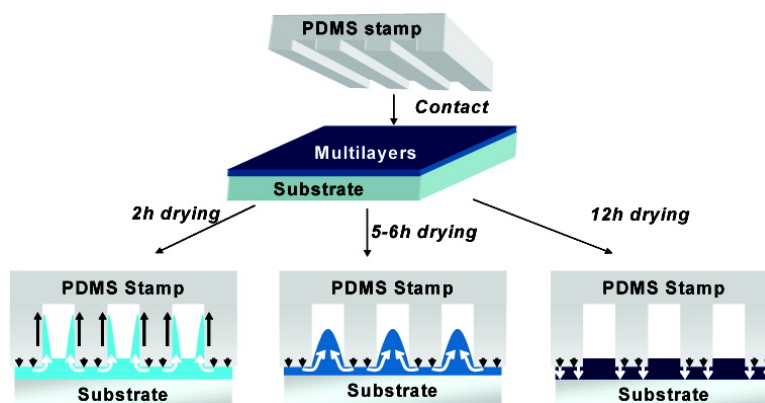


Influence of Drying Time of Polyelectrolyte Multilayers on the Compression-Induced Pattern Formation

Xiao Gong, Jie Yang, Lulu Han, and Changyou Gao

Langmuir, 2008, 24 (24), 13925-13933 • DOI: 10.1021/la802957r • Publication Date (Web): 20 November 2008

Downloaded from <http://pubs.acs.org> on January 9, 2009



More About This Article

Additional resources and features associated with this article are available within the HTML version:

- Supporting Information
- Access to high resolution figures
- Links to articles and content related to this article
- Copyright permission to reproduce figures and/or text from this article

[View the Full Text HTML](#)



ACS Publications
High quality. High impact.

Langmuir is published by the American Chemical Society, 1155 Sixteenth Street N.W., Washington, DC 20036

Influence of Drying Time of Polyelectrolyte Multilayers on the Compression-Induced Pattern Formation

Xiao Gong, Jie Yang, Lulu Han, and Changyou Gao*

Key Laboratory of Macromolecular Synthesis and Functionalization, Ministry of Education, Department of Polymer Science and Engineering, Zhejiang University, Hangzhou 310027, China

Received August 21, 2008. Revised Manuscript Received October 9, 2008

Compression of the polyelectrolyte multilayers has been found previously when they were pressed by a poly(dimethylsiloxane) (PDMS) stamp under a small pressure (*Macromolecules* 2004, 37, 8836). In this work, we further found that the pattern formation of the poly(diallyldimethylammonium chloride) (PDADMAC) containing multilayers is dependent on the drying time of the multilayers prior to compression. After the poly(4-styrenesulfonic acid-co-maleic acid) sodium salt (PSSMA)/PDADMAC multilayers were dried at 70% relative humidity and room temperature for 2, 6, and 12 h, compression of the multilayers by a PDMS stamp with linear patterns obtained double strips, high ridges and linear patterns on the multilayers, respectively. These phenomena were independent of the layer number and salt concentration and could be applied to other PDADMAC containing multilayer systems such as poly(styrene sulfonate) sodium salt (PSS)/PDADMAC and poly(acrylic acid, sodium salt) (PAA)/PDADMAC. A model was suggested to depict the process, and the influence of the water content on the multilayer structure and properties was discussed. The stability experiments revealed that the strips and high ridges obtained at shorter drying time could be erased by incubation in water for 5 h, while the compression created patterns were very stable.

Introduction

The layer-by-layer (LbL) technique, first introduced by Iler¹ in 1966 and reestablished and refined by Decher² in the 1990s, has shown great success in fabricating polymer thin films with controllable compositions, structures, and properties.³ Recently, extension of the technique onto sacrificial colloidal particles has produced hollow microcapsules, endowing the technique with more broad applications.⁴ Although other driving forces such as hydrogen bonding,^{5,6} covalent linkages,^{7,8} and hydrophobic interaction⁹ can also be applied as the driving forces, so far the electrostatic attraction dominates the assembly and the resulting multilayer films have been well investigated in terms of their physical structures and properties as well as applications.¹⁰ Many parameters governing the building process as well as the film structures and properties have been documented, including the types of the polyelectrolytes and salts, salt concentration, temperature, pH value, etc.^{11–16} In 2002, CIBA-Vision has announced the first commercially available product that is equipped with a multilayer coating.¹⁷ The ultrathin films are also

expected to be used as chemical and biological sensors,^{18–20} drug delivery carriers,^{21–23} microelectronics,^{24,25} nano-optics,^{26,27} etc.

For many of the applications, control of the surface properties and physical structures is undoubtedly important. There are several attempts to create chemical and/or physical patterns on the polyelectrolyte multilayer films. For example, Hammond and co-workers fabricated complex multilevel microstructures by patterning an initial set of multilayer films using a microcontact printing (μ CP) technique and then patterning atop the surface of the subsequently assembled multilayers.²⁸ Rubner and co-workers used a water-based subtractive patterning technique to micro-pattern multilayers such as poly(acrylic acid) (PAA)/polyacrylamide (PAAm) and poly(methacrylic acid) (PMA)/PAAm constructed by hydrogen-bonding to create more complex cell-resistant/-adhesive surfaces.²⁹ Recently, other polymeric molds such as polyurethane acrylate mold, UV-cured hard mold, and hydrophilic composite mold have also been used for the polyelectrolyte multilayer patterning.^{30–32}

*To whom correspondence should be addressed. Email:cygao@mail.hz.zj.cn. Phone/Fax: +86-571-87951108.

- (1) Iler, R. K. *J. Colloid Interface Sci.* **1966**, 21, 569.
- (2) Decher, G.; Hong, J. D. *Makromol. Chem., Macromol. Symp.* **1991**, 46, 321.
- (3) Decher, G.; Hong, J. D.; Schmitt, J. *Thin Solid Films* **1992**, 210, 831.
- (4) Caruso, F.; Caruso, R. A.; Möhwald, H. *Science* **1998**, 282, 1111.
- (5) Stockton, W. B.; Rubner, M. F. *Macromolecules* **1997**, 30, 2717.
- (6) Wang, L. Y.; Wang, Z. Q.; Zhang, X.; Shen, J. C.; Chi, L. F.; Fuchs, H. *Macromol. Rapid Commun.* **1997**, 18, 509.
- (7) Harris, J. J.; DeRose, P.; Bruening, M. J. *Am. Chem. Soc.* **1999**, 121, 1978.
- (8) Sun, J. Q.; Wu, T.; Sun, Y. P.; Wang, Z. Q.; Zhang, X.; Shen, J. C.; Cao, W. X. *Chem. Commun.* **1998**, 17, 1853.
- (9) Kotov, N. A. *Nanostruct. Mater.* **1999**, 12, 789.
- (10) Decher, G. *Science* **1997**, 277, 1232.
- (11) Salomäki, M.; Laiho, T.; Kankare, J. *Macromolecules* **2004**, 37, 9585.
- (12) Steitz, R.; Leiner, V.; Siebrecht, R.; Klitzing, R. V. *Colloids Surf. B* **2000**, 163, 63.
- (13) Büscher, K.; Graf, K.; Ahrens, H.; Helm, C. A. *Langmuir* **2002**, 18, 3585.
- (14) Shiratori, S. S.; Rubner, M. F. *Macromolecules* **2000**, 33, 4213.
- (15) Tjijto, E.; Quinn, J. F.; Caruso, F. *Langmuir* **2005**, 21, 8785.
- (16) Yoo, D.; Shiratori, S. S.; Rubner, M. F. *Macromolecules* **1998**, 31, 4309.
- (17) For a review, please see: *Multilayer Thin Films: Sequential Assembly of Nanocomposite Materials*; Wiley-VCH: 2002.

- (18) Lvov, Y. M.; Lu, Z.; Schenkman, J. B.; Zu, X.; Rusling, J. F. *J. Am. Chem. Soc.* **1998**, 120, 4073.
- (19) Kim, H.; Doh, J.; Irvine, D. J.; Cohen, R. E.; Hammond, P. T. *Biomacromolecules* **2004**, 5, 822.
- (20) Campas, M.; O'Sullivan, C. *Anal. Lett.* **2003**, 36, 2551.
- (21) Izumrudov, V. A.; Kharlampieva, E.; Sukhishvili, S. A. *Biomacromolecules* **2005**, 6, 1782.
- (22) Berg, M. C.; Zhai, L.; Cohen, R. E.; Rubner, M. F. *Biomacromolecules* **2006**, 7, 357.
- (23) Wood, K. C.; Boedicker, J. Q.; Lynn, D. M.; Hammond, P. T. *Langmuir* **2005**, 21, 1603.
- (24) Fou, A. C.; Onitsuka, O.; Ferreira, M.; Rubner, M. F.; Hsieh, B. R. *J. Appl. Phys.* **1996**, 79, 7501.
- (25) Eckle, M.; Decher, G. *Nano Lett.* **2001**, 1, 45.
- (26) Nolte, A. J.; Rubner, M. F.; Cohen, R. E. *Langmuir* **2004**, 20, 3304.
- (27) Lukkari, J.; Salomäki, M.; Viinikanoja, A.; Äärälä, T.; Paukkunen, J.; Kocharova, N.; Kankare, J. *J. Am. Chem. Soc.* **2001**, 123, 6083.
- (28) Jiang, X. P.; Hammond, P. T. *Langmuir* **2000**, 16, 8501.
- (29) Yang, S. Y.; Mendelsohn, J. D.; Rubner, M. F. *Biomacromolecules* **2003**, 4, 987.
- (30) Kim, Y. S.; Lee, H. H.; Hammond, P. T. *Nanotechnology* **2003**, 14, 1140.
- (31) Park, J.; Kim, Y. S.; Hammond, P. T. *Nano Lett.* **2005**, 5, 1347.
- (32) Lee, N. Y.; Lim, J. R.; Lee, M. J.; Park, S.; Kim, Y. S. *Langmuir* **2006**, 22, 7689.

More recently, we found an important phenomenon of the multilayer compression that can yield geometric patterns on the multilayers without alteration of their surface chemistry.³³ It proceeds very conveniently at room temperature and a low pressure (0.105–0.200 MPa, above the atmosphere pressure) but depends on several factors such as the multilayer compositions and drying conditions. At the experimental conditions, the multilayers assembled with poly(diallyldimethylammonium chloride) (PDADMAC) as one component and dried at 40–70% relative humidity (RH) for 12 h can be compressed by pressing a poly(dimethylsiloxane) (PDMS) stamp against the multilayers. The overall compression degree of poly(styrene sulfonate) sodium salt (PSS)/PDADMAC multilayers is as high as 70–90% depending on the layer numbers and salt concentrations, and thereby the absolute height of the formed patterns has a positive correlation with the film thickness. However, at these drying conditions (70% RH, 12 h), neither lateral flow of the multilayers during the compression nor the variation of the patterns in 2 M NaCl solution has been observed, implying that the patterns thus obtained is stable enough to withstand the subsequent treatments. The enhanced stability is also observed in PAA/PDADMAC multilayers assembled at pH 11. Pores with a diameter of micrometers appear in the uncompressed PAA/PDADMAC multilayers as a result of pH variation but are completely inhibited after compression.³⁴ It is understandable that after compression more densely packed microstructure is formed in the multilayer films; namely, the compression leads to shrinkage of the vacancies in the multilayer films.³⁵ Moreover, the compressed films become more hydrophobic because of the exposure of the hydrophobic groups.³⁶

Very recently, Sun and co-workers^{37,38} obtained nanopatterns on the multilayer films using an imprint lithography technique.^{39,40} They demonstrate that various pairs of the multilayers including PAA/poly(allylamine hydrochloride) (PAH), PSS/PAH, and PAA/poly(vinyl pyrrolidone) (PVP) can be lithographed into nanolines by a Ni master with a pressure of 4–6 MPa.³⁷ By use of a Norland Optical Adhesives (NOA 63) polymer mold, room-temperature imprinting is also accomplished on the PAA/PAH multilayers.³⁸ In contrast to the compression, the imprint lithography uses a high pressure to push the mold into the multilayers. Consequently, lateral flow of the multilayers is very prominent. However, influence of the drying conditions has not been observed.

In this study, we shall report that the water content which depends on the drying conditions is the most crucial issue governing the pattern formation. In contrast to the pure compression after drying for 12 h, remarkable lateral flow of the multilayers is determined at a drying time of 5–6 h, resulting in high patterns. Stability study reveals that the patterns formed by the lateral flow are unstable and can be easily erased in water, whereas the pure compressed ones keeps unchanged at the same conditions. These phenomena universally exist in all the multilayers with PDADMAC as one of the building blocks. The results not only disclose some basic properties of the multilayers

at different desiccation degree, but also augment the compression technique for obtaining patterns with different structures and stability.

Experimental Section

Materials. Polyethyleneimine (PEI, Mn 60 kDa, Mw 750 kDa), PDADMAC (very low molecular weight), poly(4-styrenesulfonic acid-co-maleic acid) sodium salt (PSSMA, SS:MA 1:1, Mw 20 kDa), poly(styrene sulfonate) sodium salt (PSS, Mw 70 kDa), and PAA sodium salt (Mw 30 kDa) were obtained from Aldrich and used as received to prepare 1 mg/mL/0.3–1 M NaCl solutions. Poly(dimethylsiloxane) (PDMS) prepolymers, Sylgard 184, were obtained from Dow Corning and was used to fabricate the PDMS stamps with desired pattern structures.

Substrate Preparation. Silicon wafers were first 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 copious amount of water, they were blown dried with a nitrogen stream.

Assembly of Polyelectrolyte Multilayers. To establish a highly charged precursor layer on the surface, a layer of PEI was first deposited on the silicon substrates. Sequential adsorption of polyelectrolytes on the silicon substrates was then performed by manually dipping. Between alternate exposures to two kinds of polymer solutions for 15 min, there were 3 rinses with triple-distilled water containing 0.1 M NaCl for 3 min. The NaCl concentration of the polyelectrolyte solutions was varied from 0.3 to 1 M. After the desired layer numbers were deposited, the PSSMA/PDADMAC and PSS/PDADMAC multilayers were rinsed with triple-distilled water, while the PAA/PDADMAC multilayers were rinsed with pH 11 water, all 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 different time. Before measurement of the multilayer thickness, the films were dried in ambient conditions (RH 40–70%) for at least one day. Results show that at such conditions the multilayer thickness is almost not changed along with the storage time.

Creation of the Patterns under Pressure. The PDMS stamps with strips or circular rings were molded from lithographically prepared masters.^{41,42} The soft PDMS stamps were put onto the polyelectrolyte multilayers with the patterned surfaces toward the multilayers and a normalized pressure of 200 g cm⁻². Two hours later, the stamps were carefully peeled off to obtain the patterned multilayers.

Post-Treatment of the Patterned Multilayers. The PSSMA/PDADMAC multilayers typically dried for 6 and 12 h in 70% RH and patterned with the PDMS stamps were incubated in water at room temperature for 5 h. The stability of the obtained patterns was then checked by scanning force microscopy (SFM).

SFM. Topographic 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 f_0 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.

Ellipsometry. The thicknesses of the multilayers were also measured by ellipsometry. The measurement was carried on a variable-angle spectroscopic ellipsometer (model VASE; 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

(33) Gao, C. Y.; Wang, B.; Feng, J.; Shen, J. C. *Macromolecules* **2004**, *37*, 8836.

(34) Wang, B.; Liu, L. L.; Chen, K.; Chen, L.; Feng, J.; Gao, C. Y. *Chem. Phys. Chem.* **2006**, *7*, 590.

(35) Wang, B.; Gao, C. Y.; Liu, L. L. *J. Phys. Chem. B* **2005**, *109*, 4887.

(36) Wang, B.; Feng, J.; Gao, C. Y. *Colloids Surf. A* **2005**, *259*, 1.

(37) Lu, Y. X.; Hu, W.; Ma, Y.; Zhang, L. B.; Sun, J. Q.; Lu, N.; Shen, J. C. *Macromol. Rapid Commun.* **2006**, *27*, 505.

(38) Lu, Y. X.; Chen, X. L.; Hu, W.; Lu, N.; Sun, J. Q.; Shen, J. C. *Langmuir* **2007**, *23*, 3254.

(39) Chou, S. Y.; Krauss, P. R.; Renstrom, P. J. *Appl. Phys. Lett.* **1995**, *67*, 3114.

(40) Guo, L. J. *Adv. Mater.* **2007**, *19*, 495.

(41) Kumar, A.; Whitesides, G. M. *Science* **1994**, *263*, 60.

(42) Xia, Y.; Whitesides, G. M. *J. Am. Chem. Soc.* **1995**, *117*, 3274.

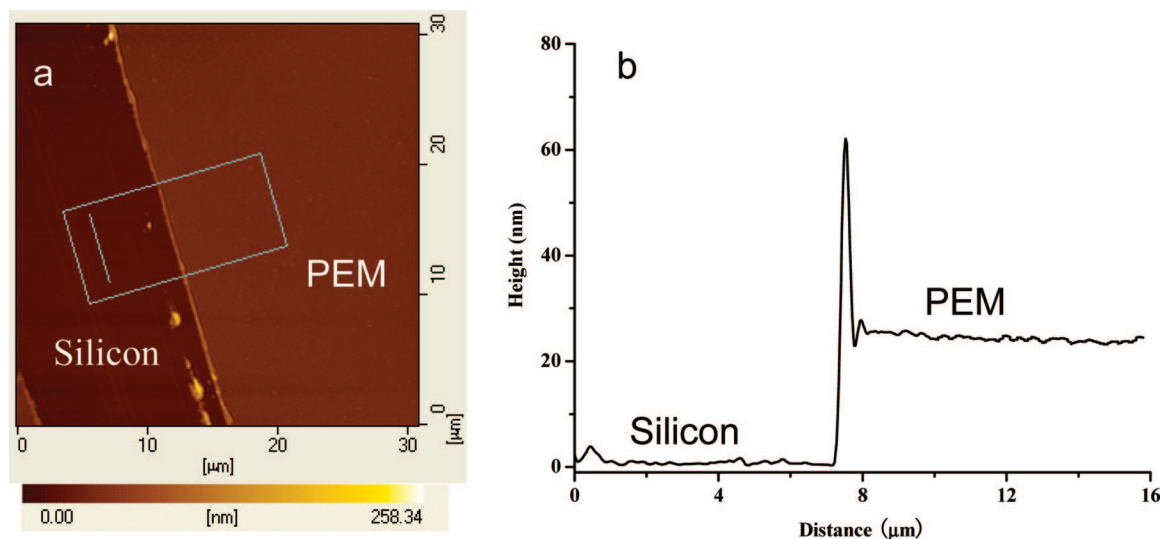


Figure 1. (a) SFM image of PEI(PSSMA/PDADMAC)₇ multilayers assembled in 0.3 M NaCl solution. One part of the multilayers was scratched off to measure the film thickness by averaging the results of the line shown in the black rectangular box. (b) The average cross section is more representative than a simple linear cross section, since every point in the profile is an average of all the points on the line within the rectangular box. The high ridge by the step edge should be ignored for thickness measurement, since it is the buildup of materials that is removed from the substrate.

Table 1. Thickness of the Multilayers Assembled with Different Building Blocks and at Different Conditions and the Formed Pattern Height at Different Drying Time^a

| samples | original thickness, ^a nm | strip height ^b 2 h drying, nm | ridge height 6 h drying, nm | pattern height 12 h drying, nm |
|---|-------------------------------------|---|--------------------------------|-----------------------------------|
| PEI(PSSMA/PDADMAC) ₇ 0.3 M NaCl | 24.0 (27.4 ± 0.8) | 34–38 (142%–158%) | 78–90 (325%–375%) | 10.5–13.5 (44%–56%) |
| PEI(PSSMA/PDADMAC) ₇ 0.5 M NaCl | 34.5 (36.9 ± 0.7) | 54–62 (156%–179%) | 103–107 (299%–310%) | 16–20 (46%–58%) |
| PEI(PSSMA/PDADMAC) ₇ 1 M NaCl | 41.9 (42.8 ± 1.3) | 59–68 (141%–162%) | 104–109 (248%–260%) | 37–39 (88%–93%) |
| PEI(PSSMA/PDADMAC) ₅ 0.5 M NaCl | 20.7 (21.0 ± 0.4) | 63–71 (304%–343%) | 112–120 (541%–580%) | 10–13 (48%–62%) |
| PEI(PSSMA/PDADMAC) ₁₀ 0.5 M NaCl | 79.8 (78.2 ± 1.4) | 105–120 (132%–151%) | 93–102 (117%–128%) | 47–53 (58%–66%) |
| PEI(PSS/PDADMAC) ₇ 0.5 M NaCl | 94.3 (93.1 ± 2.7) | 135–160 (143%–170%) | 101–105 (107%–111%) | 58–69 (62%–73%) |
| PEI(PAA/PDADMAC) ₇ 0.3 M NaCl | 53.3 (52.4 ± 3.5) | 131–155 (245%–290%) | 117–125 (220%–235%) | 33–41 (62%–77%) |

^a Data were measured by SFM, except in the brackets of the second row, which were measured by ellipsometry. ^b The data in the brackets represent the ratios of the strips, ridges, and patterns to the original thickness of the multilayers. A PDMS stamp having regular linear patterns with a width of 6 μm and a space of 6 μm was used.

calculated from the ellipsometric parameters, Δ and Ψ , by which the film thickness and refractive index was automatically fitted using a Cauchy model. Data were obtained on different place of the film and reported as mean ± standard deviation.

Results and Discussion

It has been recognized that the desiccation process is one of the most important parameters governing the compression of the polyelectrolyte multilayers.³³ Decher⁴³ and Schlenoff⁴⁴ have independently measured the number of water molecules associated with one ion pair in the polyelectrolyte complexes and conclude that the average water content inside the fully hydrated films can be larger than 40% by volume. The compression degree of 70–90% observed before³³ further reveals that the water content in the multilayers might be still higher. During the desiccation process, the water molecules are progressively evaporated, leading to the reduction of water content. At the appropriate water content, compression of the multilayers by a very small pressure can take place.

To investigate the drying extent on the compression in detail, here multilayers of PEI(PSSMA/PDADMAC)₇ were assembled in 0.3 M NaCl solution. The thickness of the fully dried multilayers

was measured as 24 nm by SFM (Figure 1), which is consistent with the ellipsometry result (27.4 nm, Table 1). This confirms the reliability of the SFM on characterization of the multilayers and pattern height, which was extensively used in this work. The PEI(PSSMA/PDADMAC)₇ multilayers were then subject to drying in 70% RH for different times before they were closely contacted with the PDMS stamp having a physical pattern structure of strips (6 μm × 6 μm in width and space with a deepness of 2 μm), above which a weight of 200 g was applied (the contacting area is about 1 cm², thus the pressure equals to 0.02 MPa without consideration of the atmosphere pressure). The formed pattern heights and structures as a function of drying time are shown in Figure 2.

At a relatively short drying time, for example 2 h, the height difference between the middles of the uncontacting areas and the contacting areas (the so-called pattern height) is not obvious, implying that at this stage the multilayers are hardly compressed. However, the topographical image (Figure 2, inset image) reveals that double thin strips on an uncontacting region with a height of 34–38 nm were formed by the contacting edges of the PDMS stamp, a phenomenon that has not been reported before. When the drying time was extended to 4 h, the created pattern height was increased to about 10 nm, accompanying with the disappearance of the thin strips by the pattern edges. At a still longer drying time of 5–6 h, the height of the formed patterns (ridges) was suddenly increased to ~80 nm, which is more than 3 times

(43) Lösche, M.; Schmitt, J.; Decher, G.; Bouwman, W. G.; Kjaer, K. *Macromolecules* **1998**, *31*, 8893.

(44) Farhat, T.; Yassin, G.; Dubas, S. T.; Schlenoff, J. B. *Langmuir* **1999**, *15*, 6621.

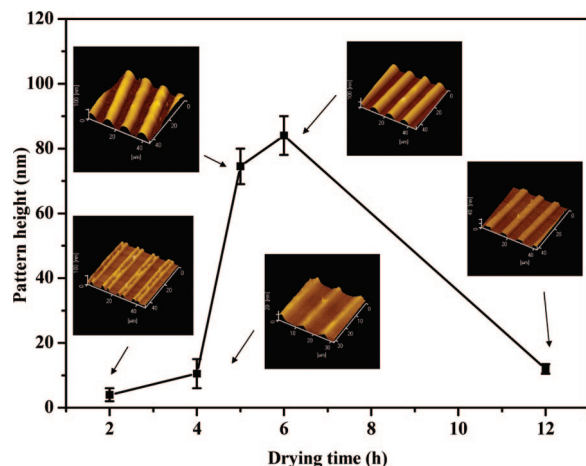


Figure 2. Pattern height of PEI(PSSMA/PDADMAC)₇ multilayers as a function of drying time. SFM topographical images of the pattern-compressed films corresponding to drying times of 2, 4, 5, 6, and 12 h, respectively. The multilayers were initially assembled in 0.3 M NaCl solution, followed by drying at 20 °C and 70% RH. Then a PDMS stamp with a strip pattern (6 $\mu\text{m} \times 6 \mu\text{m}$ in width and space) was put on the film, on which a normalized pressure of 200 g cm^{-2} was applied. Two hours later, the stamp was carefully peeled off.

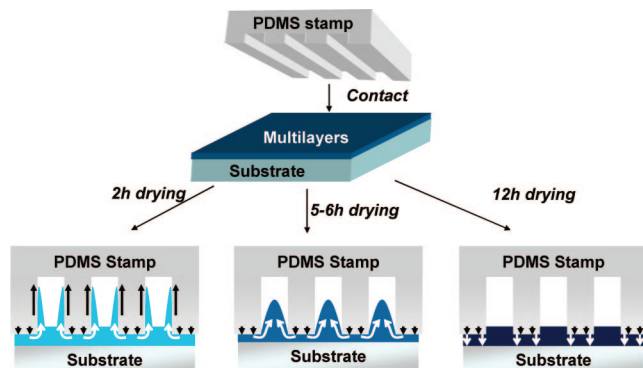


Figure 3. Schematic illustration showing the compression process and mechanism of pattern formation at different drying time. For detail, see the text.

the original film thickness. The protrudent ridges are very smooth and homogeneous in terms of their morphology and structure as illustrated in the inset images of Figure 2. Since the thickness of the multilayers is only 24 nm, it is obvious that here lateral flow of the multilayers must have occurred in addition to the compression. This phenomenon has never been observed before at such a mild processing condition. When the drying time was extended to 12 h, however, the formed pattern height was drastically decreased to 12 nm again, which is consistent with our previous observation.³³ Also the formed patterns are very homogeneous and smooth, with no sign of lateral flow of the multilayers and formation of the thin strips by the contacting edges (Figure 2, inset image). As recognized before, this is a typical result of the compression.

These findings reveal in more detail the variation of the multilayer structure during the desiccation process, which should be the decisive factor governing the formation of various patterns in contact with the PDMS stamp. Figure 3 depicts the formation mechanism of the strips, high ridges, and patterns at the typical drying time of 2, 5–6, and 12 h, respectively. At a relatively short drying period such as 2 h, the water content is large. The water molecules can function as physical cross-linkages due to the hydrogen bonds and also might enhance the hydrophobic interaction of the polyelectrolyte complexes³³ or simply endow

the multilayers with hydrostatic resistivity against press which is a common effect observed for hydrogel filled scaffold.⁴⁵ Therefore, at this stage, compression of the multilayers along the normal direction hardly occurs or at least can be neglected. However, the high water content makes the multilayers move very easily even at a very small pressure. Together with the capillary force between the hydrophobic PDMS stamp and the multilayers, the multilayers can thus climb up the pattern edges of the PDMS stamp, finally forming the thin double strips on the uncontacting region. It is worth mentioning that the very small height difference between the contacting region and the uncontacting region of the multilayers should not be caused by the compression. Instead, it reflects the occurrence of lateral flow of the multilayers, which causes inevitably height decrease of the contacting region of the multilayers.

When the drying time is 4 h or longer, the water content should be decreased to a level that the multilayers no longer move as freely as that at 2 h drying, so that the climbing up phenomenon does not appear. Nevertheless, the remained water content is still large enough to enhance the multilayers to yield a small pattern height. We believe that at this stage the patterns are formed by the lateral flow of the multilayers instead of the compression since high water content makes the compression impossible at such a small pressure.

When the drying time is extended to 5–6 h, the water content should reach to such a level that the multilayers are exactly in a gel-like or a mudlike state (comparable to the stage before the melting point of the traditional polymers). The water molecules here may function as the plasticizer softening the multilayers. Consequently, under a small pressure, the multilayers at the contacting regions of the stamp are pushed to the uncontacting regions, leading to the lateral flow of the multilayers. The high ridges are thus built up by the multilayers flowed from the two edges of the contacting regions. Indeed, occasionally unfilled valleys with the same depth could be observed in the middles of the ridges at 5 h dried samples (Figure 4), which are indicative of the building up format of the ridges, i.e., from the boundaries to the middles. According to this mechanism, the maximum height of the ridges is roughly 3–4 times the thickness of the original multilayers taking into account their nearly triangle shaped geometry. In most cases (Table 1), the height of the ridges is within this estimation, revealing that large vacancy should not exist within the high ridges. This is reasonable since during the process of ridge formation the multilayers possess good enough mobility to fill into the vacancy even if they have been formed as a result of lateral flow.

In contrast to this, the water content in the 12 h dried multilayers should have been equilibrated with the atmosphere, namely, 70% RH. At this stage, the multilayers should be in a state from rubberlike to glasslike transition (comparable to the glass transition of traditional polymers).³⁴ Hence, the polymer complex as a whole is hardly movable, but the polymer segments still possess some extent of mobility. Consequently, at this stage compression in the normal direction should dominate the process, resulting in patterns with a height smaller than that of their original multilayers.

To testify if the above phenomena and explanation are universal for this type of multilayers, in the next study the salt concentration and layer number were varied during the assembly process, resulting in the PSSMA/PDADMAC multilayers with different thickness (Table 1). The results presented in Figures 5–8 confirm

(45) Gong, Y. H.; He, L. J.; Li, J.; Zhou, Q. L.; Ma, Z. W.; Gao, C. Y.; Shen, J. C. *J. Biomed. Mater. Res. B* 2007, 82B, 192.

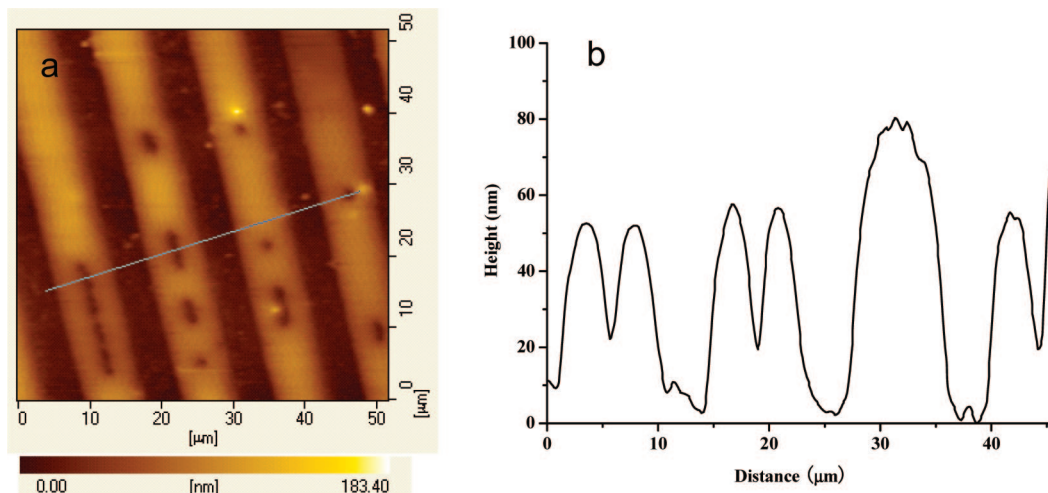


Figure 4. (a) SFM image of the pattern-compressed PEI(PSSMA/PDADMAC)₇ multilayers assembled in 0.3 M NaCl solution and dried for 5 h and (b) its corresponding cross-sectional line profile.

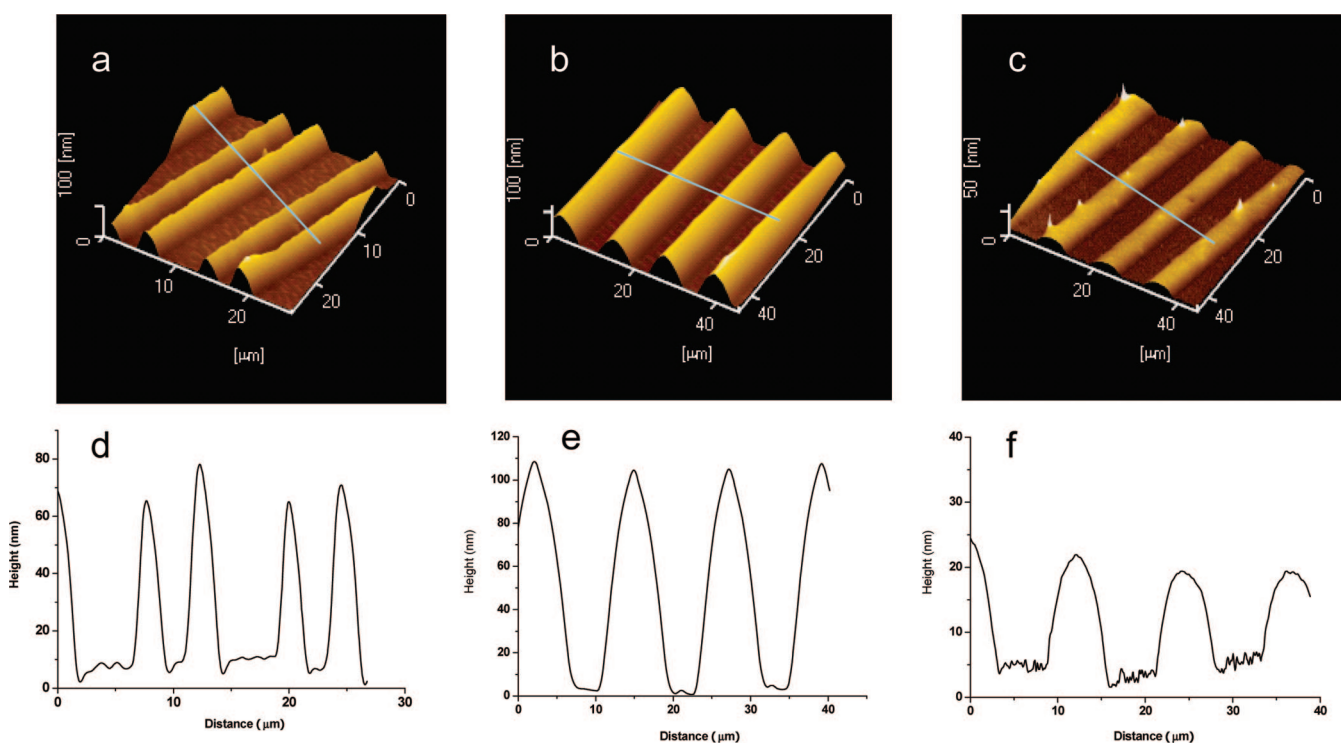


Figure 5. SFM topographical images of the pattern-compressed PEI(PSSMA/PDADMAC)₇ multilayers assembled in 0.5 M NaCl solution and dried for (a) 2 h, (b) 6 h, and (c) 12 h. (d–f) Corresponding cross-sectional profiles of parts a, b, and c, respectively.

that the above alteration tendency can be universally applied to this system.

It has been well-known that the ionic strength can significantly affect the conformation and charge density of the polyelectrolytes and thereby the growth and properties of the multilayers.^{15,46–51} As predicted, thicker multilayers were obtained at a higher salt concentration, e.g., 34.5 and 41.9 nm for the PEI(PSSMA/PDADMAC)₇ multilayers assembled in 0.5 and 1 M NaCl

solutions (Table 1), respectively. Figures 5 and 6 present the typical SFM images and line profiles of the pattern-compressed multilayers assembled in 0.5 and 1 M NaCl and dried for 2, 6, and 12 h, respectively. Again, compression of the 2 h dried multilayers yields always the thin strips by the edges of the patterns on the PDMS stamp (Figures 5a and 6a), and 6 h yields the uniform and high ridges (Figures 5b and 6b), revealing that the phenomena is independent of the salt concentration. The line profiles (Figures 5d and 6d) reveal again that between the double strips of an uncontacting region there is a deep valley which is slightly higher or almost same as the contacting region. For the series of PEI(PSSMA/PDADMAC)₇ multilayers, the height of the strips increased along with the increase of the salt concentration (namely, the multilayer thickness), but the ratios between the strips and the original thickness of the multilayers are all around

(46) Rmaile, H. H.; Schlenoff, J. B. *Langmuir* **2002**, *18*, 8263.

(47) Izumrudov, V.; Sukhishvili, S. A. *Langmuir* **2003**, *19*, 5188.

(48) Fery, A.; Schoeler, B.; Cassagneau, T.; Caruso, F. *Langmuir* **2001**, *17*, 3779.

(49) Kovacevic, D.; van der Burgh, S.; de Keizer, A.; Stuart, M. A. C. *Langmuir* **2002**, *18*, 5607.

(50) Dubas, S. T.; Schlenoff, J. B. *Langmuir* **2001**, *17*, 7725.

(51) McAloney, R. A.; Sinyor, M.; Dudnik, V.; Goh, M. C. *Langmuir* **2001**, *17*, 6655.

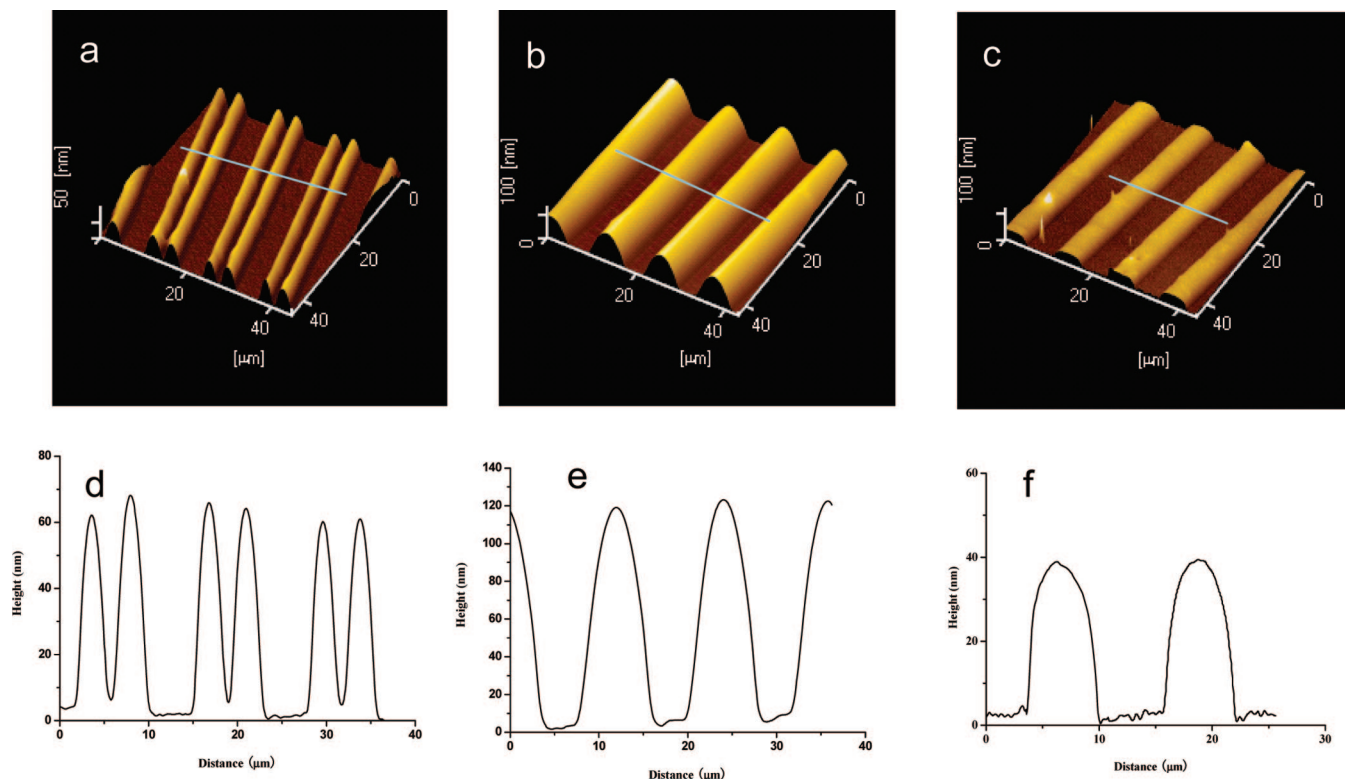


Figure 6. SFM topographical images of the pattern-compressed PEI(PSSMA/PDADMAC)₇ multilayers assembled in 1 M NaCl solution and dried for (a) 2 h, (b) 6 h, and (c) 12 h. (d–f) Corresponding cross-sectional profiles of parts a–c, respectively.

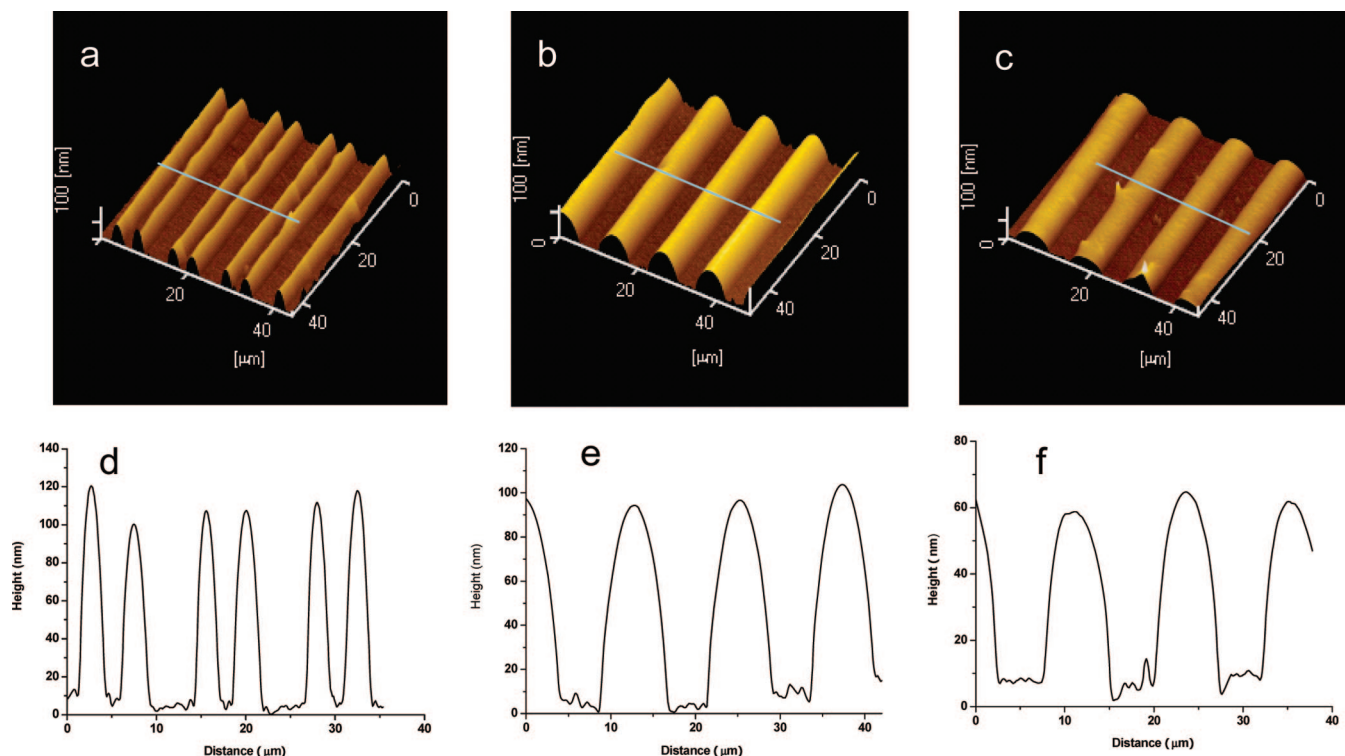


Figure 7. SFM topographical images of the pattern-compressed PEI(PSSMA/PDADMAC)₁₀ multilayers assembled in 0.5 M NaCl solution and dried for (a) 2 h, (b) 6 h, and (c) 12 h. (d–f) Corresponding cross-sectional profiles of a–c, respectively.

150% with no significant difference (Table 1). Between an uncontacting region after drying for 6 h only a single ridge (Figures 5b and 6b) was formed, whose height shows a positive correlation with the salt concentration too (Table 1). However, the ratios between the ridge and the original thickness of the multilayers

decreased from over 300% to ~250% when the salt concentration was increased from 0.3 to 1.0 M. In contrast to the high strips and ridges which are indicative of the lateral flow, the patterns obtained at 12 h drying always have a thickness smaller than their original multilayer thicknesses (Figures 5c and 6c and their

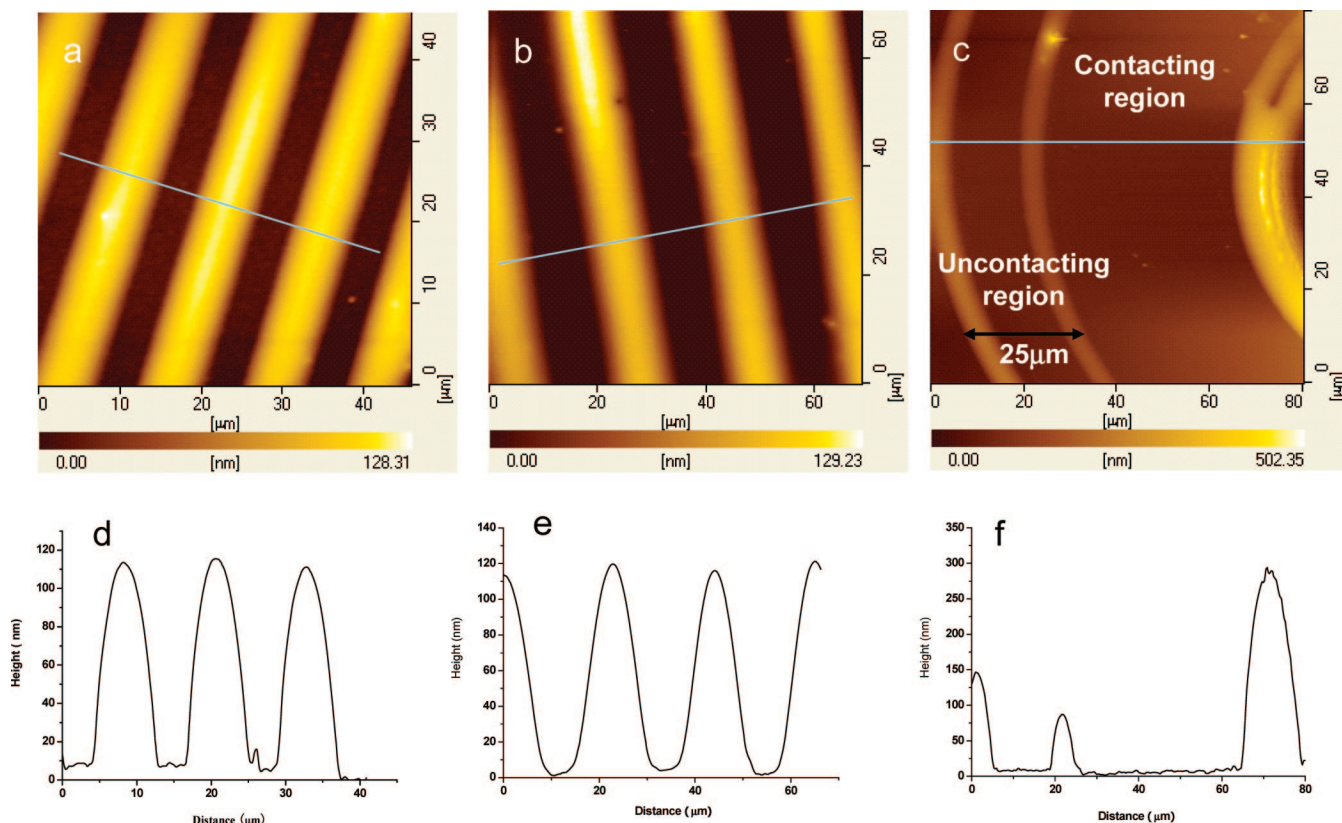


Figure 8. SFM topographical images of the pattern-compressed PEI(PSSMA/PDADMAC)₅ multilayers assembled in 0.5 M NaCl solution and dried for 6 h. The PDMS stamps with different patterns were used: (a) 6 $\mu\text{m} \times 6 \mu\text{m}$ and (b) 10 $\mu\text{m} \times 10 \mu\text{m}$ strip PDMS patterns in width and space and (c) a circular PDMS pattern with increased width and space along its in-plane normal direction. (d–f) Corresponding cross-sectional profiles of parts a–c, respectively.

corresponding line profiles), but the compression ratio was increased from 50 to 90% when the salt concentration was increased from 0.3 to 1.0 M. Although insight understanding of the salt influence still needs further investigation, it is likely that the larger ratio of defects in the multilayers assembled at a higher salt concentration^{52,53} should take a role. The defects can be healed up after compression or lateral flow in some extent, leading to higher compression ratio with lower ridges.

In the next experiment, the layer number was varied at a fixed salt concentration of 0.5 M. Similar to the PEI(PSSMA/PDADMAC)₇ multilayers, the double strips, high ridges, and the compression-created patterns were all formed on the PEI(PSSMA/PDADMAC)₁₀ (Figure 7) and PEI(PSSMA/PDADMAC)₅ multilayers (Figure 8) after drying for 2, 6, and 12 h, respectively, confirming that the layer number is not a decisive factor for these phenomena. Detail analysis (Table 1) indicates that the height of the created patterns at 12 h drying has a positive correlation with the layer number, whereas the compression ratio was within a relatively narrow range of 50–60%. As to the double strips and the single ridges formed at 2 and 6 h drying, respectively, their height ratios to the corresponding thicknesses of the original multilayers decreased markedly along with the increase of the layer number. The ridges (112–120 nm) formed on the PEI(PSSMA/PDADMAC)₅ multilayers are even 5 times higher than that of the multilayers (20.7 nm). Since the same salt concentration is used and the layer number varies within a small range, the ratio of defects in all the multilayers should not have significant difference,^{52,53} as also evidenced by the similar

compression ratio after 12 h drying. The influence of the layer number on the heights of the strips and ridges is not clear so far. One possible explanation could be that the thinner multilayers have better flowing ability and can create larger capillary force,^{54,55} which are beneficial to form the higher structures.

Figure 8 further compares the influence of the PDMS stamps having linear or circular patterns with different width and space. As shown in parts a, b, d, and e of Figure 8, the linear patterns with a width \times space of 6 $\mu\text{m} \times 6 \mu\text{m}$ and 10 $\mu\text{m} \times 10 \mu\text{m}$ created almost the same ridges in terms of height and morphology on the PEI(PSSMA/PDADMAC)₅ multilayers, illustrating that both stamps are capable of creating the nice ridges. As to the circular ring patterned stamp, when the width of the uncontacting region was 15 μm , a very high ridge (300 nm) with a circular shape was successfully obtained (Figure 8c, right side). Yet there already existed the unfilled valley (Figure 8c, upper right-hand corner). However, when the uncontacting region was increased to 25 μm , the uncontacting region could not be fully filled with the multilayers to form a single ridge but instead to form 2 ridges by the edges of the contacting regions (Figure 8c, left). This result reveals that the pressing force which causes the lateral flow has a limited distance. It can hardly work when the distance is above some limit such as 25 μm shown in the present study.

The finding of the drying time dependence of the created structures is not restricted to the PSSMA/PDADMAC system. Similar formation of the double thin strips, high ridges, and patterns as the results of lateral flow and simple compression, respectively, was also observed on other PDADMAC-containing

(52) Klitzing, R. V.; Möhwald, H. *Macromolecules* **1996**, *29*, 6901.

(53) Qiu, X. P.; Leporatti, S.; Donath, E.; Möhwald, H. *Langmuir* **2001**, *17*, 5375.

(54) Suh, K. Y.; Kim, Y. S.; Lee, H. H. *Adv. Mater.* **2001**, *13*, 1386.

(55) Suh, K. Y.; Choi, S. J.; Baek, S. J.; Kim, T. W.; Langer, R. *Adv. Mater.* **2005**, *17*, 560.

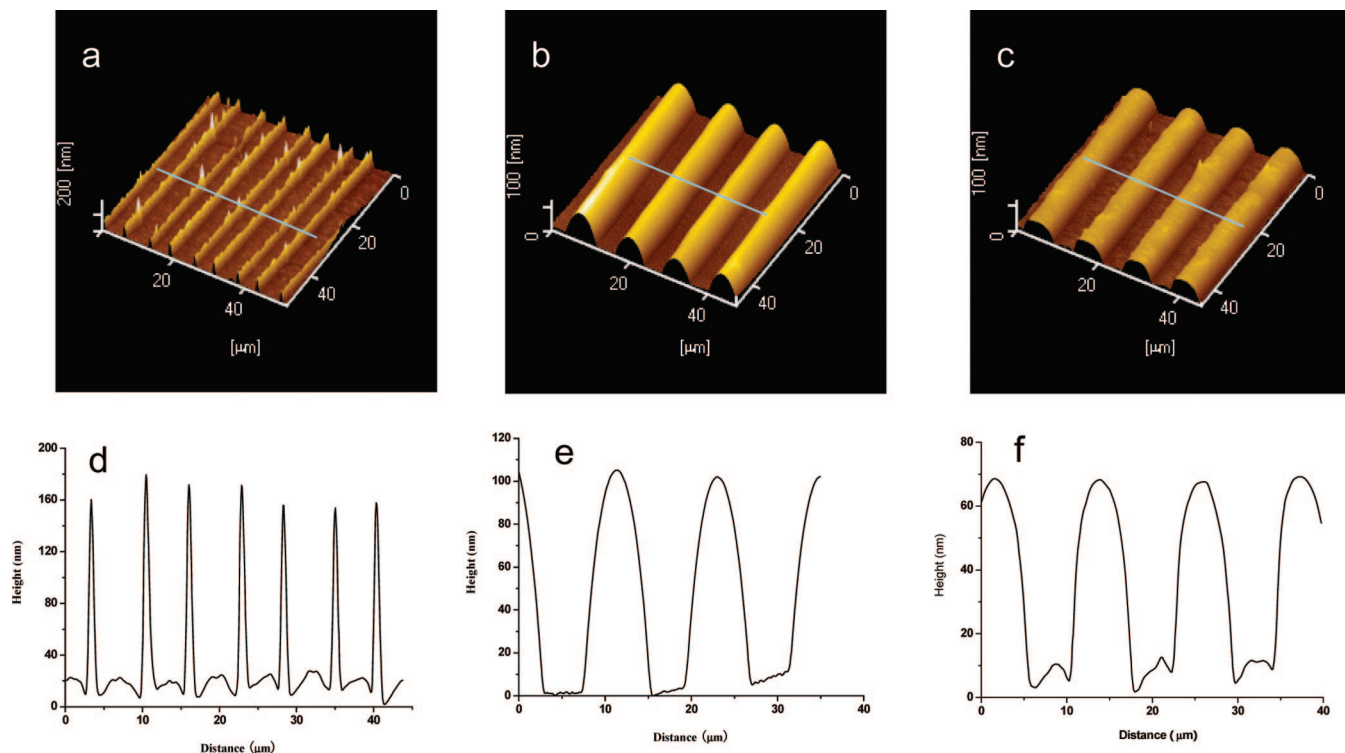


Figure 9. SFM topographical images of the pattern-compressed PEI(PSS/PDADMAC)₇ multilayers assembled in 0.5 M NaCl solution and dried for (a) 2, (b) 6, and (c) 12 h. (d–f) Corresponding cross-sectional profiles of parts a–c, respectively.

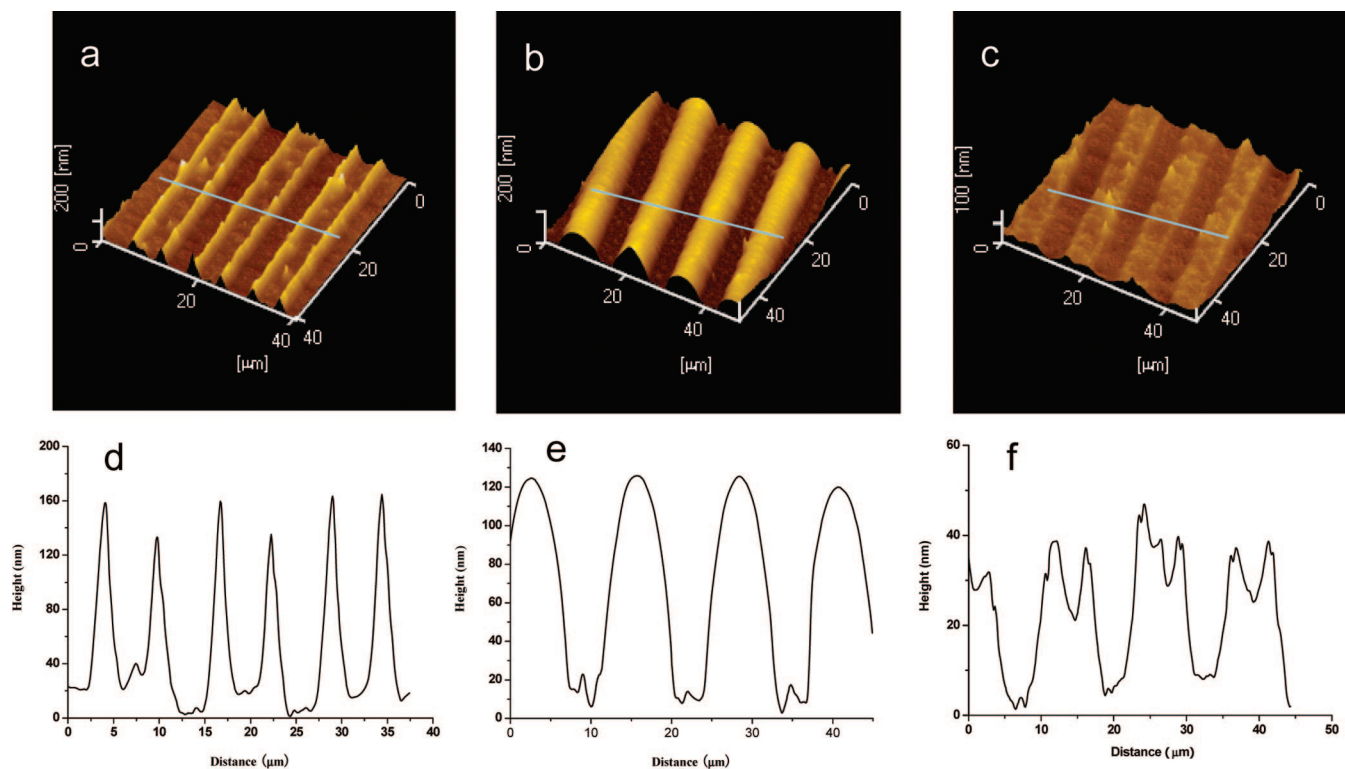


Figure 10. SFM topographical images of the pattern-compressed PEI(PAA/PDADMAC)₇ multilayers assembled in 0.3 M NaCl solution at pH 11 and dried for (a) 2, (b) 6, and (c) 12 h. (d–f) Corresponding cross-sectional profiles of parts a–c, respectively.

polyelectrolyte multilayers such as PSS/PDADMAC (Figure 9) and PAA/PDADMAC (Figure 10). Therefore, the drying time dependency is a universal rather than an occasional phenomenon and can be applied to the PDADMAC-containing multilayers regardless of the other building block, layer number, and salt concentration. Works are still needed to be done to explore if

this phenomenon can be applied to other polyelectrolyte pairs such as PSS/PAH.

Lastly, we examined the stability of the formed structures in water. After incubation for 5 h, the height of the as-prepared strips was largely reduced (image not shown), while the ridges were almost diminished as representatively shown in Figure 11a.

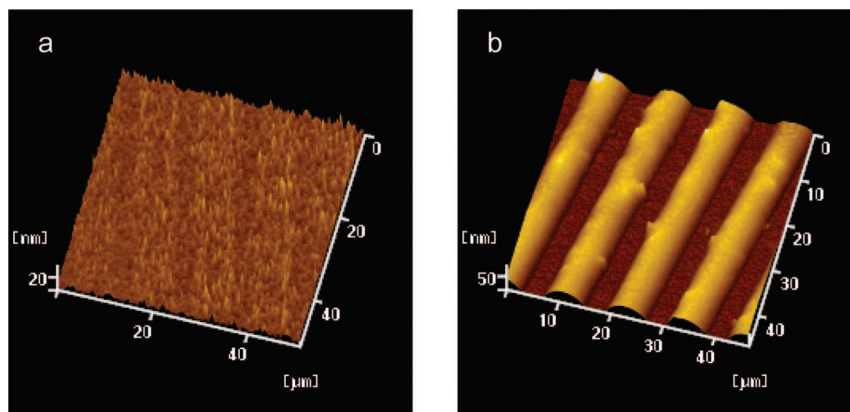


Figure 11. SFM topographical images to show the development of the formed patterns after incubation in water for 5 h. The initial patterns of (a) and (b) were obtained from the PEI(PSSMA/PDADMAC)₇ multilayers assembled in 1 M NaCl solution and dried for 6 and 12 h before the patterned compression, respectively.

By contrast, the patterns created by the compression kept unchanged after the same treatment (Figure 11b). This difference is consistent with their formation mechanism. The ridges formed by the lateral flow are lack of strong interaction and thereby recover their morphology after relaxation in water. However, the compression can make the polyelectrolytes approach closer, forming more permanent electrostatic pairs and hydrophobic interaction which stabilize the compressed structures.³⁴

Conclusion

We find in this work the phenomena of drying time dependency of the patterned structures on polyelectrolyte multilayers with PDADMAC as one building block. Along with the prolongation of drying of the multilayers, compression of the multilayers by a PDMS stamp with linear patterns can create double strips, high ridges, and linear patterns on the PSSMA/PDADMAC multilayers. A model is suggested to depict the process, and the influence of the water content on the multilayer structure and properties is discussed. With relatively higher water content, the multilayers are more likely in a gel-like state, which have a lower strength and easily flow along the lateral direction.

Consequently, the multilayers in contact with the PDMS patterns are pushed to the uncontacting regions, leading to the lateral flow and formation of the ridges whose height is as high as 3–5 times the initial multilayers. After drying for 12 h, the multilayers are more likely in a transition state from the gel to glass, which inhibits the free flow of the whole polymer complex but can permit the movement of the segments. As a result, the multilayers can be permanently compressed in the normal direction. These phenomena are independent of the layer number and salt concentration and can be applied to other PDADMAC containing multilayer systems such as PSS/PDADMAC and PAA/PDADMAC. Because of the lack of strong interaction, the formed strips and high ridges can be erased by incubation in water for 5 h. By contrast, the compression created patterns are very stable.

Acknowledgment. We thank Profs. J. C. Shen and H. Möhwald for valuable discussion and continuous support. This study is financially supported by the Natural Science Foundation of China (Nos. 20774084 and 20434030) and the National Science Fund for Distinguished Young Scholars (No. 50425311).

LA802957R