Compression-Inhibited Pore Formation of Polyelectrolyte Multilayers Containing Weak Polyanions: A Scanning Force Microscopy Study


Morphological changes of poly(acrylic acid)/poly(diallyldimethylammonium chloride) multilayers induced by low pH were investigated by scanning force microscopy. The weakened interaction between the charged polymer chains in the protonation process is believed to be the reason for this variation. Kinetic studies have shown that during protonation phase separation and dissociation of the multilayers took place successively. The compression of the multilayers, however, caused a transition of the multilayers from a rubbery state to a glassy state. As a result, the closely compacted multilayers lost their sensitivity to pH change. An increase of electrostatic and hydrophobic interactions, can decrease the free energy of the multilayers, and stabilize the films. By compression of the multilayers with a rubber stamp having geometric patterns, films with spatially localized pores were produced.

1. Introduction

Over the past decades, electrostatic layer-by-layer (LbL) assembled multilayers have attracted much interest.[1] In the deposition process, oppositely charged species are adsorbed on a substrate sequentially. This simple method has several advantages over other surface modification approaches. Firstly, it is quite convenient to design, modify, and functionalize the surfaces without involvement of harsh conditions. Extensive studies have been carried out to introduce small organic molecules or inorganic compounds, bio-macromolecules, dendrimers, and colloids or latex particles into the layered architectures.[2] Compared with physical adsorption, more substances can be deposited in the multilayers. Secondly, both the molecular organization and the properties of the multilayers can be tuned easily by assembly conditions or post-treatments, such as salt concentration and pH value. The most typical example is the pH-controlled assembly of weak polyelectrolytes, originally developed by Rubner and co-workers.[3] The substance encapsulation in microparticles, with polyelectrolyte multilayers (PEMs) as walls, is also established based on tunable permeability in response to stimuli.[4] Thirdly, the Lbl assembly is a low-cost, environment-friendly, wet-bench technique that can be employed in industrial processes. CIBA-Vision has announced the first commercially available product that is equipped with a multilayer coating in 2002.[1] Moreover, all proteins and most polysaccharides are polyelectrolytes as well. Studies of the PEMs also provide meaningful information to understand biomacromolecules adsorbed on surfaces and interfaces. Finally, as the thickness of the multilayers can be varied from nanometer to micrometer scales, it is possible to fabricate three-dimensional structures on surfaces by the LbL technique. Patterned assembly[5] and compression[6] are two typical examples.

Recently, we have reported the irreversible compression of polyelectrolyte multilayers assembled with poly(diallyldimethylammonium chloride) (PDADMAC) by pressing a poly(dimethylsiloxane) (PDMS) stamp against the films.[6] The compression extent varies from several to hundreds of nanometers showing a positive correlation with the multilayer thickness, which can normally be tuned by the layer number or salt concentration. The effect of the desiccation degree on the ability of the compression illustrates that the structural water content plays an important role for the intrinsic properties of PEMs. The number of water molecules associated with one ion pair in a polyanion/polycation complex has been measured independently by Decher[7] and Schlenoff.[8] The average water content inside the fully hydrated films is larger than 40% by volume. Consequently, the film thickness is reduced by 30% after drying.[7]

Small hydrophilic dye molecules are further used to study the volumetric behavior of the compressed PEMs.[9] The diffusion coefficient of the probe decreases dramatically and loses the sensitivity to salt addition after compression.[10,11] It is understandable that the compression leads to shrinkage of the vacancies in the PEMs. Here, the concept of free volume can be applied to some extent.[12]

Herein, the effect of the compression on pore formation of the poly(acrylic acid) (PAA)/PDADMAC multilayers will be reported. As visualized and analyzed by scanning force microscopy (SFM), pores with a diameter of microns in the control PAA/PDADMAC multilayers were identified as a result of pH varia-
tion. However, the compression of the multilayer film completely inhibits the emergence of the pores. It shall be demonstrated that the compression induces a transition from a rubbery state to a glassy state by desolvation. A thermodynamic analysis based on a free energy model for compression has been adopted to explain the results accordingly.

2. Materials and Methods

2.1 Materials

Polyethyleneimine (Aldrich, PEI, $M_n$ 60 000, $M_w$ 750 0000), PDADMAC (Aldrich, $M_n$ 200 000–350 0000) and PAA (Fluka, $M_w$ 20 000, if not otherwise indicated) were used as received to prepare $10^{-4}$ M aqueous solutions, supplemented with 0.3 mM sodium chloride (99 + %). The pH value of the solution was adjusted to 11 by adding trace amounts of sodium hydroxide which did not affect the ionic strength. Under these assembly conditions, thickest multilayers were obtained. Poly(dimethylsiloxane) (PDMS) prepolymers were obtained from Dow Corning, Sylgard 184. Silicon wafers were cleaned in 70% H$_2$SO$_4$ (concentrated)/30% H$_2$O$_2$(aq.) (“piranha”, caution: piranha is a strong oxidizer and should not be stored in a closed container) and then in hot H$_2$O$_2$/ammonia/water, 1:1:5 (vol/vol), rinsed in water, and dried in a nitrogen stream.

2.2 Methods

Assembly

To obtain a homogeneous growth of the multilayers, a precursor layer of PEI was deposited on the pre-treated substrate. Sequential adsorption of the polyelectrolytes was performed by manual dipping. Between alternate exposures to two kinds of polymer solutions for 20 min, there were 3 rinses, each for 3 min. Then the films were dried under the desired relative humidity for 12 h.

Compression

A PDMS stamp with holes each measuring 50 $\mu$m in diameter, 10 $\mu$m in space and 4 $\mu$m in height, was molded from lithographically prepared masters. The stamp was then pressed on the multilayers with a normalized pressure of 200 g cm$^{-2}$. The pressing time was 20 min.

SFM Imaging

Topographic images as well as phase images were collected simultaneously using a SPI3800N Probe Station and a SPA400 SPM Unit (Seiko Instruments Inc.) in dynamic force mode. Silicon tips with a resonance frequency $f_0$ of 150 kHz and a spring constant of 20 N m$^{-1}$ 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).

Film Thickness Measurements

To measure the film thickness, parts of the multilayers were scratched off using a razor blade. The SFM probe tip was then scanned across the newly exposed regions to verify that very little, if any, material was left. The height of the film above the substrate was thus obtained directly. To verify the reliability of the method, a fresh silicon wafer was similarly scratched and examined. No visible scratch or damage was detected. The thickness measurement of PEI(PAA/PDADMAC)$_7$ is shown in Figure 1 as an example.

Figure 1. a) The thickness of PEI(PAA/PDADMAC)$_7$ was measured by SFM after scratching off all the polyelectrolyte multilayers from one area. The rectangular box depicts the area where the average cross-section (indicated by the dashed line) was taken along the direction of the arrow. b) The average cross-section which is more representative than a simple linear cross-section, since every point in the profile is an average of all the points on the dashed line. It is worth noting that the high ridge with a width of 10 $\mu$m at the step edge should be ignored for thickness measurements, since it is the buildup of materials which was removed from the substrate. Because neither the film surface nor the scratched region was perfectly flat, the film thickness was averaged from several samples.

Lateral Force Measurements

To investigate the relaxation behavior of the multilayer surface, frictional force measurements were carried out at 20°C in a closed chamber with certain humidity. The lateral force curve was obtained in contact force mode under a repulsive force of 25 nN. A triangle 100 $\mu$m cantilever with a force constant of 0.09 N m$^{-1}$ and an integrated silicon nitride (Si$_3$N$_4$) tip were applied. The magnitude of the lateral force was evaluated with the line scan mode. The scan rate is equal to $2 \times$ (scan length) $\times$ (scan frequency). Six friction loop cycles were averaged for every measurement to improve the signal-to-noise ratio.

Surface Spectrum

The topographic images were transformed into digital data by FIS ASCII converter (Seiko Instruments Inc.). The “height spectroscopy” data, that is, the histograms of the number of image pixels in incremental height intervals were calculated by SPSS (Statistical Program for Social Sciences).
Based on the analysis in ref. [17], power spectral density (PSD) functions were determined as follows by a homemade computer program. A two-dimensional fast Fourier transformation algorithm was applied to the SFM image data, followed by calculations of the squares to obtain density values. Then all the values were normalized to the scanned area. The mathematical description of this process is presented in Equation (1):

\[ I(f_x, f_y) = \frac{1}{L_x L_y} \left[ \sum_{m=1}^{N_x} \sum_{n=1}^{N_y} z_{mn} e^{-2\pi i (f_x m + f_y n)} (\Delta L)^2 \right] \]

where \( I(f_x, f_y) \) denotes the two-dimensional PSD, \( L_x \) is the scanned area, \( N \) is the number of data points per line and row, \( z_{mn} \) is the height value at position \((x=m, y=n)\), \( f_x \) and \( f_y \) are the spatial frequencies in the \( x \) and \( y \) directions, and \( \Delta L \) is the sampling distance. The transformation was followed by a transition to polar coordinates for the frequencies. The final PSD function was obtained by angular averaging (Eq. (2)):

\[ I(f) = \frac{1}{2\pi} \int_0^{2\pi} I(f_x, f_y) \, df_y \]

### 3. Results and Discussion

At an assembly condition of 0.3 M NaCl and pH 11, PEI(PAA/PDADMAC) multilayers exhibit flat and featureless surface morphology as visualized by SFM (Figure 2a). The thickness of the films is on the order of 64 ± 5 nm (Figure 1). Since the ionization degree of PAA is pH sensitive, it should, in principle, be possible to modulate electrostatic interaction of the PAA/PDADMAC chains by controlling the solution pH. By immersing the film assembled at pH 11 into a solution of pH 5 for 3 min, large granular features with dimensions from several tens to hundreds of nanometers were formed (Figure 2b). Moreover, retuse pits with depths of nanometers and diameters of micron scale were observed. However, the flat regions still kept their original thickness without detectable variations. By prolonging the time to 15 min, a highly porous microstructure was observed as depicted in Figure 2c. The length scale of the pores is 1-5 μm with a characteristic depth around 50 nm, which is only slightly lower than the original film thickness. On the other hand, the thickness of the protuberant parts remains almost as constant as the original PEM thickness. When the treatment time was extended to 30 min, a vermiculate surface morphology was observed (Figure 2d). This interesting morphology has been reported for poly(4-styrenesulfonic acid) (PSS)/PDADMAC multilayers assembled in high salt concentrations, and is probably caused by aggregation of polymers.[15] However, in our case, the thickness of the film decreased to 17 ± 3 nm, only ≈25% of the original thickness. This observation is consistent with the ellipsometry results measured by Schlenoff and co-workers.[13] Even though the possibility of some shrinkage of the multilayers cannot be ruled out absolutely, the loss of the polyelectrolytes at low pH values was confirmed by this series of measurements.

This process can be analyzed via the PSD function (Figure 2) as well. The PSD gives the power of each of these constituted waveforms, and hence, allows the analysis of the most frequent wavelength and conveys the greatest influence to the surface topography. The spatial frequency is the inverse of the in-plane spatial wavelength of the roughness features. The most interesting result is that the power of the surface, which was treated with a pH 5 solution for 15 min (Figure 2c), concentrates in the low-frequency region, indicating that the surface presents a periodicity to some extent. The intensity at a high spatial frequency increased upon acidic solution treatment (Figure 2b). This shows quantitatively that the roughness increases dramatically, mainly due to random features of very small length scale. However, the PSD functions retained the tapered profiles regardless of the duration of the treatment, which is characteristic of isotropic surfaces. These plots confirm that the images consist of a composite of multiple waveforms.

By magnifying the pore structure (Figure 2c) as shown in Figure 3, the remaining polyelectrolytes at the bottom of the pores showed up clearly. Furthermore, the morphology at the pore bottom was not uniform. Instead, some small pits were found as indicated by the arrows in Figure 3b, which were imprinted by the released polyelectrolyte complexes. The height spectrum shows that pores occupy ≈20% of the surface area (Figure 3c). This pore structure is quite interesting and regular/ reproducible. In the sections below, it is considered as a measure of the pH sensitivity of the multilayers.

These results indicate that in acidic solution the change of the multilayer morphology develops gradually from nanometer scaled granular features to micrometer-scaled pores, while the thickness of the multilayers (unchanged regions) remains rather constant. As for the transition of PAA/poly(allylamine hydrochloride) (PAH) multilayers reported by Rubner and co-workers, the reason for the morphological changes of the PAA/PDADMAC multilayers described here should be attributed to the chain rearrangement and/or the phase separation (formation of granular features), followed by dissolution of the polyelectrolytes. The whole process should be caused by a
decrease in the degree of ionization. Following the procedure described by Granick and co-workers, the degree of ionization of the carboxylic groups in the PEMs was measured and actually decreased from 100 to 40% after acidic treatment for 15 min, which is consistent with the results reported by Rubner and co-workers.

Basically, below a critical charge density, the enthalpic energy required to maintain the chains in a more extended flat conformation as in the multilayers is no longer able to overcome the entropic penalty associated with this conformational state. The destruction of the multilayers may actually yield very loosely associated complexes. These complexes have insufficient structural integrity to maintain a layer but do not fully dissociate. Classical polymer adsorption theory also suggests a small loss of conformational entropy (of order $0.2kT$ per segment) when a polymer adsorbs on a surface. A complex in solution might be a little more stable than a complex within a multilayer film since an additional degree of freedom is afforded in the former. Moreover, the formation of a more hydrophobic hydrogen bonded PAA complex in acidic environment can expedite the process of forming the final structure.

Additionally, accommodating excess positive charge within multilayers by rearrangement into an elevated surface area is the reason for the rougher surface, such as pores and a vermiculate morphology.

It is worth mentioning that very thick films can in fact be obtained when PAA/PDADMAC multilayers are assembled at pH 5. However, dissolution of the film with a pH 5 solution during post-treatment was observed in our study. Furthermore, only a very thin PAA/PDADMAC film was formed under such conditions, which is consistent with results from Schlenoff and co-workers. This inconsistency might be caused by the different molecular weight of PAA adopted in these studies. In fact, we assembled a film using PAA with higher molecular weight ($M_w \approx 100,000$, Sigma–Aldrich), no such transition was observed after the same treatment. The cooperative charge coupling effect is crucial for multilayer formation and stability. For example, longer polyelectrolytes are more tightly bound and thus restricted in their positions. Sukhishvili and co-workers also observed that, controlled by the phase diagram, smaller amounts of polyacids were adsorbed on a surface or precipitated in a polyelectrolyte complex when the molecular chains were shorter, especially when the molecular weight of the oppositely charged polymer was large. It is also much easier for polymers of small molecular weight to move and, as a result, to be stripped from the surface, because few attachment points exist on the shorter chains. This mobility is quite important for our studies, which is the reason why we chose such small polyacids.

Following the process we reported previously, partially dehydrated polyelectrolyte multilayers (dried under 75% relative humidity) were compressed by a PDMS stamp with patterned features (Figure 4). From the profile shown in Figure 4b, the height difference between the compressed and the uncompressed regions was measured to be $45 \pm 4$ nm. Hence, the compression ratio is an estimated 75% of the original thickness. The remaining thickness of the multilayers after homogeneous compression with a flat PDMS film has also been examined by SFM using the scratching method (Figure 5).
resulting height ($\approx 15$ nm) measured from the profile (Figure 5b) matches roughly the remaining value of the compressed regions shown in Figure 4b (65 nm-45 nm). It is worth noting that the dustlike particles in Figure 5a are residual materials produced during the scratching procedure. Compared with the case shown in Figure 1 and the extremely flat compressed surface (Figure 4a),\textsuperscript{[6]} one can conclude that the compressed multilayers are more fragile and easily pulverized.

The compression has also been characterized by the phase image of SFM (Figure 4c). The phase lag between the resonance signal and the cantilever response is a parameter that contains relevant information about the interaction between tip and sample. The topographic component has been separated from material-dependent contributions to the phase shift.\textsuperscript{[28]} It has been proved that the topographic component of the phase lag is almost constant when the height changes gradually.\textsuperscript{[28]} For elastic materials, the absolute value of the phase decreases from 90° to 0° as the cantilever approaches the sample. This is a consequence of the resonance frequency displacement of the cantilever to higher frequencies due to the tip–sample contact. The shift is smaller for softer samples because the frequency change is smaller.\textsuperscript{[30]} Variations of the capillary force in samples with regions of different hydrophilic/hydrophobic properties could also be a source of phase contrast.\textsuperscript{[31]} The phase contrast profiles presented in Figure 4d show that the compressed regions display harder and hydrophobic properties, which is consistent with the results of other characterization approaches.\textsuperscript{[32]} The deviating low absolute value of the phase lag on the boundaries should be attributed to the heterogeneous stress distribution in these regions.\textsuperscript{[33]}

When the pattern-compressed multilayers were immersed in a pH 5 solution for 15 min, the porous structure emerged only in the uncompressed regions (Figures 6a and 6b for a magnified view). The length scale and the depth of the pores were quite consistent with the uncompressed films (Figure 6c for line profile). This locally porous film might find wide applications in areas of controlled release, personal care, sensors, and filtration.\textsuperscript{[34]}

It is quite hard to imagine that the compression closes up voids and channels in the polymer matrix that facilitate small ion diffusion. As prepared, the polyelectrolyte multilayers contain no mobile small ions within their bulk.\textsuperscript{[35]} Actually, upon compression the oppositely charged polyelectrolyte chains can approach each other much closer to produce a higher density of ion cross-linking and physical entanglement, which in turn can effectively enhance their stability against chain rearrangement and/or phase separation.\textsuperscript{[36]} A compact packing of the molecules might result in reduced diffusion. Consequently, the dissolution of the films needs longer time. Furthermore, upon compression the positive charges approach the polycations, which moves the barrier to ionization of a carboxylic acid group to lower pH than for the uncompressed multilayers,\textsuperscript{[20,21,36]} However, when we immersed these locally porous films in a pH 1 solution for 48 h, no change was found. Actually, in contrast to the uncompressed films,\textsuperscript{[37]} compressed ones were not swollen in 2 M NaCl.\textsuperscript{[38]} All these proofs point out that the compressed multilayers become thermodynamically and not just kinetically much more stable. The ionization degree also remained as high as 82% after incubation in a pH 5 solution for 2 h. Electrostatic couplings possibly provide a sufficient source of stabilization energy (or rather enthalpy) to counterbalance unfavorable entropy changes. An increased hydrophobic interaction in the compact polymer complex can be another source of stabilization energy as well.\textsuperscript{[21,38]}

With stronger interactions among polymer chains, the energy barrier of polymer rearrangement should become much higher. The molecular surface motion can be measured by the frictional force on the surface. A typical example of the lateral force loop is shown in Figure 7a. The frictional force, being nonconservative, is quantified as the difference of the average lateral force scanned in opposite directions.\textsuperscript{[16]} The data at the extreme left and right ends of the scanning interval correspond to the static friction region, where the tip has not yet attained a sliding state.\textsuperscript{[39]} They should thus be neglected in the calculation. Since the magnitude of the frictional force is almost proportional to the loss modulus,\textsuperscript{[40]} the frictional force
is larger at the glassy–rubbery transition than in either the glassy or rubbery state. The friction of the multilayers completely dried under 15% relative humidity (Figure 7b) does not show any frequency dependence (the frequency shows a positive correlation with the scanning rate), illustrating that the film is in a glassy state. In contrast to this, as seen from the frictional force curve displayed in Figure 7c, the multilayers dried under 75% relative humidity show a glass transition with an increase of the scanning rate. This demonstrates that the partially dehydrated film is in the rubbery state. The different behaviors confirm the lower modulus of a wetting film compared with a fully dried one.[41] However, the rubbery film becomes glassy after compression, as evidenced by the frequency independent friction curve (Figure 7d). The distinct transition from a rubbery to a glassy nature of the multilayers is further supported by the following experiment: small areas of the uncompressed and the compressed film (both dried under 75% relative humidity) were scanned at a larger load force (100 nN). The uncompressed multilayers could be abraded mechanically, while the compressed films could not. This phenomenon is comparable with the result of Cohen-Stuart and co-workers for an ionic induced glass transition of multilayers.[42]

So far, the mechanism of the compression has been partially unveiled (Figure 8). In the process of compression, the water molecules (left) which function as plasticizers in the partially dehydrated films are squeezed out. Consequently, the polymer chains approach each other closer (right) and the free space for molecular motion is diminished. Moreover, due to the formation of more temporary ionic bonds and microhydrophobic complexes, the motions of the polymer chains are retarded to some extent. Thus, a pressure induced glass transition has occurred. This is the reason for the property variation, such as stability, permeability, stiffness, wettability and so on.

4. Conclusions

Driven by weakened interactions between charged polymer chains, low/high pH values induce morphological variation of PAA/PDADMAC multilayers. The multilayers present granular features, micropores, or a vermiculate morphology tuned by pH and incubation time. The kinetics shows that in the process of protonation phase separation and film dissociation occur successively. However, after compression the closely compacted multilayers lose their sensitivity to pH changes, and undergo a glass transition. It has been demonstrated that electrostatic or hydrophobic interactions, can decrease the free energy of the multilayers, thus stabilizing the film. Based on this study and our previous results, the molecular mechanism of compression is revealed. The locally microporous films may find potential applications in areas of controlled release, personal care, sensors, and filtration.

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