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<td>RMS (nm)</td>
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<td>1.3</td>
</tr>
<tr>
<td>Refractive index</td>
<td>1.5045</td>
<td>1.5058</td>
<td>1.5675</td>
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Fig. 3. (a) UV–vis spectra of the PEI(PSSMA/PDADMAC)$_7$ multilayers before and after in situ synthesis of Ag nanoparticles. (b) XRD patterns of the compressed and uncompressed PEI(PSSMA/PDADMAC)$_7$ multilayers after in situ synthesis of Ag nanoparticles. (c) TEM and (d) SEM images of the uncompressed PEI(PSSMA/PDADMAC)$_7$ multilayers after in situ synthesis of Ag nanoparticles. The assembly pH was set at 4.
multilayer morphology and roughness (Fig. 4a and b), as well as thickness and refractive index (Table 1), demonstrating that the multilayer structure is maximally preserved. By contrast, reduction by NaBH4 solution caused significant change. The multilayers became smoother (Fig. 4c) with a smaller roughness of 1.3 nm. Nanoparticles on the multilayer surface were visible too, which agrees well with the SEM observation (Fig. 3d). Moreover, the multilayer thickness decreased pronouncedly from 45 nm to 33 nm, accompanying with an increase of the refractive index from 1.5058 to 1.5675 (Table 1). Control experiment revealed that when the multilayers without Ag+ ions were immersed in the NaBH4 solution for the same time, the thickness and morphology of the multilayers did not obviously change.

Since the UV–vis spectra did not record the mass loss during the synthesis process, the thickness decrease and refractive index increase implies the densification of the multilayers as a result of Ag nanoparticles formation and rearrangement of the polyelectrolyte conformation. During the synthesis process, the Ag+ ions first complex with the carboxylic acid groups, then were reduced into nanoparticles by NaBH4. After Ag+ ions were reduced, a fraction of carboxylic groups in the multilayers were released, leading to the increase of ionization degree of the carboxylic acid groups in the water at neutral pH [23]. The polyelectrolyte molecules thus adopt a more flat conformation. At the same time, the synthesized Ag nanoparticles may function as physical cross-links which cause the structure of the multilayers denser and regular.

Different from the above results, when the PEI(PSSMA/PDADMAC)7 multilayers assembled at pH 2 was suffered from the same treatments, considerable mass loss was found (Fig. S1a). Again, the compression caused similarly the reduction of Ag nanoparticles synthesized inside the multilayers, as confirmed by the UV–vis spectra and XRD (Fig. S1). The multilayers assembled at pH 6 and either compressed or not were subject to the Ag nanoparticles synthesis too. No mass loss was found during the synthesis process (Fig. S2a). However, compared with pH 4, the content of the Ag nanoparticles inside the multilayers was so small that it could not be determined by the UV–vis spectroscopy (Fig. S2a) and XRD (Fig. S2b) regardless of the compression. TEM characterization confirmed the formation of the Ag nanoparticles in the uncompressed multilayers, whose size was about 5–10 nm (Fig. S2c). At this pH, the ionization degree of the carboxylic acid groups is pretty large, leading to the inefficient coordination of the Ag+ ions and thereby the smaller amount of the Ag nanoparticles synthesized. Since the ionization degree of the multilayers is already large enough at this pH, the compression is hardly to further create significant difference and thus no influence is observed.

### 4. Summary

In this work the effects of assembly pH on compression and Ag nanoparticle synthesis of polyelectrolyte multilayers were explored. A homogeneous compression by PDMS stamp increased significantly the water contact angle to a same value which was independent on the original assembly pH anymore. Compression of the multilayers with the PDMS stamp having linear patterns found that the one assembled at pH 4 had the maximum compression ratio, which well agrees with the loose multilayer structures as a result of the thickest thickness. The Ag nanoparticles could be in situ synthesized within the flat compressed and uncompressed multilayers, but their amount was significantly smaller inside the compressed multilayers assembled at pH 4. Comparatively, a fewer number of the Ag nanoparticles were synthesized inside the multilayers assembled at higher pH, for example, pH 6. This is attributed to the decrease of the protonated carboxylic acid groups, with which the Ag+ ions are complexed. Reduction of the Ag+ containing multilayers by NaBH4 solution caused substantial changes of surface morphology, thickness, and refractive index of the multilayers due to the rearrangement of the conformation of the polyelectrolyte chains.

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### Appendix A. Supplementary material

UV–vis spectra of the PEI(PSSMA/PDADMAC)7 multilayers before and after in situ synthesis of Ag nanoparticles, and XRD patterns of the compressed and uncompressed PEI(PSSMA/PDADMAC)7 multilayers after in situ synthesis of Ag nanoparticles (the assembling pH was set at 2 and 6). Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.jcis.2010.12.054.

### References