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The Effect of Assembly Technique on Weak Polyelectrolyte Multilayer Film Morphology and Humidity Swelling/Deswelling Behavior

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The Effect of Assembly Technique on Weak Polyelectrolyte Multilayer Film Morphology and Humidity Swelling/Deswelling Behavior

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Name

Chemical Engineering
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EXAMINATION COMMITTEE:

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PASSED x **FAILED** ____

ABSTRACT

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M.S.Ch.E

Rose-Hulman Institute of Technology

February 2016

The Effect of Assembly Technique on Weak Polyelectrolyte Multilayer Film Morphology and Humidity Swelling/Deswelling Behavior

Thesis Advisor: Dr. Adam Nolte

Summary:

The goal of this research is to investigate the film morphology and humidity swelling/deswelling behavior of polyelectrolyte multilayers (PEMs) that are constructed from poly(allylamine hydrochloride) (PAH) and poly(acrylic acid) (PAA) by two assembly techniques: automated dipping layer-by-layer (LbL) and spin-assisted (SA) LbL. Two sets of pH polyelectrolyte solution conditions were tested: (PAH7.5/PAA3.5) and (PAH7.0/PAA7.0). It was found that when the films were constructed with the same number of bilayers (=20 bilayers), SA-LbL (PAH7.5/PAA3.5) has a greater thickness than (PAH7.0/PAA7.0). (PAH7.5/PAA3.5) thin films constructed by automated dipping LbL did not result in a uniform film morphology, making thickness comparisons between techniques for those assembly conditions difficult. On the other hand, the thickness of $(PAH7.0/PAA7.0)_{20}$ thin films constructed by automated dipping LbL was a tenth of the thickness of $(PAH7.0/PAA7.0)_{20}$ thin films constructed by SA-LbL.

In addition, film morphology was studied for the uneven automated dipping LbL $(PAH7.5/PAA3.5)_{20}$ thin film using contact mode AFM. Silane treatment and an adsorbed polyethylenimine (PEI) underlayer were attempted to produce a smooth film surface.

However, neither surface treatments gave a smooth film surface for the uneven automated dip-coated LbL $(PAH7.5/PAA3.5)_{20.}$ Therefore, the assembly technique is an important factor on the thin film thickness and film morphology.

Humidity swelling/deswelling tests were carried out on SA-LbL $(PAH7.5/PAA3.5)_{20}$, SA-LbL $(PAH7.0/PAA7.0)_{20}$, and automated dip-coated LbL $(PAH7.0/PAA7.0)_{20}$. SA-LbL $(PAH7.5/PAA3.5)_{20}$ and SA-LbL $(PAH7.0/PAA7.0)_{20}$ demonstrated a maximum swelling of approximately 40% under a humid air environment. However, the humidity hysteresis effect for the automated dipping LbL $(PAH7.0/PAA7.0)_{20}$ was hard to tell due to the high uncertainty in the film thickness.

DEDICATION

I would like to dedicate this thesis to my wonderful parents who have always supported me with my studies in all means. My parents, Lubing Yin and Lanping Wang, have supported me with their love and care throughout my study journey in the U.S. I would not have gone this far without them. Thanks for your amazing parenting and constant support. I am about to embark a new journey of my life. Thank you very much!

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LIST OF ABBREVIATIONS

LbL	Layer-by-Layer
RH	Relative Humidity
RMS	Root Mean Square
SA	Spin-Assisted
PAH	Poly(allylamine hydrochloride)
PAA	Poly(acrylic acid)
PEI	Polyethylenimine
PEM	Polyelectrolyte Multilayer

1. INTRODUCTION

1.1 Background

Polyelectrolyte multilayers (PEMs) are thin films traditionally formed by using the layer-by-layer (LbL) technique, which involves dipping a substrate back and forth between positively and negatively charged polyelectrolyte solutions. After each deposition step, water rinse steps are used to ensure that only well-adsorbed polymer stays in the film. In this study, two layer-by-layer techniques were used: automated dipping assembly and spin-assisted (SA) assembly. The automated dipping assembly uses a robotic dipping machine along with a computer program to execute the dipping process as shown in Figure 1.1.1(a). On the other hand, the spin-assisted LbL (SA-LbL) assembly instead uses alternating spin coating of polymer and rinse solutions as shown in Figure 1.1.1(b). The latter technique speeds up the polymer adsorption process. Even though the chemical composition of SA-LbL assembly is similar to the one of dipping assembly, due to the forced adsorption, the chain structure can be different [1].

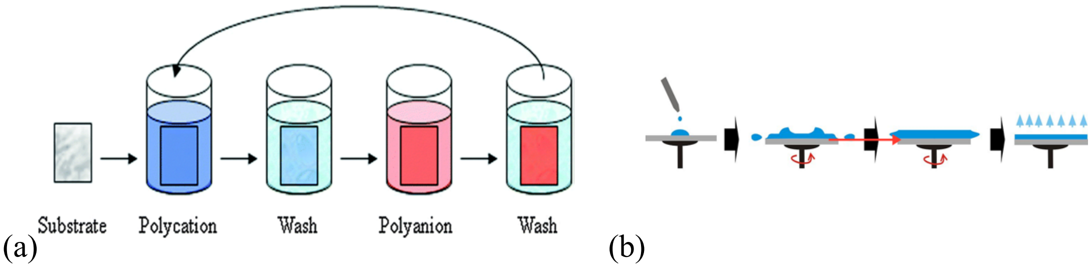

Figure 1.1.1 Illustrations of (a) the traditional dipping LbL assembly process and (b) the spin-assisted coating assembly process [2][3]

The layer-by-layer assembly has been utilized in various applications. For example, the layer-by-layer assembly has been used in nanoparticle coating on fibers, H_2 sensing in industrial processes utilizing H_2 gas, and optical coatings [4]. PEMs have been known to be suitable for sensing in humid environments because they can respond differently to different chemical environments such as humidity and to rearrange within the film in nanoscale. In addition, PEMs have been used in the semiconductor industry to produce thin-film transistors [5].

PEMs are prepared by using either strong polyelectrolytes, which remain fully charged with change in pH, or weak polyelectrolytes, which may be partially charged depending upon the pH**.** Strong polyelectrolytes and fully charged weak polyelectrolytes can be deposited to form films with very thin layers. This is because the charges from the polyelectrolytes cause the chains to stretch out on the surface. Therefore, those polyelectrolytes can adhere to the substrate in multiple locations. Partially charged weak polyelectrolytes allow the chains in solution to have a more globular morphology and to adhere at fewer points to the surface, forming chain loops on the surface and thicker adsorbed layers. The resulting films constructed by such partially charged weak polyelectrolytes are thicker for an equivalent number of deposition steps.

1.2 Scope of the work

In this study, LbL thin films were constructed from positively charged poly(allylamine hydrochloride) (PAH) and negatively charged poly(acrylic acid) (PAA) polyelectrolyte solutions. The structures of these polyelectrolytes are shown in Figure 1.2.1.

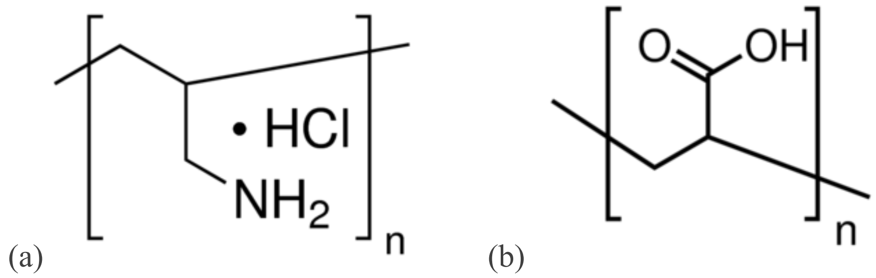

Figure 1.2.1 The structures of (a) poly(allylamine hydrochloride) (PAH) and (b) poly(acrylic acid) (PAA)

Two different types of LbL films were assembled from PAH and PAA for each assembly technique; these are distinguished by listing the pH values of the polyelectrolyte solution used during film construction. (PAH7.5/PAA3.5) conditions result in both adsorbing polyelectrolytes being only partially charged during the deposition steps, while the neutral pH (PAH7.0/PAA7.0) conditions result in each polyelectrolyte being fully charged during the deposition steps [6]. The film deposition processes were carried out by automated dipping and spin-assisted dipping. By alternating back and forth between the weak polyelectrolyte solutions, electrostatically crosslinked thin films were constructed. Since two different deposition conditions and two different deposition methods were used, the film properties could be expected to vary as a result of both of these factors. Therefore, the goals of this study are:

(a) To compare film thickness and topology of PEM thin films constructed at the same pair of pHs with different assembly techniques
(b) If uniform films were constructed, to perform humidity swelling/deswelling tests to determine the extent of swelling and any swelling hysteresis effects that may exist.

Therefore, pH of polymer solutions and assembly methods are important to the morphology and internal chemistry of the PEM thin films.

1.3 Literature Review

The layer-by-layer assembly method is a fairly recent approach to fabricate nanoscale thin films. The discovery of the LbL assembly method was by R.K. Iller in 1965, who utilized this technique to build charged particle films; however, it did not become popular until 1997 with the rediscovery by Gero Decher and its application to polyelectrolytes

[7,8]. There are several advantages of using the LbL assembly method. First, it can accommodate a range of substrate sizes and shapes, and a wide range of materials can be deposited onto different substrates. Second, materials for LbL assembly method are not limited to polyelectrolytes. Functional macromolecules including proteins and DNA, biological nanoparticles, and magnetic and gold nanoparticles are all on the list for constructing LbL multilayer films. The substrates can be glass, silicon or optical fibers [9]. Lastly, LbL assembly in itself is a simple and relatively inexpensive method of depositing alternate layers of functional materials [10].

Dip-coating and spin-assisted are two major LbL assembly techniques. Dip-coating LbL assembly relies on diffusion of a charged species to the surface of a growing film when a substrate is immersed in the polymer solution [6]. For a long immersion time, the amount of polymer molecules adsorbed will be limited by charge repulsion between chains on the surface and chains in the solution. There are several factors that contribute to the dip-coated film structures and thickness: submersion time (for short times), initial substrate surface functionality, rinse steps, pH of solutions, etc. Dip-coating LbL assembly can be done either by hand or using an automated robotic system.

In previous research, a study on how solution pH affected the dip-coating LbL assembly of PAH and PAA on the Si substrate was carried out [6]. Both polyelectrolyte solutions were made at 0.01 M based on the repeat unit molecular weight. Films constructed by all possible pH combinations between pH 2.5 and pH 9.0 were tested. Two of these conditions are directly relevant to this study.

When depositing with PAH and PAA solutions each at the same pH near neutral (pH 7), both polyelectrolytes were fully charged and the resulting films were flat and thin. In the study, the authors described these conditions in “region III” (pH 6.0-7.5), where both PAH and PAA were fully ionized. The resulting PAH/PAA bilayer thickness was very thin, ranging from 0.3-0.5 nm. Similar results were expected for the PAH7.0/PAA7.0 pH conditions in this study.

In addition, this previous research also carried out a study keeping PAA at a constant pH of 3.5 and varying pH of PAH solution from 2.5 to 8.5. In the pH range of 2.5- 4.5, the PAH/PAA bilayer thickness increased with the increasing pH of PAH within a range of 3-6 nm. When the pH of PAH was higher than 4.5, however, adsorbing chains would adopt a more loopy conformation which resulted in a substantially thicker bilayer thickness [6]. Therefore, when depositing PAH7.5/PAA3.5 system, the adsorbing chains are expected to be only partially charged, which would result in a thicker film.

In contrast to dip-coating LbL assembly, PEMs that were constructed by spin-assisted (SA) LbL assembly uses forced-adsorption along with centrifugal force to deposit polymer solutions on a flat, spinning substrate. There are many advantages for using SA-LbL including decreasing assembly time and minimizing solution usage compared to dip-coating LbL assembly. In addition, different deposition methods could result in different film morphology when using the same polymer solutions [11].

In a previous study on the effect of LbL deposition methods on the surface morphology, hydrogen-bonding multilayer thin films constructed by hydrophobically modified poly(ethylene oxide) (HM-PEO) and PAA were prepared using dip-coating LbL and SA-LbL. It was found that the surface morphology constructed by the same polymer solution using different deposition techniques was different. For the SA-LbL assembly, the adsorption and rearrangement on the surface was limited during the short spinning time (~20 s). In addition, HM-PEO micelles were easily deformed by imposed shear force; therefore, during the deposition process, the micelles could not retain their shape. On the contrary, dip-coating LbL allowed HM-PEO to diffuse and adsorb onto the substrate due to a long deposition time (~15 minutes). It also allowed a longer time for the surface rearrangement, resulting in different surface morphology than the SA-LbL sample. Therefore, the finalized thin films constructed by the two assembly techniques looked different. The dip-coated LbL films appeared to be cloudy, which indicated a high surface roughness due to light scattering, whereas the spin-assisted LbL films appeared to be transparent [11].

PEMs are known to be sensitive to external factors such as pH, temperature, or humidity [12]. Therefore, it is vital to know about humidity swelling/deswelling effects in the PEMs. The swelling of PEMs can be attributed to the increasing availability of additional absorption sites for water to enter [13]. In a previous work, a humidity swelling/deswelling study of was carried out for SA-LbL $(PAH7.5/PAA3.5)_{20}$ thin films. Data collected in the swelling period was called “absorption”, whereas data collected in the deswelling period was called “desorption”. It was found that humidity swelling hysteresis occurred in this thin film between dry state conditions (~10% RH) and hydrated state conditions (~100% RH). Overall, the thin film swelled up to approximately 40% of its dry state thickness. In addition, the swelling was not linear with humidity. PEMs demonstrated a substantial increase in swelling above 90% RH, as the external water activity approached unity [13]. However, when desorption occurred from ~100% RH to 90% RH, the film quickly reached its 90% RH absorption film thickness, which indicated that water that entered above this humidity was not tightly bound [13]. The hysteresis became apparent when desorption occurred below 90% RH. The rearrangement of the film structure upon swelling gave more binding interactions with water and hindered the desorption of water from within the film. Furthermore, these interactions prevented the film from reforming the same electrostatic cross-linking interactions that were present during absorption, which resulted in thicker films at the same humidity levels during deswelling; hence, the hysteresis effect [13].

2. METHODS

2.1 Deposition process of PEMs

All PEMs were constructed on (100) p-type (University Wafer) silicon wafer by using spin-coating (Laurell Technologies Inc., model WS-400BZ-6NPP/Lite) or an automated dipping system (nanoStrata Inc., StratoSequence VI). Before deposition, silicon wafers were treated by a Novascan Digital UV ozone system for 30 minutes to eliminate organic containments on the wafers. Aqueous solution of PAH (Alfa Aesar, MW=120K-200K) and PAA (Polyscience Inc, 25% solids in water, MW > 200,000) were prepared with deionized water (Millipore, 18 MΩ•cm) to a concentration of 0.01 M by repeat unit. Afterwards, solutions were adjusted to desired pH values using 0.01 M solutions of either NaOH or HCl. The same pH-adjusted polyelectrolyte solutions were used in spin-assisted and automated dipping assemblies. PAH was first deposited, followed by two rinse steps of water. Then, PAA was deposited, followed by two rinse steps of water. This process was considered as one bilayer of film, and the process was repeated until reaching the targeted bilayer number (=20 bilayers). The SA-LbL PEMs were constructed using a spin step at 2000 rpm for 20 s, whereas the dipping PEMs were constructed by immersion in the solution for 5 min in each step. Both spin-assisted and dipping PEMs are denoted as $(\text{PAH x/PAA y})_z$, where x and y indicate the pH of the polyelectrolyte solution, and z indicates the number of bilayers used to construct the film. In this study, two sets of pH conditions of PEMs were studied by two assembly methods: $(\text{PAH7.5/PAA3.5})_{20}$ and $(\text{PAH7.0/PAA7.0})_{20.}$ The film thickness measurements were carried out by a reflectometer (Filmetrics F20, as shown in Figure 2.1.1)

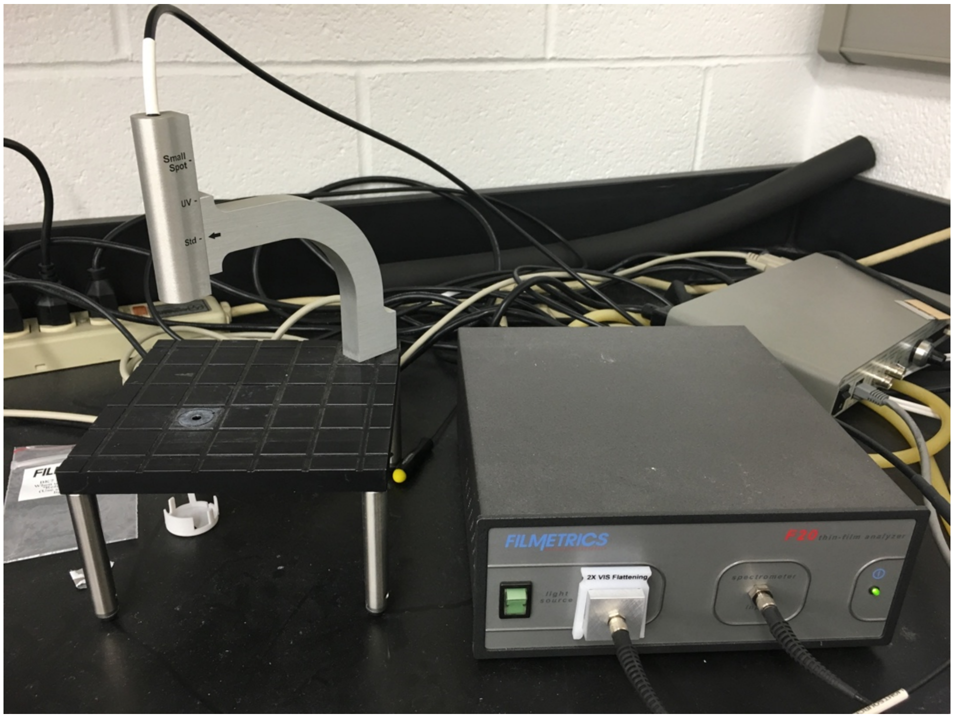

Figure 2.1.1 Thin film thickness measurement instrument: Filmetrics F20

The thickness of thin film is measured by the reflectance from the top and bottom of the thin film. The reflective index and the extinction coefficient will also be generated. The thickness of spin-assisted LbL film was recorded every 5 bilayers; the thickness of dipped LbL film was recorded at 3 bilayers and 20 bilayers.

2.2 Film morphology study with silane treatment and PEI underlayer

Because dip-coated LbL $(PAH7.5/PAA3.5)_{20}$ did not have a uniform surface, two different surface modifications on the Si substrates were subsequently investigated to see if more uniform films could be produced: silane treatment and the pre-adsorption of a PEI adhesion underlayer. Chloro(dimethyl)octylsilane (Sigma Aldrich, 97%) was used for the silane treatment. First, the ozone-treated Si substrate was put on an elevated surface in a petri dish. Then, one part of silane by mass and four parts of toluene by mass were mixed right before the treatment. The treatment was carried out in a vacuum oven (Thermo

Scientific™ Lindberg/Blue M™ Vacuum Oven) to let the mixture deposit from the vapor phase onto the Si at a pressure of 15 in Hg, temperature of 70ºF for 15 minutes. After the treatment, thin films were deposited in the same automated dipping process.

In addition, linear PEI (Polysciences Inc, MW=25,000) was used to help the adhesion of PAH and PAA onto the wafer for the thin films where the morphology was cloudy [14]. 0.02M PEI solution was adjusted to pH 5.0. Then, the ozone-treated Si substrates were immersed in the PEI solution for 10 minutes, followed by a 2-minute water rinse. Afterwards, the dip-coated deposition steps were carried out according to the usual procedure.

Film surface morphology studies were carried out using contact mode AFM (as shown in Figure 2.2.1) with a cantilever spring constant of 0.2 N/m and a scan speed of 0.5 lines/s. The AFM was used to characterize sample surface at high resolution. In a contact mode AFM, the cantilever tip is scanned in close proximity over a sample surface. As the scanning proceeds, the surface roughness would cause the cantilever to bend and produce a measurement.

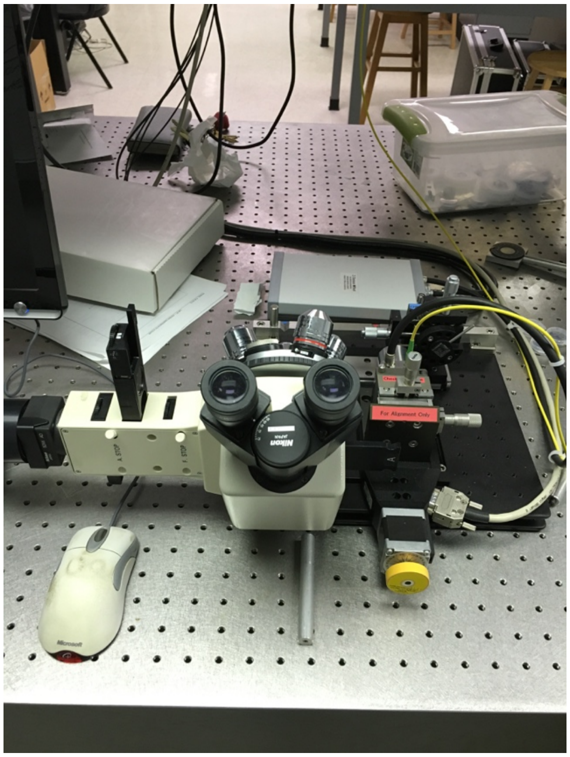

Figure 2.2.1 Surface roughness measurement instrument: Atomic Force Microscope

In this study, the surface roughness for PEMs was measured based on RMS roughness as measured over a 10 μm square area. An ozone-treated Si substrate was also used as a standard to compare its measured surface roughness, which should be very small, with the PEM thin films.

2.3 Humidity swelling/deswelling studies

The effect of humidity on both SA-LbL and dip-coated PEM thicknesses was studied by using a reflectometer (as shown in Figure 2.1.1). Measurements were carried out in a humidity-controlled glovebox (Electro-Tech Systems, Inc.). The thickness of the film was measured at least 5 times after reaching equilibrium. Relative film thickness was used for the analysis where the film thickness was normalized to the thickness value at 10% RH of each sample. Thin films were equilibrated at 10% RH overnight, and film thickness was taken when the reading was stabilized. Then, RH was increased by 10%

increment until it reached 100% RH. At each RH value, 5 minutes were allowed to achieve equilibrium before recording data. Data collected in this swelling period was called absorption. After reaching 100% RH, desorption data was collected by decreasing RH by 10% increment until it reached 10% RH.

3. RESULTS AND DISCUSSIONS

3.1 Thin film thickness measurements

The thin film thickness versus number of bilayers for SA-LbL and automated dipping LbL samples are recorded in Figure 3.1.1. The ambient temperature was about 21 ºC, and the room humidity was about 22 %RH when the deposition process and thickness measurements took place. As seen in Figure 3.1.1, thin films deposited by dip-coating and SA-LbL assembly demonstrated a nearly linear growth in film thickness with increasing bilayer number. Moreover, SA-LbL (PAH7.5/PAA3.5)$_{20}$ samples were relatively thicker than (PAH7.0/PAA7.0)$_{20}$ samples using the same assembly technique.

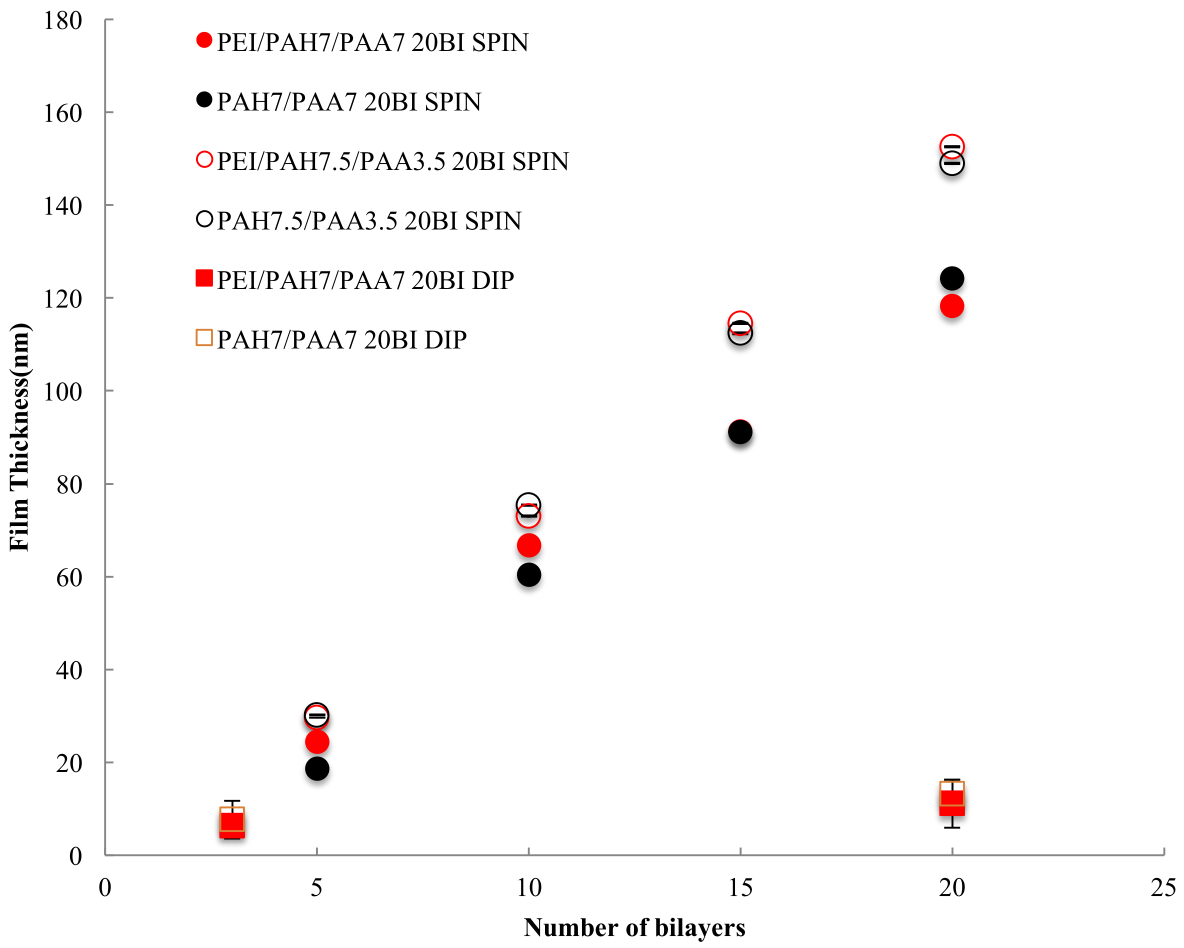

Figure 3.1.1 Thin film thickness growth by two deposition methods

The film thickness (and respective per bilayer thickness) of the two fabrication methods were summarized in Table 3.1. The difference in thickness between an adsorbed PEI underlayer samples and no underlayer samples was really small for samples that appeared to form uniform films. However, film morphology of dip-coated samples for (PAH7.5/PAA3.5)$_{20}$, silane treated (PAH7.5/PAA3.5)$_{20}$ and PEI underlayer (PAH7.5/PAA3.5)$_{20}$ appeared to be non-uniform and splotchy, regardless of surface treatment. Hence, the thickness of those samples could not be measured by a reflectometer. Therefore, no data for these films appears in Figure 3.1.1, and such films were not included in the humidity tests. The surface morphology dip-coated (PAH7.5/PAA3.5)$_{20}$ samples were however further investigated by AFM.

Table 3.1 Summary of total and per-bilayer film thickness for the two fabrication methods and assembly pH conditions

	SA-LbL film thickness (nm)	Bilayer thickness for spin-coated (nm)	Dip-Coated LbL film thickness (nm)	Bilayer thickness for dip-coated (nm)
(PAH7.5/PAA3.5)$_{20}$	149.0±0.2	7.5	N/A	N/A
PEI underlayer (PAH7.5/PAA3.5)$_{20}$	152.5±0.1	7.6	N/A	N/A
(PAH7.0/PAA7.0)$_{20}$	124.3±0.5	6.2	13.3±3.1	0.7
PEI underlayer (PAH7.0/PAA7.0)$_{20}$	118.3±1.7	5.9	11.1±5.2	0.6

The film thickness of dip-coated $(PAH7.0/PAA7.0)_{20}$ was very thin. This result was consistent with what has been found in the previous literature [6]. At this condition, both PAH and PAA were fully ionized, leading to fewer chain loops within the film. Moreover, in the dip-coating assembly process, the polymer molecules diffused freely onto the substrate, and, due to charge repulsion or other thermodynamic effects, would have self-limited their growth at each deposition step [11]. Then, the water rinse steps would wash off any unbound polymer molecules. Therefore, the amount of polymer adsorbed on the substrate was presumably less than what would be possible via spin coating. In contrast, during spin coating, a thick film of polyelectrolytes is forced onto the surface via centrifugal force and precipitation from the drying solvent (water). It is unclear whether subsequent rinse steps can remove all the excess material, perhaps resulting in a larger bilayer thickness. Even though the film thickness of dip-coated $(PAH7.5/PAA3.5)_{20}$ was not able to be determined by a reflectometer, based on the AFM topography from Figure 3.2.3, the estimated film thickness should be at least 100 nm, as its peak to valley distance was about 200 nm. Based on these results, where the same assembly technique was used, the film thickness of PAH7.5/PAA3.5 was much thicker than PAH7.0/PAA7.0, which was consistent with previous literature results [6].

Even though dip-coated $(PAH7.5/PAA3.5)_{20}$ samples did not give a uniform surface films, the SA-LbL $(PAH7.5/PAA3.5)_{20}$ samples appeared to be uniform and clear. Comparing SA-LbL (PAH7.0/PAA7.0) with SA-LbL (PAH7.5/PAA3.5) thin films, the per bilayer thickness did not differ that much. Although it has been shown that the thickness of PAH7.0/PAA7.0 films are substantially smaller than the thickness of PAH7.5/PAA3.5 films when constructed by dip-coating, films constructed at the same conditions using SA-LbL seem to have very similar thicknesses. This finding could be beneficial to those who would like to fabricate thick PAH7.0/PAA7.0 films using dip-coating assembly. Now, they could use SA-LbL to fabricate the same thickness of PAH7.0/PAA7.0 film and cut down the fabrication time. Therefore, the assembly technique could be a factor on the film morphology and the film thickness.

Finally, an adsorbed PEI underlayer was used to promote adhesion of thin film in the deposition process. Using this method could increase the polycationic charge on the surface, which could provide more adsorption sites for the polymer molecules to attach to the substrate. However, based on the film thickness measurement, it did not seem to affect the ultimate film thickness too much compared to samples without the treatment [14].

3.2 Thin film topography study with AFM

Film surface topography studies were carried out using contact mode AFM. The surface roughness for PEMs was measured based on RMS roughness as measured over a 10 µm square area. The image in Figure 3.2.1 was the AFM of a bare Si substrate after ozone treatment. Since there was nothing deposited on the substrate, the surface should be relatively smooth with an RMS roughness value of 0.143nm [15]. An RMS roughness value of 10.9 nm indicated that the surface of the film was smooth, as compared to the multilayer film samples, but that value was more than an order of magnitude higher than would be expected for a Si wafer [15]. It was speculated that room noise was the cause for this higher roughness value. Because this noise would presumably be present for all of the samples measured, the silicon roughness value was treated as a standard for the roughness study of the films, although in light of the high value for the silicon, roughness values in the following were only used for comparative purposes between samples.

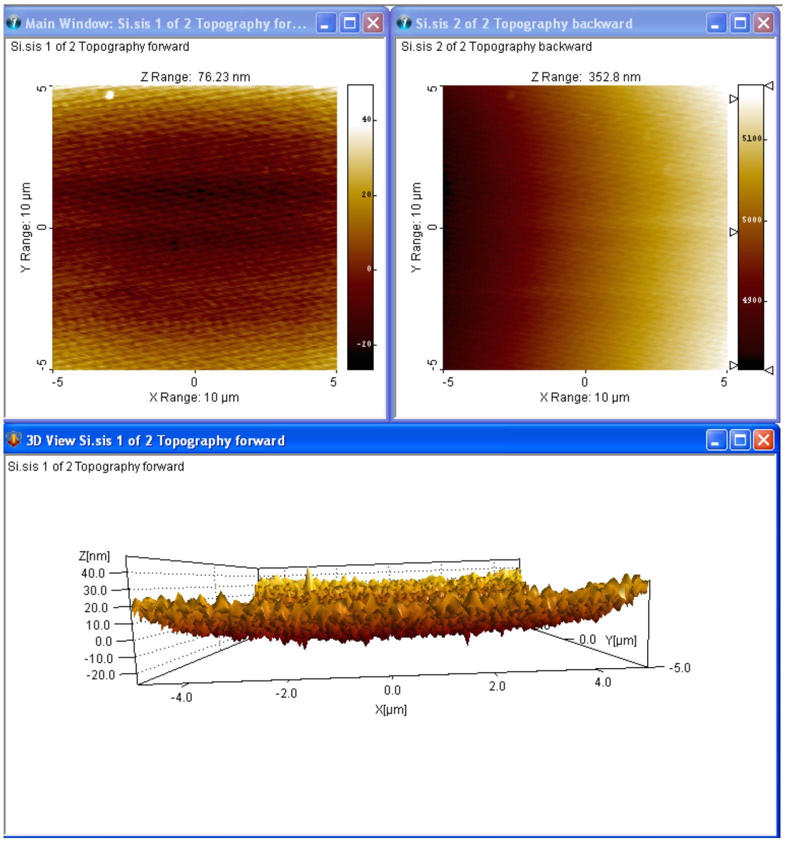

Figure 3.2.1 Topographic image of a clear Si substrate with RMS=10.9nm

The topographic image of the spin-coated (PAH7.5/PAA3.5)$_{20}$ was shown in Figure 3.2.2. The RMS roughness value (= 13.6nm) of the spin-coated (PAH7.5/PAA3.5)$_{20}$ thin film was only slighter higher than that of the bare Si substrate, indicating a very smooth surface morphology. These films also appeared very uniform visually.

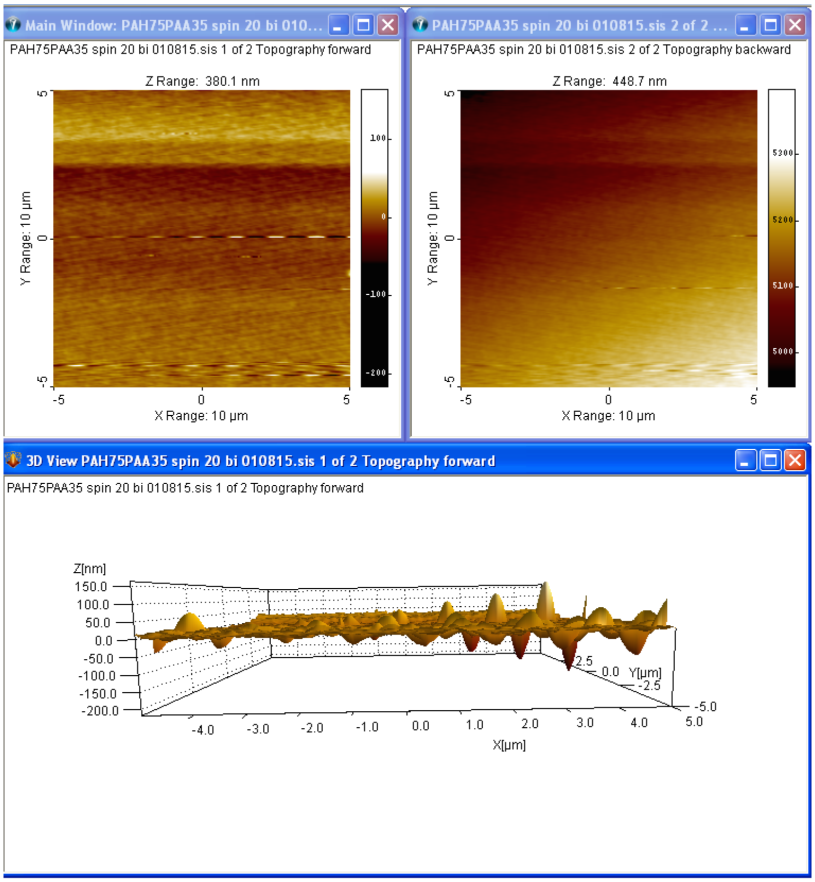

Figure 3.2.2 Topographic image of spin-coated $(PAH7.5/PAA3.5)_{20}$ with RMS = 13.6nm

In contrast to their spin-assembled counterparts, dip-coated $(PAH7.5/PAA3.5)_{20}$ films appeared non-uniform and cloudy. Based on the topographic image from Figure 3.2.3, the film had several peaks and valleys, which indicated the unevenness of the film. The RMS roughness value was 20 times greater than the spin-coated $(PAH7.5/PAA3.5)_{20}$ sample.

As mentioned previously, the uneven dip-coated (PAH7.5/PAA3.5) film morphology led to an investigation of whether a surface treatment could be used to produce smoother films. Two surface treatment techniques were attempted: silane treatment and an adsorbed PEI underlayer. Using silane treatment before deposition would make the substrate hydrophobic and potentially encourage alternate types of surface binding interactions. For example, others have shown that the PAH7.5/PAA3.5 system can adsorb directly onto hydrophobic poly(dimethylsiloxane) surfaces [16]. In addition, an adsorbed PEI underlayer was used to attempt to promote adhesion of thin film during the deposition process as PEI is a strong polycation which could introduce more surface charge and make the first few bilayers of PAH/PAA adhere more strongly onto the substrate.

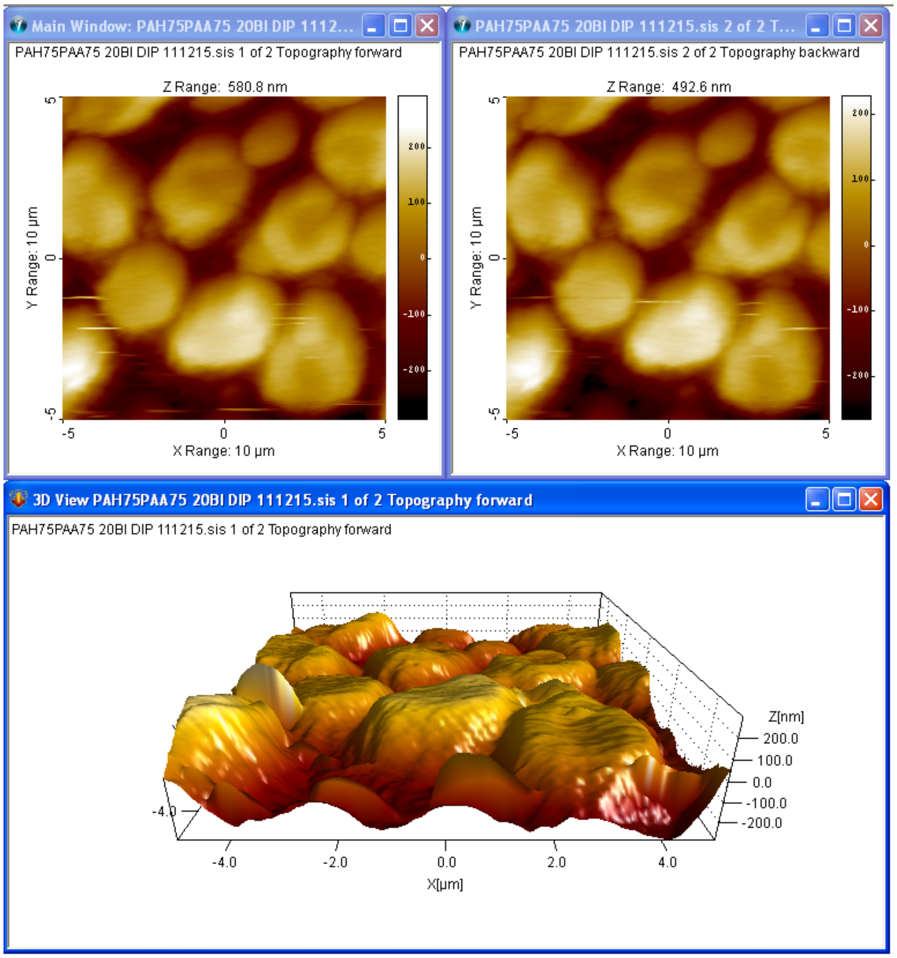

Figure 3.2.3 Topographic image of dip-coated $(PAH7.5/PAA3.5)_{20}$ with RMS=386.2nm

The topographic image of silane treated dip-coated $(PAH7.5/PAA3.5)_{20}$ was shown in Figure 3.2.4. The RMS roughness value of 61.4 nm decreased drastically after the treatment compared to the sample without the treatment (RMS = 386.2 nm). This result indicated that the silane treatment did help to decrease surface roughness in the deposition process. However, this thin film still appeared cloudy visually, and there were still several peaks and valleys on the film surface based on the topography image. Therefore, silane treatment before deposition of dip-coated $(PAH7.5/PAA3.5)_{20}$ did not work well enough to enable reflectometry, and samples were not as smooth as their SA counterparts.

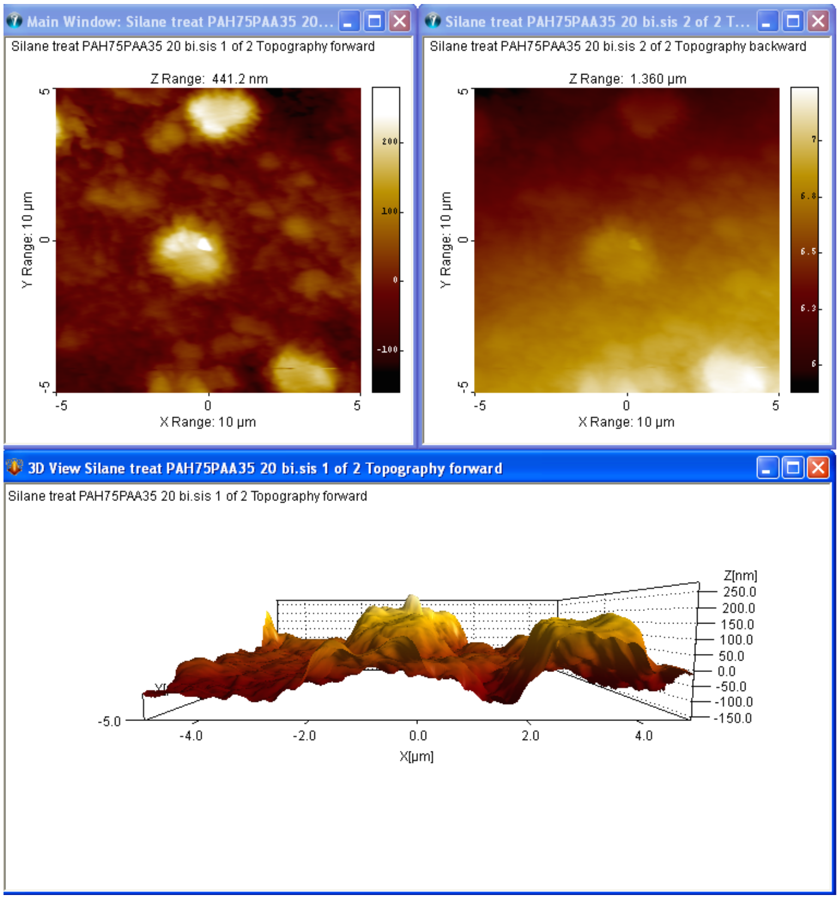

Figure 3.2.4 Topographic image of silane treated dip-coated $(PAH7.5/PAA3.5)_{20}$ with RMS=61.4nm

The topographic image of dip-coated $(PAH7.5/PAA3.5)_{20}$ with an adsorbed PEI underlayer is shown in Figure 3.2.5. Compared to the sample without any treatment, the thin film with an adsorbed PEI underlayer had a much smaller RMS roughness value of 35.2 nm. This could due to the fact that the strong polycationic PEI helped with the adhesion of the deposited thin film in the deposition process. However, even with a PEI underlayer and an order of magnitude decrease in the surface roughness from samples with an untreated substrate, the film appeared to be cloudy, and the film was still too rough to characterize using optical techniques.

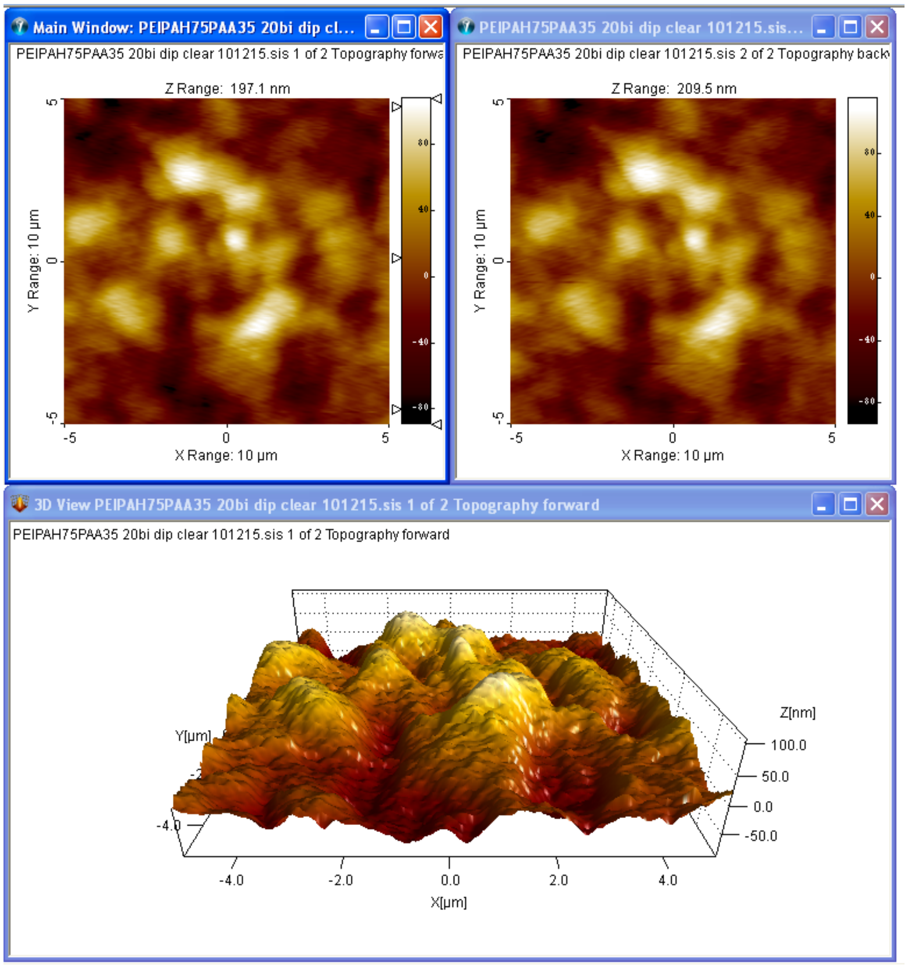

Figure 3.2.5 Topographic image of dip-coated $(PAH7.5/PAA3.5)_{20}$ with a PEI underlayer with RMS=35.2nm

Based on the two surface treatment findings, they both gave a smaller RMS roughness value compared to the thin film without any surface treatments. Even though neither treatment made the thin films visually uniform and clear, the roughness of the thin films decreased drastically. The adsorbed PEI underlayer on the dip-coated $(PAH7.5/PAA3.5)_{20}$ produced a smaller RMS roughness than the silane treated sample.

As mentioned before, an adsorbed PEI underlayer promoted better adhesion for the thin film because of the increase in surface polycationic charge, which would presumably provide adsorption sites for the polymer molecules to attach onto the surface.

3.3 Humidity hysteresis study

Swelling and deswelling measurements were performed on SA-LbL $(PAH7.5/PAA3.5)_{20}$ and SA-LbL $(PAH7.0/PAA7.0)_{20}$ films. The temperature for the testing condition was 25.3±0.17 ºC. The results of these studies are shown below in Figures 3.3.1 and 3.3.2, respectively. Both of the samples exhibited a hysteresis effect. In addition, they both swelled up to a maximum of nearly 40% of the dry-state thickness, which was similar to previous results [13]. However, neither system collapsed back to its original thickness at 10 %RH, which has been previously observed. This could be due to the decreased chain mobility in the PEM at low humidity [13].

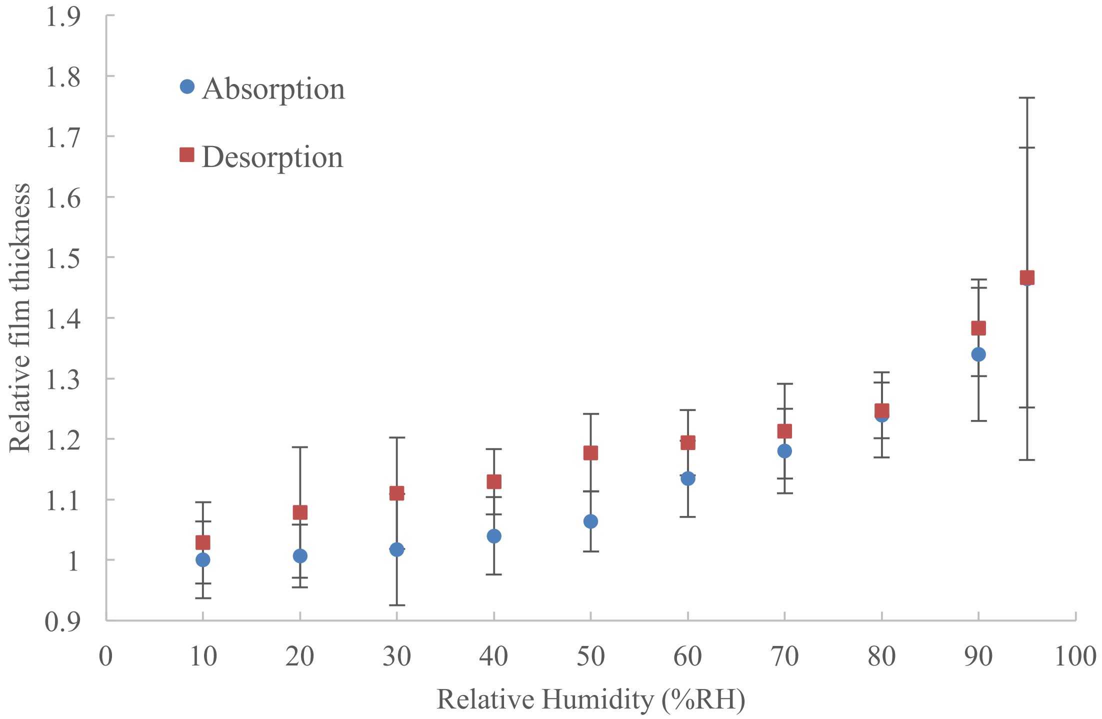

Figure 3.3.1 Humidity swelling/deswelling of SA-LbL $(PAH7.5/PAA3.5)_{20}$ (The uncertainty represents the standard deviation of at least 5 times of film thickness measurements)

As can be seen on both plots (Figure 3.3.1 and Figure 3.3.2), there was a comparatively larger change of thickness from 90% RH to ≈100%RH in swelling. This could be due to increased mobility of chains in the film at the highest humidity values. From 10% RH up until 90% RH, the film was hysterestically stable, meaning that a different thickness was observed for absorption and desorption measurements [13].

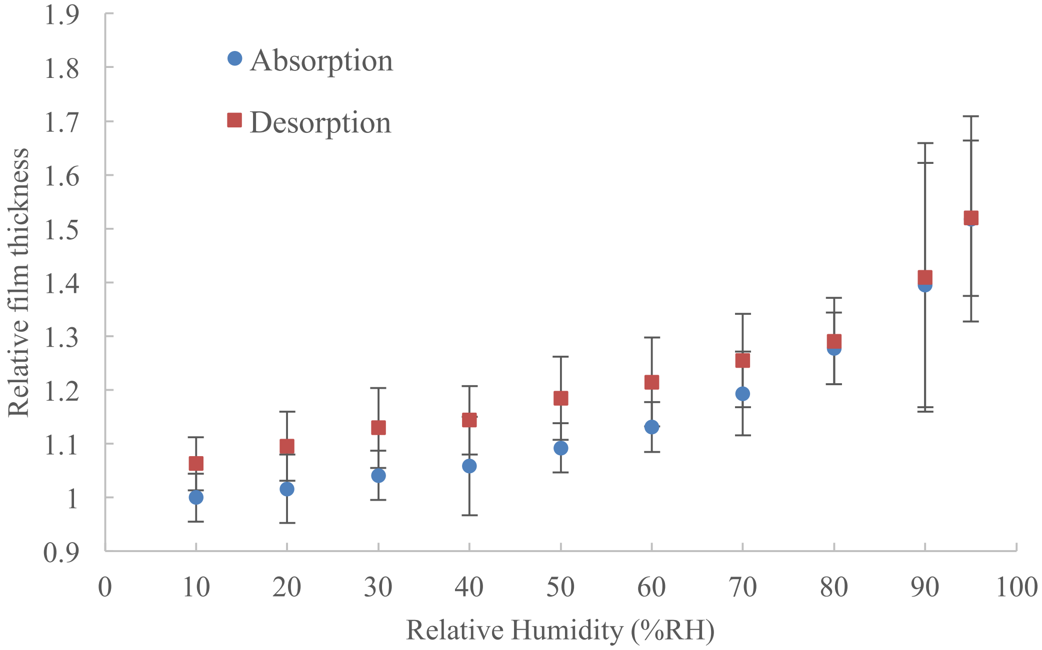

Figure 3.3.2 Humidity swelling/deswelling of SA-LbL $(PAH7.0/PAA7.0)_{20}$(The uncertainty represents the standard deviation of at least 5 times of film thickness measurements)

It was interesting to find in this case that at different pH conditions using SA-LbL assembly, the thin films demonstrated similar humidity hysteresis effect. At room temperature, the bilayer thickness of SA-LbL $(PAH7.0/PAA7.0)_{20}$ was very close to the bilayer thickness of SA-LbL $(PAH7.5/PAA\ 3.5)_{20}$. In addition, according to Figure 3.1.1, the thin film growth pattern for both conditions was relatively similar. Based on these observations, a speculation could be made that using SA-LbL to construct PAH/PAA system, even though the pH of polymer solutions was different, the resulting thin film structure could be similar. However, this speculation needs to be further investigated.

The humidity hysteresis effect was difficult to analyze in the dip-coated LbL $(PAH7.0/PAA7.0)_{20}$ due to the high uncertainty in film thickness as well as its small film thickness. As can be seen from Figure 3.3.3, the film thickness was not stable and thickness measurements varied widely at each humidity condition. Although it is feasible that the water entering the film was rearranging the crosslinking in a dramatic way or that the substrate was having an effect on the swelling properties due to the thinness of the film, it should be noted that the film thickness of dip-coated LbL (PAH7.0/PAA7.0)$_{20}$ was really small (≈13nm), making film thickness measurements by reflectometry extremely challenging. Without additional measurements on thicker dip coated (PAH7.0/PAA7.0) films, it difficult to say anything conclusive about the swelling properties of that system.

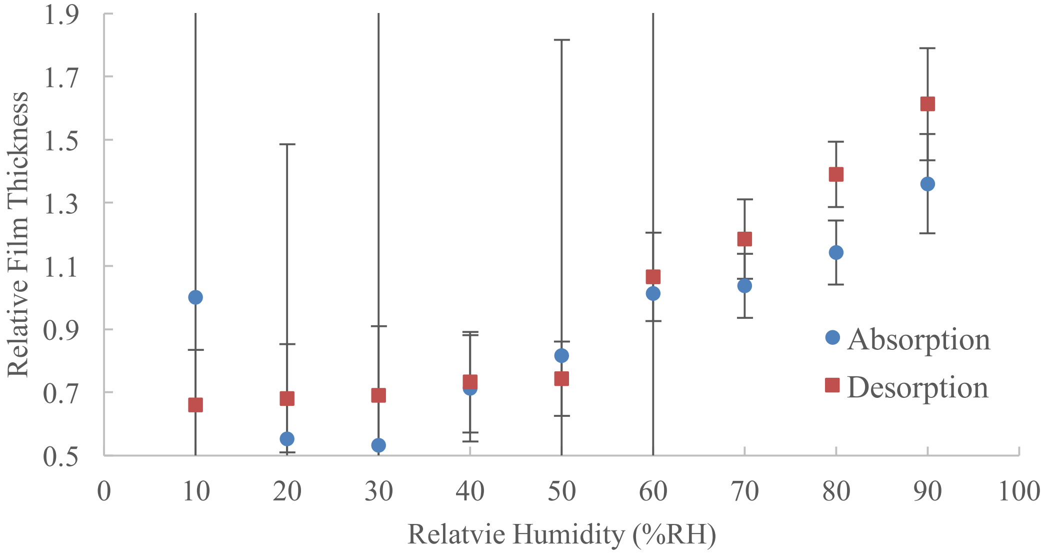

Figure 3.3.3 Humidity swelling/deswelling of dip-coated LbL (PAH7.0/PAA7.0)$_{20}$ (there is a point not shown at %RH≈100 where the swelling ratio is near 3)

4. CONCLUSIONS

PEMs in this study were constructed at two different pH assembly conditions and by two different techniques: automated dipping assembly and spin-assisted assembly. The difference in assembly methods at the same assembly conditions resulted in different film thickness and film morphology.

The adsorption of polyelectrolyte chains in dip-coating LbL assembly is limited by diffusion and charge repulsion between adsorbing and adsorbed chains, which is mediated by the solution pH. PEMs constructed by dip-coated LbL had very different film thicknesses and morphology depending upon the pH of the polymer solutions. On the other hand, SA-LbL assembly utilizes a forced adsorption method. The resulting film thicknesses for both SA-LbL $(PAH7.5/PAA3.5)_{20}$ and SA-LbL $(PAH7.0/PAA7.0)_{20}$ did not vary much. Therefore, SA-LbL assembly appears to yield films whose morphology is less sensitive to the pH of the polyelectrolyte solutions.

The film morphology of dip-coated LbL $(PAH7.5/PAA3.5)_{20}$ was non-uniform, and AFM tests suggested a film thickness of several hundred nanometers. Even though different surface treatments were tested on the substrate and were able to decrease the roughness considerably, it did not decrease the film roughness to the same level as SA-LbL films, and thickness measurements with the reflectometer could not be performed. For the dip-coated LbL $(PAH7.0/PAA7.0)_{20}$, the film morphology looked uniform, but the films were considerably thinner. In the PAH7.0/PAA7.0 system, different assembly techniques could result in different film thickness. The SA-LbL PAH7.0/PAA7.0 sample resulted in a thicker film compared to the dip-coated LbL PAH7.0/PAA7.0 sample. In this case, SA-LbL could produce a thicker film in a much shorter time. Therefore, the assembly technique is important to film thickness and morphology.

In addition, humidity swelling hysteresis effects were found in both SA-LbL $(PAH7.5/PAA3.5)_{20}$ and SA-LbL $(PAH7.0/PAA7.0)_{20.}$ However, for the dip-coated LbL $(PAH7.0/PAA7.0)_{20}$, even though the film morphology looked uniform, the films were considerably thinner, making film swelling/deswelling measurements and an evaluation of swelling hysteresis difficult to quantify. The humidity swelling hysteresis effect at this condition needs to be further investigated with a thicker film thickness.

Based on the similar humidity hysteresis effect found in SA-LbL $(PAH7.0/PAA7.0)_{20}$ and SA-LbL $(PAH7.5/PAA3.5)_{20}$, it would be beneficial for the future work to determine whether the films were chemically similar internally. In addition, different pH condition pairs of PAH and PAA could be investigated to see if similar humidity hysteresis persisted over wider ranges of assembly conditions.

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