Force-Free Patterning of Polyelectrolyte Multilayers under Solvent Assistance

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Physical patterns were created on hydrated PSS/PDADMAC multilayers without using external force. A typical process was to put a PDMS stamp onto the wet and swollen multilayers, which were then put into an oven and maintained for a period of time to micromold the multilayers. The influence of molding temperature and time, multilayer thickness, solvent quality, and multilayer compositions on pattern formation were elucidated. Evolution of the patterns from double lines, double strips, and meniscus-shaped ridges to high ridges was observed under all conditions, revealing that this is a universal principle for this process. Finally, patterns on PAA/PAH and PSS/PAH multilayers were also prepared at the optimal conditions, highlighting its wide generality on the multilayer patterning.

Introduction

Layer-by-layer (LbL) assembly, first introduced by Iler[1] and re-established and refined by Decher,[2] has been widely investigated and used to build up ultrathin films on various substrates. It employs different driving forces such as hydrogen bonding,[3,4] covalent linking,[5,6] hydrophobic interaction,[7] and especially electrostatic attraction[8] to sequentially deposit the building blocks such as polymers, multivalent ions, dyes, and nanoparticles. The well-defined nanostructures and properties, including compositions, thickness, surface functional groups, and internal linkage between layers, can be governed by many parameters during the building process and post-treatment, for example, the types of the polyelectrolytes and salts, salt concentration, temperature, pH value, etc.[9–14] Therefore, the polyelectrolyte multilayers (PEMs) have attracted much interest in chemical and biological sensors,[15–17] drug delivery carriers,[18–20] microelectronics,[21,22] nano-optics,[23,24] biomimetics,[25,26] and tissue engineering.[27–29]

On the other hand, the micrometer- and nano-scale patterns are important for a wide range of applications such as integrated circuits, information storage devices, microfluidic devices, sensors, biochips, etc.[30] So far the physical and/or chemical features have been created on the PEMs. Among the techniques employed, the lithographic techniques are more widely adopted for the PEMs, which include surface selective deposition,[31] inkjet imprinting,[32] photopattern technology,[33,34] lift-off technology,[35,36] multilayer transfer printing,[37] and microcontact printing.[38,39] These techniques produce mainly the chemical patterns by chemical bonding and linking of other desirable substances on the PEM surfaces. However, due to the differences of chemical properties among the PEM surfaces, it is hard to find a universal method to pattern most of the PEMs.

In 2004, we reported a phenomenon of irreversible compression of PEMs.[40] In this way, physical features are fabricated at room temperature and a low pressure (200 g cm−2), depending on several factors such as the
multilayer compositions and desiccation conditions before compression. So far we have found that the multilayers assembled with poly(diallyldimethylammonium chloride) (PDADMAC) as one component and dried for 12 h at 40–70% relative humidity (RH) can be compressed with an extent of 70–90%. The vertical compression-induced patterns on the multilayers are chemically homogeneous but physically heterogeneous. The compressed multilayers have caused alterations of their inner structures and properties such as the glass transition temperature ($T_g$), surface roughness, permeability, solubility, and wettabiliy.$^{[41–43]}$ More recently, we have further quantified the influence of drying time on the pattern formation.$^{[44]}$ Along with decrease of the drying time in RH 70%, the water content in the multilayers increases and lateral flow occurs in parallel with the vertical compression, resulting in sharp linear structures and high ridges whose height is several times higher than that of the PEMs.

Another method to make the physical patterns on the PEMs has been reported recently by Lu et al.$^{[45–47]}$ by room-temperature nano-imprinting lithography, which can be applied to almost all kinds of the multilayers including the hydrogen bonded ones. The appropriate water content in the film can facilitate the multilayer films to be imprinted at room temperature; however, the films dried in an oven or a nitrogen stream could not be imprinted. Since the height of the patterns after imprinting is much higher than that of the original multilayers, the pattern formation is not only the result of direct vertical compression of the films but also the result of lateral flow toward the non-contact regions under a high pressure.

Recently, Hammond and coworkers$^{[48]}$ developed a simple method to imprint the PEMs by capillary force with the assistance of water vapor. Consequently, only a few bars were required to prepare the same patterns. Although patterns of different heights were created by changing the molding time, several hours were needed to obtain higher patterns.

All the results reveal a fact that the solvent may take the most important role than others such as pressure in the multilayer patterning. It is understandable that the water decreases viscosity of the PEMs, which in turn facilitates the movement of the multilayers during the micromolding process.$^{[40]}$ However, by all the previous micromolding methods the multilayers are equilibrated in humid air and therefore a relatively long time (at least several hours) and some extent of pressure are needed. In contrast, in liquid water the swelling finishes within the first minutes$^{[49]}$ and achieves the greatest extent, which offers great ease on the micromolding. Therefore, in this work we directly put the stamp onto the PEMs which are highly swollen by solvent, and then place the system into an oven without involving any external force to make the physical patterns within minutes. As shown in Figure 1, along with evaporation of the solvent, water for example, driven by capillary force lateral flow of the PEMs from the contacting regions to the uncontacting regions of the polydimethylsiloxane (PDMS) stamp shall occur. After complete drying and removal of the PDMS stamp, a negative structure of the PDMS is formed on the PEMs. By this method, no external force is necessarily applied, and the micromolding time can be substantially reduced from hours to minutes (≈15 min). Moreover, the pattern features can be easily tuned by the factors such as molding temperature and time, multilayer thickness, as well as solvent quality, for example, ethanol solution. Besides the PDADMAC-containing PEMs, this method can also be applied to other PEMs such as poly(acrylic acid) (PAA)/poly(allylamine hydrochloride) (PAH) and poly(styrene sulfonate) (PSS)/PAH, demonstrating its generality.

**Experimental Part**

Polyethyleneimine ([PEI], $M_w \approx 25$ kDa), PDADMAC ($M_w \approx 200–350$ kDa), PSS ($M_w \approx 70$ kDa), PAH ($M_w \approx 15$ kDa), and PAA ($M_w \approx 30$ kDa) were obtained from Aldrich. The polyelectrolytes were prepared into 1 mg mL$^{-1}$ aqueous solutions optionally supplemented with NaCl, whose pH values were adjusted with HCl and NaOH. PDMS prepolymer were obtained from Dow Corning. Sylgard 184. Quartz and silicon wafers (1 × 2–3 cm$^2$) were cleaned in Piranha solution [H$_2$SO$_4$ (concentrated)/H$_2$O$_2$ (30%) = 7:3 v/v. Caution: Piranha solution is a strong oxidizer and should not be stored in a closed container]. After rinsed in copious amount of water, they were dried with a smooth stream of N$_2$.

To ensure the successful adsorption, a precursor layer of PEI was deposited on the silicon wafers. Sequential adsorption of the polyelectrolytes was then performed by manually dipping. Both...
PSS and PDADMAC were dissolved in 1 M NaCl. Between alternate exposures to two kinds of polymer solutions for 20 min, there were three rinses with 0.1 M NaCl solution for 3 min. At the last step, the films were rinsed with triple-distilled water for at least 5 min to eliminate the adsorbed salt. The multilayers are represented as PEI(PSS/PDADMAC)$_n$, where $n$ denotes the number of PSS/PDADMAC bilayers. The PSS/PAH multilayers were assembled in 1 M NaCl and rinsed with 0.1 M NaCl solution. The PAA/PAH multilayers were assembled at pH $= 3.5$ PAA and pH $= 7.5$ PAH solutions, respectively, and were rinsed with triply distilled water.

The PDMS stamps with strips were molded from lithographically prepared masters.$^{[50,51]}$ The flat stamps were obtained after the prepolymer was cured between two flat glasses. Before patterning, a drop of water or ethanol solution was dropped on the surface of the PEMs, and then a PDMS stamp (typically $0.5 \times 0.5–0.8 \times 0.8 \text{cm}^2$) was carefully put onto the wet PEMs (make sure no bubble existed between the PEMs and the PDMS). They were immediately put into an oven at a given temperature and maintained for a period of time to ensure complete evaporation of the water. Finally, the stamps were carefully peeled off to obtain the patterned multilayers. During this process, no external pressure was applied except for the PSS/PAH multilayers.

Thickness and refractive index of the PEMs were determined from 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 400–1700 nm. The thickness and refractive index were calculated from the ellipsometric parameters, $\Delta$ and $\psi$, by using a Cauchy model.

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 of 150 kHz and a spring constant of 20 N m$^{-1}$ were utilized. The scanning frequency was 1 Hz. The contact force between the tip and the samples was kept as low as possible ($<2.5$ nN). The samples were scanned randomly on the patterned surface, except of the edge area.

UV-Vis spectra were obtained from a UV-Vis spectrophotometer (Shimadzu, UV2550) within a wavelength range of 200–400 nm to detect the absorbance of the benzene ring of PSS at 225 nm.

**Results and Discussion**

**Characterization of the PEMs and Pattern Formation**

Alternative assembly of PSS and PDADMAC on PEI covered silicone slides yielded PEI(PSS/PDADMAC)$_n$ multilayers with a smooth surface morphology, as shown in Figure 2a. Their thickness was measured by both atomic force microscopy (AFM) and ellipsometry, giving a very close value. For example, 205 (Figure 2b) and 198 nm (Figure 2c) were measured for the PEI(PSS/PDADMAC)$_7$ multilayers by AFM and ellipsometry, respectively, confirming the reliability of AFM on characterization of the multilayers and pattern height. The thickness of the PEI(PSS/PDADMAC)$_n$ multilayers exhibited an exponential growth behavior as a function of bilayer number (Figure 2c), which is understood as a result of interpenetration of the polyelectrolytes in their neighboring layers.$^{[52,53]}$

Micromolding of the PEMs has been well established so far, exclusively on the basis of external force up to tens of atmosphere pressure. The high pressure could lead to asymmetric patterns and breakage of the substrates or the hard molds in some cases.$^{[154]}$ To create pattern structures by force-free micromolding, the PEI(PSS/PDADMAC)$_n$ multilayers were first covered with a water layer, onto which a PDMS stamp with a physical pattern structure of strips was put closely. For a typical process, the system was then placed into an oven at 70 °C for 30 min (Figure 1). Since the
strip height of the PDMS stamp was much higher (2 μm) than that of the PEMs, the water could evaporate through the gap between the multilayers and the PDMS during this process. The PDMS was then peeled off carefully, leaving behind strip patterns on the PEMs. Here no external force was necessarily applied, since the multilayers were highly swollen and plasticized by the water, resulting in softer materials which are easily molded by capillary force. As shall be demonstrated in the following study, it is very powerful to obtain the physical patterns with different topography and height on the PEMs at very short time and simple conditions.

**Influence of Molding Temperature**

To demonstrate the ease of control over the pattern height and topography, the molding temperature and molding time were varied during the process of micromolding. Firstly, the assembled PEI(PSS/PDADMAC)₇ multilayers were molded in an oven at 23, 31, 40, 50, 60, and 70 °C for long enough time until the water were fully evaporated, respectively (Figure 3a). At 23 °C, the height difference between the middles of the uncontacting areas and the contacting areas (the so-called pattern height) was only about 14 nm, forming simultaneously double line stripes at the edges of the PDMS with a height of ≈50 nm over the middles of the uncontacting areas (Figure 3b). When the temperature rose to 40 °C, the pattern height reached to 59 nm. The double line stripes appeared also with a height of 90 nm. At 50 °C, the line stripes disappeared, and the height of the ridges was further increased to 149 nm (Figure 3c). When the temperature was increased to 60 and 70 °C, the pattern height was pronouncedly raised to 249 ± 29 and 320 ± 45 nm, respectively, which were higher than that of the initial multilayers (≈200 nm). At 90 °C, however, the PEMs were broken and detached from the substrates as also previously observed by Qin et al. In this sense, the process may also be universally applied to determine the Tₘ of ultrathin polymer films. However, clear patterns could still be created below the Tₑ, e.g., at 23 °C, confirming the macroscopic fluidity of the PEMs at this temperature. Since the multilayers were in a highly swollen state, the superficial molecules, whose Tₑ are generally lower than that of the bulky materials, could still possess the ability of movement, in particular under the capillary force produced during the dehydration process. Actually, this could be comparable to the Vicat deflection measurement. When the PSS/PDADMAC multilayers were treated in water with an extremely high temperature, i.e., 90 °C, they were damaged and detached from the substrates as also previously observed by Qin et al. Nevertheless, an appropriate molding temperature can facilitate the fluidity of the multilayers and thereby is favor of formation of high patterns.

**Influence of Molding Time**

In the next experiment, the molding time was varied at a fixed temperature of 70 °C. In this process, 4 μL water was dropped onto the PEI(PSS/PDADMAC)₇ multilayers and the size of the PDMS stamp was fixed at 0.5 × 0.5 cm². After incubation at 70 °C for a given time period, the stamp was peeled off quickly and the water was blown dried by N₂ flow immediately, if any. When the molding time was below 12 min, no clear pattern was found on the PEMs (Figure 3d and e). By contrast, when the molding time was extended to...
15 min, the ridge-like patterns were obtained immediately (Figure 3d and f). The pattern height (295 ± 67 nm), which was consistent with the previous experiment at 70 °C for 30 min, kept almost unchanged at still longer molding time (Figure 3d). This is reasonable since the polymer chains are frozen and the patterns are fixed upon complete evaporation of the water. On the other hand, if plenty of water is remained, the pattern cannot be formed as reported previously.[40] Actually, before 12 min water could still be seen on the multilayers after the PDMS was peeled off. There might be two possibilities for the “unobserved patterns”: (1) no patterns are formed at all; (2) the formed patterns are not stable and recovered upon peeling off PDMS in the existence of water. To answer this question, after molded for 10 min the system was frozen at 0 °C so that recovery of the patterns could be restricted. The multilayers were then blown dried. No patterns were found on these multilayers either. Therefore, the pattern should be formed within a very short period, most possibly upon full evaporation of the liquid water.

**Dependence of Bilayer Number**

Another way to control the pattern height is alteration of the initial thickness of the multilayers, e.g., the deposition cycles. Figure 4a shows that the pattern height was increased along with the deposition cycle, following a very similar profile as that of the film thickness (Figure 2c). For example, for the PEI(PSS/PDADMAC)n multilayers, the pattern height was only 15–19 nm, accompanying with appearance of the double thin strips with a height of 27–38 nm at the contacting edges to the PDMS stamp (Figure 4b). When the bilayer number was 4, the pattern height was increased slightly to 24 nm, but the height of the lines was pronouncedly increased to ≈100 nm. The double thin strips disappeared and the pattern height was increased remarkably upon the bilayer number over 5, forming smooth and uniform ridges (Figure 4c). On the 10 bilayer PEMs, the ridge height was as high as 795 nm (Figure 4d). It is understandable that a thicker film has plenty of mass to be filled into the uncontacting areas under the capillary force, and thereby high ridges can be formed. This result discloses that the pattern height as well as the pattern structure can be easily tuned by the initial multilayer thickness, which is very facile to control.

**Driving Force for the Micromolding**

So far by this molding method, clear patterns have been successfully fabricated on the PEI(PSS/PDADMAC)n multilayers at very mild conditions. In order to demonstrate this is a true “force-free” molding process, the minor contribution of weight of the PDMS stamp was further ruled out by inversely putting the PDMS stamp on the wet PEI(PSS/PDADMAC)n multilayers. They were then put on the edge of an empty chamber (Figure 5a). The PDMS still could stably adhere onto the PEMs by overcoming its gravity in the existence of water. After treatment at 70 °C for 1 h, regular ridges with a height of 300 ± 22 nm were similarly created on the PEMs (Figure 5b and c), which were exactly same as those fabricated by the normal way shown in Figure 1 and 3f. Therefore, in this force-free molding process, no external force is needed to create the patterns.
Nevertheless, force must be applied to direct the flow or movement of the PEMs so that the physical patterns can be eventually formed. This is contributed by the capillary force between the PDMS stamp and the PEMs. It is known that the capillary pressure of drainage between two planes separated by distance $l_z$ (Figure 1a) creates the force. The capillary force which pulls the two planes toward each other is inversely proportional to the distance $l_z$. When the water layer between the PDMS and the PEMs remains thick, very small capillary force shall be produced, which is difficult to push the contacting PEMs into the voids during the molding. When the water evaporation approaches completely, i.e., the water layer is very thin, the capillary force becomes big enough to cause lateral flow of the PEMs, resulting in the high ridges consequently. During this process, vertical compression of the multilayers at the contacting regions and lateral flow toward the uncontacting reasons should occur simultaneously, yielding ridges higher than the multilayer thickness. Since the compression alone can yield patterns whose height is smaller than that of the multilayers, we believe that the lateral flow should dominate this process. According to this analysis, the water here takes two roles: plasticizer for the PEMs and the medium providing big enough capillary force. Both are necessary for making the physical patterns.

The molding process preserves almost all the mass of the multilayers, as demonstrated by the following experiment. After the PEMs were molded with a flat PDMS following the same process, their thickness was reduced to 90% of the original value. UV-Vis characterization found no mass loss by referring to the absorbance at 225 nm, which is assigned to benzene ring of the PSS molecule. The PDMS stamp used here had low surface energy, and thus was very easily released after molding although it adhered tightly to the PEMs during the molding. If the PDMS stamp was treated with plasma to endow its surface with better hydrophilicity, it was hard to be peeled off after molding because of the stronger interaction, which was observed previously too. In this case, the PEMs are usually torn off and adhered to the PDMS surface, as were the quartz and the glass stamps.

### Influence of Solvent Quality

So far only water could be used as the plasticizer for micromolding the PEMs by methods of compression and imprinting. To the best of our knowledge, organic solvents, which were usually used to regulate thickness, porosity, and mechanical properties of the PEMs, have not been used to assist patterning of the PEMs by any of the above methods. In this study, we found that the pattern height and topography could also be conveniently controlled by using ethanol solution. Ethanol can be ideally mixed with water, and does not swell the PDMS stamp (if swelling of the stamp does occur, the microstructures will be distorted). Moreover, since the evaporation rate of ethanol is faster than that of water, the ethanol content...
used here was over 50%, otherwise at the last stage only water was remained in the PEMs. Figure 6 presents the molded PEI(PSS/PDADMAC)_{10} multilayers by the force-free method at 70 °C for 0.5 h using different concentration of ethanol solution as the solvent. When the PEMs were molded with 50% ethanol solution, the uniform ridges were formed with an average height of 771 ± 106 nm (Figure 6a), which was same as that molded with pure water (Figure 4d). Molded with 75% ethanol solution resulted in the same result too. When the ethanol concentration was increased to 90%, the pattern height was dramatically decreased to 60 ± 21 nm, and the pattern topography was changed to double line strips with a height of 437 ± 245 nm too (Figure 6b). At 95% ethanol concentration, the height of the contacting regions was same as the uncontacting ones, and only thin lines at the contacting edges with a height of 117 ± 13 nm remained (Figure 6c). Furthermore, 100% ethanol could not obtain any clear patterns. Most organic solvents like ethanol have much smaller dielectric constants compared with pure water, and thus can decrease electrostatic intra- and interchain repulsions and enhance hydrophobic interactions between the polyelectrolyte chains. Therefore, it has weaker swelling effect to the multilayers as the water, and may not effectively decrease the $T_g$ of the PSS/PDADMAC multilayers. The faster evaporating rate of ethanol leaves shorter time for the multilayers to re-arrange their confirmation and to flow too. Moreover, its lower surface tension creates smaller capillary force. All are disadvantageous for making the patterns. Nevertheless, the results confirm that both the pattern topography and height can be easily tuned by the quality of solvents as well.

Micromolding of the PEMs was further studied by addition of 95% ethanol solution from one side of the PDMS stamp for several times. By this way, the PDMS stamp was not peeled off after the solvent was evaporated completely. Instead, another drop of 95% ethanol solution was dropped on one side of the PDMS stamp (Figure 7a). By capillary effect, the open channels between the PDMS stamp and the PEMs could spontaneously suck in the ethanol solution of low surface tension. After the multilayers were molded in the oven, 95% ethanol solution was repeated dropped as above, and totally 3 times of solution dropping were performed. As shown in Figure 6c and 7b–d, along with increase of the addition time, the pattern topography and height regularly changed from thin double lines, double strips to meniscus-shaped ridges, and finally to uniform high ridges. Since ethanol is evaporated very fast, the action time of capillary force is rather short. Repeating addition of the ethanol solution is equal to prolongation of the action time. It is also possible that the water content in the PEMs is increased to some extent after repeating addition of the ethanol solution, since water may have stronger interactions with the PEMs and thus evaporated more slowly. Both are beneficial of lateral flow of more PEMs, and thereby the various patterns are progressively formed depending on the addition times.

**Mechanism of the Pattern Formation**

The above results unveil that formation of the final high ridges experiences all the previous stages, in other word, the double lines, double strips, and meniscus-shaped ridges can all be regarded as the intermediate stages of the high ridges. Different types of patterns are thus formed when the process stops at different points. In summary, evolution of the pattern topography is universal for this type of force-free micromolding process as a function of temperature (Figure 3a), bilayer number (Figure 4a), ethanol concentration (Figure 6), and addition time of ethanol solution (Figure 7). Similar phenomenon has also been observed by changing the molding time when the polyelectrolyte multilayers were patterned in a saturated water vapor environment. Therefore, it unveils a common physiochemical mechanism, which is believed to be decided by the lateral flow of the PEMs. When the lateral flow is hard to take place at lower temperature,
thinner layer thickness, or higher ethanol concentration, the capillary effect drives the PEMs to climb up the well walls of the PDMS stamp to some extent, resulting in thin double lines and strips (Figure 8a and b), a typical morphology formed by capillary force. For the thinner PEMs, there is another reason that the available mass for the lateral flow is not sufficient enough. This was also evidenced when the distance between the uncontacting features of the PDMS stamp were large enough, in which only high strips (Figure 9) were formed even at the suitable micromolding conditions. It is worth mentioning that the very inner layer of the PEMs contributed by PEI and PSS on the substrate are rather stable and thereby are not easy to flow as the upper ones, which provide sufficient stickiness for final formation of the patterns. At the conditions such as a higher temperature and water content, and a larger layer thickness, the PEMs are sufficiently plasticized in a state above the \( T_g \) and thus soft enough, leading to ease of deformation and lateral flow under the capillary force. Consequently, uniform high ridges are eventually formed (Figure 8d). During this process, all the PEMs regardless of their positions move toward the center of the microwells. Due to geometric restriction of the stamp, some PEMs at the contacting regions are pushed to the uncontacting voids, forming the segregated pattern structure. In between these two topographies are the meniscus-shaped ridges (Figure 8c), which are formed by the incomplete filling of the microwells as a result of certain degree of lateral flow of the PEMs. We have shown in this work that all these topographies can be facially obtained in a controlled manner.

**Generality of the Micromolding Method**

This patterning method can also be applied to other PEMs systems such as PAA/PAH and PSS/PAH (Figure 10). The PEI(PAA/PAH)\(_7\) multilayers (initial height 140 nm) could be easily molded at 90 °C to form high ridges with a height of 110 nm. For the PEI(PSS/PAH)\(_7\) multilayers, the molding was performed at 90 °C for 30 min under the assistance of minor external pressure (0.08 MPa or 800 g·cm\(^{-2}\)). Figure 10b shows that clear patterns with an average height of 17 nm were formed. A comparable study showed that clear patterns were hardly formed on the PSS/PAH multilayers without external force. These results reveal also the different structures and properties of the multilayers assembled from different building blocks. It is known that the PSS/PDADMAC multilayers are much softer than the PSS/PAH multilayers, since the distribution of charges along the PDADMAC chain mismatch with that of PSS. Other study has also observed that the PSS/PAH multilayers are more resistant to force-induced deformation, even at higher pressure (0.5 MPa) for a prolonged period of time, since they are more hydrophobic and tougher compared with the PAH/PAA and the PDADMAC containing multilayers. Therefore, the only PSS/PAH physical patterns were fabricated by imprinting at a high pressure previously. In this study, the existence of water and high capillary temperature can enhance mobility of the PEMs. The capillary force and the minor external pressure can then compress the PSS/PAH multilayers vertically, leading to pattern formation. Therefore, the micromolding technique reported in this study can be widely applied to PEMs of different compositions and properties under the assistance of solvents and capillary force, without or with only minor external forces.

**Conclusion**

Herein we report a force-free micromolding technique to prepare various patterns on PEMs under the assistance of water and elevated temperature. During this process no
Figure 10. AFM topographical images of (a) PEI(PAA/PAH)7 and (b) PEI(PSS/PAH)7 multilayers with an original height of 140 and 48 nm after micromolding at 90 °C, respectively.

Studies also found that evolution of these pattern topographies is universal for the force-free micromolding process; formation of the final high ridges experiences all intermediate stages of the high ridges. Different types of patterns are thus formed when the process stops at different points. All these results confirm that this micromolding technique is a simple but versatile method to pattern the multilayers, with the merits of force-free, shorter molding time, mild conditions and easy operation, and is expected to be used to prepare functional structures for various applications.

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