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Chemical Fixation of Polyelectrolyte Multilayers on Polymer Substrates

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Abstract: A simple chemical fixation method for the fabrication of layer-by-layer (LbL) polyelectrolyte multilayer (PEM) has been developed to create a large area, highly uniform film for various applications. PEM of weak polyelectrolytes, i.e., polyallylamine hydrogen chloride (PAH) and poly(acrylic acid)(PAA), was assembled on polymer substrates such as poly(methyl methacrylate)(PMMA) and polycarbonate (PC). In the case of a weak polyelectrolyte, the fabricated thin film thickness of the polyelectrolyte multilayers was strongly dependent on the pH of the processing solution, which enabled the film thickness or optical properties to be controlled. On the other hand, the environmental stability for device application was poor. In this study, we utilized the chemical fixation method using glutaraldehyde (GA)-amine reaction in order to stabilize the polyelectrolyte multilayers. By simple treatment of GA on the PEM film, the inherent morphology was fixed and the adhesion and mechanical strength were improved. Both surface tension and FT-IR measurements supported the chemical cross-linking reaction. The surface property of the polyelectrolyte films was altered and converted from hydrophilic to hydrophobic by chemical modification. The possible application to antireflection coating on PMMA and PC was demonstrated.

Keywords: chemical fixation, polyelectrolyte multilayer, glutaraldehyde, crosslinking, antireflection.

Introduction

In recent years, the ability of plastics to function as optical devices, semiconductors, diodes has been interested in large area processing and patterning without the use of vacuum technology. Among the possible various techniques, fabrication of layer-by-layer (LbL) polyelectrolyte multilayer (PEM)[1] has received much attention as a simple and versatile technique for this purposes. PEM method can afford to assemble ultra-thin film for various applications such as anti-reflection coatings,[2] micro-patterning,[3-5] organic electroluminescence device[6-11] and membrane,[12-14] humidity sensor,[15] etc. Typically, oppositely charged polyelectrolytes are able to be alternatively adsorbed on glass, Si-wafer or polymer substrate. The use of weak polyelectrolytes in LbL PEM assembly process gives additional versatility to control thickness, morphology, swellability of PEM film depending on pH of the processing solution.[16] Many of these applications make use of the micro-structural change due to the phase separation behavior upon changing pH. For example, when poly(allylamine hydrogenchloride) (PAH) and poly (acrylic acid)(PAA) have been used to make PEM, PAH/PAA film can be easily assembled under certain pH condition. Subsequent exposure of PAH/PAA film to more acidic condition induces the morphological structure change or film removal. It have been attributed to the breaking of electrostatic interaction between cationic and anionic moiety within PAH/PAA film resulting in micro-phase-separated or water-soluble film.[16]

Although the micro-structural change of PEM offers the application advantages in one aspect, the environmental meta-stability as device applications may be a drawback in another aspect. Several methods have been employed to overcome this structural meta-stability. One of the well known methods is the amide formation between the amine group of PAH and the carboxylic acid group of PAA by thermal[17,18] or chemical method.[19-21] Although the thermal amide formation is simple and easy, it requires high temperature and may not be used for polymer substrate which is one of most important material for commercial optical application. Whereas chemical cross-linker such as 1-ethyl-3-(3-dimethyl aminopropyl)carbodiimide (EDC) is commonly used to form amide bonding, especially in aqueous solution. However, the cost of EDC is rather expensive and becomes crucial for large area commercial application purpose. Another method to stabilize the PEM structure is to use the photo-crosslinker which is embedded in polyelectrolyte moiety by chemical modification. Sun *et al.*[22] have demonstrated that PEM film containing diazo-resin and PAA was used to prevent the selective film etching by UV-induced

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photo-linking. Park *et al.*[23] adopted benzophenone-modified poly(acrylic acid) and poly(allylamine hydrochloride) and they prepared the stable PEM films with pH-switchable ion permselectivity by photo-crosslinking. Similarly, Olugebefola *et al.*[24] reported the alternative chemistry to modify PAA with photocross-linkable vinyl benzyl side group and successfully demonstrated to create 2-D and 3-D patterning. These methods, however, required substantial chemistry to modify polyelectrolytes.

In this study, we utilized the chemistry of aldehyde and amine reaction to stabilize the micro- or nano structured film without perturbing integrity. Glutaraldehyde (GA) has been known for a long time to fix the living tissue or protein.[25] It may be chemically cross-linked with PAH in proper pH range and mild reaction condition since PAH has amine moiety as shown in Scheme I. To demonstrate this method is easy and simple, anti-reflection film with PAH/PAA was fabricated on polymer substrates and compared with and without the treatment of GA.

Experimental

Commercially available polymer substrates such as poly (methyl methacrylate)(PMMA), polycarbonate (PC) were used as received. PAH (M_w ~70,000) was purchased from Aldrich Chemical. PAA was synthesized and obtained in aqueous solution as described earlier.[26] Poly(acrylic acid) (PAA) was prepared by polymerization of acrylic acid in 1,4-dioxane using AIBN as an initiator at 65 °C for 12 h under a nitrogen atmosphere. The solution was poured into an excess of petroleum ether to precipitate PAA. PAA was dried at room temperature under vacuum. Its viscosity-average molecular weight was measured in 1, 4-dioxane at 30 °C and was determined to be M_w~100,000. Glutaraldehyde (GA) as cross-linker was purchased from Sigma-Aldrich. All chemicals were used without further purification. 20 mM polyelectrolyte dipping solutions based on the repeat unit molecular weight were prepared from 18 MΩ deionized water. pH of PAH and PAA solution was adjusted to pH 7.5, 3.5, respectively.

The layer-by-layer deposition technique involves the repeated sequential dipping of a substrate (PMMA; PC; Si-wafer) into dilute polycation and polyanion solutions with rinsing between each deposition step as described earlier.[16,27] One bilayer in this paper denotes each PAH and PAA layer deposition. The substrates such as PMMA and PC were surface-modified by O_2 plasma or mixture of LiOH/MeOH/H_2O_2 3% for 4 h. Si wafer was cleaned by Piranha solution for 12 h. After the desired number of layers had been assembled, the substrates were dried with filtered air and subsequently oven-dried at 80 °C at least 2 h. In order to have anti-reflection film, the PEM film was further treated with $MgCl_2$ according to the literature.[2] To stabilize PAH/PAA film, it was immersed in aqueous glutaraldehyle (GA) 2.5% solution for the desired time at 30 °C.

The Phoenix 300 system was used to measure the contact angle of water on films. The contact angles presented in this paper are advancing contact angle. Two different types of PEM film were prepared to measure the contact angle: One for as-prepared and the other for vacuum dried at 60 °C for 1 h and stored in ambient air for 12 h. Three different locations on each sample were measured to ensure a representative value of the contact angle.

Buker IFS66V Fourier transform infrared (FT-IR) spectrophotometer was used to confirm the reaction between GA and PAH. For IR measurement, 200 μm Si wafer was used as substrate. After PEM film was deposited onto Si wafer, it was further treated as described above. To enhance the intensity of FT-IR spectra, the multilayer films were deposited up to 40 bilayers. FT-IR measurements were carried out for the samples before and after cross-linking with GA for desired time. UV-Vis spectroscopy was used to measure the transmittances of the PEM film at near-normal incidence. SIS AFM system was used to obtain AFM image.

Results and Discussion

In order to assemble PEM film on the polymer substrates, it is better to generate the surface charge on the substrate by either chemical or physical means. In the case of PMMA, it is often treated with basic LiOH/methanol solution for several hours to hydrolyze the ester group of PMMA. According to the contact angle measurement, however, O_2 plasma treatment gave better hydrophilic surface. Figure 1 shows the water contact angle difference of PMMA and PEM coated film. Both bare PMMA gave high contact angle close to 75° whereas the O_2 plasma treatment makes polymer surface hydrophilic. The initial contact angle of O_2 plasma treated substrate became 18.7° and increased to 35.6° after 2 h heat-treatment at 60 °C. To have fresh surface of substrate, all polymer substrates were immediately used after O_2 plasma treatment. Since the treated surface became negatively charged, the substrate was immersed first in PAH solution and subsequently in PAA solution. The 9.5 bilayer denotes the outmost layer is PAH whereas 9 bilayer means PAA is a surface layer. The contact angle of layered PEM is dependent upon the outmost layer of polyelectrolyte due to its characteristics as shown in Figure 1. We found that the contact angle is very much dependent on how to prepare the PEM sample. This is because polyelectrolyte has the moisture-absorbing character. Sample was vacuum-dried at 60 °C for 1 h and stored in ambient air for 12 h to have consistent contact angle measurement. The contact angle of 9.5 bilayer was initially 23.2° although not shown in Figure 1 and then became 55.8° after drying process. All reported values on Figure 1 are given after this process. Contact angle of PAH was observed slightly larger than that of PAA, which is previously reported by others.[27] The value of

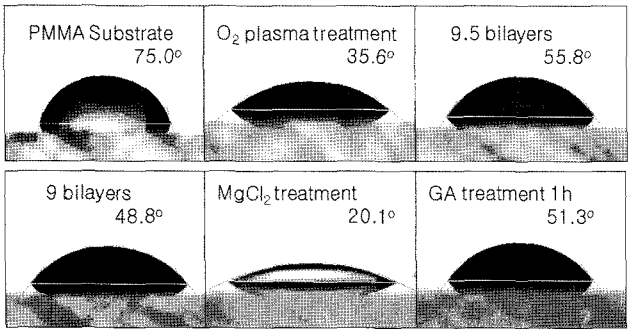
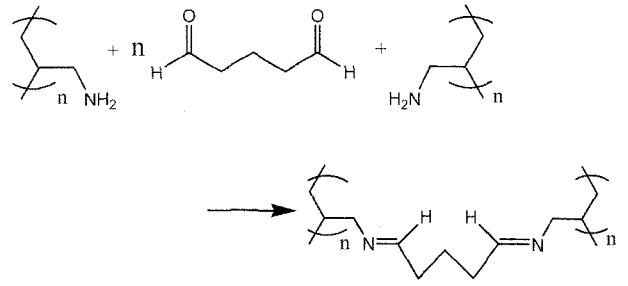


Figure 1. Contact angle measurements of various conditions on PMMA substrate.



Scheme I. Reaction of glutaraldehyde and polyallylamine.

reported contact angle is slightly different from ours. This is because of sample treatment difference.

After 9.5 bilayer deposition, the sample was immersed in pH 2.3 solution in order to induce the phase-separation of PEM film and subsequently treated with $MgCl_2$ as reported previously by Rubner *et al.*.[2] This process makes the contact angle changed quite much because of the morphology transformation by pH and the electrostatic effect by Mg^{2+} ion. Figure 2(A) shows the surface image of PEM film. With pH 2.3 treatment, the morphology of the PEM surface became porous due to the phase separation. Since the phase separation behavior is kinetically controlled, the overall porosity depends on how long the film exposes to pH 2.3 solution. Rubner *et al.*[2] has clearly shown that PAH/PAA multilayers became reversibly erasable nanoporous anti-reflection coatings by pH cycling treatment and $MgCl_2$ solution. We have also observed similar results. The overall porosity and surface roughness of PEM film became larger as the dipping time on pH 2.3 solution increased. With 1 min treatment of pH 2.3, the contact angle was significantly changed from 55.8° to 20.1° and the porosity as well as surface roughness of film changed due to phase-separation as shown in Figure 2(B). This porosity and roughness increment results in the reduction of density as well as refractive index of PEM film, which in fact is one of main conditions of anti reflection film as described earlier. Prolonged treatment of pH 2.3 solution will further increase the porosity and surface roughness although not shown.

pH and $MgCl_2$ treated PEM is unstable againt environmental condition although it is anti-reflective. In order to stabilize the anti-reflective film, it is necessary to lock the porous structure. For this purpose, glutaraldehyde and amine reaction was utilized. Glutaraldehyde (GA) treatment on PEM film makes significant change in contact angle from 20.1° to 51.3° as shown in Figure 1. Since GA and amine reaction takes place according to Scheme I, hydrophilic amine moiety of PAH layers becomes less. It makes PEM film more hydrophobic. However, as compared with Figure 2(B), the overall morphology and surface roughness of PEM film seems not to perturb very much as shown in Figure 2(C). In fact, this observation may be proved indirectly by transmission measurements of PEM films before and after GA treatment, which will be discussed later.

In order to show the reaction between GA and amine, IR spectroscopy was utilized with 200 μm Si wafer as substrate and 40 bilayered PEM film on Si wafer was used to have enough IR intensity. As shown in Figure 3, free acid, base and salt form such as COOH (1713 cm^{-1}), COO^- (1561, 1398 cm^{-1}), NH_2 (1627 cm^{-1}) and NH_3^+ (1318, 850 cm^{-1}) peaks were observed even though the PEM film was treated with pH 2.3. When PEM film was assembled, salt form from anionic $-COO^-$ and cationic $-NH_3^+$ moieties was formed and not easily dissolved at acidic or basic condition except extreme condition. Otherwise, the IR spectra of both pH 2.3 and 11.0

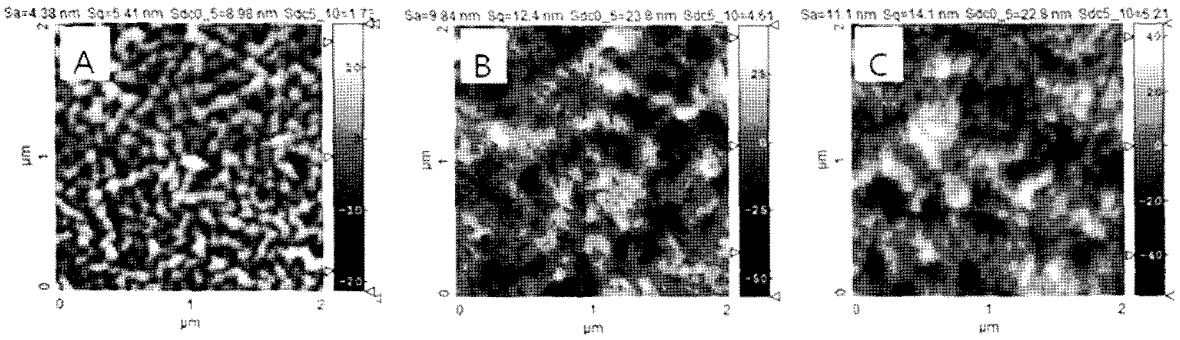


Figure 2. AFM images of 9.5 bilayered PAH/PAA film: (A) as-prepared, (B) pH 2.3 and $MgCl_2$ treatment for 1 min, (C) GA treated after pH 2.3 and $MgCl_2$ treatment.

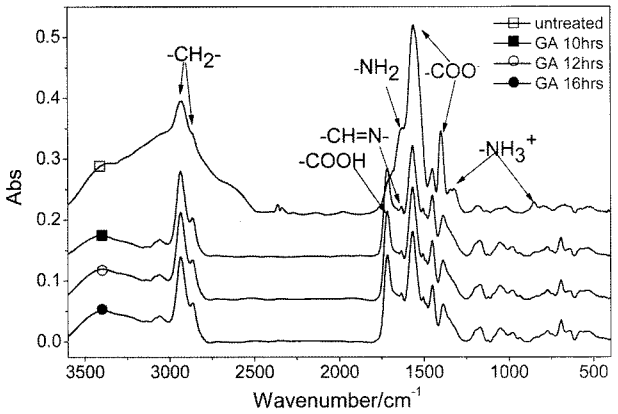
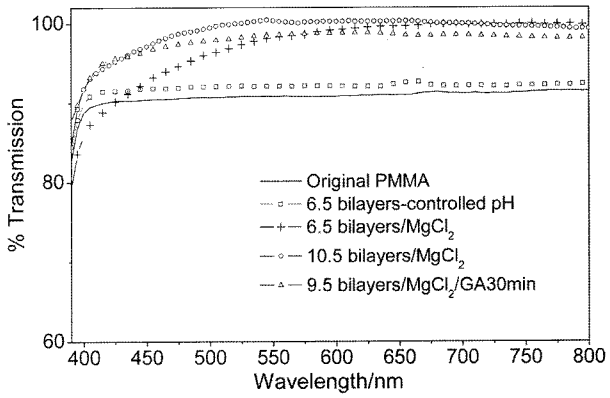


Figure 3. After dipping on pH 2.30 solution, FT-IR spectra of forty-bilayer PAH/PAA films untreated and treated with glutaraldehyde for given hours as indicated.

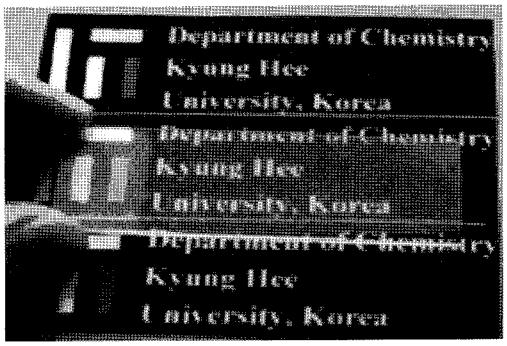
are almost identical. This is because COOH/COO- ratio is almost constant above pH 4.0.[16] However, below pH 1.75, PEM film could be dissolved easily.[16] With GA treatment, available free amine group may react with aldehyde of GA. Consequently, IR peak of amine diminished and imine peak appeared in 1635 cm^{-1} as shown in Figure 3 although it is small. As the reaction proceeded, the –COOH peak became dominant which was buried and weakly shown on the $-NH_2$ shoulder before GA treatment. The reaction rate with GA at pH 11.0 seemed to be slightly faster than at pH 2.3 although it was not shown here. This may due to the abundance of free amine group at high pH. Also, CH_2 stretching vibration peaks at 2925 and 2862 cm^{-1} became apparent due to the incorporation of methylene group from GA.

Knowing that GA really reacted with amine group of PAH, antireflection coating films on PMMA and PC were prepared. As shown in Figure 4, bare PMMA has about 90% transmission and 6.5 bilayer of PAH/PAA on PMMA has slightly improved in transmission. With pH and $MgCl_2$ treatment, T% of 9.5 bilayer increases substantially up to nearly 99%. According to Rubner *et al.*,[2] the porous features of anti-reflection film can be advantageously controlled by varying the pH of the porosity-inducing steps, as well as by the addition of low concentrations of various salts, such as NaCl and $MgCl_2$, to the acidic bath. Without added salt, the phase separation proceeded slowly. Hence, it is rather difficult to control porosity and antireflection condition.

PEM film treated with GA gave about 1% reduced transmission compared with pH and $MgCl_2$ treated sample. As shown in Figures 2(b) and 2(c), the overall structure did not seem to change very much and is persistent after crosslinking. The apparent 1% transmission reduction after crosslinking may come from aldehyde and amine reaction inside of porous structure. It may result in density as well as refractive index increase although PEM film preserves the porous structure. In order to have perfect antireflection coating, it requires the following two conditions: $n_f \sim (n_{sub} \cdot n_{air})^{0.5}$ and



(a)



(b)

Figure 4. (a) Transmission spectra of PMMA substrate before and after PAH/PAA multilayer coatings with various treatments. (b) A photograph image of 9.5 bilayers/$MgCl_2$/GA 30 min treated sample.

$T_f \sim \lambda/4n_f$ where n_f, n_{sub}, n_{air}, T_f, λ denote refractive indices of antireflection film, substrate, air, film thickness and wavelength, respectively. Since refractive index (RI) of air is 1 and RI of substrate is in the range of 1.4 to 1.5, RI of film needs to be about 1.22 and film thickness about 100~160 nm, which

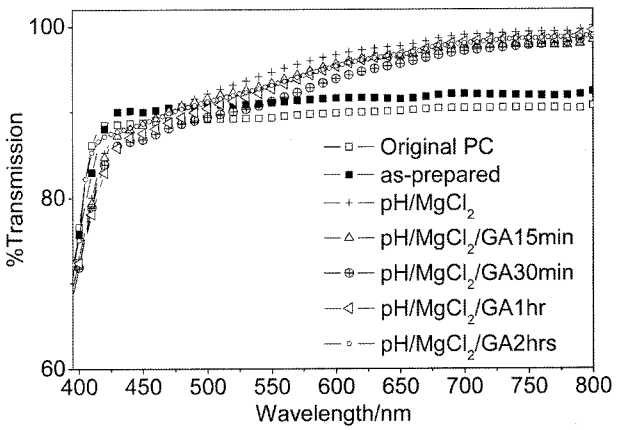


Figure 5. Transmission spectra of 9.5 bilayer of PAH/PAA on PC substrate before and after various treatments. pH and $MgCl_2$ denoted pH and $MgCl_2$ treatment. GA were treated for given time as indicated.

Table I. Stability Test of PEM Films

Treatment			Test Conditions	
pH 2.3	pH 11	GA treatment at 30 °C	Dipping in 1 M HCl	Cotton rubbing with 1 M HCl
x	x	x	removed	removed
1 min	1 min	x	removed	removed
x	x	0.5; 1; 2 h	stable	stable
1 min	2 min	0.5; 1; 2 h	stable	stable
1 min	2 min	0.5, 1, 2 h	stable	stable

requires porous film to fulfill the requirement for most of substrates.[2] Cross-linking of PEM film somewhat fills up the porous voids by GA. RI of GA treated film will slightly increase and hence its transmission will decrease. The observation of Figure 4 is in accord with expectation. In order to have perfect antireflection film, it needs to match the conditions for overall wavelength range. However, this is beyond the scope of this work. In the case of PC substrate, similar results were obtained as shown in Figure 5.

To test the film stability, several samples were prepared. The test summary was given in Table I. As-prepared or pH 2.3 or 11.0 treated samples were not stable against 0.1 M HCl and completely removed as soon as acid solution was touched on the surface of PEM film. However, the PEM film treated with GA for 30 min remained intact with 0.1 M HCl solution whether the films were pre-process with either pH 2.3 or 11.0 not. This indicated the chemical fixation of PEM film on polymer substrate works readily within 30 min. Further test was performed under the cotton swab rubbing condition with 0.1 M HCl and the GA cross-linked PEM film remained stable and intact. Also, the adhesion test gave much better result. With GA treatment, PEM film was not able to remove from the substrate by simple Scotch tape peel test whereas some part of the film was removed without GA treatment. It indicates that GA treatment improved mechanical and chemical stability as well as adhesion by cross-linking.

Conclusions

We have demonstrated that layer-by-layer assembled multilayers of the weak polyelectrolytes PAH and PAA can be further stabilized by glutaraldehyde. The chemical cross-linking of PEM did not alter the morphology of film very much but the surface tension of film changed quite much due to the elimination of amine moiety by GA. IR spectra of PEM film on Si substrate did not change even after the film was treated on different pHs such as 2.3 and 11.0, which indicates the formed PAH/PAA complex cannot dissolve in this pH range. Also, it was clearly shown that GA can easily react with PAH according to IR spectra. With this chemical treatment, antireflection films on PMMA and PC substrates have been shown to be environmentally stable such as pH or mechanical rubbing. This simple treatment may be used to fabricate large area AR film using various polymer substrates.

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References

(1) G. Decher, J. D. Hong, and J. Schmitt, *Thin Solid Films*, **210-211**, 831 (1992).
(2) J. Hiller, J. D. Mendelsohn, and M. F. Rubner, *Nature Mater.*, **1**, 59 (2002).
(3) S. L. Clark, M. F. Montague, and P. T. Hammond, *Macromolecules*, **30**, 7237 (1997).
(4) P. T. H. Sarah and L. Clark, *Adv. Mater.*, **10**, 1515 (1998).
(5) H. Zheng, I. Lee, M. F. Rubner, and P. T. Hammond, *Adv. Mater.*, **14**, 569 (2002).
(6) A. C. Fou, O. Onitsuka, M. Ferreira, M. F. Rubner, and B. R. Hsieh, *J. Appl. Phys.*, **79**, 7501 (1996).
(7) A. C. Fou and M. F. Rubner, *Macromolecules*, **28**, 7115 (1995).
(8) O. Onitsuka, A. C. Fou, M. Ferreira, B. R. Hsieh, and M. F. Rubner, *J. Appl. Phys.*, **80**, 4067 (1996).
(9) P. K. H. Ho, J.-S. Kim, J. H. Burroughes, H. Becker, F. Y. L. Sam, T. M. Brown, F. Cacialli, and R. H. Friend, *Nature*, **404**, 481 (2000).
(10) M. Eckle and G. Decher, *Nano Lett.*, **1**, 45 (2001).
(11) J. Cho, K. Char, S. Y. Kim, J. D. Hong, S. K. Lee, and D. Y. Kim, *Thin Solid Films*, **379**, 188 (2000).
(12) D. M. Sullivan and M. L. Bruening, *J. Am. Chem. Soc.*, **123**, 11805 (2001).
(13) S. T. Dubas, T. R. Farhat, and J. B. Schlenoff, *J. Am. Chem. Soc.*, **123**, 5368 (2001).
(14) H. H. Rmaile and J. B. Schlenoff, *J. Am. Chem. Soc.*, **125**, 6602 (2003).
(15) C.-W. Lee, J.-G. Kim, and M.-S. Gong, *Macromol. Res.*, **13**, 265 (2005).
(16) J. D. Mendelsohn, C. J. Barrett, V. V. Chan, A. J. Pal, A. M. Mayes, and M. F. Rubner, *Langmuir*, **16**, 5017 (2000).
(17) J. J. Harris, P. M. DeRose, and M. L. Bruening, *J. Am. Chem. Soc.*, **121**, 1978 (1999).
(18) J. L. Stair, J. J. Harris, and M. L. Bruening, *Chem. Mater.*, **13**,

2641 (2001).
(19) P. Schuetz and F. Caruso, *Adv. Func. Mater.*, **13**, 929 (2003).
(20) L. Richert, F. Boulmedais, P. Lavalle, J. Mutterer, E. Ferreux, G. Decher, P. Schaaf, J. C. Voegel, and C. Picart, *Biomacromolecules*, **5**, 284 (2004).
(21) S. Y. Yang, D. Lee, R. E. Cohen, and M. F. Rubner, *Langmuir*, **20**, 5978 (2004).
(22) J. Sun, T. Wu, F. Liu, Z. Wang, X. Zhang, and J. Shen, *Langmuir*, **16**, 4620 (2000).
(23) M. K. Park, S. Deng, and R. C. Advincula, *J. Am. Chem. Soc.*, **126**, 13723 (2004).
(24) S. C. Olugebefola, S. W. Ryu, A. J. Nolte, M. F. Rubner, and A. M. Mayes, *Langmuir*, **22**, 5958 (2006).
(25) D. D. Sabatini, K. Bensch, and R. J. Barrnett, *J. Cell Biol.*, **17**, 19 (1963).
(26) M. Okubo, K. Ikegami, and Y. Yamamoto, *Colloid Polym. Sci.*, **267**, 193 (1989).
(27) D. Yoo, S. S. Shiratori, and M. F. Rubner, *Macromolecules*, **31**, 4309 (1998).