Poly(vinyl alcohol) Based Hydrogen-Bonded Multilayers: From pH-Controlled Multi-Stage Dissolution to Zwitter-Wettable Surfaces

by

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ABSTRACT

Understanding the mechanisms that govern the structure and function of synthetic polymer thin films is of fundamental and practical significance for developing a diverse range of functional surfaces including antifogging coatings, switchable surfaces and stimuli-responsive hydrogels. The first part of this thesis is focused on extending hydrogen-bonding driven polymer thin film assembly by developing a novel systematic framework in which poly(vinyl alcohol) (PVA) can be incorporated into LbL assembled multilayer thin films. Incorporation of PVA into multilayer thin films is advantageous due to its biocompatibility and ease of chemical functionalization and cross-linking. The optimal assembly conditions of PVA multilayer films were discovered through extensive investigation on the degree of PVA hydrolysis, molecular weight and the type of weak polyacids. Subtle variations due to the prevalence of PVA acetate moieties, characterized by the degree of hydrolysis, were shown to cause drastic differences both in self-assembly with its hydrogen-bonding partners as well as its overall pH-stability.

The library of materials that can be hydrogen-bonded with PVA was further extended by assembling films with biologically relevant molecules such as tannic acid. This leads to enhanced pH-stability as a result of the high pKₐ value of tannic acid. Multiple stacks of hydrogen-bonded LbL structures with differing composition and properties were also assembled resulting in complex heterostructured architectures that sequentially dissolve with an increase in local pH conditions.

The abundance of free hydroxyl and carboxylic acid groups in the PVA/PAA multilayer allows for enhanced pH stability up to physiological conditions using thermal and chemical methods which offer numerous opportunities for post-assembly functionalization. This was demonstrated by functionalizing PVA/PAA multilayers with poly(ethylene glycol methyl ether) (PEG) to generate a novel antifogging coating with switchable surface properties. To facilitate the characterization of the antifogging coatings a new protocol was developed that enables quantitative analysis of antifogging performance via real-time monitoring of transmission levels as well as image distortion.

The antifogging PVA/PAA multilayers were shown to exhibit “zwitter-wettable” behavior, whereby the multilayer film exhibited a facile, rapid absorption of molecular-level water into a film from the gas phase while simultaneously exhibiting very high contact angles for macroscopic liquid drops of water placed on the surface of the same film. An additional step of functionalizing this nano-blended PVA/PAA multilayer with PEG segments produced significantly enhanced antifog and even frost-resistant behavior which was due to the increase in the nonfreezing water capacity of the multilayer film.
The PEG-functionalized PVA/PAA multilayers exhibited transient and reversible water contact angle behavior which was studied by both goniometry and dynamic tensiometry. The time-dependent wetting behavior of these coatings was attributed to the transient surface rearrangement of hydrophilic functional groups towards the surface in response to exposure to a liquid water environment. Using a simple first-order thermally-activated model, the kinetics of surface rearrangement was explored in detail.

Finally, a model system was designed to study the zwitter-wettable phenomenon in more detail. The complex network of hydrophilic and hydrophobic moieties was decoupled into a heterostructured film consisting of a hydrophilic reservoir and a hydrophobic capping layer. Surface chemistry and roughness were previously believed to be the main factors controlling condensation of water on the film, however, the capacity of the film to transport water molecules was also found to be important for designing functional zwitter-wettable films.

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3. INTRODUCTION AND BACKGROUND

3.1 Introduction
This chapter introduces several concepts and ideas related to Layer-by-Layer assembly, poly(vinyl alcohol), and antifogging coatings. The aim of this introduction section is to provide basic knowledge for readers outside this specific technical field and facilitate understanding of results and discussion presented in this thesis. Detailed literature reviews on relevant works are described in each chapter with individual introduction sections.

3.2 Motivation
Understanding and developing a novel thin film platform in which various physicochemical properties can be easily tuned and prepared in a cost-effective way is of fundamental and practical significance for various applications including antifogging coatings, switchable surfaces, and stimuli-responsive hydrogels. Previously, Cohen and Rubner group has largely focused on engineering multilayered thin films using Layer-by-Layer (LbL) self-assembly technique to impart desirable functionalities. In particular, multilayered thin films that exhibit superhydrophobic, superhydrophilic, antibacterial, antireflective, pH-responsive, temperature-responsive, drug delivery systems, and antifogging properties have been fabricated and characterized. Among the various systems utilized to achieve such functional films, hydrogen-bonding driven polymer thin film assembly was chosen and extended by introducing a new way to incorporate poly(vinyl alcohol)(PVA) into multilayered film. Then this framework was applied to design heterostructured architecture that sequentially dissolves with increase in local pH condition as well as films that exhibit zwitter-wettable behavior and frost-resisting capabilities.

In the following part of this chapter, we will start by introducing the LbL self-assembly technique and discuss in detail how this general processing technique is expanded to hydrogen-bonding driven assembly. We will then introduce the advantage of incorporating PVA into the hydrogen-bonded LbL assembly and exploit wide range of applications in detail by introducing two major themes of this thesis: (i) PVA-based
film fabrication and its applications, and (ii) Design and fabrication of zwitter-wettable surfaces for antifogging/frosting applications.

3.3 Layer-by-Layer Assembly

Layer-by-Layer (LbL) assembly technique has been known to be one of the simple and versatile methods to prepare functional thin films. In the conventional LbL process, a substrate is dipped into aqueous solution of oppositely charged polyelectrolyte (i.e., a polyanion and a polycation) with rinsing steps in between as shown in the Figure 3-1 below.

![Figure 3-1 Schematic of the LbL film deposition process.](image)

During the assembly, adsorption is typically driven by electrostatic interactions with a charged substrate. Adsorption results in charge overcompensation, which then facilitates the subsequent adsorption of another oppositely charged polyelectrolyte. This process creates alternating bilayers of polyelectrolyte in a very controlled manner due to self-limiting adsorption and desorption of polyelectrolytes in each dipping cycle. In some cases, polyelectrolytes contain weak acid or base functional groups such as amine and carboxylic acid groups whose degree of ionization is dependent on the pH of the solution. As a result, the conformation of polyelectrolyte molecules in solution as well as the way in which it adsorbs during the dipping process changes. This gives an opportunity to control the structure of an adsorbed polymer layer which at the end determines the physicochemical properties of the resulting multilayered film. For example, by changing the assembly pH and the type of polyelectrolyte used, precise tuning of film thickness, roughness, porosity, surface wettability, cytotoxicity, anti-bacterial and mechanical properties
was achieved earlier.\textsuperscript{3, 17, 18} It is also noteworthy to mention that molecular weight as well as ionic strength have been reported to have effect on the conformation of polyelectrolyte molecules in solution and serve as additional parameters to tune the properties of multilayer film.

While electrostatic interactions are most commonly used to assemble multilayer films, over the past decade, LbL technique has been extended to prepare films based on wide range of interactions such as hydrogen-bonding,\textsuperscript{19-21} covalent bonding,\textsuperscript{22} molecular recognition,\textsuperscript{23} and hydrophobic interactions.\textsuperscript{24} This led to incorporation of broader range of materials to the system and increased the spectrum of potential applications and usefulness of LbL technique.

3.4 Hydrogen-Bonded Layer-by-Layer Assembly

Among the variety types of interactions used to assemble multilayered films, hydrogen-bonding interaction is of particular interest due to ease of producing stimuli-responsive films and the ability to incorporate uncharged polymers. First discovered a decade ago by our research group,\textsuperscript{25} significant amount of research has been done on the development of hydrogen-bonded multilayer films with these promising properties. In particular, aqueous solutions based hydrogen-bonded LbL assembly was considered highly advantageous since water is environment-friendly and adequate for biological applications and drug delivery systems.

Hydrogen-bonded LbL assembly of water-soluble polymers often involves a weak polyelectrolyte such as polyacids, and a neutral polymer. Unlike the electrostatically assembled counterparts, hydrogen-bonded LbL assembly consisting of polyacid is often performed in acidic conditions where polyacid is protonated and act as hydrogen donating polymer while the neutral polymer act as the complementary hydrogen accepting polymer. It was also demonstrated earlier that various assembly parameters such as polymer type, assembly pH, molecular weight, ionic strength of the medium can be used to control the growth of hydrogen-bonded films.\textsuperscript{20, 21} Details on the effect of various assembly conditions on growth can be found in one of the well-written review papers on hydrogen-bonded LbL films.\textsuperscript{20, 21}
One of the unique features of hydrogen-bonded LbL films involving polyacids is their pH-sensitive stability. Polyacids incorporated in these films become increasingly ionized at pH conditions above the assembly pH, a trend which continues until the critical pH (pH_{crit}), when the film disassembles primarily due to the enhanced swelling driven by the ionization of the polyacids. Depending on the strength of hydrogen-bonding interactions within the film, the value of pH_{crit} can be fine-tuned for controlled delivery systems where the film dissolves above a certain pH condition. On the other hand, several strategies have also been developed recently to stabilize hydrogen-bonded films at neutral or even basic conditions for applications where pH-stability in physiological conditions is required. Furthermore, these systems have been utilized to create free floating films as well as pH-responsive polymeric capsules by applying on colloidal substrates.

3.5 Poly(vinyl alcohol)

Poly(vinyl alcohol)(PVA) is a well-known hydrophilic synthetic polymer that has been broadly used in the hydrogel area due to its biocompatibility and ease of chemical functionalization and cross-linking.

![Chemical structure of poly(vinyl alcohol)](image)

Figure 3-2 The chemical structure of poly(vinyl alcohol)(PVA).

Although PVA is commonly known as a simple linear polymer with hydroxyl groups along the polymer chain, PVA has some residual acetate moieties as shown in Figure 3-2. Because PVA cannot be directly synthesized, poly(vinyl acetate) is prepared first and hydrolyzed in basic environment to result in PVA. Thus, depending on how much residual acetate moieties are remaining in the polymer chain, there exists a parameter, degree of hydrolysis (DH) which shows how much hydroxyl groups are present in the polymer chain versus acetate groups. There are two grades of commercially available PVAs, partially hydrolyzed
PVA \((\text{PVA}_g)\) with 84-87% of hydroxyls and fully hydrolyzed PVA \((\text{PVA}_f)\) with 97-99% of hydroxyl groups.

PVA is extensively utilized in many applications including antifogging coatings, \(^2\) controlled release systems \(^2\), arthroplasty and tissue engineering \(^3\). However, PVA is subjected to rapid dissolution in water due to its hydrophilic nature which limits its broad applicability as a thin film. One of the conventionally used methods to avoid this problem is to chemically cross-link PVA with bifunctional compounds capable of reacting with the hydroxyl groups. This enhances resistance to dissolution and improves mechanical properties. Heat-treating above the glass transition temperature, \(^3\) as well as repeated freezing-thawing cycles, \(^3\) are also used as means of achieving the same goal mainly by increasing the crystallinity of the polymer, which acts as a physical network. It is noteworthy to mention that PVA is a semi-crystalline material that exhibits crystallinity as hydroxyls are small enough to fit into the lattice and also has inter-, and intra- hydrogen bonding capability.

Another method of stabilizing this water-soluble PVA is to from hydrogen-bonded complex by introducing a complementary polymer pair. When two initially soluble polymers are bound within a complex through multiple hydrogen bonds along the polymer chain, water-insoluble product is formed by screening of hydrophilic moieties. Conventional solvent-casting methods are widely employed to deposit such complexes at surfaces for generating interpenetrating polymer network (IPN) and hydrogel systems. However, these methods often results in poor control of film quality and thickness. Thus, it is highly desirable to develop a way to incorporate PVA into hydrogen-bonded LbL assembly which allows precise tuning of physicochemical properties. It should be noted that only few reports \(^2\), \(^3\), \(^3\) have been published on the successful incorporation of PVA into multilayer films. Beyond our first demonstration that hydrogen-bonded multilayers can be formed from PVA by assembling with polyaniline, \(^2\) very little progress has been made in this area.
3.6 Antifogging Coatings

When cold surfaces are introduced into a hot and humid environment, water molecules in the vapor
phase start to nucleate and grow on the surface. When condensed water droplets grow large enough to
scatter light, these are called (surface-induced) fog. These fog cause visibility and perception issues on
transparent substrates which is a detrimental to their function. Often times, it takes couple of minutes to
clear out until the surface equilibrates with the exposed environment which can raise severe safety issues
in applications such as car windshields by obstructing the view.

A number of different approaches have been put forth to alleviate this fogging issue where the main
design principle was to alter the surface wetting characteristics to become hydrophilic. It has been well-
accepted that equilibrium contact angle is the primary factor that determines whether a surface will fog or
not. For instance, if a surface has high water contact angle, the condensates will be in discrete droplet
form acting as individual scatter points whereas surfaces with low water contact angle would form a
continuous sheet of water layer where this fogging is mitigated.

Previously, Galvin et al. \textsuperscript{35} investigated the effect of surface wettability (determined by the water contact
angle value) and the size of the water droplet on light scattering. From theoretical calculations based on
Snell's law, it was concluded that for low contact angle water droplets (less than ~ 40°), the internal
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observed as contact angle increases. Also it was demonstrated that as the droplet size increases due to
coalescence, the relative area which scatters light is confined to the edge of the droplet. Based on these
calculations, significant amount of research has focused on developing experimental methods to alter the
surface to become hydrophilic and facilitate film-like condensation.

In our research group, hydrophilic polysaccharides such as chitosan and carboxymethyl cellulose have
been electrostatically assembled by LbL technique to result in antifogging coatings.\textsuperscript{15} These hydrophilic
coatings remained optically clear in condensing environments due to their superior water-absorbing
characteristics that form a uniform, non-light-scattering film of water on the surface. Also, silica and
titania oxide nanoparticles were LbL assembled to generate nano-porous multilayer films where water completely spreads on the surface with nearly zero degree contact angle and exhibit anti-fog behavior.\textsuperscript{3,4}

While these superhydrophilic coatings have its own unique characteristics, either due to the photocatalytic effect of titania dioxide nanoparticles or capillary condensation provided by the nano-porous structure, these films suffer from issues such as short life time under humid conditions, excessive fouling and poor mechanically durability.

Another technical difficulty in the antifogging community is the absence of rationally designed quantitative method to evaluate the antifogging performance. Although others\textsuperscript{22,36} have attempted to quantitatively characterize antifogging performance by measuring time-dependent light transmission or haze values using ASTM standards, these methodologies may not always capture the true optical performance of the coating. Not to mention that majority of the previously reported antifogging coatings were evaluated by simple qualitative tests such as the Erlenmeyer steam test and the cold-fog test.\textsuperscript{3,4,15,22,36-64} Thus, it is indeed necessary to design an experimental setup that allows quantitative analysis of the antifogging performance.

3.7 Thesis Outline

3.7.1 PVA-Based Film Fabrication and Its Applications

The first part of this thesis (chapter 4-6) focuses on developing PVA-based hydrogen-bonded multilayer platform in which various physicochemical properties can be easily tuned to achieve smart pH-responsive hydrogels.

Chapter 4 explores the interpolymer complexation of various PVAs with weak polyacids and relates LbL assembly parameters to the film growth behavior, and pH-stability of the hydrogen-bonded films.

Through the systematic study in Chapter 4, optimal assembly condition of PVA-based multilayer films is investigated. Also, pH-responsive hydrogels as well as the potential opportunities for post-assembly functionalization is investigated in detail.
In Chapter 5, the library of materials that can be hydrogen-bonded with PVA is further extended by assembling films with tannic acid. The optimal assembly condition as well as the effect of DH of PVA, and concentration on film growth behavior is explored. Incorporation of tannic acid enhances the pH-stability of PVA-based multilayer films up to physiological pH conditions without thermal crosslinking suitable for biological applications.

In Chapter 6, pH-sensitive nature of PVA-based multilayer film is combined with the advantage of LbL assembly technique to assemble multiple stacks, each with different pH-stability to generate heterostructured architecture. By varying the stacking sequence, pH-controlled multi-stage dissolution of the multilayer film as well as multi-functional freestanding film with tunable film thickness is generated.

3.7.2 Design and Fabrication of Zwitter-Wettable Surfaces for Antifogging/frosting Applications

The second part of this thesis (chapter 7-9) focuses on design, fabrication, and characterization of zwitter-wettable surface and their application in antifogging/antifrosting coatings.

In chapter 7, PVA/PAA multilayer film assembled in Chapter 4 is used to generate a novel antifogging coating with zwitter-wettable characteristics. Antifrosting coatings are produced by post-functionalization with poly(ethylene glycol) segments which increases the nonfreezing capacity of the film. Also, an experimental protocol that enables quantitative analysis of antifogging performance is introduced.

In Chapter 8, the transient and reversible water contact angle behavior of PEG-functionalized PVA/PAA multilayer film is investigated. It is demonstrated that the time-dependent wetting behavior was attributed to the rearrangement of functional groups towards the surface in response to exposure to a liquid water environment. In addition, the kinetics of surface rearrangement is explored in detail by both goniometry and dynamic tensiometry.

Chapter 9 explores the underlying mechanism of zwitter-wettable phenomenon by designing a model system. Decoupling a complex hydrogel system into a heterostructured film consisting of a hydrophilic reservoir and a hydrophobic capping layer allowed various experimental characterization techniques to be
employed for systematic studies. From this study, it is revealed that the capacity of the film to transport water molecules is important for designing functional zwitter-wettable surfaces.
4. HYDROGEN BONDING BASED LAYER-BY-LAYER ASSEMBLY OF POLY (VINYL ALCOHOL) WITH WEAK POLYACIDS

This was a research project with Mensire, R., a visiting student from Ecole Polytechnique. Mensire, R. carried out the spray LbL assembly portion of this work. Reproduced in part with permission from Lee, H., Mensire, R., Cohen, R.E, and Rubner, M.F., Macromolecules, 45 347-355. Copyright 2012 American Chemical Society.

4.1 Introduction

Poly(vinyl alcohol) (PVA) is extensively utilized in many important technologies due to its wide ranging attributes including, for example, a high level of biocompatibility and hydrophilicity, excellent barrier properties and ease of chemical functionalization, cross-linking and crystallization. The incorporation of this important water soluble polymer into Layer-by-Layer (LbL) assembled multilayer thin films, however, remains limited to only a few material combinations that tend to exploit the strong hydrogen bonding ability and often limited water solubility of the PVA assembly partner. Previous hydrogen bonding partners used to form LbL multilayers with PVA include polyaniline, and clay particles. Although these multilayer systems provide unique property combinations, they clearly lack the level of versatility and post-assembly chemical and physical manipulation that is now well established with polyelectrolyte multilayers based on weak polyelectrolytes such as poly(acrylic acid) (PAA). In fact, it is quite interesting to note that PVA stands out as one of the few water soluble, hydrogen-bonding polymers that has not been successfully assembled into a multilayer thin film with suitable polycids or other often-utilized hydrogen bonding partners. This is in contrast to poly(ethylene oxide) (PEO), which readily forms LbL assembled polymer multilayers with PAA. It should also be noted that others have assembled PVA multilayers using a borax complex, hydrophobic interactions, covalent bonding, and polymer mixtures.

In this chapter of my thesis, we demonstrate that it is possible to fabricate high quality, hydrogen bonded multilayer films from PVA and PAA or poly(methacrylic acid) (PMAA). As expected, it was found that
the assembly solution pH must be low enough to avoid ionization of the carboxylic acid groups of PAA. However, it will be demonstrated that the degree of hydrolysis of PVA and its molecular weight are also critical parameters that determine whether hydrogen bonded LbL assembly is possible. To realize high quality multilayer thin films, it is also necessary to utilize suitable surface chemistry to anchor the first layer of PVA. It will be further shown that the pH stability of the resultant multilayer thin films can be enhanced significantly with a short heat treatment that introduces ester cross-links between PVA and PAA. Thus, with suitable heat treatment, robust multilayer thin film hydrogels with reversible swelling behavior can be created that are stable at physiological pH. The presence of an abundance of free alcohol and carboxylic acid groups in the lightly cross-linked films provides numerous opportunities for post-assembly functionalization as will be demonstrated by the covalent attachment of a protein to the acid groups and a PEO modified dye to the alcohol groups. This PVA based multilayer system represents a new, stable and quite versatile platform for applications ranging from biological to optical. For example, in a future publication, we will show that suitably functionalized optical quality coatings with outstanding anti-fog properties can be fabricated from this system.

4.2 Interpolymer Complexes of PVA in Aqueous Solution

In order to identify solution assembly conditions that would favor robust multilayer growth, we first studied interpolymer complex formation between a variety of PVA samples and the complementary polyacids PAA and PMAA. Others have reported that polycarboxylic acids and proton-accepting polymers can form interpolymer complexes through hydrogen bonding interactions. These water insoluble complexes are often readily detected by simple turbidity, transmission measurements or by visual inspection of the mixed solutions. These simple tests are known to be a helpful predictor of the ability of complimentary polymer pairs to assemble into LbL films. Mixing PAA and proton-accepting polymers such as PEO in suitable aqueous solutions, for example, leads to interpolymer hydrogen bonding interactions that screen the hydrophilic functional groups and result in insoluble polymer
complexes. Conditions that favor the formation of these water-insoluble complexes are good candidates for successful LbL assembly.

Although the repeat unit of PVA is isomeric with that of PEO, its hydrogen bonding properties are very different due to the presence of hydroxyl groups. The hydroxyl groups of PVA can form hydrogen bonds with other hydroxyl groups within the same chain (intra-chain hydrogen bonding) or on other PVA chains (inter-chain hydrogen bonding). PVA is made by the hydrolysis of poly(vinyl acetate), and the fraction of residual acetate groups along the chain typically varies from as high 15% to as low as 1%. Since the degree of hydrolysis determines the linear density of hydroxyl groups along the chain, it will also affect the behavior of PVA in solution and its ability to engage in inter- and intra-molecular hydrogen bonds. As might be expected, polymer complex formation is also strongly influenced by the molecular weight of the interacting polymers.

To explore these different parameters, various PVA samples with different degrees of hydrolysis and different molecular weights were mixed with complimentary hydrogen bond donors (PAA and PMAA) to test for interpolymer complex formation.
Figure 4-1 (a) Cartoon showing interpolymer complexation of PVA and PAA. (b) pH / PVA matrix showing the attenuation of transmitted light (I) expressed as $\Delta I/I_0$ where $\Delta I = I_0 - I$ and $I_0$ is the incident light intensity averaged over the 370-750 nm range. (c) Photographs of PVA/PAA and PVA/PMAA mixtures. PVA and PAA were mixed in equal volume ratios. The concentration of each solution before mixing was 1 mg/mL and the pH was adjusted to 2.0 using HCl. All solutions were transparent before mixing and the light transmittance was measured 10 min after mixing for (b).

Figure 4-1(b) displays the fractional attenuation of light ($\Delta I/I_0$) of various solutions of PVA and PAA. When PAA is the proton-donating polymer, complexation with PVA depends strongly on the pH of the aqueous solution. While turbidity is observed in several cases at pH 2.0, as the pH increases, hydrogen bonding decreases due to the increased ionization of the PAA chains and, consequently the measured light attenuation decreases towards zero. The results show that even in pH 2.0 DI water where PAA is known to be fully protonated, complexes are not formed readily for both low and high molecular weight fully hydrolyzed PVA (F1, F2). However for partially hydrolyzed PVA (P1 and P3) and especially for the high molecular weight sample PVA$_3$, there is a noticeable change in solution turbidity upon mixing the polymer solutions. For PVA$_3$/PAA, the solution turbidity is also apparent even at pH 3.0, where PAA starts to ionize. These results clearly show that the degree of hydrolysis and molecular weight of PVA are
important parameters controlling polymer complexation with PAA. PMAA was also used to evaluate the effect of the degree of hydrolysis on interpolymer complexation. Others have reported that PEO/PMAA complexes are more stable and more strongly interacting than PEO/PAA complexes due to the α-methyl group of PMAA. As shown in Figure 4-1(c), all PVA solutions became turbid upon mixing with PMAA. From this, we conclude that the effect of the extent of PVA hydrolysis is significant only for weakly interacting polymer pairs such as PVA and PAA. The analog of Figure 4-1(b) for PVA/PMAA was also produced and is included in the Supplemental Information (Figure 4-9).

4.3 Layer-by-Layer Assembly of PVA with PAA or PMAA

With the insight gained from the interpolymer complex formation screening test, we explored how complex formation relates to the LbL assembly process. It should be noted at this point that high quality LbL films were obtained only if suitable surface chemistry was applied to the substrate prior to the deposition of the first PVA layer. In the case of PEO/PAA hydrogen bonded films, it has been reported that reproducibility issues exist as well as batch-to-batch variability even for carefully controlled assembly conditions. We observed similar behavior in our preliminary experiments with the PVA/PAA system in which the only pretreatment of the glass substrate was oxygen plasma. In particular, overall film quality was poor, exhibiting agglomerates and non-uniform thickness across the film. Luzinov’s group recently introduced a robust method to anchor various polymers to surfaces by attaching a macromolecular anchoring layer rich in epoxy functional groups to the substrate. PGMA serves as an anchoring interlayer to attach functional polymers, providing a strong bond between the grafted layer and the substrate. Using this method, the first layer of PVA was covalently bonded to the substrate. The film subsequently assembled on top of this layer showed enhanced thickness reproducibility and increased smoothness as shown in Supplemental Information (Figure 4-10). The enhanced adhesion of the LbL films to the substrates greatly simplified the swelling characterization and spectroscopy analysis. Due to these many advantages, all multilayers were assembled from aqueous solutions of pH 2.0 with no added
salt onto PGMA-modified glass substrates with the first layer of PVA covalently attached as described above. Both dip and spray assembly were utilized to fabricate the multilayer thin films.

Figure 4-2 shows the growth profiles of the various PVA/PAA multilayers examined in this work. As predicted by the solution complexation studies, multilayer growth was dramatically dependent on the molecular weight and degree of hydrolysis of PVA. Whereas the PVA<sub>n</sub>/PAA systems (fully hydrolyzed PVA) exhibited very small thickness increments per deposition cycle even with the higher molecular weight PVA, multilayer growth of the PVA<sub>p</sub>/PAA systems (partially hydrolyzed PVA) was strongly dependent on the molecular weight of PVA. Only multilayers created from the highest molecular weight PVA showed high thickness increments per bilayer. Table 4-1 presents the average thickness increment per bilayer for all of the PVA<sub>n</sub>/PAA systems assembled in this study.

![Diagram](image)

Figure 4-2 Growth behavior of (PVA<sub>n</sub>/PAA) (■ black squares), (PVA<sub>p</sub>/PAA) (● red circles), (PVA<sub>p</sub>/PAA) (▲ blue triangles), (PVA<sub>f</sub>/PAA) (▼ green triangles), and (PVA<sub>f</sub>/PAA) (◆ pink triangles) systems assembled at pH 2.0 on glass substrates modified with PGMA. Figure 2 (a) shows results obtained by dip assembly and Figure 2 (b) shows data obtained on films produced by spray assembly.

For PVA/PAA multilayers assembled at pH 2.0 with fully hydrolyzed PVA, small incremental thicknesses were observed and the multilayers were generally rough compared to the film thicknesses. In sharp contrast, a large bilayer thickness was observed for the PVA<sub>p</sub>/PAA system with an average value of 54.7 nm obtained by using the dip assembly process and 20.6 nm obtained by using the spray LbL assembly process. The former bilayer thickness is comparable to the ~80 nm per bilayer value reported
for dip assembled PEO/PAA,\textsuperscript{72,75} which also features weak intermolecular hydrogen bonding. For the multilayers assembled with partially hydrolyzed PVA, the average bilayer thickness depends strongly on the molecular weight of the PVA used in the assembly process. Similar observation have been reported previously for the PEO/PAA system, where a sevenfold increase in bilayer thickness was observed when the molecular weight of PEO was increased from 1.5 to 20 kDa.\textsuperscript{72} However, as seen in Figure 4-2 and Table 4-1, the average bilayer thickness observed for the dip assembled PVA/PAA system increases by a factor of about 100 when the molecular weight ($M_a$) of partially hydrolyzed PVA increased from 12 kDa to 87 kDa. The spray assembly results show that this multilayer system can be fabricated by using spray approaches. In these preliminary studies, the dip assembled multilayers exhibited a larger thickness per bilayer compared to spray assembled films and lower roughness values. We anticipate that further optimization of the spray assembly process will result in more comparable films. In any event, it is clear that, if needed, it will be possible to take advantage of the faster processing times inherent in the spray assembly process (see Table 4-1).

<table>
<thead>
<tr>
<th>System</th>
<th>Thickness per bilayer (nm)</th>
<th>Roughness ($R_a$) (nm)</th>
<th>Time required to obtain a 500 nm film (min)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Dip assembly</td>
<td>Spray assembly</td>
<td>Dip assembly</td>
</tr>
<tr>
<td>(PVA\textsubscript{P1}/PAA)</td>
<td>0.4</td>
<td>0.6</td>
<td>1.3</td>
</tr>
<tr>
<td>(PVA\textsubscript{P2}/PAA)</td>
<td>5.7</td>
<td>-</td>
<td>0.8</td>
</tr>
<tr>
<td>(PVA\textsubscript{P3}/PAA)</td>
<td>54.7</td>
<td>20.6</td>
<td>0.6</td>
</tr>
</tbody>
</table>

\textsuperscript{a}The linear regime was considered to be from 10-30 bilayers.

\textsuperscript{b}Roughness was measured using profilometry.

As anticipated by the complexation experiments, in the case of the PVA/PMAA multilayer system, reasonable multilayer growth was obtained for all PVA samples examined (Figure 4-3). The use of the
more strongly interacting polyacid PMAA results in average thickness increments comparable to the best PVA/PAA system, regardless of the molecular weight and the degree of hydrolysis of the PVA utilized to fabricate the multilayer.

![Graph showing growth behavior of different multilayer systems](image)

**Figure 4-3** Growth behavior of (PVA<sub>n</sub>/PMAA) (■ black squares), (PVA<sub>m</sub>/PMAA) (○ red circles), (PVA<sub>m</sub>/PMAA) (▲ blue triangles), and (PVA<sub>F</sub>/PMAA) (▼ green triangles) systems dip-assembled at pH 2.0 on glass substrates modified with PGMA.

As mentioned briefly in the introduction, polycarboxylic acids incorporated into a hydrogen bonded multilayer become ionized when exposed to pH conditions higher than the assembly pH. When multilayer films are exposed to this critical higher pH, the hydrogen bonds are disrupted and the film dissolves. The critical pH at which film disintegration occurs depends upon the strength of the hydrogen bonding interactions within the multilayer film, with weaker interactions resulting in lower critical pH values.²¹,²⁶ Among the pH-degradable hydrogen-bonded multilayer systems reported so far, the PEO/PAA system is known to be one of the weakest, with a critical dissolution pH of 3.5.²² When PMAA was used as the hydrogen bonding partner with PEO, the critical pH shifted to a slightly higher value of 4.6.²¹
In order to determine the critical film dissolution pH, multilayer films were immersed into a pH-adjusted solution for 2 hr and the dry film thickness was measured and compared to the original thickness. As shown in Figure 4-4, (PVA<sub>3</sub>/PAA) multilayers start to dissolve between pH 2.5 and 3.0, well below the value of 3.5 observed for PEO/PAA. When PVA is assembled with the more strongly interacting polymer PMAA, the critical pH shifts to higher values as expected. In contrast to the PEO/PAA multilayer system (~1.1 pH units<sup>21,72</sup>), a more substantial increase of 3.75 pH units is observed when comparing PVA<sub>3</sub>/PAA to PVA<sub>3</sub>/PMAA. The enhanced pH stability of PVA<sub>3</sub>/PMAA is attributed to the presence of the methyl groups in PMAA, which along with the acetate moieties in the PVA, lead to stronger hydrophobic interactions that stabilize the film.<sup>77</sup> Figure 4-4 shows that it is possible to tune the critical pH value of PVA containing multilayers from a very low value (about 2.5, (PVA<sub>3</sub>/PAA)) to as high as about 6.5 (PVA<sub>3</sub>/PMAA) by simply changing the hydrogen bonding polyanion partner or by using PVA materials with different degrees of hydrolysis.

The effect of PVA molecular weight on film disintegration was also examined. Although the molecular weight of the depositing polymer significantly affects the film growth behavior as shown in Figure 2, we observed that films containing PVA chains of different molecular weights exhibit essentially the same critical pH value, consistent with results reported for other hydrogen-bonded systems.<sup>21,78</sup> Indeed, as shown in Supplemental Information (Figure 4-11), the PVA<sub>3</sub>/PAA and PVA<sub>3</sub>/PAA multilayers show similar critical pH values even though the film growth behavior is significantly different for these two systems. Dissociation of polymer segments is apparently governed by the destruction of cooperative sequences of associating functional groups, and with sufficiently long exposure to a solution, the molecular weight has only a kinetic effect.
4.4 Composition Analysis and Heat-Induced Cross-Linking Studies of (PVA₃/PAA)₁₀₀

The chemical composition of (PVA₃/PAA)₁₀₀ multilayer films was characterized by dissolving free-standing films in a deutrated solvent (D₂O) and carrying out ¹H-NMR spectroscopy on the solutions as shown in Supplemental Information (Figure 4-12). As a baseline, the degree of hydrolysis for the fully hydrolyzed and partially hydrolyzed PVA samples of similar molecular weight was determined. NMR analysis revealed that the fully hydrolyzed PVA sample has a degree of hydrolysis of 97% whereas the partially hydrolyzed PVA sample is 84% hydrolyzed; both of these values agree well with the manufacturers’ stated values. Using the determined degree of hydrolysis and the PAA spectrum as a reference, the overall composition of a (PVA₃/PAA)₁₀₀ multilayer film was determined to be approximately 47% PVA and 53% PAA.

Several methods have been developed in the literature to extend the pH stability of hydrogen-bonded films to physiological conditions.¹¹ These methods include blending hydrogen-bonded films with an electrostatically interacting pair,⁷⁹,⁸⁰ and cross-linking of the constituent polymers.⁸¹,⁸² In the case of the
PVA/PAA multilayer films, the presence of both carboxylic acid and alcohol groups makes it possible to form cross-links via a simple thermally induced esterification reaction.\textsuperscript{83, 84} Figure 4-5 shows how pH-dependent film stability varies with the extent of heat treatment for the PVA\textsubscript{p3}/PAA system. As-prepared films had a critical pH between 2.0 and 3.0 and dissolved completely at higher pH values. When a (PVAp\textsubscript{p}/PAA)\textsubscript{30} multilayer film was subjected to 105 °C for 5 min, the film became somewhat more stable than the as-prepared films but still exhibited partial dissolution. For reference, the glass transition temperatures of PVA\textsuperscript{85} and PAA\textsuperscript{18} are 55-65 °C and 90-100 °C respectively. When samples were heated for 5 min at 140 °C and for 45 min at 150 °C, however, they were rendered completely stable over a wide range of pH values for up to one week. FT-IR analysis confirmed that heat treatment at these higher temperatures results in the formation of ester crosslinks (see Figure 4-13).

Figure 4-5 pH-triggered disintegration of hydrogen-bonded (PVAp\textsubscript{p}/PAA)\textsubscript{30} film after heat-induced esterification. Subjecting the film to heat-treatment allows control of the disintegration pH.

The pH-dependent swelling behavior of heat treated multilayer films was monitored using \textit{in situ} ellipsometry. The swelling ratio is defined here as the ratio of the thickness of a film in contact with excess water at stated conditions to that of a dry film, both thicknesses measured via ellipsometry. Figure 4-6 (a) shows the swelling ratio in pH 2.0 DI water versus time for a series of (PVAp\textsubscript{p}/PAA)\textsubscript{30} films subjected to a variety of heat treatment protocols. For the untreated sample, the swelling ratio was ~5.5
and as the heating temperature (and time) increased from 105°C (5 min) to 140 °C (5 min) to 150 °C (45 min), a decrease in swelling ratio was observed: the corresponding values of swelling ratio were ~3.2, ~2.3, ~1.4, respectively. This gradual decrease in swelling ratio is consistent with increased esterification cross-linking. Comparing the swelling of (PVA/PAA)30 films subjected to different heat treatments in pH 7.4 phosphate buffer saline (PBS), it is evident from Figure 4-6 (b) that only those films heated for 5 min at 140 °C and for 45 min at 150 °C were stable at physiological pH. Interestingly, a comparison of the swelling ratio at the extremes of the pH range investigated revealed that the swelling ratio of films in pH 2.0 DI water and pH 7.4 PBS were ~1.4 and ~1.8 respectively for multilayer films treated for 45 min at 150 °C. However for the multilayer films heated for 5 min at 140 °C, a significant difference in swelling ratio was observed with a value of ~2.3 for pH 2.0 DI water and a value of ~4.3 for pH 7.4 PBS. Similar behavior was observed previously for a bicomponent hydrogel consisting of PVA and PAA prepared by solvent casting and heat treated to give pH-responsive hydrogels. It was reported that the amount of pH-responsive swelling was reduced by increase of heating time due to enhanced cross-linking in these blends.33, 84

Figure 4-6 Swelling experiments using in-situ ellipsometry measurements of (PVA/PAA)30 films to verify the effect of thermal cross-linking. a) pH 2.0 DI water, b) pH 7.4 PBS buffer.

The thickness of a (PVA/PAA)30 film heated for 5 min at 140 °C was monitored by in situ ellipsometry over five cycles of immersion in either pH 2.0 DI water or pH 7.4 PBS with drying after each step (Figure...
Each film was immersed in solution for 10 minutes and dried at room temperature for several minutes with N₂ before measurements. The thickness increases and decreases observed using in-situ ellipsometry were accompanied by commensurate decreases and increases of the refractive index, indicating that film loss was negligible during pH cycling. These results confirm the excellent pH stability that results from the thermal cross-linking step. Figure 4-7 (b) is a schematic of the key features of a heat treated multilayer film including covalent linkages in the form of ester bonds, ionized carboxylic acid groups, and hydroxyl groups. Changes in the degree of ionization of the acid groups primarily drive the pH-responsive swelling behavior.

![Figure 4-7](image)

**Figure 4-7** (a) pH-dependent reversible swelling behavior of a (PVAP₃/PAA)₃₀ film heated for 5 min at 140 °C in pH 2.0 DI water and pH 7.4 PBS. Films were immersed in the solution for 10 min and dried with N₂. (b) Cartoon showing a pH-dependent reversible swelling.

We used methylene blue adsorption to verify the presence of ionized carboxylic acids existing in the film. The procedure simply involved adsorbing positively charged methylene blue dye into the film and observing whether the film remained stained after thorough rinsing. Figure 4-15 in the Supplemental Information shows that a significant amount of ionized carboxylic acid groups is present in the film even after rigorous rinsing with PBS.

### 4.5 Biofunctionalization with FITC-BSA and RB-PEG

Cross-linked (PVAPₓ/PAA), multilayers are essentially swellable thin film hydrogels, replete with free carboxylic acid and alcohol groups. This combination of properties and functionality makes this
multilayer system an extremely versatile platform for exploring various types of bioengineered surfaces.

To demonstrate that the hydroxyl and carboxylic acid groups can be utilized to add additional functionality to the multilayer, specific post-functionalization chemistries were examined. By selective targeting of these functional groups, it is possible to covalently attach multiple synthetic and biological molecules to the multilayer in a controlled fashion. To accomplish this, a model protein, BSA labeled FITC (FITC-BSA) end-functionalized with a primary amine and a PEG labeled Rhodamine B (RB-PEG) molecule end-functionalized with a hydroxyl group were used as probe molecules. PEG molecules are known to confirm biocompatibility to thin films. As shown in Figure 4-8(a), the multilayer film was first functionalized with FITC-BSA using carbodiimide chemistry. In this case, the carboxylic acid groups embedded in the film were first activated by EDC/NHS chemistry and subsequently reacted with the amine terminated FITC-BSA. To confirm that the FITC-BSA was covalently attached and not simply physically absorbed, a control experiment was done by placing samples with and without the EDC/NHS treatment in a 0.1% (v/v) Tween-20 PBS solution for 3 hrs on a shaker plate. Tween-20 is known to facilitate the removal of physically absorbed proteins. The results shown in Figure 4-16 (a) in the Supplemental Information confirm that in the case of samples activated with EDC/NHS chemistry, a significant fraction of the FITC-BSA is covalently attached to the multilayer and hence not removed by treatment in the Tween solution.

After FITC-BSA attachment, the film was immersed for 30 min into a 0.5 mg/mL RB-PEG solution. The film was then immersed into a 30°C, 0.13% (w/w) glutaraldehyde containing PBS solution for 10 min, rinsed with DI water and dried. When the film is introduced into the 0.13% (w/w) glutaraldehyde PBS solution, it is expected that reactions with both the hydroxyl terminated RB-PEG molecules and the hydroxyl groups of the PVA chains are possible. In the latter case, further chemical cross-linking of the multilayer would occur. Also, given the positive charge of the RB-PEG molecules, one would expect an uptake of dye due to electrostatic binding with the free carboxylic acid groups of PAA. This was confirmed by control experiments in which multilayer films without the FITC-BSA attached were
exposed to solutions of RB-PEG and subsequently treated for 15 hrs in a Tween-20 solution (in Figure 4-16 (b) in the Supplemental Information). Even after the extensive Tween treatment, about half of the dye initially loaded onto the film remained. Thus, it is also possible to use electrostatic binding to add functional molecules to this multilayer. This might be desirable if pH triggered release of the functional molecule is important. For films prior loaded with FITC-BSA, there would be fewer acid groups available for electrostatic binding of the RB-PEG.

Figure 4-8 shows the emission spectra of multilayer films functionalized with the various molecules as well as confocal microscopy images of a multilayer film functionalized with both FITC-BSA and RB-PEG. In the case of the emission spectra, samples excited at a wavelength of 440 nm that have been treated only with FITC-BSA, only with RB-PEG and with both molecules reveal the characteristic emission of each dye (green curve, FITC-BSA only; red curve, RB-PEG only) and the combination spectrum expected when both dyes are present (yellow curve). The confocal microscopy images of the film functionalized with both FITC-BSA and RB-PEG also clearly reveal that the multilayer is emitting both a green and red signal, indicating that both molecules are present in the film.

![Scheme of a film being functionalized with FITC-BSA and RB-PEG. Upper-right hand corner shows the emission spectra of three individual samples excited at a single wavelength of 440 nm (Green : FITC-BSA only, Red : RB-PEG only, Yellow : both).](image-url)

Figure 4-8 (a) Scheme of a film being functionalized with FITC-BSA and RB-PEG. Upper-right hand corner shows the emission spectra of three individual samples excited at a single wavelength of 440 nm (Green : FITC-BSA only, Red : RB-PEG only, Yellow : both). (b) A, C: Confocal microscopy image of the film functionalized with both FITC-BSA and RB-PEG measured at two
different excitation wavelengths of 488 nm (for FITC) and 543 nm (for RB), respectively. B: Plain image to distinguish the coated area, D: Overlay image excited at both wavelengths (488 nm, 543 nm).

4.6 Conclusions

In summary, we have demonstrated that hydrogen-bonded LbL films containing PVA and PAA can be assembled successfully at low pH by using a relatively high molecular weight sample of partially hydrolyzed PVA. By comparing films containing PAA with those containing a more strongly interacting polyacid, PMAA, it was demonstrated that the extent of PVA hydrolysis becomes a significant factor only when weak hydrogen bonding pairs such as PVA and PAA are used. We also demonstrated by pH-triggered dissolution experiments that the degree of hydrolysis can be used as an additional parameter by which to tune the pH stability of the film. This feature may be very useful in the fabrication of sacrificial multilayers for controlled release of overlying multilayers or of therapeutic agents. Thermal treatment of the PVA/PAA multilayer system was found to introduce covalent ester cross-links that stabilize the film to physiological conditions. These heat-treated films were stable to repeated exposure to aqueous solutions of wide ranging pH and swelled reversibly in response to these pH changes. Also, suitably end-functionalized biologically relevant molecules (FITC-BSA and RB-PEG) were successfully covalently attached to the PVA/PAA multilayer to validate that this system is a stable platform, suitable for further functionalization. This new multilayer system opens the door to the exploration of a wide variety of biofunctional thin films and optical coatings.

4.7 Materials and Methods

Materials: To investigate the effect of degree of hydrolysis and molecular weight on the interpolymer complexation behavior and thus on growth behavior and stability of films, a number of PVA samples were obtained from Sigma-Aldrich (P1: $M_w = 24\,500$ g/mol, PDI = 1.99, 87-89% hydrolyzed, P2: $M_w = 88\,400$ g/mol, PDI = 1.18, 87-89% hydrolyzed, P3: $M_w = 131\,000$ g/mol, PDI = 1.50, 87-89% hydrolyzed, F1: $M_w = 21\,400$ g/mol, PDI = 1.22, 98-99% hydrolyzed, F2: $M_w = 144\,000$ g/mol, PDI = 1.34, 98-99% hydrolyzed). The codes P and F indicate partial versus full hydrolysis while molecular weight increases with the integer in the sample code. Each sample was dissolved in a pH 7.0 buffer solution (0.2 M sodium...
nitrate, 0.01 M sodium phosphate) at a concentration of 2 mg/mL and characterized using gel permeation chromatography (GPC) (Agilent Technology 1260 Infinity, Wyatt Optilab T-rEX detector, PL Aquagel -OH column). The resulting molecular weight and polydispersity values are summarized in Table 4-2.

Table 4-2 The number average molecular weight ($M_n$), weight average molecular weight ($M_w$) and the polydispersity index (PDI = $M_w / M_n$) of the PVA samples used in this work.

<table>
<thead>
<tr>
<th>PVA Samples</th>
<th>$M_n (10^4 \text{ g/mol})$</th>
<th>$M_w (10^4 \text{ g/mol})$</th>
<th>PDI ($M_w / M_n$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>P1</td>
<td>1.23</td>
<td>2.44</td>
<td>1.99</td>
</tr>
<tr>
<td>P2</td>
<td>7.50</td>
<td>8.84</td>
<td>1.18</td>
</tr>
<tr>
<td>P3</td>
<td>8.73</td>
<td>13.1</td>
<td>1.50</td>
</tr>
<tr>
<td>F1</td>
<td>1.76</td>
<td>2.14</td>
<td>1.22</td>
</tr>
<tr>
<td>F2</td>
<td>10.8</td>
<td>14.4</td>
<td>1.34</td>
</tr>
</tbody>
</table>

P: partially hydrolyzed (87–89 percent) PVA, F: fully hydrolyzed (98–99 percent) PVA.

2-butanone (MEK, 99+% A.C.S. reagent), Methylene blue dye, Albumin-fluorescein isothiocyanate conjugate (FITC-BSA), Glutaraldehyde solution (Grade II, 25% in H$_2$O), N-(3-Dimethylaminopropyl)-N'-ethylcarbodiimide hydrochloride (EDC), N-Hydroxysulfosuccinimide sodium salt (NHS), MES sodium salt, and Tween-20 were obtained from Sigma-Aldrich. Poly(acrylic acid) (PAA, $M_w = 225,000$ g/mol, 20% aqueous solution), poly(methacrylic acid) (PMAA, $M_w = 100,000$ g/mol), and poly(glycidyl methacrylate) (PGMA, $M_w = 25,000$ g/mol, 10% solution in MEK) were obtained from Polysciences. Rhodamine B labeled polyethylene glycol (RB-PEG) was obtained from Nanocs. Standard (soda lime) glass microscope slides and phosphate buffer saline (PBS) were obtained from VWR. Deionized water (DI, 18.2 MΩ·cm, MilliQ) was used in all aqueous polymer solutions and rinsing procedures.

**PGMA Surface Anchoring Chemistry:** The glass substrates were degreased by sonication in a 4% (v/v) solution of Micro-90 (International Products Co.) for 15 min, and subsequently sonicated twice in DI
water for 15 min and dried with compressed air. They were then treated with oxygen plasma (PDC-32G, Harrick Scientific Products, Inc.) for 2 min at 150 mTorr. A plasma-treated glass slide was immediately immersed in a 0.1% (w/v) PGMA/MEK solution for 20 sec and then placed in a 110 °C oven for 30 min to covalently bond PGMA to the glass substrate. After cooling to ambient temperature, the PGMA-coated glass substrate was immersed in a 1 mg/mL aqueous solution of PVA (pH 2.0) for 20 min. The PVA-coated substrate was then dried at ambient temperature and again placed in the oven at 110°C for 30 min to induce a chemical reaction between the residual epoxy groups present in PGMA and the PVA hydroxyl groups. Silicon wafers were treated using the same protocol.74

**Thin Film Assembly:** Films were constructed using a Stratosequence VI spin dipper (Nanostrata Inc.) controlled using StratoSmart v6.2 software. PGMA-treated substrates that were reacted with a layer of PVA were first rinsed three times using DI water of the same pH as the preceding PVA solutions to remove loosely bound PVA from the substrate. LbL assembly was then commenced with dipping times of 10 min for the polymer solutions, followed by three rinses of 2, 1, and 1 min. The concentration of the polymer solutions used was 1 mg/mL and the pH of these solutions and the rinse water were adjusted with 0.1 M HCl or 0.1 M NaOH. PVA/PAA films were also produced by spray assembly using automated equipment described in a previous publication.88 For the spray assembly, we used the same concentrations and pH conditions as employed in the dip assembly but the cycle times (polymer solution 12 sec / delay time 6 sec / rinsing 20 sec twice) to produce a bilayer were significantly smaller. The nomenclature for LbL films follows the convention (hydrogen bonding acceptor/donor)z where Z is the total number of bilayers deposited. Typically the pH conditions are specified for individual polymer solutions but here all the LbL films were assembled at pH 2.0 conditions and were omitted for simplicity.

**Functional Modification with FITC-BSA / RB-PEG:** (PVA<sub>Py</sub>/PAA)<sub>10</sub> films on glass substrates were heated for 5 min at 140 °C. Then the film was immersed in 0.1 M EDC and 0.1 M NHS solution in 50 mM MES buffer (pH 5.0) for 30 min. The sample was then rinsed with 50 mM MES buffer (pH 5.0) for 10 sec and immediately immersed in 1 mg/mL FITC-BSA in MES buffer (pH 6.0) for 2 hrs. After rinsing
with DI water, the sample was soaked in 0.1% (v/v) Tween-20 in PBS (pH 6.0) for either 3 hrs or 15 hrs on the shaker plate set at 100 rpm. Samples were rinsed thoroughly with DI water and dried with compressed air. Control samples were prepared with the exact same protocol without the EDC / NHS. After FITC-BSA was attached to the film, sample was immersed in 0.5 mg/mL RB-PEG solution for 30 min. Then the sample was soaked in 30°C 0.13% (w/w) glutaraldehyde in PBS for 10 min, rinsed with DI water and dried with compressed air. Similarly, a control sample was prepared without the glutaraldehyde cross-linking.

**Characterization:** Dry film thicknesses were measured using a Tencor P16 surface profilometer with a 2 μm stylus tip, 2 mg stylus force, and a scanning rate of 50 μm/s. To determine wet film thicknesses *in situ*, a custom-built quartz cell was used in conjunction with a J.A. Woollam XLS-100 spectroscopic ellipsometer as described previously. Data were collected between 400 and 1000 nm at a 70° incidence angle and analyzed with WVASE32 software. To measure the extent of reversible swelling, the thickness of each film was measured first when immersed for 10 minutes in water of a designated pH and then after drying with compressed air. Topographical images of the multilayers were obtained using a Veeco Nanoscope V Dimension 3100 AFM microscope in tapping mode.

The extent of polymer complexation in various pH conditions was determined by measuring the attenuation of light using UV-VIS spectroscopy (Varian Cary 50 Bio) over the 370-750 nm range 10 min after the mixing of two hydrogen bonding polymer solutions. IR spectra of films deposited on ZnSe plates were taken using a Nicolet 4700 FT-IR Spectrometer (Thermo Scientific). The extent of pH-triggered disintegration was determined by measuring the ratio of the dry film thickness before and after 2 hr incubation in pH-adjusted DI water. NMR spectra of samples dissolved in deuterated water were obtained on a Varian Mercury-300 spectrometer. The degree of hydrolysis for the fully hydrolyzed and partially hydrolyzed PVA samples of similar molecular weight was determined by the analysis of NMR spectra. Peak areas of hydrogen atoms attached to the alpha carbon (H_b, and H_b" - peaks near 4.0 ppm) in PVA were set to 1.00. The peak area near 2.1 ppm which corresponds to the acetate hydrogen H_a, was then
used to calculate the fraction of acetate groups in the overall PVA chain. The amount of each polymer within the freestanding (PVA$_{P2}$/PAA)$_{100}$ film was calculated by normalizing with respect to the peaks associated with the hydrogen atoms on the alpha carbon (H$_b$ and H$_{b''}$) and subtracting out the contribution of PVA in the upfield region (1.0-2.5 ppm) where only the hydrogen atoms of PAA appear. The presence of carboxylic acid groups was probed using methylene blue as described previously. The emission spectra of the films that contained fluorescent dyes were obtained from Horiba Fluorolog-3 spectrofluorometer. The fluorescence emission was visualized with Zeiss LSM 510 confocal laser scanning microscopy (CLSM) with the excitation wavelengths set at 488 nm, and 543 nm.

4.8 Supplemental Information

**Interpolymer Complexation:** Although it is highly desirable to quantify the extent of complexation and to determine the cutoff point at which the driving force (mainly hydrogen bonding in our case) is insufficient for LbL assembly, the light attenuation values such as those reported above are not suitable for predicting LbL assembly if very strong precipitation occurs. This problem is evident in Figure 4-9 where the behavior of the strongly complexing pair PVA/PMAA is shown. The attenuation at pH 2.0 is highest for PVA$_{P2}$. Other PVA samples at the same conditions precipitated out within 10 minutes after mixing, resulting in lower light attenuation. In this case, the visual observation of precipitation is a better indicator of a system's ability to LbL assemble.
Figure 4-9 pH / PVA matrix showing the attenuation of transmitted light (I) expressed as ΔI/I₀, where ΔI=I₀ – I and I₀ is the incident light intensity to determine whether PVA and PMAA form water-insoluble complexes.

![Graph showing pH / PVA matrix and transmitted light intensity attenuation.]

Figure 4-10 (a), (b) AFM image of the (PVAP2/PAA)₃₀ film on PGMA-modified glass substrate showing roughness (Rₛ: 0.15 nm, Rₒ: 0.19 nm) for ~1.5 μm thick film. Scale bars are from + 10 nm / - 10 nm.
Figure 4-11 pH-triggered dissolution of untreated hydrogen bonded thin films: (PVA<sub>P3</sub>/PAA)<sub>30</sub> ( ■ black squares), (PVA<sub>P2</sub>/PAA)<sub>30</sub> ( ○ red circles).

Figure 4-12 <sup>1</sup>H-NMR spectra in D<sub>2</sub>O. (a) PVA<sub>P2</sub>, (b) PVA<sub>P3</sub>, (c) PAA, (d) (PVA<sub>P3</sub>/PAA)<sub>100</sub>

FT-IR analysis – Heat-Induced Esterification: To further explore this stability enhancement and to confirm the origin of this effect, PVA<sub>P</sub>/PAA films were prepared on ZnSe substrates and then subjected to different heat treatments. Figure 4-13 (a) presents the FT-IR spectra of the various PVA<sub>P3</sub>/PAA samples. The FT-IR spectra of the individual polymers are given in Figure S6. Close ups of the carboxyl region in Figure 4-13 (b) - (d) were examined in more depth to determine the effect of heating on the
change in chemical nature. Protonated carboxylic acids (COOH) typically have two separate peaks at ~1710 cm\(^{-1}\) and ~1740 cm\(^{-1}\) ("dimerized" or "free" state, respectively.) Also acetate and ester peaks show up at ~1735 cm\(^{-1}\). Due to the initial presence of acetate in PVAP, and also the possibility of having "free" state protonated carboxylic acids, a shoulder appears even in the untreated sample (see Figure 4-13 (b)). As the extent of heat treatment increases, however, it is clear that the ester ratio in the overall carboxyl peak increases. While the film heated for 5 min at 105 °C does not change significantly after heat treatment, the films that were stable to high pH show noticeable changes in their acetate/ester/acid distribution. Interestingly, the anhydride peak at ~1805 cm\(^{-1}\) only becomes apparent when the sample was subjected to 150 °C 45 min heat treatment. Also, thermal analysis of this sample confirmed no sign of crystallization in the film (data not shown).

Figure 4-13 (a) IR spectra for a series of (PVAP/PAA)\(_{30}\) films on ZnSe substrates subjected to various heat treatment protocols. (b) A close up of the anhydride peak (1805 cm\(^{-1}\)) which only appears for the sample treated for 45 min at 150 °C. Heat treatment increases the area of the carboxyl peak (C=O) assigned to the acetate, ester and "free" state PAA (COOH).
Figure 4-14 IR spectra for (a) PVA$_{P2}$, (b) PVA$_{P3}$, and (c) PAA dip-coated films on ZnSe substrates.

Figure 4-15 Methylene blue adsorption test to verify the presence of ionized carboxylic acid groups in a (PVA$_{P3}$/PAA)$_{30}$ film treated for 5 min at 140 °C.
Figure 4-16 Emission spectra of films coated with either FITC or RB. (a) Comparison study of FITC and its control. Both samples were soaked in 0.1% (v/v) Tween-20 PBS (pH 6.0) for 3 hr on a shaker plate set at 100 rpm. The films were excited at 440 nm. (b) Comparison study of RB and its control. Both samples were soaked in 0.1% (v/v) Tween-20 PBS (pH 6.0) for 15 hr on a shaker plate set at 100 rpm. Films were excited at 520 nm.
5. HYDROGEN BONDING BASED LAYER-BY-LAYER ASSEMBLY OF POLY (VINYL ALCOHOL) WITH TANNIC ACID

This was a research project with Sample, C., an undergraduate student from Department of Materials Science and Engineering, under my supervision. Sample, C. carried out fabrication of multilayer films, measured film thicknesses and conducted QCM-D measurements.

5.1 Introduction

Layer-by-Layer (LbL) assembled multilayer films driven by hydrogen-bonding interactions have been utilized in many applications due to their ability to incorporate uncharged polymers and dissolve at a designated pH condition (pH_{int}).

Previously, it was demonstrated that poly(vinyl alcohol) (PVA), a hydrophilic biocompatible polymer with hydroxyl groups, can be LbL assembled with weak polyacids such as poly(acrylic acid) (PAA) and poly(methacrylic acid) (PMAA) via hydrogen-bonding interactions. By varying the degree of hydrolysis (DH) of PVA and the type of weak polyacids, the pH-stability of the film was tuned. For all these PVA-based hydrogen-bonded multilayers assembled with polycabonylic acids, however, films dissolved at physiological conditions. One way to achieve multilayers stable at physiological pH is to thermally crosslink the hydroxyl groups and carboxylic acids to form ester-linkage by thermal treatment. While this approach enhances the pH-stability significantly by covalent linkage formation, post-assembly thermal crosslinking may limit the incorporation of biologically relevant molecules. Another approach widely used to impart high pH-stability to hydrogen-bonded multilayers without crosslinking is to incorporate polymers with pK_{a} values higher than those for poly(carboxylic acid)s such as tannic acid (TA). TA has pK_{a} value of ~8.5 resulting in the complementary hydrogen-bonding interactions to persist even at neutral pH.

In this chapter of my thesis, we focus on hydrogen-bonded LbL assembly of PVA and TA. In addition to its high pK_{a} values, TA is an attractive molecule for inclusion for its biofunctional properties, such as antimitagenic, antioxidant, and antibacterial activities and its prevalence in nature. It is noteworthy that TA containing hydrogen-bonded LbL films has been reported earlier by other groups.
However, only few have investigated systems where TA has been assembled with weakly binding hydrogen-accepting polymer such as poly(ethylene oxide) (PEO)\textsuperscript{92, 93} where the resulting film has been reported to exhibit film fouling after certain number of layers and were rough and appeared visibly opaque.\textsuperscript{92} In this work, the optimal assembly conditions for TA containing hydrogen-bonded LbL multilayer films with PVA which is also in the category of weakly interacting hydrogen-accepting polymer was investigated.\textsuperscript{21, 89} Optimal assembly condition for conformal thin film was studied in detail by varying the assembly conditions such as pH, DH and molecular weight of PVA, and material concentration.

In contrast to previous published studies, TA based hydrogen-bonded system was approached from another perspective focusing on properties related to material concentrations. While concentration of materials used for LbL assembly ideally should not significantly affect the overall multilayer film growth behavior since LbL assembly is a self-limiting adsorption/desorption process, drastic difference in film growth behavior depending on the DH of PVA was observed. For partially hydrolyzed PVA (PVAp), lower concentration of materials resulted in thicker films while the trend was the opposite for fully hydrolyzed PVA (PVAF). It is noteworthy to mention that TA has been reported previously to form self-associated aggregates either by aromatic stacking interactions between TA rings\textsuperscript{97} or intra- and intermolecular hydrogen bonds.\textsuperscript{28} Also, deposition of TA layer in aggregated state was shown when TA solution concentration was high by Lvov \textit{et al.}\textsuperscript{28}

In this work, the dynamic adsorption and desorption behavior was monitored for various PVA/TA systems with different DH of PVA and concentration by using a quartz crystal microbalance with dissipation monitoring (QCM-D) to investigate this rather unexpected result in detail.
5.2 Fabrication of PVA/TA Multilayer Films

![Chemical Structures of PVA and TA](image)

**Figure 5-1 Chemical Structure of PVA and TA.**

The LbL films were fabricated from PVA and TA, whose structures are shown in Figure 5-1. In order to identify solution assembly conditions that would have sufficient driving force for the multilayer growth, interpolymer complex formation between fully hydrolyzed PVA (PVA_F) and TA at various pH conditions was performed similar to previously described. Figure 5-2a shows the PVA_F/TA mixtures when two solutions were mixed in equal volume ratio at various pH conditions. While significant turbidity is observed at pH 2.0, turbidity of the mixture decreases as the pH increases due to the increased ionization of the TA. The results show that for pH 7.5, no apparent water-insoluble complexes are formed. TA became colored (yellow) before mixing for pH 7.5, which is an indication that TA is in its oxidized state at this pH due to reaction with atmospheric oxygen. Then, how interpolymer complexation result relates to the LbL assembly was explored in detail. Figure 5-2b shows the 30-bilayer thicknesses of PVA_F/TA multilayers assembled at various pH conditions along with their R_a roughness values measured via profilometry. It should be noted that the first layer of PVA was covalently bonded to the substrate using poly(glycidyl metharylate)(PGMA) to obtain high-quality LbL films as previously described. Also, concentration of 1.0 mg/mL was used for both PVA_F and TA where the molecular weight of PVA_F was 146-186 kDa. As predicted by the solution complexation studies, multilayer film thickness was significantly dependent on the assembly pH. Optimal film growth was achieved at pH 4.0, which contrasted with uncontrollable assembly at lower pH and lack of growth at higher pH. For the multilayer
film assembled at pH 2.0, the 30- bilayer film thickness was 2649 ± 1088 nm, while at pH 4.0, the thickness was only 354 ± 5 nm. As shown in Figure 5-2c and 2d with the atomic force microscopy (AFM) topography images, film assembled at pH 2.0 presents an extremely rough surface. With increased assembly pH from pH 2.0 to pH 4.0, however, both the Rₐ and Rₚ roughness values decreased from 350 nm and 483 nm to 4.7 nm and 5.9 nm, respectively. As anticipated by these roughness values, amount of particle-like features and their sizes reduced significantly when the assembly pH increased. This observation may be attributed to the increased aggregation of TA molecules at low pH due to less charge density.

Figure 5-2 (a) Photographs of PVAF/TA mixtures. PVAF and TA were mixed in equal volume ratios. The concentration of each solution before mixing was 1 mg/mL, and the pH was both adjusted as indicated. All solutions were transparent before mixing except for pH 7.5, TA solution where it was slightly yellowish in color. (b) 30- bilayer film thickness and roughness (Rₐ) of (PVAF/TA) systems assembled at various pH conditions (from pH 2.0 to pH 7.5) on glass substrates modified with
PGMA. (c) AFM topography images of (PVA<sub>f</sub>/TA)<sub>30</sub> assembled at pH 2.0, (d) AFM topography image of (PVA<sub>f</sub>/TA)<sub>30</sub> assembled at pH 4.0.

Figure 5-3 (a), (b) 30-bilayer film thickness of (PVA<sub>f</sub>/TA) (black bar), (PVA<sub>f</sub>/TA) (red bar) systems assembled at pH 2.0, 3.0, and 4.0 on glass substrates modified with PGMA. The concentration of each solution was 1 mg/mL. (a) High M<sub>n</sub> PVA (131-144 kDa), (b) Low M<sub>n</sub> PVA (21-25 kDa). (c) Film growth behavior of (PVA<sub>f</sub>/TA) systems assembled at pH 4.0 with various concentrations: 0.1 mg/mL (■ black squares), 0.5 mg/mL (○ red circles), 1.0 mg/mL (▲ blue triangles). (d) Film growth behavior of (PVA<sub>f</sub>/TA) systems assembled at various concentrations: 0.1 mg/mL (■ black squares), 0.5 mg/mL (○ red circles), 1.0 mg/mL (▲ blue triangles).

In order to study the effect of DH of PVA on the assembly, 30-bilayer thicknesses of PVA<sub>f</sub>/TA and PVA<sub>f</sub>/TA multilayer films assembled at various pH conditions were measured as shown in Figure 5-3a. Consistent with Figure 5-2b, the overall trend of film thickness decrease with increase in assembly pH was observed. Also, partially hydrolyzed PVA(PVAp) had thinner film thickness at equivalent conditions in all three pH conditions tested. However, as shown in Figure 5-3b, when analogous experiment was performed with low molecular weight PVAs (21-25 kDa versus 131-144 kDa), lack of growth was
observed regardless of DH of PVA and the assembly pH. Similar behavior was observed earlier with PEO/PAA systems where film constructed from low molecular weight PEO were of poor quality (very thin with high roughness). Since individual complementary hydrogen-bonding interactions are weak, cooperative binding with sufficient binding sites were assumed to be necessary, especially for films comprising of weak hydrogen atom acceptors such as PEO and PVA.

5.3 The Effect of concentration on PVA/TA Multilayer Films

As shown in Figure 5-3c, the concentration at which a film is assembled significantly changed the growth rate of the film. When TA was assembled with PVA, increase in concentration of both PVA and TA resulted in the film to grow more rapidly. In general, concentration should not significantly affect the growth rate since LbL assembly is a self-limiting adsorption/desorption process as long as the substrate is immersed in each polymer solution for sufficient amount of time for diffusion to occur and depletion of material can be ruled out. However, the change in concentration from 0.1 mg/mL to 1.0 mg/mL resulted in the average incremental bilayer thickness to increase from 1.1 nm to 13.3 nm, and 16.7 nm, respectively. Nevertheless, this trend is completely reversed by simply varying the portion of acetate moieties in PVA from 1-2 % to 11-13 % (PVA versus PVA). When TA was assembled with PVA with varying concentration as shown in Figure 5-3d, the change in concentration from 0.1 mg/mL to 1.0 mg/mL resulted in negligible film thickness and decreased the average incremental bilayer thickness from 7.2 nm to 5.6 nm, and -0.2 nm, respectively. Here, the average incremental bilayer thickness was determined by calculating the slope of the linear portion in each growth curve (after 10- bilayer).

Comparing with the assembly pH effect results shown earlier in Figure 5-2, these results clearly suggest that even though the primary driving force for the film buildup is hydrogen-bonding interaction between PVA and TA, there is an additional interaction that needs to be taken into consideration during the assembly, presumably the interaction among TAs. As described in earlier LbL studies involving TA, TA has the ability to form self-aggregates in solution. Depending on the assembly pH and the concentration, TAs can exist in water-soluble complexes in solution and deposit in such aggregates.
Similar observation was reported earlier in PAH/TA system$^{28}$ where TA layer was reported to adsorb in its aggregated state at high concentration.

In order to confirm the self-association behavior of TA molecules in solution, dynamic light scattering (DLS) experiments were performed at various concentrations and pH conditions. As shown in Table 5-1, the effective diameter of TA aggregates in solution decreases from $47 \pm 5$ nm to $14 \pm 5$ nm as the pH increases and the concentration decreases. Indeed, TA molecules exist in drastically different form depending on the pH and concentration.

Table 5-1 The effective Diameter (nm) of the TA Used in This Work.

<table>
<thead>
<tr>
<th>Concentration / pH</th>
<th>pH 2.0</th>
<th>pH 4.0</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.0 mg/mL</td>
<td>47 ± 5</td>
<td>38 ± 5</td>
</tr>
<tr>
<td>0.1 mg/mL</td>
<td>-</td>
<td>14 ± 5</td>
</tr>
</tbody>
</table>
Figure 5-4 pH-triggered dissolution of PVA/TA systems assembled at the concentration of 0.5 mg/mL at pH 4.0: (PVA\textsubscript{f}/TA) (black squares), (PVA\textsubscript{r}/TA) (red circles).

The effect of DH of PVA on pH-stability was also examined. As shown in Figure 5-4, both PVA\textsubscript{f} and PVA\textsubscript{r} exhibit higher pH\textsubscript{crit} values when they were LbL assembled with TA instead of poly(carboxylic acid). PVA\textsubscript{f}/TA has pH\textsubscript{crit} of ~7.2 and PVA\textsubscript{r}/TA has ~8.3, higher than the most pH-stable pair with poly(carboxylic acid) which is PVA\textsubscript{r}/PMAA with pH\textsubscript{crit} of 6.5.\textsuperscript{89} Here, PVA\textsubscript{r}/TA pair being more pH-stable than PVA\textsubscript{f}/TA pair is attributed to the extra hydrophobic forces by acetate moieties in partially hydrolyzed PVA (PVA\textsubscript{r}).\textsuperscript{89,91} However, it is interesting to note that unlike the previously studied systems with sharp transition in pH-stability, gradual transition is observed for PVA/TA systems. Similar gradual transition in pH-stability was observed for weakly binding PEO/TA system\textsuperscript{92} and we anticipate that this may be attributed to the loosely bound TA aggregates initially present in the film leaching out upon exposure to higher pH conditions.
Figure 5-5 *In-situ* adsorption/desorption behavior of various systems: (a) PVA<sub>F</sub>/TA, pH 4.0, 0.1 mg/mL, (b) PVA<sub>F</sub>/TA, pH 4.0, 1.0 mg/mL, (c) PVA<sub>F</sub>/TA, pH 4.0, 0.1 mg/mL, (d) PVA<sub>F</sub>/TA, pH 4.0, 1.0 mg/mL.

In order to study the effect of DH of PVA and concentration on LbL assembly in detail, QCM-D was employed. QCM-D measurements allow the *in-situ* monitoring of the multilayer build-up by detecting changes in frequency and dissipation, which provides additional insight into the details of the dynamic adsorption/desorption phenomena that occur during LbL assembly. Figure 5-5 shows the hydrated mass evolution during the multilayer film build-up on silica-coated quartz crystal using PVA and TA. Silica-coated quartz crystal was first assembled with 3.5- bilayers of (poly(diallyldimethylammonium chloride) (PDAC) / poly(sodium 4-styrene-sulfonate) (SPS)) to improve subsequent assembly of (PVA/TA).

Consistent with the profilometry measurement results in Figure 5-3c and d, same overall trend of film growth with variation in DH of PVA and concentration was observed. Net hydrated mass increase was
more significant when concentration is higher (1.0 mg/mL) for PVA_f/TA while it was more significant when the concentration is lower (0.1 mg/mL) for PVA_p/TA. Typical growth behavior\textsuperscript{28} observed for LbL deposition using QCM-D is either linear growth, i.e., linear increase in hydrated mass with each polymer deposition step, or zigzag-type growth, i.e., an increase in hydrated mass at one polymer deposition step, followed by some loss in mass during deposition of the other polymer. However, for all combination of systems investigated in this study, hydrated mass increase was accompanied by immediate partial removal in each polymer addition step. Although the hydrated mass evolution is very complex as it is, there are two key observations that are worthwhile to mention. One is that with addition of high concentration of TA (1.0 mg/mL) in both cases (PVA_f and PVA_p), the increase in hydrated mass is more than its analogous lower concentration case (0.1 mg/mL) denoted by orange arrow. The other is that for PVA_f at high concentration (1.0 mg/mL) (Figure 5-5d), there exists a significant increase in hydrated mass followed by immediate drastic reduction in hydrated mass upon addition of PVA_p.
Figure 5-6 Schematic representation of the effect of concentration on growth behavior of (a) PVA/TA, (b) PVA/TA.

As shown in Figure 5-6, more TA is adsorbed initially when TA is higher in concentration (1.0 mg/mL) due to self-association (or aggregate formation). The dotted orange line surrounding the TA molecules in Figure 5-6 represents the TA molecules in its aggregate form. Also, when the complementary interaction between TA and hydrogen-accepting polymer (PVA in this case) is stronger compared to the interaction among TAs, more material is lost in net during the next PVA addition step. We’ve shown earlier in Figure 5-4 with pH-stability test that the PVA/TA pair interacts relatively stronger than PVA/TA pair.

With an assumption that the interaction strength among TAs lies within these two hydrogen-bonding pairs, following hypothesis can be made. When relatively weakly interacting PVA is introduced into TA aggregate adsorbed in the prior deposition step, faster film growth is observed due to prevalent binding site offered by the TA aggregate. In the other case of PVA, addition of PVA solubilizes the TA aggregates adsorbed in the prior deposition step and results in negligible film growth. In order to validate
our hypothesis, poly(vinyl pyrrolidone) (PVPON) which is classified as strongly interacting hydrogen-accepting polymer\textsuperscript{21} was assembled with TA at various concentrations and pH conditions as shown in Figure 5-7.

![Figure 5-7 Film growth behavior of (PVPON/TA) systems assembled at various concentration and pH: pH 2.0, 1.0 mg/mL (■ black squares), pH 4.0, 1.0 mg/mL (○ red circles), pH 4.0, 0.1 mg/mL (▲ blue triangles).](image)

As shown in Figure 5-7, decrease in assembly pH from pH 4.0 to pH 2.0 resulted in the PVPON/TA film to grow more slowly while decrease in concentration from 1.0 mg/mL to 0.1 mg/mL at pH 4.0 resulted in the film to grow more rapidly which is consistent with our current hypothesis. When strongly interacting polymer (PVPON in this case) is introduced into TA aggregate at high concentration (1.0 mg/mL), addition of PVPON solubilizes the TA aggregates adsorbed in the prior deposition step and results in slower growth rate compared to lower concentration (0.1 mg/mL) analogue.

5.4 Conclusion

In summary, we have demonstrated that hydrogen-bonded LbL films containing PVA and TA can be successfully assembled at pH 4.0 by using a high molecular weight sample of PVA. The pH\textsubscript{crit} value of PVA/TA films were higher than previously investigated PVA based systems assembled with weak polyacids, which is consistent with the high pK\textsubscript{a} value of TA. By varying the degree of DH of PVA, as
well as the concentration of the two components, it was demonstrated that PVAF at a concentration of 1.0 mg/mL and PVAp at a concentration of 0.1 mg/mL resulted in more rapid growth behavior. It was also hypothesized that self-association behavior of TA at high concentration and its competing interaction with its hydrogen-bonding partner PVA results in this rather unexpected growth behavior respect to DH of PVA and concentration. Although further experiments are necessary to fully validate our current hypothesis, we believe that this study may assist in designing self-assembled multilayer films involving building blocks that can self-associate to form aggregates.

5.5 Materials and Methods

Materials: Partially hydrolyzed poly(vinyl alcohol)(PVAp, low molecular weight: \(M_w = 24,500\) g/mol, PDI = 1.99, 87-89% hydrolyzed, Sigma-Aldrich; high molecular weight: \(M_w = 131,000\) g/mol, PDI = 1.50, 87-89% hydrolyzed, Sigma-Aldrich), fully hydrolyzed poly(vinyl alcohol) (PVAF, low molecular weight: \(M_w = 21,400\) g/mol, PDI = 1.22, 98-99% hydrolyzed, Sigma-Aldrich; high molecular weight: \(M_w = 144,000\) g/mol, PDI = 1.34, 98-99% hydrolyzed, Sigma-Aldrich), tannic acid (TA, \(M_w = 1,701\) g/mol, Sigma-Aldrich), poly(diallyldimethylammonium chloride)(PDAC, \(M_w = 200 - 350,000\) g/mol, 20% aqueous solution, Sigma-Aldrich), poly(sodium 4-styrene-sulfonate)(SPS, \(M_w = 70,000\) g/mol, Sigma-Aldrich), poly(vinyl pyrrolidone)(PVPON, \(M_w = 360,000\) g/mol, Sigma-Aldrich), 2-butanone (MEK, 99+% A.C.S. reagent, Sigma-Aldrich), poly(glycidyl methacrylate) (PGMA, \(M_w = 25,000\) g/mol, 10% solution in MEK, Polysciences) were used as received. Standard soda lime glass microscope slides and phosphate buffer saline (PBS) were obtained from VWR. Deionized water (DI, 18.2 MΩ·cm, MilliQ) was used in all aqueous polymer solutions and rinsing procedures.

Layer-by-Layer assembly of the polymer thin films: The glass substrates were degreased and oxygen plasma treated using previously published protocols. PGMA was used as the binder to covalently bond the first layer of PVA to the glass substrate prior to multilayer film assembly to obtain high quality LbL films. Films were constructed using a Stratosequence VI spin dipper (Nanostrata Inc.) and StratoSmart v6.2 software. The LbL assembly process included dipping times of 10 min for the polymer solutions,
followed by three rinses of 2, 1, and 1 min. The pH of polymer solutions and the rinse water were adjusted with 0.1 M HCl or 0.1 M NaOH with no extra salt. For the polymers used in adhesion layers, 100 mM sodium chloride was added before adjusting pH. The nomenclature for LbL films follows conventions depending on the primary driving force: (polycation/polyanion)_z for electrostatic interactions, and (hydrogen bonding acceptor/donor)_z for hydrogen-bonding interactions, where Z is the total number of bilayers deposited. Most of the LbL films were assembled at pH 4.0 conditions, and therefore the pH conditions are not specified unless other conditions were used.

**Thickness measurement/pH-stability test:** Dry film thicknesses were measured using a Tencor P16 surface profilometer with a 2 μm stylus tip, 2 mg stylus force, and a scanning rate of 50 μm/s. The extent of pH-triggered dissolution was determined by measuring the dry film thickness before and after 2 hr incubation in pH-adjusted DI water.

**Dynamic Light Scattering Experiment (DLS):** Dynamic light scattering (DLS) experiments were performed on TA solution at various concentration and pH conditions using ZetaPALS (Brookhaven Instruments Corp.).

**Quartz Crystal Microbalance with Dissipation Monitoring (QCM-D):** Silica-coated QCM-sensors (Q-Sense Inc.) are cleaned with UV/ozone treatment for 10 min, then immersed in 2% (v/v) Sodium Deodecyl Sulfate (SDS) for 30 min in room temperature, rinsed with DI water, and finally blown dry with compressed air. Also, another UV/ozone treatment was done for 10 min before the baseline measurement. The baseline frequency and dissipation are first recorded with a blank crystal under pH 4.0 adjusted DI water (assembly pH) and calibrated to zero for the QCM-D measurements. All the multilayer films are then formed on the crystals through flowing the polymer solution and rinsing solution at a flow rate of 150 μL/s. Films were first built by depositing 3.5- bilayers of PDAC and SPS to improve subsequent assembly. Then, alternating deposition of TA and PVA with variation in DH of PVA and concentration was performed. TA and PVA were left to adsorb for 5 minutes, followed by 2 minutes of rinsing with DI
water at the pH of assembly. The measured frequency and dissipation are fitted using the Voigt viscoelastic model incorporated in Q-Sense analysis software (QTools) to calculate the hydrated mass evolution at various conditions.
6. PH-PROGRAMMABLE SEQUENTIAL DISSOLUTION OF MULTILAYER STACKS OF HYDROGEN-BONDED POLYMERS

This was a research project with Sample, C., an undergraduate student from Department of Materials Science and Engineering, under my supervision. Sample, C., carried out film fabrication, measured film thicknesses and conducted pH-stability experiments. Reproduced in part with permission from Lee, H., Sample, C., Cohen, R.E, and Rubner, M.F., ACS Macro Lett., 2, 924-927. Copyright 2013 American Chemical Society.

6.1 Introduction

Layer-by-Layer (LbL) assembled multilayer films driven by hydrogen-bonding interactions have been utilized in many applications where incorporating uncharged polymers and obtaining stimuli-responsive properties are desired, including controlled delivery systems, cellular and bacterial adhesion, biomimetic materials, and microreactors. For example, in the area of drug delivery, hydrogen-bonding LbL structures offer the unique advantages of (i) dissolution at a designated pH condition (pH_{lim}), and (ii) the option to assemble multiple stacks, each with different composition and properties, to generate heterostructured architecture suitable for "programmable" release of multiple functional elements within one system. However, the development of multicompartment LbL films with distinctive functional regions has been limited due to interlayer diffusion, which results in a blended internal structure. Although much work has been done to resolve this issue in analogous electrostatically assembled LbL structures, control of interlayer diffusion in purely hydrogen-bonded LbL films remains an unsolved problem. Therefore, of particular interest are strategies to control the internal structure of these hydrogen-bonded layer systems assembled in multiple stacks to generate complex functional platforms.

In this chapter of my thesis, we demonstrate a simple method to minimize interlayer diffusion of polymer chains within multi-stack hydrogen-bonded multilayer films by assembling the constituent polymers in a specific stacking order. When a low pH stability hydrogen-bonding pair is assembled on
top of a high pH stability pair, interlayer diffusion is minimized, resulting in selective removal of the low pH stability section of the stack while preserving the high pH stability region. The net result is an ability to create a complex hydrogen-bonded heterostructured architecture that sequentially dissolves with an increase in local pH conditions. In addition to generating this pH-programmable platform, we show that a freestanding film with tunable film thickness can be generated through appropriate stacking and subsequent thermal crosslinking. Also, we functionalize the freestanding multilayer film with fluorescent dye and magnetic nanoparticles to demonstrate that functional materials can be incorporated into these nano-scale freestanding films.

6.2 Sequential pH-Programmed Release of the Multilayer Film

As a basis for these studies, we selected poly(vinyl alcohol) (PVA), either fully hydrolyzed (PVAf) or partially hydrolyzed (PVAp) and the weak polyacids, poly(acrylic acid) (PAA) and poly(methacrylic acid) (PMAA) as the hydrogen bonding pairs, which have been reported to successfully assemble at low pH conditions (pH 2.0) and exhibit conformal and reproducible growth behavior (30 – 50 nm / bilayer). Polyacids incorporated in these hydrogen-bonded multilayer films become increasingly ionized at pH conditions above the assembly pH, a trend which continues until the critical pH (pHcrit), when the film disassembles primarily due to the enhanced swelling driven by the ionization of the polyacids. By varying the polyacid and the degree of hydrolysis of PVA, we observed distinctive pHcrit values. The pH stability of the complementary hydrogen-bonding pairs investigated in this paper decreased in the following order, (PVAp/PMAA: pHcrit = 6.5) > (PVAp/PMAA: pHcrit = 4.5) > (PVAf/PAA: pHcrit = 2.5).

Here, the difference in the pHcrit is attributed to the contribution of extra hydrophobic forces by acetate moieties in partially hydrolyzed PVA (PVAp), similar to reported previously.

It has been well established that diffusion of an adsorbing polymer into a multilayer film can occur during the assembly, which can dramatically alter the physical properties of the film. To illustrate this effect with PVA-based multilayer film, differently stacked films consisting of (PVAf/PAA: pHcrit = 2.5) and (PVAp/PMAA: pHcrit = 6.5) were fabricated and subsequently exposed to pH 4.0 conditions as shown
in Figure 6-1. The nomenclature for hydrogen-bonding based multilayer films follows conventions, 
(hydrogen bonding acceptor/donor)$_Z$, where $Z$ is the total number of bilayers deposited.

Figure 6-1 (a) Dry film thickness of (PVA/PAA: pH$_{crit}$ = 2.5)$_{30}$ and (PVA/PAA)$_{30}$(PVA/PMAA: 
pH$_{crit}$ = 6.5)$_{30}$ film on the substrate before and after exposure to pH 4.0 DI water for 2 hr. (b) Dry 
film thicknesses of (PVA/PMAA)$_{30}$ and (PVA/PMAA)$_{30}$(PVA/PAA)$_{30}$ multilayers on the substrate 
before and after exposure to pH 4.0 DI water for 2 hr. Schematic representation of film disassembly 
for two differently stacked multilayer films is shown on the right.

In the first case (Figure 6-1a), where the 30 bilayers of high pH stability pair, (PVA/PMAA), were 
assembled on top of 30 bilayers of (PVA/PAA) film, exposure to pH 4.0 did not selectively dissolve the 
underlying layer of (PVA/PAA) and generate a freestanding film of (PVA/PMAA). Instead, only a 
slight decrease in overall film thickness was observed. A similar result has been reported previously, where the high pH stability polymer pair (poly(N-vinylcaprolactam) (PVCL) / tannic acid (TA)) 
assembled on low pH stability polymer film enhanced the overall film pH stability. Additional related 
analysis on PVA-based system is shown in the Supplemental Information (Figure 6-5).

In the other case (Figure 6-1b), where 30 bilayers of (PVA/PAA: pH$_{crit}$ = 2.5) film were assembled on 
top of 30 bilayers of (PVA/PMAA: pH$_{crit}$ = 6.5) film, exposure to pH 4.0 DI water for 2 hr completely 
removed the (PVA/PAA)$_{30}$ while the film retained on the glass substrate was similar in thickness to 
(PVA/PMAA)$_{30}$. This result suggests that when the low pH stability hydrogen-bonding pair is assembled 
on top of the high pH stability pair, interlayer diffusion is minimized. A similar explanation for this 
asymmetric (in $z$-direction) diffusion has been reported based on an exchange of polymer chains in 
solution and those within the film during the assembly.
Given that it is possible to assemble less pH-stable polymer pairs onto more pH-stable multilayer films without significant diffusion, more complex systems were explored in detail. Here, the stacking order and exposure pH of these individual systems were varied while the number of bilayers was kept constant (10 bilayers for individual stacks). Four groups consisting of three different combinations of polymer pairs were studied: (PVAp/PAA: pH<sub>crit</sub> = 2.5), (PVAp/PMAA: pH<sub>crit</sub> = 4.5), and (PVAp/PMAA: pH<sub>crit</sub> = 6.5).

All four groups were assembled at pH 2.0, and the dotted line in Figure 2 represents the dry film thicknesses measured between the assemblies of each 10 bilayers of a polymer pair. In contrast, the solid line represents the measured dry film thickness after incubation in designated pH condition for 2 hr. The first group (Figure 6-2) was prepared on a glass substrate in a descending order of pH stability by assembling (PVAp/PMAA: pH<sub>crit</sub> = 6.5)<sub>10</sub>(PVAp/PMAA: pH<sub>crit</sub> = 4.5)<sub>10</sub>(PVAp/PAA: pH<sub>crit</sub> = 2.5)<sub>10</sub>, i.e. the (PVAp/PAA) region is on the top. As shown in Figure 2A, stepwise dissolution behavior with increasing pH conditions was observed, revealing that interlayer diffusion is not significant and the critical pH behavior of the individual stacks is preserved despite the reported highly diffusive behavior of weakly associating hydrogen-bonding pairs. \(^{20, 90}\)
Figure 6-2 pH-triggered dissolution of (a) (PVA
/PMAA: pH_{crit} = 6.5)_{10}(PVA
/PMAA: pH_{crit} = 4.5)_{10}(PVA
/PAA: pH_{crit} = 2.5)_{10}, (b) (PVA
/PAA)_{10}(PVA
/PMAA)_{10}(PVA
/PMAA)_{10}, (c) (PVA
/PMAA)_{10}(PVA
/PAAA)_{10}(PVA
/PMAA)_{10}, and (d) (PVA
/PMAA)_{10}(PVA
/PAAA)_{10}(PVA
/PMAA)_{10}. The shaded area represents the portion of the film where high pH stability polymer pairs were assembled on top of low pH stability polymer pairs.

The second group (Figure 6-2b) was prepared on a glass substrate in an ascending order of pH stability by assembling (PVA
/PAA: pH_{crit} = 2.5)_{10}(PVA
/PMAA: pH_{crit} = 4.5)_{10}(PVA
/PMAA: pH_{crit} = 6.5)_{10}.

Compared to the previous case, the dissolution profile shows a monotonic decrease in film thickness with increase in pH up to pH 7.4, at which point the film completely dissolved. Similar behavior was observed previously\textsuperscript{26} and was explained on the basis of partial removal of the weakly interacting polymer components from the film. Also, although the pH_{crit} of the bottommost stack (close to the substrate, (PVA
/PAA)_{10}) implies complete dissolution of the bottom stack above pH 3.0, this did not occur. Instead, complete dissolution took place at pH 7.4, which suggests that the individual stacks lost their independent stability characteristics as a result of interlayer diffusion of polymer chains during assembly. The same
experiment in Figure 6-2a and Figure 6-2b was conducted at exposure pH of 4.0, 6.0, and 8.0 for longer times (up to 1 day) to reveal that a 2 hr exposure is indeed sufficient to rule out the kinetic effects (data not shown). However as discussed in more detail in the Supplemental Information (Figure 6-6), it was observed that multiple wet-to-dry cycles in pH conditions just below pH$_{cr}$ may facilitate dissolution of that film.

The third group (Figure 6-2c) was prepared with the two polymer pairs close to the substrate in increasing order of pH stability and the lowest pH stability polymer pair on top (PVA$_p$/PMAA: pH$_{crit}$ = 4.5)$_{10}$ (PVA$_p$/PMAA: pH$_{crit}$ = 6.5)$_{10}$ (PVA$_p$/PAA: pH$_{crit}$ = 2.5)$_{10}$. Upon exposure to pH 3.0, the top layer (PVA$_p$/PAA) dissolved completely while the underlying two polymer pairs with higher pH stability remained intact. With increase in pH conditions, monotonic decrease in film thickness occurred similar to the second group (Figure 6-2b) until pH 7.0 where the local pH condition exceeds the pH$_{crit}$ of the (PVA$_p$/PMAA) pair and complete film dissolution was observed.

The last group (Figure 6-2d) was prepared on a glass substrate by assembling (PVA$_p$/PMAA: pH$_{crit}$ = 6.5)$_{10}$ (PVA$_p$/PAA: pH$_{crit}$ = 2.5)$_{10}$ (PVA$_p$/PMAA: pH$_{crit}$ = 4.5)$_{10}$. In this case, unusual dissolution behavior was observed. At pH 6.0, a 790 ± 16 nm thick film remained on the glass substrate even though both the polymer pairs assembled close to the surface, (PVA$_p$/PAA) and (PVA$_p$/PMAA), have pH$_{crit}$ < 6.0. Furthermore, in the case of exposure to pH 7.0, the residual film remaining on glass substrate was 425 ± 4 nm thick, which is close to the as-prepared (PVA$_p$/PMAA)$_{10}$ thickness of 372 ± 4 nm and non-dissolving freestanding films were generated. One possible explanation for this observation is interlayer diffusion or intermixing between layers, resulting in a new combination of polymer pairs. This four component (PVA$_p$, PVA$_f$, PAA, PMAA) intermixing could result in the combination of PVA$_p$/PMAA, which may explain the non-dissolving freestanding film at pH 7.0.
6.3 PVA-Based Multi-Functional Freestanding Film

The ability to generate multi-compartment hydrogen-bonded structures can be further extended to fabricate multifunctional freestanding films containing PVA with controllable film thicknesses. Previously, we have demonstrated that the PVA<sub>p</sub>/PAA polymer pair has low pH stability (pH<sub>crit</sub> = 2.5), but the presence of alcohol groups in PVA allows the formation of crosslinks with carboxylic acid groups in PAA via thermally induced esterification, which enhances the pH stability to physiological pH conditions. Thus, it was anticipated that a PVA-containing freestanding film could be generated by assembling a hydrogen-bonding polymer pair prior to the deposition of (PVA<sub>p</sub>/PAA) layers with the following characteristics: (i) higher pH stability than the (PVA<sub>p</sub>/PAA) pair to minimize interlayer diffusion and (ii) the inability to crosslink during thermal crosslinking to allow dissolution as a sacrificial layer. Here, poly(ethylene oxide) (PEO)/PAA was chosen because its dissolution pH has been reported to be 3.5, which is higher than PVA<sub>p</sub>/PAA (pH<sub>crit</sub> = 2.5); it also has been reported that the PEO/PAA system does not crosslink severely upon mild thermal treatment. As shown in Figure 6-3, 15.5 bilayers of (poly(diallyldimethylammonium chloride (PDAC) / poly(sodium 4-styrene-sulfonate) (SPS)) were first assembled on a glass substrate to improve subsequent assembly of (PEO/PAA)<sub>30</sub>. 15.5 bilayers were chosen arbitrarily; fewer bilayers (e.g. 5.5) work just as well. Then, 30 bilayers of (PVA<sub>p</sub>/PAA) multilayers were assembled on top of the (PEO/PAA) layers and thermally crosslinked at 140°C for 5 min. Subsequent immersion in PBS buffer produced a freestanding film of crosslinked (PVA<sub>p</sub>/PAA)<sub>30</sub> with thickness of ~700 nm (Supplemental Information, Figure 6-7). A control experiment was performed on a thermally treated system containing solely (PEO/PAA)<sub>30</sub> to confirm that the underlying layer completely dissolves after the selected heating protocol (Figure 6-4a).
Figure 6-3 Fabrication of a PVAp/PAA freestanding film and its functionalized form.

Figure 6-4 (a) Multilayer film retained on glass substrate before and after exposure to PBS buffer solution (pH 7.4) for 2 hr. (b) Fe$_3$O$_4$ superparamagnetic nanoparticles embedded in the freestanding multilayer film drives the film to a magnet by the external magnetic force.

Fabrication of nano-scale multifunctional freestanding films has been of significant interest in the field of layer-by-layer assembly.$^{110}$ Although hydrogen-bonded freestanding films have been generated through
other methods, precise control over film thickness is often limited. On the other hand, our experimental technique allows not only facile pH-triggered release from the substrate but also robust additional functionalization capabilities to achieve PVA-based multifunctional freestanding films. A fluorescent-labeled freestanding film with potential in magnetic applications was prepared by subsequently assembling functional materials on top of the (PDAC/SPS)$_{10.3}$(PEO/PAA)$_{30.5}$(PVA$_p$/PAA)$_{30}$ multilayer film crosslinked at 140°C for 5 min. Anionic Fe$_3$O$_4$ superparamagnetic nanoparticles (MNP) were alternately deposited with fluorescein-labeled poly(allylamine hydrochloride) (PAH-FITC) on top of this system and exposed to PBS buffer (pH 7.4) as shown in Scheme 1. As long as the subsequent functional LbL layers were assembled at pH conditions where thermally treated PEO/PAA is stable (below pH = 4.0), successful generation of a functionalized freestanding film was achieved. The freestanding multilayer film mounted on a glass substrate after exposure for 2 hr in PBS buffer, as well as the control samples are shown in the Supplemental Information (Figure 6-8). Fe$_3$O$_4$ superparamagnetic nanoparticles embedded in the freestanding multilayer film can drive the film to a magnet through external magnetic forces as shown in Figure 6-4b. This freestanding film was stable in PBS buffer for over a month.

6.4 Conclusions
We show that when a low pH stability hydrogen-bonding pair is assembled on top of a high pH stability pair, interlayer diffusion can be minimized, whereas it is significant in the opposite case. In addition, the fabrication of fluorescently-labeled freestanding films with magnetically responsive properties revealed that understanding the nuances of interlayer diffusion in hydrogen-bonded system can assist in the design of multifunctional freestanding ultrathin heterostructured films.

6.5 Materials and Methods
Materials: Partially hydrolyzed poly(vinyl alcohol)(PVA$_p$, Mw = 131 000 g/mol, PDI = 1.50, 87-89% hydrolyzed, Sigma-Aldrich), fully hydrolyzed poly(vinyl alcohol) (PVA$_f$, Mw = 144 000 g/mol, PDI = 1.34, 98-99% hydrolyzed, Sigma-Aldrich), poly(acrylic acid) (PAA, Mw = 225 000 g/mol, 20% aqueous
solution, Sigma-Aldrich), poly(allylamine hydrochloride) (PAH, 56 000 g/mol, Sigma-Aldrich), poly(diallyldimethylammonium chloride) (PDAC, Mw = 200 - 350 000 g/mol, 20% aqueous solution, Sigma-Aldrich), poly(fluorescein isothiocyanate allylamine hydrochloride) (PAH-FITC, Mw = 56 000 g/mol, Sigma-Aldrich), poly(sodium 4-styrene-sulfonate) (SPS, Mw = 70 000 g/mol, Sigma-Aldrich), 2-butane (MEK, 99+% A.C.S. reagent, Sigma-Aldrich), poly(glycidyl methacrylate) (PGMA, Mw = 25 000 g/mol, 10% solution in MEK, Polysciences), poly(methacrylic acid) (PMAA, Mw = 100 000 g/mol, Polysciences), poly(ethylene oxide) (PEO, Mw = 100 000 g/mol, Sigma-Aldrich), Iron oxide magnetic nanoparticle (Fe$_3$O$_4$ NP or MNP, average diameter = 10 nm, anionic, 3.9 % vol. aqueous suspension stabilized with anionic surfactant, Ferrotec EMG 705) were used as received. Standard soda lime glass microscope slides and phosphate buffer saline (PBS) were obtained from VWR. Deionized water (DI, 18.2 MΩ·cm, MilliQ) was used in all aqueous polymer solutions and rinsing procedures.

Thin Film Assembly: The glass substrates were degreased and oxygen plasma treated using previously published protocols. PGMA was used as the binder to covalently bond the first layer of PVA to the glass substrate prior to multilayer film assembly in the cases where other adhesion layers were not used. Films were constructed using a Stratosequence VI spin dipper (Nanostrata Inc.) and StratoSmart v6.2 software. The LbL assembly process included dipping times of 10 min for the polymer solutions, followed by three rinses of 2, 1, and 1 min. The concentration of the polymer solutions used was 1 mg/mL and the pH of these solutions and the rinse water were adjusted with 0.1 M HCl or 0.1 M NaOH with no extra salt. For the polymers used in adhesion layers, 100 mM sodium chloride was added before adjusting pH. The nomenclature for LbL films follows conventions depending on the primary driving force: (polycation/polyanion)$_z$ for electrostatic interactions, and (hydrogen bonding acceptor/donor)$_z$ for hydrogen-bonding interactions, where Z is the total number of bilayers deposited. Most of the LbL films were assembled at pH 2.0 conditions, and therefore the pH conditions are not specified unless other conditions were used. In cases where (PEO/PAA) multilayer films were assembled as sacrificial layers to
generate freestanding films, adhesion layers consisting of \((\text{PDAC/SPS})_{10.5}\) were used prior to deposition of sacrificial layer instead of starting with covalent attachment of PVA.

**Functional Modification with Fluorescent Dye and Magnetic Nanoparticles:**

\((\text{PDAC/SPS})_{10.5}\)(PAA/PEO)\(_{30}\)(PVA\(_p/PAA\))\(_{30}\) multilayer film was assembled on glass substrate at low pH conditions (pH 2.0) and crosslinked at 140°C for 5 min. Then, a 10 bilayer film of (PAH-FITC\(_{3.0}\)/MNP\(_{4.0}\)) was LbL assembled subsequently on this multilayer film using a previously published protocol.\(^{14}\) Briefly, Fe\(_3\)O\(_4\) superparamagnetic nanoparticle (MNP) solution was prepared by adding 0.5 mL of a 3.9% w/v stock solution in 400 mL DI water and adjusting the pH to 4.0. The concentration of PAH-FITC was 1 mg/mL and adjusted to pH 3.0.

**Characterization:** Dry film thicknesses were measured using a Tencor P16 surface profilometer with a 2 \(\mu\)m stylus tip, 2 mg stylus force, and a scanning rate of 50 \(\mu\)m/s. The extent of pH-triggered dissolution was determined by measuring the dry film thickness before and after 2 hr incubation in pH-adjusted DI water. For the pH 7.4 case, PBS buffer was used instead of pH adjusted DI water for the reference purposes. Exposure time for fluorescence microscopy images was 958 ms.
6.6 Supplemental Information

Figure 6-5 (a) Schematic representation of (PAH/SPS), blocking layers sandwiched between (PVA/PMAA: pH_{crit} = 6.5), and (PVA/PAA: pH_{crit} = 2.5), layers. Dry film thickness before (black) and after (red) exposure to pH 5.0 DI water for 2 hr is shown with variation in x and y. (b) y = 0, x = 0, 3.5, 5.5, 10.5, 30.5, (c) y = 1.5, x = 0, 3.5, 5.5, 10.5, 30.5, (d) y = 10.5, x = 0, 3.5, 5.5, 10.5, 30.5.

The mode of disassembly of the PVA-based system is dependent on the number of high pH stability pairs in the surface stack, with an increase in the number of bilayers of more stable polymer pairs (PVA/PMAA) resulting in an increase in the portion of the film remaining on the glass substrate after exposure to intermediate pH conditions as shown in Figure 6-5b. Moreover, it was found that conventional methodology\textsuperscript{104} of using a blocking layer to inhibit the diffusion of subsequently assembled more stable polymer pairs into the underlying layer fails for PVA-based systems. As shown in Figure 6-5c, and d, blocking layers (PAH/SPS) are somewhat effective in suppressing interlayer diffusion up to certain extent but starts to fail as the number of bilayers of more stable polymer pairs increases. Also, the presence of blocking layer facilitates uncontrollable deposition of subsequent polymer layers and irregular
disassembly behavior which may introduce multiple complication if intend to design two distinctive regions of layers with desired thickness and functionality.

Figure 6-6 pH-triggered dissolution of (PVA/p/PMAA: pH$_{crit}$ = 6.5)$_{10}$(PVAc/PMAA: pH$_{crit}$ = 4.5)$_{10}$(PVA/p/PAA: pH$_{crit}$ = 2.5)$_{10}$ assembled at pH 2.0 and subsequently exposed to pH conditions of 4.0, 6.0 and 8.0, respectively. The dotted line in Figure S2 represents the dry film thicknesses measured between the assemblies of each 10 bilayers of polymer pair. Sample 1 (■) was exposed to multiple wet-to-dry cycles at pH 4.0 and starts to dissolve away after exposure to pH 6.0 for 1.5 hr. Sample 2 (○) was conditioned at pH 4.0 for 4 hr (one wet-to-dry cycle) and starts to dissolve away after exposure to pH 6.0 for 2 hr and completely dissolves at 3 hr. Sample 3 (▲) was conditioned at pH 4.0 and pH 6.0 for 4 hr each (two wet-to-dry cycle in total) and dissolved immediately after exposure to pH 8.0.

While conducting multiple thickness measurements on a single sample at shorter intervals, it was observed that multiple wet-to-dry cycles in pH conditions just below pH$_{crit}$ may facilitate dissolution of that film as shown in Figure 6-6. Comparison between samples in Figure 6-6 shows that the pH-triggered dissolution of multilayer film is dependent not on the total amount of time exposed but rather on how many wet-to-dry cycles the sample went through in pH conditions close to the pH$_{crit}$. 
Figure 6-7 (a) A photograph of PVA-based freestanding film suspended in PBS buffer solution (pH 7.4)., (b) A photograph of PVA-based freestanding film stained with methylene blue for better image contrast., (c) A photograph of PVA-based freestanding film removed from solution and dried at ambient lab conditions.

Figure 6-8 (a) (PDAC/SPS)$_{15.5}$ (PEO/PAA)$_{30.5}$ (PVAp/PAA)$_{30}$ (PAH-FITC/MNP)$_{10}$ multilayer film on glass substrate before exposure to PBS buffer solution. (b) Residual on glass substrate after immersion in PBS buffer for 2 hr. (c) Freestanding multilayer film ((PVAp/PAA)$_{30}$ (PAH-FITC/MNP)$_{10}$) mounted on a glass substrate after exposure to PBS buffer solution for 2 hr. Scale bar is 100 μm and exposure time is 958 ms.
7. ZWITTER-WETTABILITY AND ANTIFOGGING COATINGS WITH FROST-RESISTING CAPABILITIES

This was a research project with Alcaraz, M.L., an undergraduate student from Department of Chemical Engineering, under my supervision. Alcaraz, M.L. conducted the experiments involving quantification of antifogging performances. Reproduced in part with permission from Lee, H., Alcaraz, M.L., Cohen, R.E., and Rubner, M.F., ACS Nano, 7, 2172-2185. Copyright 2013 American Chemical Society.

7.1 Introduction

Over the past decade, many research groups\[^{3, 4, 15, 22, 36-64}\] have worked to develop stable, effective antifogging (AF) coatings capable of handling a wide range of environmental challenges. Although many of these AF coatings perform satisfactorily in specifically defined antifogging challenges including such tests as the erlenmeyer steam test and the cold-fog test,\[^{3, 4, 15, 22, 36-64}\] there is no single quantitative test that provides all the information needed to assess the full optical performance of the coating. For example, even coatings that maintain high levels of light transmission during an aggressive fogging challenge, under specific conditions may produce significant image distortion due to excess or non-uniform water condensation (Supplemental Information Figure S1a). Thus, to truly understand the key parameters necessary for designing widely applicable antifogging coatings, it is essential to evaluate both light transmission and image distortion effects under a wide range of controlled environmental conditions.

In this chapter of my thesis, we establish an experimental protocol that allows for the exploration of a variety of aggressive antifogging challenges by controlling not only the initial substrate temperature ($T_I$) but also the environmental conditions in which the AF behavior is recorded, such as temperature ($T_f$) and relative humidity ($\%RH_f$). This protocol also enables quantitative analysis of the antifogging performance via real-time monitoring of transmission levels as well as image distortion. Although others\[^{22, 64}\] have attempted to quantitatively characterize antifogging performance by measuring time dependent light transmission or haze values in accordance with ASTM standards, these methodologies may not always reveal the true optical performance of the coating.
In the process of using this new protocol to evaluate our antifog coatings, we realized that, under some extreme conditions, many coatings fail to maintain high transmission levels coupled with low image distortion values. As a result, we worked to develop a superior antifog coating that could handle aggressive temperature/humidity conditions including those that would normally produce severe frosting on surfaces. Herein, we describe the development of a new coating system that maintains excellent optical clarity under conditions that would normally produce extreme fogging and/or frosting.

This new coating system is based on a layer-by-layer (LbL) assembled multilayer comprised of poly(vinyl alcohol) (PVA) and poly(acrylic acid) (PAA). Previously, we have shown that hydrogen bonded multilayer thin films consisting of PVA and PAA can be assembled under acidic conditions (pH 2.0) and further stabilized to withstand higher pH conditions by a thermal crosslinking treatment.\textsuperscript{89} Although this multilayer coating exhibits good anti-fog properties, we find that an additional step of adding poly(ethylene glycol methyl ether) (PEG) segments throughout the resultant LbL-assembled multilayer film produces significantly enhanced antifog and anti-frosting behavior. Anti-frosting in this context refers to the ability of a coating to resist frost formation when a sample is held at very low initial substrate temperatures (\(T_i\); where \(T_i\) is less than the freezing temperature of water) and then exposed to higher temperatures and high humidity.

In contrast to many antifogging coatings with hydrophilic\textsuperscript{15} or even superhydrophilic\textsuperscript{3,4} wetting behavior, PEG functionalized PVA/PAA LbL assembled multilayer films exhibit abnormally high initial water contact angles (\(\sim 110^\circ\)), followed by a transient decay to lower contact angle values over the period of several minutes. These unusually high initial water contact angles are quite remarkable considering that the multilayer coating is comprised of only very hydrophilic polymers that are water soluble in non-crosslinked forms and well known for their ability to strongly interact with water molecules. Unlike conventional hydrophobic surfaces, these coatings have the distinct capacity to alter reversibly their surface structure in order to minimize their interfacial free energy with a surrounding medium. In addition, this new nanostructured multilayer coating can simultaneously present a very hydrophobic...
character to water droplets (close to a Teflon-like surface) and exhibit the capacity to absorb a substantial amount of molecularly dispersed, non-freezing water via hydrogen bonding interactions.\textsuperscript{112-114} We refer to this unique combination of properties as 'zwitter-wettability' and note that such behavior requires a specific combination of molecular and structural features that are readily created by controlling the processing parameters and materials used in the layer-by-layer nanoscale assembly process.

7.2 Fabrication and Quantification of Antifogging/Frosting Coatings

We previously reported that multi-functional thin film coatings comprised of PVA and PAA could be layer-by-layer assembled under low pH conditions and subsequently stabilized to high pH by either post-assembly thermal or chemical treatments.\textsuperscript{89} We anticipated that the resultant hydrogel-like multilayers would be good candidates for preparing hydrophilic-type antifogging coatings with performance similar to coatings based on multilayers assembled from hydrophilic polysaccharides.\textsuperscript{15} To screen these coatings and compare to other control surfaces, samples were conditioned at -20°C and subsequently exposed to ambient lab conditions (22 ± 1°C, 40 ± 10% RH).
Layer-by-Layer assembly of PVA/PAA by hydrogen bonding

Thermal crosslinking (Esterification)

PEG functionalization using glutaraldehyde

Figure 7-1 a. Schematics showing the fabrication of the antifogging coating including reacting a thermally stabilized PVA/PAA multilayer film with poly(ethylene glycol) (PEG) molecules. b. Photographs taken immediately and 30 seconds after transfer to ambient lab conditions (22 ± 1°C, 40 ± 10% RH) from a -20°C freezer. Only the PEG functionalized 30 bilayer PVA/PAA multilayer film resisted frost formation at the early and later stages of exposure.

As revealed in Figure 7-1b, under these conditions, hydrophilic glass (soda lime glass substrate treated with oxygen plasma using the procedure described previously\(^8\)) and a 30 bilayer PVA/PAA multilayer film both exhibit initial high levels of frost formation followed by a slow clearing to a more transparent state. In the case of a hydrophobic fluorosilane-treated glass, the frosting persists for at least 30 seconds. Thus, under this particular challenge, both hydrophobic and hydrophilic glass as well as glass coated with a PVA/PAA multilayer thin film did not exhibit acceptable anti-frost behavior.

To enhance the anti-frost behavior of the PVA/PAA multilayer film, PEG molecules were reacted into the film as schematically illustrated in Figure 7-1a. The abundance of free hydroxyl and carboxylic acid groups in the as-assembled film allows for facile thermal and chemical modifications that enhance the
stability of the film and provide additional functionality. As-assembled films (30 bilayers – 1610 ± 7 nm in thickness) were thermally crosslinked at 140°C for 5 min to form ester linkages. Hydroxyl terminated poly(ethylene glycol methyl ether) (PEG, Mw = 5000 g/mol) molecules were then reacted with the pH stabilized films in PBS buffer solutions (pH ~ 7.4) using glutaraldehyde chemistry. The reaction was performed while the films are in a highly swollen state and after the PEG molecules have been allowed ample time (20 min) to diffuse throughout the film structure. Thus, the PEG molecules are dispersed throughout the entire film and not simply grafted onto the surface. Successful loading of the covalently attached PEG molecules throughout the multilayer film was confirmed by using a probe molecule as previously described (for more details, see Supplemental Information (Figure 7-9)). In addition, no significant change in thickness was observed after the PEG chemistry (thickness after reaction; 1600 ± 29 nm), consistent with the conclusion that this reaction is not producing a dense grafted surface layer of PEG molecules. The final PEG functionalized multilayer exhibited excellent optical quality and was uniform except at the edges of the glass slide, as is sometimes observed when glass slide size samples are coated with multilayers. Figure 7-1b shows the dramatic enhancement of anti-frost behavior that results from this additional PEG chemistry. In contrast to the as-assembled multilayer and the control glass samples, the PEG functionalized multilayer remains frost-free during the entire experiment.
To more completely assess the antifog/anti-frost capability of this promising new coating system, real-time monitoring of both light transmission and image distortion were conducted under a variety of temperature/humidity profiles relevant to common fogging conditions as shown in Figure 7-2. In order to provide context, PEG functionalized multilayers were compared to a number of different control surfaces and coatings. A complete description of the testing apparatus and procedures can be found in the experimental section.
Figure 7-3 Normalized light transmission versus time of various coatings on glass after exposure to 37 °C, 80 % RH conditions (Black: T_i = 22.5 °C, Red: T_i = -11.2 °C, Blue: T_i = -19.6 °C). Light transmission was normalized to the incident light intensity averaged over the 421-573 nm range without any sample present. Below are images recorded through the sample at the indicated times and their corresponding α values. a. Hydrophilic glass, b. Hydrophobic glass, c. PVA/PAA multilayer film (140°C, 5 min), d. PEG functionalized PVA/PAA multilayer film.

Figure 7-3 shows the normalized light transmission versus time of various coatings after exposure to 37 °C, 80 % RH conditions with variation in T_i. Light transmission was normalized to the incident light intensity without any sample present. The level of image distortion observed from video images and the corresponding correlation coefficient values (α) are also shown. The correlation coefficient (α) has a scale of 0 to 1, where 1 means no distortion and complete matching of the two images and 0 means no
correlation among the images. Values of \( \alpha \) above 0.95 correspond to essentially distortion-free behavior while \( \alpha \) below 0.5 corresponds to unacceptably poor visual clarity. Compared to the results shown in Figure 7-1b, these experiments were conducted in a more challenging environment for antifogging, i.e., in more humid final conditions (37 °C, 80 % RH) compared to ambient lab conditions (22 ± 1°C, 40 ± 10% RH).

In the case of hydrophilic glass (water advancing contact angle of 8 ± 1°), high transmission and low image distortion levels are observed under the least challenging fogging conditions. (\( T_i = 22.5 ^\circ C \)) This behavior is consistent with what has been reported\textsuperscript{15} for hydrophilic surfaces. In sharp contrast however, under more aggressive fogging conditions, there is an initial sharp drop in transmission levels followed by a recovery to values above 90%. This early stage drop in transmission is due to frost formation facilitated by a conditioning temperature (\( T_i \)) that is below the freezing point of water. Of particular note is the fact that even though high transmission levels are recovered after the frost clears, images viewed through the glass samples are clearly distorted as revealed by visual observation and by decreasing \( \alpha \) values with lower temperature conditioning. Relatively high transmission levels are promoted in part by the presence of a low refractive index layer of water condensed on the surface (\( n_{\text{water}} \sim 1.33 \)) compared to that of the glass substrate (\( n_{\text{glass}} \sim 1.5 \)). Condensed water layers on both sides of the substrate enhance transmission levels via an antireflection mechanism, even though their presence also produces image distortion that would be undesirable for many optical applications. These very hydrophilic surfaces also become less water wettable with aging under normal laboratory conditions. The net result as shown in the Supplemental Information Figure 7-10a ('bare glass') is lower transmission levels and corresponding decreasing \( \alpha \) values during fog testing. This is a well-known problem that occurs with highly energetic, very hydrophilic surfaces.\textsuperscript{115}

Figure 7-3b shows the normalized light transmission and image distortion for the hydrophobic (advancing water contact angle of 112 ± 1°) fluorosilane-treated glass. Results reveal that this hydrophobic coating exhibits not only significant distortion due to frosting and fogging, but also the
transmission values remain very low during the entire testing period. Clearly, typical hydrophobic surfaces are not well suited for handling an aggressive fogging challenge. In the case of a glass slide coated with the polymer PMMA (advancing water contact angle of $72 \pm 2'$), it was also found that low transmission values and high image distortion occurred during testing (Supplemental Information Figure 7-10b).

When the PVA/PAA multilayer film was subjected to the same testing protocols (Figure 7-3c), it was found that samples conditioned at room temperature ($T_i = 22.5^\circ C$), maintained high transmission and low image distortion values during the entire testing period. However, decreasing $T_i$ to $-11.2^\circ C$ and further to $-19.6^\circ C$, results in significant frost formation in the initial stages of the experiment, and in corresponding reductions in $\alpha$, to 0.79 and 0.58, respectively. Note also that after 10 seconds in these later cases, the transmission levels are high even though the sample promotes significant image distortion. In sharp contrast to all of the samples tested, adding PEG segments to the PVA/PAA multilayer film produced a coating that maintained high normalized transmission levels (above 90%) and low image distortion ($\alpha$ values of .98) regardless of the initial conditioning temperature (Figure 7-3d). Thus, even under the most aggressive testing conditions, this coating effectively inhibits both frost formation and fogging.

Based on the full set of antifogging results for the various surfaces examined in this study, the following conclusions can be made. Hydrophilic glass surfaces can be effective at preventing fogging under mild conditions but are not able to prevent initial stage frost formation when samples are conditioned at temperatures below the freezing point of water. In addition, such surfaces can promote significant image distortion even after clearing of the frost. Commonly prepared hydrophobic surfaces, on the other hand, are unable to prevent fogging or frost formation under the conditions explored in this study. It is generally accepted that good anti-fog behavior is typically associated with surfaces that exhibit an advancing water droplet contact angle of less than $40^\circ$. Hydrophobic surfaces are classically defined as having an initial advancing water droplet contact angle of $90^\circ$ or higher and are generally not considered to be effective at preventing fog or frost formation. As will be discussed shortly, PVA/PAA multilayers, both
as-prepared and PEG-functionalized, exhibit hydrophobic character when probed with water droplets (initial advancing contact angle ~100° or higher). Clearly the excellent anti-frost and antifogging capability of the PEG-functionalized multilayers is not consistent with conventional wisdom and warrants further clarification and understanding.

![Diagram](image)

Figure 7-4 a. Schematic representation of the spherical cap model used for the calculation of wetted surface area and droplet volume. b. Water contact angle evolution over time (600 s) for three samples exhibiting hydrophobic behavior. c. The wetted surface area evolution over time (600 s) for the three samples expressed as $\Delta S/S_0$ where $\Delta S = S - S_0$ and $S_0$ is the initial wetted surface area at $t=0$. d. The water droplet volume evolution over time (600 s) for three samples expressed as $\Delta V/V_0$ where $\Delta V = V - V_0$ and $V_0$ is the initial water droplet volume at $t=0$. Filled symbols denote the average of three or more independent data points every 20 sec.

7.3 Wetting Properties of PEG Functionalized PVA/PAA Multilayer Films

To investigate the origin of the excellent anti-frost capabilities of PEG-functionalized PVA/PAA multilayers, time dependent contact angle measurements were conducted for the three hydrophobic
surfaces examined in this study; hydrophobic glass, as-prepared PVA/PAA multilayers and PEG-
fuctionalized PVA/PAA multilayers. As shown in Figure 7-4b, the surfaces of all of these coatings 
exhibited initial advancing water droplet contact angles of greater than 100°. In the case of the 
hydrophobic fluorosilane-treated glass (initial contact angle 112 ± 1°), the contact angle remains nearly 
constant with time. For the PVA/PAA multilayers and PEG-functionalized PVA/PAA multilayers, the 
initial contact angle (111 ± 3° for PVA/PAA multilayers and 117 ± 12° for PEG-functionalized PVA/PAA 
multilayers), drops slowly to much lower values over the course of the experiment, reaching about 70° for 
the PVA/PAA multilayer and about 50° for the PEG-functionalized PVA/PAA multilayer after 600 
seconds. Not unexpectedly, the multilayer systems exhibit time dependent behavior that is often attributed 
to transient surface reconstruction associated with a reorganization of hydrophilic functional groups to the 
surface in response to the water droplet.\textsuperscript{116-121} Also note that the initial water contact angle of the PEG 
functionalized PVA/PAA multilayer is essentially the same as that measured for the unmodified 
multilayer film. The observation of similar contact angles is consistent with the conclusion that a dense 
top layer of PEO is not grafted onto the surface.

In order to investigate this change in water contact angle more in depth, a drop shape analysis method 
was applied as reported previously.\textsuperscript{117} Goniometry allows extraction of the droplet height (h), droplet 
width (r_0) and also its contact angle (θ) versus time as shown in Figure 7-4a. The spherical cap model was 
employed to determine the wetted surface area and the droplet volume. The initial droplet volume 
calculated using this model matched well with the actual water dispensed. The wetted surface area and 
droplet volume changes with time for the various samples were compared by using the equation given 
below.
\[ S(t) = \pi r_e^2(t) \quad (7-1) \]
\[ V(t) = \frac{\pi r_e^3(t) h(t) (2 + \cos \theta(t))}{3 (1 + \cos \theta(t))} \quad (7-2) \]

where \( S(t) \) and \( V(t) \) define the wetted surface area and volume of the drop as a function of time, respectively. Figure 7-4c shows how the normalized wetted surface area changes with time for these samples. While the surface area for the hydrophobic fluorosilane-treated glass does not change with time, the data for the multilayer samples indicate an increase in the wetted surface area consistent with spreading of the water drops. For the PEG functionalized PVA/PAA multilayer film, the wetted surface area increased nearly 300% over the 600 sec time interval. However, from Figure 7-4d where the normalized volume change with time is plotted, no significant difference in volume was observed (small 10 – 20% decreases in volume can be anticipated due to evaporation of water from the droplets). From the multilayer results, it was concluded that the spreading of the water droplet dominates relative to the absorption of water into the film from the droplet over the 600 seconds of the experiment. Furthermore, PEG functionalized PVA/PAA multilayer films exhibit a much faster-evolving spreading of a water drop than the PVA/PAA multilayer films, suggesting that the surface reconstructs from a high initial to a lower final water contact angle more quickly for the PEG functionalized PVA/PAA multilayer film.

It was unexpected for the PVA/PAA multilayer film and PEG functionalized PVA/PAA multilayer film to exhibit such high values of the initial advancing water droplet contact angle \( \theta_a \). Two main factors were considered as possible sources of this unusual behavior; (A) the presence of hydrophobic acetate groups in the partially-hydrolyzed PVA polymer, and (B) water droplet induced surface deformation at the three-phase contact line due to the intrinsically “soft” nature of the PVA/PAA multilayer film.

In the former case, it is to be recognized that the PVA used in the PVA/PAA multilayer films contains 11-16% acetate-bearing repeat units. It is possible that these relatively hydrophobic moieties preferentially orient and become trapped at the film/air interface during the heating process used to thermally crosslink the film (140°C for 5 min in vacuum). Similar abnormally high water contact angles
have been reported before.\textsuperscript{122-125} For example, nanocomposite poly (N-isopropylacrylamide)(PNIPA) films with clay network structures exhibited $\theta_w$ values in the range of $100^\circ$ - $131^\circ$. The authors attributed this behavior to the alignment of N-isopropyl groups of PNIPA chains at the gel-air interface. Consistent with the notion that the acetate groups are sufficiently hydrophobic to influence wettability, measurements of $\theta_w$ of poly(vinyl acetate) and partially hydrolyzed PVA with 11-16 \% acetate groups (films covalently bonded to a glass substrate and heated at 140\textdegree C for 5 min in vacuum) revealed advancing contact angles of $75 \pm 2^\circ$ and $75 \pm 5^\circ$, respectively. In contrast, fully hydrolyzed PVA with 1-3 \% acetate groups exhibits a contact angle of $58 \pm 1^\circ$ after a similar heat treatment (see Supplemental Information (Figure 7-11)).

With regard to the latter possibility, it was reported recently\textsuperscript{126} that on thin soft substrates, Young's law fails when there is substantial deformation near the three-phase contact line. Under such circumstances, the macroscopically observed contact angle increases and the substrate is effectively less wettable. As shown in Supplemental Information (Figure 7-12), PVA/PAA multilayer films that have been thermally crosslinked at 140\textdegree C for 5 min show significant substrate deformation at the three phase contact line after a hemispherical droplet of water is fully evaporated; more heavily crosslinked systems (140\textdegree C, 10 min and 30 min) do not show this behavior. Based on the previous predictions,\textsuperscript{126} one would expect the contact angle to increase by a maximum of about 10\degree as a result of this effect. The additional enhancement in contact angle may be attributed to the chemical structure/mobility of the polymer matrix. It has been reported that the extent to which a gel surface may become hydrophobic by reorientation and conformational changes depends on the chemical structure of the polymer in the gel matrix and also on the mobility of the individual chain segments.\textsuperscript{122} The effect of polymer mobility on the hydrophobicity of a hydrogel has been studied previously\textsuperscript{125} where a soft mobile gelatin gel with over 95\% water content was found to have water contact angle in the range of 90 - 120\degree.

It should be noted that others have suggested\textsuperscript{127} that a rough surface could also contribute to the observation of very high values of $\theta_w$. However, as reported previously,\textsuperscript{69} PVA/PAA multilayer films
have Rₐ roughness values of about 0.6 nm for ~1.5 µm thick films while the roughness of PEG functionalized PVA/PAA multilayer films is about 1.8 nm. Thus an enhancement of θₑ due to high surface roughness was assumed to be negligible for both surfaces. We therefore conclude that the abnormally high initial values of θₑ observed on both PVA/PAA multilayer films and PEG functionalized PVA/PAA multilayer films derive from the combined effects of the initially-surface-enriched hydrophobic acetate moieties, the softness of the multilayer film and the mobility of chain segments near the surface.

Figure 7-5 a. Photographs of water drop profiles versus time on a PEG functionalized PVA/PAA multilayer film in 37°C, 80% RH conditions. b. Water contact angle evolution over time (600 s) for a PVA/PAA multilayer film in ambient condition and 37°C, 80% RH condition. c. Water contact angle evolution over time (600 s) for a PEG functionalized PVA/PAA multilayer film in ambient lab condition (22 ± 1°C, 40 ± 10% RH) and 37°C, 80% RH condition. d. Photograph of water drop placed on PEG functionalized PVA/PAA multilayer film after being transferred to ambient lab conditions (22 ± 1°C, 40 ± 10% RH) from -20°C. Inset photograph shows the zoomed-in image of the water drop with a contact angle above 90’. Only the PEG functionalized PVA/PAA multilayer coated part of the glass resist frost formation. e. Schematic representation of zwitter-wettability.
7.4 Condensation Experiments

One might expect that more hydrophobic surfaces inhibit the condensation of water by suppressing nucleation and that this effect might play a role in anti-fogging behavior.\textsuperscript{128-131} To determine if the various surfaces investigated exhibited differences in water condensation during fogging conditions, the maximum amount of water condensed from moist air and steam was investigated. Various coatings (PVA/PAA multilayer film, PEG functionalized PVA/PAA multilayer film, hydrophilic glass, and hydrophobic glass) were incubated at -20°C for 1 hr, and the mass change versus time was measured immediately after transfer to ambient lab conditions (22 ± 1°C, 40 ± 10% RH). The maximum amount of water condensed was more or less the same (5-7 mg) for all of the coatings investigated regardless of their wetting properties except for the PVA/PAA multilayer film which exhibited a larger amount of condensed water (9 mg) during the measured time period. Thus, no correlation between the amount of water condensed and anti-frost/antifogging behavior was observed.

7.5 Effect of Elevated Temperature and Relative Humidity on Macroscopic Water Drop Profiles

The transient nature of the contact angle with time for the PVA/PAA based multilayer coatings (Figure 7-4b) was previously attributed to surface functional group reorganizations in response to the presence of the probe water droplet. To examine if conditioning (for 1 hr before water droplets added) the coatings in humid environments at higher temperatures would influence this effect, the evolution of macroscopic water drop profiles were examined in controlled environments at elevated temperature and higher humidity (37°C, 80% RH). Both the PEG functionalized and as-assembled PVA/PAA multilayers show faster decreases in contact angles with time and reach lower values of the contact angle when incubated and then probed in a higher humidity, higher temperature environment as shown in Figure 7-5a, b and c. However, even after conditioning in an environment that would be expected to render the coatings more hydrophilic due to reorganization of hydrophilic groups to the surface as reported previously by others,\textsuperscript{119} the PEG functionalized multilayer stills exhibits an initial water droplet contact angle above 90° for the first 25 seconds of the experiment. In order to study this behavior in detail, another simple test was performed. A water drop was placed on a PEG functionalized PVA/PAA multilayer film after being
transferred to ambient lab conditions (22 ± 1°C, 40 ± 10% RH) from a -20°C freezer as shown in Figure 7-5d. As revealed in this image, the coated section of the glass remains frost-free indicating that molecularly condensed water has been effectively absorbed by the film. However, a water drop placed on top of this frost-free coating exhibits a water contact angle above 90°. Thus, this unusual surface simultaneously presents a very hydrophobic character, but also has the capacity to absorb a substantial amount of molecularly dispersed water. We refer to this unique combination of properties as ‘zwitter-wettability’ as shown in Figure 7-5e.

Figure 7-6 a. Normalized transmission versus time after exposure to 37 °C, 80 % RH conditions of PVA/PAA multilayer films thermally crosslinked with different heating times (5, 10, 30 min). Right photos are images recorded through the samples after 30 seconds and their corresponding α values. b. Swelling ratio of PVA/PAA multilayer films with varying crosslinking treatments. c. Water contact angle evolution over time (600 s) for PVA/PAA multilayer films in ambient conditions varying crosslinking treatments. Open symbols denote the average of three independent data points every 10 sec.

7.6 Effect of Thermal Crosslinking on Wetting Behavior

PVA/PAA multilayer films were thermally treated to varying extents to ascertain how increased crosslinking might influence wetting and anti-frost behavior. Previously, we have reported that
increasing the heating extent either by time or temperature alters the crosslink density of the multilayer film. Figure 7-6b shows how the swelling ratio (defined here as the ratio of the thickness of a film in contact with DI water to that of a dry film) changes with increase in heating time. For the 140°C, 5 min treated sample, the swelling ratio was 3.6 and as the heating time increased from 5 min to 30 min, a decrease in swelling ratio was observed: the corresponding values of swelling ratio were 2.9 and 2.3, respectively. Decreasing swelling ratios are consistent with an increase in crosslink density (Supplemental Information Table 7-1). Figure 7-6a shows the transmission versus time plots of PVA/PAA multilayer films after exposure to 37 °C, 80 % RH conditions for samples with the different thermal treatments. It is evident from the transmission experiment as well as the distortion analysis that increasing the crosslinking density is detrimental to the antifogging performance. Furthermore, a comparison of the transient water contact angle profiles of the PVA/PAA multilayer films with increasing crosslinking density (Figure 7-6c) revealed that the initial water contact angle of a PVA/PAA multilayer film decreases from 111 ± 3° to 77 ± 4°, and 70 ± 3°, with increasing crosslinking times. The abnormally high initial water contact angle (−110°) shown for the 140°C, 5 min treated PVA/PAA multilayer film is lost for the more heavily crosslinked systems and becomes closer to what was found for a poly(vinyl acetate) coated glass (75 ± 1°). Thus, a more crosslinked film behaves as a more conventional hydrophilic coating. This result supports the hypothesis that the enhanced contact angle is due to the combined effects of a flexible surface enriched in hydrophobic acetate moieties and the softness of the multilayer film as mentioned earlier.

7.7 Effect of Overall Film Thickness and Type of Polymer Top Layer on Antifog /Anti-Frosting Behavior

The effect of bilayer number (or overall film thickness) and the type of polymer that was used in the last deposition step of the LbL assembly on antifog/anti-frosting capabilities were investigated. The PVA/PAA multilayer films mentioned throughout this article are prepared by thermally crosslinking a 30 bilayer PVA/PAA multilayer film ((PVA/PAA)30) on a glass substrate for 5 min at 140°C; the 30 bilayer films are typically approximately ~1.5 μm in overall film thickness. In order to explore the effect of
overall film thickness, a 6 bilayer PVA/PAA multilayer film (~100 nm) and its PEG functionalized counterpart were prepared. Transmission experiments and distortion image analysis on these thinner samples were performed, and the results (Supplemental Information, Figure 7-14) show clearly that the antifog/antifrost performance of the 6-bilayer films was inferior to the 30 bilayer films. Similar observations have been reported previously, where a minimum critical thickness of the film was necessary to achieve acceptable antifogging performance.

The outermost layer effect was also investigated by ending the multilayer assembly with PVA: (PVA/PAA)_{30}. The noninteger value of Z indicates that the assembly process ends with the same polymer used to start the process, that is, the film is topped with the hydrogen bonding acceptor PVA. As shown in the Supplemental Information (Figure 7-15), regardless of which layer is on the top, functionalizing the PVA/PAA multilayer film with PEG results in excellent frost resisting films.

![Figure 7-7 Frost formation experiment of PEG functionalized PVA/PAA multilayer films with different water pretreatments. Samples were subjected to -19.6 °C freezer for 1 hr and exposed to ambient conditions (22 ± 1°C, 40 ± 10% RH). a. Schematic representation of how condensed water](image-url)
is presented after exposure to ambient conditions for differently pretreated PEG functionalized PVA/PAA multilayer films. I. A dry PEG functionalized PVA/PAA multilayer film, II. A wet PEG functionalized PVA/PAA multilayer film, III. A water soaked PEG functionalized PVA/PAA multilayer film. b. Corresponding photos taken immediately, 30 seconds and 60 seconds after exposure to ambient conditions for differently pretreated PEG functionalized PVA/PAA multilayer films. Arrow indicates the direction of increase in time.

7.8 Inhibition of Frost Formation

PVA/PAA multilayer films and PEG functionalized PVA/PAA multilayer films are essentially soft coatings that have an abundance of hydrophilic functional groups that can absorb a substantial amount of water vapor from moist air. This property makes this system an extremely interesting platform for antifogging applications. However, it still remains a question why PEG functionalized PVA/PAA multilayer films inhibit frost formation after incubation at very low temperatures and manage condensed water in such a way that minimizes image distortion. It has been reported that water absorbed in certain polymer systems can exist in different states including nonfreezing (molecularly bound) and melting point depressed states. In this case, the water molecules are presumably molecularly dispersed as a result of strong polymer-water hydrogen bonding interactions and hence are not capable of freezing at the usual temperature. One might expect that if this is the case in the PEG functionalized PVA/PAA multilayer coatings, excess water on the surface could freeze but water dispersed throughout the film would experience a depressed freezing point or none at all. In order to explore this hypothesis, samples were pre-exposed to different amounts of water prior to cooling (-20°C) and subsequently tested under frost forming conditions (Figure 7-7). Pretreatments before incubating in a freezer included (I) drying in ambient conditions, (II) immersion in DI water for 20 seconds followed by an exposure to compressed air just to remove the excess water layer on the top and (III) immersion in DI water for 20 seconds followed by immediate transfer into the freezer. The observation of interference patterns after the treatment for sample (II) confirmed that the film absorbed a substantial amount of water prior to incubation in a freezer. As shown in Figure 7-7b, only sample III exhibited ice formation, with the surface ice eventually sliding across the film top surface. Sample II supports the idea that water existing in the multilayer film is non-
freezing and therefore imparts a resistance to frost formation even when a film is treated at temperatures below the normal freezing point of water.

### 7.9 Discussion

Classically, a hydrophobic surface is defined as a surface that supports a water droplet advancing contact angle of $90^\circ$ or higher. The PVA/PAA multilayer coatings, both as-prepared and PEG functionalized, satisfy this simple definition. Both multilayer systems also exhibit a zwitter-wettable character. That is, the ability to rapidly absorb molecular water from the environment while simultaneously appearing hydrophobic when probed with water droplets. However, in the case of the PEG-functionalized multilayer, its special chemical and molecular architecture imparts a combination of physical properties that turns out to be uniquely suited for the prevention of frost formation and fogging. This combined zwitter-wettable and frost resistant character requires a number of key molecular and structural features including (1) a surface enriched in hydrophobic moieties and (2) an abundance of available hydrophilic functional groups within the material that strongly hydrogen bond with water to produce a sufficient amount of non-freezing water molecules. When these elements are in place, it is possible to create frost resistant coatings that simultaneously exhibit both hydrophobic and hydrophilic characteristics.

The as-prepared PVA/PAA multilayer comes close to achieving all of the required elements, but only after adding PEG molecules does it become fully capable of resisting frost formation. The hydrophilic segments of both PEG and PVA are known to interact strongly with absorbed water molecules via hydrogen bonding interactions to produce a non-freezing bound state. Ultimately, however, it is the amount of non-freezing water the material can accommodate that determines its effectiveness as an anti-frost coating. The capacity of a material for absorbing a large amount of non-freezing water is determined by its crosslink density (both physical and covalent), level of crystallinity and level of competitive hydrogen bonding of the system. In all of these cases, increases of the parameter will decrease the amount of non-freezing water the system can accommodate. For the as-prepared multilayer, the molecularly blended hydrogen bonded complex created by the nanoscale layer-by-layer
assembly process insures that crystallization of the PVA molecules will be limited or non-existent. This same complexation, on the other hand, also reduces the amount of molecular interactions possible with water molecules (competitive hydrogen bonding). Likewise, the low level of covalent crosslinking needed to stabilize the multilayer also decreases the non-freezing water capacity of the system. Thus, the addition of PEG segments is needed to further increase the non-freezing water capacity of the multilayer.

The nanoscale layer-by-layer process for creating these PEG-containing multilayer films makes it possible to optimize many of the key parameters responsible for the anti-frost behavior. We therefore anticipate that further optimization of the structures of the polymers used and the assembly process could result in an as-prepared multilayer that exhibits anti-frosting properties comparable to the PEG functionalized system. It should also be noted that in absence of nanoscale LbL assembly, cast films of the same PVA-PAA composition are rough and turbid (clearly not of optical quality) as shown in Figure 7-13. The enabling role of this nanoscale processing methodology is thus very apparent and critically important to the results presented in this paper.

The unusual hydrophobic nature of the multilayer is also a consequence of the structure and surface organization of the molecular complex formed by the layer-by-layer assembly process and subsequent chemical crosslinking. Previous reports of hydrophilic gels with unusually high advancing water droplet contact angles conclude that this attribute is associated with the stable alignment of hydrophobic chain segments at the substrate surface. To achieve this alignment, the level of crosslinking and inter-chain molecular complexation (for multi-component polymer systems) must be low enough to allow sufficient molecular mobility for the surface segments to achieve the required stable molecular conformations. As noted in this paper, increasing levels of crosslinking reduce the advancing contact angle to levels expected for a crosslinked homopolymer of partially hydrolyzed PVA (about 75°).

Increasing levels of crosslinking and complexation also would be expected to decrease the compliance of the multilayer, thereby reducing the enhancement in contact angle due to the "softness effect" described in the results section. Thus, to realize hydrophobic behavior that is observed even when a sample is
incubated in a high humidity environment and pre-loaded with non-freezing water, it is essential that the energetics favor surface alignment of the hydrophobic chain segments even when exposed to gas phase water. This was accomplished in the PVA/PAA multilayers by utilizing partially hydrolyzed PVA (provides the needed hydrophobic acetate groups), assembling under controlled pH conditions (controls the complexation process) and limiting the level of post-assembly crosslinking. It should be noted that the hydrophobic character of this multilayer system may help to overcome a major problem with anti-fog coatings based on extremely hydrophilic, high surface energy materials; namely a high susceptibility to fouling by low-surface-energy contaminants.\textsuperscript{47,136} Additional work is required to confirm this possibility.

Finally, we note that the observation of 'zwitter-wettability' is possible due to differences in the way water interacts with a surface when it is in a gas phase molecular state versus a droplet state. In the latter case, the liquid surface tension of water ($\gamma_{LV}$) dominates the initial interaction of the drop with the surface due to strong hydrogen bonding of water molecules within the water droplet. In contrast, molecularly dispersed water molecules in the atmosphere can directly diffuse into the multilayer film and interact with the abundant embedded hydrophilic groups. The net result is an ability to present simultaneously both hydrophobic character to water droplets and hydrophilic character to gas phase water molecules. This is possible, even after the thin film has absorbed a significant amount of water as has been observed in certain polymer hydrogels.\textsuperscript{122-125}

\textbf{7.10 Conclusion}

In summary, we show that zwitter-wettable surfaces, surfaces that simultaneously present a hydrophobic character and have the capacity to absorb a substantial amount of molecularly dispersed water, can be prepared using hydrogen-bonding assisted LbL assembly of PVA and PAA. Real-time monitoring of transmission as well as distortion image analysis revealed that when PEG segments were reacted throughout the PVA/PAA multilayer, a coating was produced that maintained high normalized transmission levels and low image distortion regardless of the initial conditioning temperature. The net result was a coating system that effectively inhibited both frost formation and fogging.
Static water contact angle and swelling experiments indicated that the abnormally high initial advancing water contact angle of the multilayer platform (>100°) was attributed to the presence of surface enriched hydrophobic acetate groups and the softness of the multilayer film. An abundance of hydrophilic functional groups within the material allows water droplets placed on a surface to spread by surface reconstruction and for molecularly dispersed water molecules to strongly hydrogen bond to produce non-freezing water molecules. The addition of PEG to the PVA/PAA multilayer film provides an additional capacity to absorb non-freezing water and an improvement in anti-frost behavior.

7.11 Materials and Methods

**Materials:** Asahiklin (AK225, Asahi Glass Company), poly(vinyl alcohol)(PVA, Mw = 131 000 g/mol, PDI = 1.50, 87-89% hydrolyzed, Sigma-Aldrich), poly(acrylic acid) (PAA, Mw = 225 000 g/mol, 20% aqueous solution, Sigma-Aldrich), glutaraldehyde solution (Grade II, 25% in H2O, Sigma-Aldrich), 2-butane (MEK, 99+% A.C.S. reagent, Sigma-Aldrich), poly(glycidyl methacrylate) (PGMA, Mw = 25 000 g/mol, 10% solution in MEK, Polysciences), poly(methyl methacrylate) (PMMA, Mw = 540 000 g/mol, Scientific Polymer Products), poly(ethylene glycol methyl ether) (PEG, Mw = 5 000 g/mol, Sigma-Aldrich), 1H,1H,2H,2H-perfluorodecyltrichlorosilane (Sigma-Aldrich) were used as received. Standard soda lime glass microscope slides and phosphate buffer saline (PBS) were obtained from VWR. Deionized water (DI, 18.2 MΩ cm, MilliQ) was used in all aqueous polymer solutions and rinsing procedures.

**Glass Substrate Pretreatment:** The glass substrates were first degreased by sonication in a 4% (v/v) solution of Micro-90 (International Products Co.) for 15 min, and subsequently sonicated twice in DI water for 15 min and dried with compressed air. They were then treated with oxygen plasma (PDC-32G, Harrick Scientific Products, Inc.) for 2 min at 150 mTorr. This glass is denoted here as hydrophilic glass and was used as the substrate for all the polymer coatings that were produced by layer-by-layer assembly. However, specifically for PVA/PAA system, additional PGMA anchoring chemistry was included in
order to covalently bond the first layer of PVA to the substrate, following the protocol described in our previous work. 8 9

**Coating Methodology:** LbL assemblies of PVA and PAA were constructed using a Stratosequence VI spin dipper (Nanostrata Inc.) controlled using StratoSmart v6.2 software. LbL assembly employed dipping times of 10 min for the polymer solutions, followed by three rinses of 2, 1, and 1 min. The concentration of the polymer solutions was 1 mg/mL and the pH of these solutions and the rinse water were adjusted to pH 2.0 with 0.1 M HCl or 0.1 M NaOH. The nomenclature for LbL films follows the following conventions, (hydrogen bonding acceptor/donor)z where Z is the total number of bilayers deposited. The PVA/PAA multilayer film mentioned throughout this article is prepared by thermally crosslinking (PVA/PAA)30 on glass substrate for 5 min in 140°C, unless other conditions are specified. PEG functionalized PVA/PAA multilayer film was prepared by immersing PVA/PAA multilayer film in 10 mg/mL PEG solution (pH 2.0) for 20 min. Then the sample was soaked in 30°C, 0.13% (w/w) glutaraldehyde in PBS for 10 min, rinsed with DI water and dried with compressed air. PMMA coated glass was prepared by dissolving PMMA in Asahiklin at a concentration of 10 mg/mL. Approximately 150 nm thick coating was deposited onto a pretreated glass substrate by dip-coating for 1 hr and heating the film for 1 hr at ~60°C to completely evaporate the solvent. Pretreated glass substrates were treated with 1H,1H,2H,2H-per-fluorodecytrichlorosilane by first placing them, along with a few drops of the reactive fluoroalkylsilane liquid, inside a Teflon canister under an inert nitrogen atmosphere and then sealing the canister and heating it overnight at 110°C to result in hydrophobic fluorosilane-treated glass. 137

**Film Characterization:** Dry film thicknesses were measured using a Tencor P16 surface profilometer with a 2 μm stylus tip, 2 mg stylus force, and a scanning rate of 50 μm/s. Water contact angle measurements were performed using a Rame-Hart model 590 goniometer after vertically dispensing droplets of deionized water on various coatings. Water contact angles were measured as deionized water was supplied via a syringe into sessile droplets (drop volume ~10 μL). Measurements were taken at three different spot on each film, and the reported uncertainties are standard deviations associated with these
contact angle values. The evolutions of water drop profiles in a controlled environment (37°C, 80% RH) were measured by taking movies of the water drop inside the environmental chamber. Then, ImageJ software was used to fit the extracted images with the built-in angle tool. To determine the swelling ratio, a custom-built quartz cell was used in conjunction with a J.A. Woollam XLS-100 spectroscopic ellipsometer as described previously. Data were collected between 400 and 1000 nm at a 70° incidence angle and analyzed with WVASE32 software. Condensation experiments were performed by preparing the samples on glass substrates of dimension 37.5 mm x 25.0 mm and equilibrating in the freezer set at -20°C for 1 hr and measuring the mass change versus time immediately after transfer to ambient lab condition using a digital scale balance (model Ag204, Mettler Toledo Instruments).

**Antifogging Characterization:** The quantitative antifogging performance on various coatings was evaluated in part by a customized setup in an environmental chamber as shown in Figure 2. Measurements were conducted by performing visible light transmission measurements (Light source: tungsten lamp (421 nm – 573 nm), Detector: InstaSpec II, Oriel Instruments, Monochromator: 125mm spectrography / monochromator, model 77400, Oriel Instruments) on a sample in a controlled-humidity glove box (environmental chamber, Electro-Tech Systems, Inc.) Optical fibers were used to measure the normalized transmission values inside the environmental chamber. Before measuring the real-time transmission behavior inside the controlled environment, the samples were first allowed to equilibrate for 1 hr in a freezer set at designated temperature (T_i) before being moved to the environmental chamber, which was maintained at 37°C, 80% RH. Samples were transferred using a secondary container and the exposure time was measured within 3 sec after the sample was placed in the environmental chamber.

For the image distortion analysis, styrofoam was used as an insulator to inhibit the condensation of water vapor on the inner wall of the environmental chamber. A microscopy test chart was used for the test image. Reference video was taken with no sample between the camera and the test image. Exposure time was measured within 3 sec after the sample was placed between the camera and the test image. Photos were extracted from the video at 5 sec, and 30 sec after exposure and referred as target images. Distortion
image analysis\textsuperscript{38} was conducted by examining pixel intensity array subsets on two corresponding images (reference and target images) and extracting the deformation mapping function that relates the images, allowing a correlation coefficient to be obtained as shown in Supplemental Information (Figure S1b). Also, it should be noted that transmission measurement and image distortion analysis were conducted consecutively on the same sample with drying steps (in ambient conditions) in between.

7.12 Supplemental Information

Figure 7-8 a. A Photograph showing significant distortion of image through a coating due to excess water condensed on both sides of the glass. b. Digital Image analysis on two corresponding images.
Figure 7-9 Spectrofluorometry study of a PEG functionalized PVA/PAA multilayer film. Comparison study of Rhodamine labeled PEG (Mw = 3400 g/mole) reacted with a PVA/PAA multilayer film and its control. The control was prepared in the same manner without the crosslinker. Both samples were soaked in DI water for 12 hr. Emission spectra of films excited at 440 nm.

Figure 7-9 shows the emission spectra of a PVA/PAA multilayer film reacted with a crosslinker and a Rhodamine labeled PEG molecule end-functionalized with a hydroxyl group after extensive washing to remove unreacted molecules and a control film without the cross-linker. The emission spectra clearly reveal that the PEG molecules are strongly bonded to the underlying PVA/PAA multilayer film only when the crosslinker is used.

UV-VIS measurements were performed to estimate the overall PEG concentration in the multilayer film by using a probe molecule (Rhodamine labeled PEG, Mw = 3400 g/mole). PVA/PAA multilayers with three thicknesses were prepared, 1180 ± 20 nm, 980 ± 27 nm and 340 ± 4 nm, respectively, to examine whether the PEG molecules were only grafted to the surface or were distributed throughout the entire film. The multilayers were thermally crosslinked at 140°C, 5 min prior to Rhodamine labeled PEG functionalization. The Beer-Lambert law was employed to determine the molar concentration of the probe molecule in the multilayer. The extinction coefficient of the probe molecule was calculated to be 1.48×10^4 M^-1 cm^-1 (at 557 nm). The multilayers were immersed in Rhodamine labeled PEG solutions (0.2
mg/mL ~ 0.059 mM) for 20 min and dried. Then the multilayers were soaked in 30°C, 0.13% (w/w) glutaraldehyde in PBS for 10 min.

After the glutaraldehyde treatment that covalently attaches the PEG molecules to the PEM network and extensive rinsing with DI water and drying, the dry basis concentration of labeled PEG in the film was found to be 4.6 mM, 4.5 mM, and 5.8 mM, respectively. These concentrations are similar in amount even though the thicknesses vary by a factor of about 3.4. This supports the idea that the PEG molecules exist throughout the entire film.

Figure 7-10 Normalized light transmission versus time of various coatings on glass after exposure to 37 °C, 80 % RH conditions (Black: \(T_i = 22.5\) °C, Red: \(T_i = -11.2\) °C, Blue: \(T_i = -19.6\) °C). Inset photograph shows the water advancing contact angle. Below are images recorded through the sample at the indicated times and their corresponding \(\alpha\) values. a. Bare aged glass, b. PMMA coated glass.
Figure 7-11 Water contact angle measurements on various coatings. a. poly(vinyl acetate), b. partially hydrolyzed poly(vinyl alcohol) – 16% are acetate groups, c. fully hydrolyzed poly(vinyl alcohol) – 3% are acetate groups.

Figure 7-12 Substrate deformation at the three phase contact line of PVA/PAA multilayer film (140°C, 5 min) after hemispherical droplet of water is fully evaporated. Shown are profilometry and optical microscopy data.

The crosslink densities of the multilayers (defined here as $\frac{v_e}{V_0}$, where $v_e$ is the number of moles of elastically effective chains in the network and $V_0$ is the initial volume of the film) was estimated using the Flory-Rehner equation (Paul J. Flory, Principles of Polymer Chemistry, 1953, p 580), assuming $x_1 = 0$. 
\[-[\ln(1 - v_{2m}) + v_{2m} + \chi v_{2m}^2] = v_i(V_i / V_o)(v_{2m}^{1/2} - v_{2m} / 2)\]  \hspace{1cm} (7-3)

where \(v_{2m} = V_o / V_f\) and \(V_f\) is the final volume at swelling equilibrium and \(v_i\) is the molar volume of water (at 298K, 18.079 cm\(^3\)/mol).

The results are shown in the following table:

<table>
<thead>
<tr>
<th>Time at 140°C (min)</th>
<th>Equilibrium Swelling Ratio (V_d/V_o)</th>
<th>Crosslink Density (moles/cm(^3))</th>
</tr>
</thead>
<tbody>
<tr>
<td>5</td>
<td>3.6</td>
<td>(5 \times 10^{-3})</td>
</tr>
<tr>
<td>10</td>
<td>2.9</td>
<td>(8 \times 10^{-3})</td>
</tr>
<tr>
<td>30</td>
<td>2.3</td>
<td>(14 \times 10^{-3})</td>
</tr>
</tbody>
</table>

A simple test was performed to prove that nanoscale control of film growth and film composition that is afforded by the layer-by-layer (LbL) assembly is necessary to construct topographically smooth, optically transparent, hydrogen-bonded films. Here, two aqueous polymer solutions, of the same PVA and PAA concentrations used in the LbL assembly reported in the paper, were blended macroscopically and cast onto a petri dish. The resulting turbid film is shown in Figure 7-13. The enabling role of the nanoscale processing methodology is thus very apparent.
Figure 7-13 PVA and PAA solutions (1 mg/mL, pH 2.0, 5 mL each) were mixed and cast onto a petri dish and dried in ambient conditions.

Figure 7-14 Normalized light transmission versus time of various coatings on glass after exposure to 37 °C, 80 % RH conditions (Black: $T_i = 22.5^\circ$C, Red: $T_i = -11.2^\circ$C, Blue: $T_i = -19.6^\circ$C). Light transmission was normalized to the incident light intensity averaged over the 421-573 nm range without any sample present. Below are images recorded through the sample at the indicated times.
and their corresponding $\alpha$ values. a. PVA/PAA multilayer film (6 bilayers), b. PEG functionalized PVA/PAA multilayer film (6 bilayers).

Figure 7-15 Photographs taken a few seconds after transfer to ambient lab conditions from a -20°C freezer. Only the PEG functionalized PVA/PAA multilayer films resisted frost formation regardless of the top layer.
8. EXPLORING THE KINETICS OF SWITCHABLE POLYMER SURFACES WITH DYNAMIC TENSIOMETRY

This was an intra-research group collaborative project where the transient water contact angle behavior of PEG-functionalized PVA/PAA multilayer film was explored in detail with Justin A. Kleingartner. Both authors, Kleingartner, J.A. and Lee, H. equally contributed to this work. Both Kleingartner, J.A. and Lee, H. conceived the idea and designed the experiments. Lee, H. performed the film fabrication, wetting characterization and analysis using goniometry. Kleingartner, J. A. performed the wetting characterization and analysis using dynamic tensiometry and modeling of surface rearrangement. J. A. Kleingartner, H. Lee, M. F. Rubner, G. H. McKinley and R. E. Cohen, Soft Matter, 2013, 9, 6080 DOI: 10.1039/C3SM50596K – Published by The Royal Society of Chemistry.

8.1 Introduction

Switchable polymer surfaces have the ability to molecularly rearrange in response to changes in their surrounding environments. A number of research groups have developed surfaces that can switch their surface wetting in response to environmental stimuli. Many experimental tools have been employed to investigate surface reconstruction phenomenon, including electron spectroscopy for chemical analysis (ESCA) or x-ray photoelectron spectroscopy (XPS), sum-frequency generation microscopy (SFM), surface acidity titration, and contact angle goniometry. Although each technique has specific advantages depending on the intended probing depth and sensitivity, contact angle measurements generally offer a very simple, convenient method of characterizing solid/liquid interfaces that are undergoing surface reconstruction. Contact angle measurements probe the top molecular layer of a surface (typically less than 1 nm deep), making them appropriate for elucidating the details of surface phenomena, which are primarily governed by local molecular motions and short-range interactions. Advancing and receding contact angles of a probe liquid are used to provide an upper and lower bound on the thermodynamic equilibrium contact angle. In the measurement of an advancing water contact angle (θ_{adv}), the advancing three-phase contact line of the expanding liquid drop
always sees the solid-air interface where primarily low surface energy moieties are present; whereas, the receding three-phase contact line of a contracting liquid drop moves across a solid-liquid interface that has been enriched with higher surface energy moieties due to local molecular reorientation that provides preferential interactions with the wetting liquids. This procedure provides measurements of two distinct interfacial states that bracket the equilibrium behavior of the three phase system.

Previous work has primarily focused on measuring contact angle hysteresis \( \Delta \theta = \theta_{\text{adv}} - \theta_{\text{rec}} \) to quantify surface reconstruction phenomena. Although large contact angle hysteresis has been associated with significant surface reconstruction, surface roughness and chemical heterogeneity also result in hysteresis even in the absence of surface reconstruction. A more insightful characterization of surface reconstruction can be accomplished through quantitative investigation into the kinetics of surface rearrangement. Recently, time dependent measurements of contact angles on various reconfigurable surfaces have been used to probe the rate of the surface rearrangement of biopolymer coatings, poly(methyl methacrylate) (PMMA), and siloxane-based polymeric surfaces. Morra et al. have previously used dynamic tensiometry to investigate rearranging hydrogel surfaces.

In this chapter of my thesis, we show that rate and temperature dependent tensiometry measurements provide a powerful framework for completely characterizing the forward (hydrophobic to hydrophilic) and reverse (hydrophilic to hydrophobic) reconstruction phenomena as well as the temperature dependencies of these thermally-activated kinetic processes. In a dynamic tensiometer, force and relative position data are collected while a container of probe liquid is raised and lowered at a constant velocity such that the liquid contact line advances (or recedes) across the solid surface at a programmed speed. In the quasi-static limit, when viscous forces are negligible, the net force acting on the sample results from a combination of interfacial and buoyant forces and is given by \( F = P \gamma_n \cos \theta - \rho g A x \), where \( P \) is the total perimeter of the solid-liquid-air contact line, \( \gamma_n \) is the probe liquid surface tension, \( \rho \) is the liquid
density, \( g \) is the gravitational acceleration, \( A \) is the cross-sectional area of the immersed solid, and \( x \) is the immersed depth of the solid.\(^{152,153}\) This force balance can be conveniently nondimensionalized, scaling the resultant tensiometric force by \( P\gamma_n \) (the maximum possible interfacial force in the vertical direction) and the immersed depth by \( \sqrt{2}\ell_{\text{cap}} \) (the maximum height associated with capillary rise of a liquid meniscus on the solid in the limit of perfect wetting \( \theta \to 0 \)).\(^{154}\) This scaling allows for a more insightful analysis of the shape of tensiometric force traces and results in the compact expression

\[
\hat{F} = \cos \theta - B\hat{x}
\]

where \( \hat{F} = F/P\gamma_n \) is the scaled force, \( \hat{x} = x/\sqrt{2}\ell_{\text{cap}} \) is the scaled immersion depth, and \( B = \sqrt{2}A/P\ell_{\text{cap}} \) is a dimensionless group quantifying the buoyant force acting on the immersed solid. By measuring the transient force \( F(t) \) in the system as the liquid contact line advances or recedes across the surface (at a specified rate \( \dot{x} = \pm V \)) dynamic changes in the advancing or receding contact angle (denoted as \( \theta(t) \)) can be calculated.

In the search for a mechanically robust antifrost, and antifogging coating, we have recently developed a new multilayer system.\(^9\) This system exhibited two interesting characteristics: One is zwitter-wettable behavior whereby the multilayer film exhibits a facile, rapid absorption of water into a film from the gas phase while simultaneously exhibiting very high contact angles for drops of liquid water placed on the surface of the same film, and the other is transient water contact angle behavior. The former feature has been discussed in detail previously.\(^9\) In the present study, we investigate the time dependent wetting behavior of these coatings, which results from the transient surface rearrangement of hydrophilic functional groups towards the surface in response to exposure to a liquid water environment.
8.2 Measuring the Kinetics of Surface Rearrangement using Goniometry

Figure 8-1 Procedure for the fabrication of PEG-functionalized PVA/PAA multilayer film on glass substrate.

Thin multilayer coatings comprised of PVA and PAA were produced via LbL assembly at low pH conditions (pH = 2), stabilized for use at higher pH by post-assembly thermal or chemical treatments, and then further functionalized with poly(ethylene glycol methyl ether) (PEG) using glutaraldehyde chemistry. A graphic representation of this process is shown in Figure 8-1. This procedure results in a dry coating that rearranges on a molecular scale with time when contacted with liquid water.

The dynamics of this molecular-scale, surface rearrangement was first investigated through the measurement of changes in the surface wetting properties of the coatings. Goniometric measurements of the time-dependent advancing contact angle with water were conducted for PEG-functionalized PVA/PAA multilayer films and fluorosilane-treated glass slides as shown in Figure 8-2a. The surfaces of all of these coatings exhibited initial advancing water contact angles greater than 100°. In the case of the fluorosilane-treated glass (initial advancing contact angle of 112 ± 1°), the water contact angle decreased by less than 10° over the period of 20 min, which can be attributed to evaporation of fluid from the static
drop over the elapsed time of the experiment. For the PEG-functionalized PVA/PAA multilayer film, the initial advancing water contact angle ($\theta_{adv,i} = 117 \pm 1^\circ$) decreased monotonically dropping to approximately 40° after 20 min. After the initial stage of rapid decay, the water contact angle decreased linearly with time in a similar fashion to the fluorosilane-treated glass slide. The linear decrease in contact angle at long times is expected as a result of evaporation and has been reported by others.\textsuperscript{117,118}

The PEG-functionalized PVA/PAA multilayer films possess two particularly striking features: they have an unusually high initial water contact angle for a coating that is produced entirely from water-soluble polymers, as well as a very strong transient water contact angle behavior (exhibiting a large decay in advancing contact angle upon exposure to a liquid water drop). The former feature has been discussed in detail previously\textsuperscript{99} and results from the combined effects of an initial surface enrichment of hydrophobic acetate moieties and the softness of the multilayer film. The latter feature can be rationalized in the context of surface reconstruction, specifically the time-dependent spatial orientation of hydrophobic and hydrophilic functional groups at the liquid water / solid polymer interface.\textsuperscript{116-121} To test the latter hypothesis, contact angle measurements were performed on the same samples using two nonpolar liquids, diiodomethane (DM) and hexadecane (HD), with surface tension values $\gamma^\text{DM}_L = 50.8 \text{ mN/m}$ and $\gamma^\text{HD}_L = 27.5 \text{ mN/m}$, respectively. These results are shown in the Supplemental Information (Figure 8-8).

Both liquids exhibited low contact angle hysteresis ($CAH \approx 15^\circ$) on the LbL films and only a weak linear time dependence in their advancing contact angles, which can again be attributed to evaporation. There was no evidence of the strong exponential transient response in the contact angle measured with liquid droplets of DM or HD. This suggests that the hydrophilic groups buried just beneath the surface of the initially-dry films are not driven to the solid/liquid interface when nonpolar liquids are used to probe the surface.
Figure 8-2 a. Time dependence of advancing water contact angles $\theta_{\text{adv}}$ for PEG-functionalized PVA/PAA multilayer film and fluorosilane-treated glass at room temperature (22 ± 1 °C). Open boxes, and circles represent individual data points averaged every 10 sec while the bold line represents the model fit; b. Changes in advancing water contact angles $\theta_{\text{adv}}$ by alternating between dry and hydrated conditions for PEG-functionalized PVA/PAA multilayer film.

The reversibility of the surface reconstruction, shown in Figure 8-2b, was investigated by measuring the initial advancing water contact angle while alternating the environment between hydrated and dry states. The PEG-functionalized PVA/PAA multilayer film, which exhibits an initially hydrophobic contact angle, was repeatedly placed in hydrated conditions (submerged in water) and then dried in ambient lab conditions (22 ± 1 °C, 40 ± 10% RH) for 15 min. In the hydrated state the film exhibited an advancing water contact angle near zero, which is likely due to a thin residual layer of adsorbed water covering the surface. As the surface is gradually dried under ambient conditions, the initial advancing water contact angle increased from 0° to more than 100° indicating that the surface of the multilayer film reconfigures as water molecules are removed to enrich the concentration of lower energy hydrophobic acetate moieties to the hydrophobic state. After five cycles the film still displayed complete reversibility (Figure 8-2b).
Figure 8-3 a. Time dependence of the advancing water contact angle $\theta_{adv}$ for PEG-functionalized PVA/PAA multilayer film at $T = 10, 20, 30, 40$ °C. The individual data points represent the average value of three separate measurements over 10 sec intervals; b. A plot of $\ln \tau_f$ versus $1/T$ where $\tau_f$ is obtained from fits of the transient data of (a) after correcting for evaporation.

The initial rapid response of the surface reconfiguration can be characterized by an exponential of the form $-\exp(-t/\tau_f)$ where $\tau_f$ is a material-dependent time constant. Furthermore, if this surface reconstruction is viewed as a thermally-activated process, the characteristic time scale ($\tau_f$) of the mechanism should depend on temperature according to an Arrhenius or similar formalism. This aspect of the film behavior was explored goniometrically by performing time dependent measurements of the advancing contact angle at $T = 10, 20, 30, \text{and } 40$ °C. The results of these experiments are shown in Figure 8-3a. The initial exponential decay of the advancing water contact angle clearly proceeds more rapidly at higher temperatures. The forward surface rearrangement occurs within the first half of the experiment and the subsequent linear decrease in the measured contact angle was used to estimate the evaporation rate. The time constant for the forward surface rearrangement ($\tau_f$) was then determined after removing the effects of evaporation. The surface rearrangement was modeled as a first-order process:
\[
\cos \theta(t) - \cos \theta_{phi} = \exp\left(-t/\tau_f\right)
\]

where \( \theta_{phi} \) indicates the equilibrium value of the advancing contact angle in the low-contact-angle hydrophilic state and \( \theta_{phob} \) indicates the equilibrium value of the advancing contact angle in the high-contact-angle hydrophobic state, respectively.

Table 8-1 \( \theta_{phob}, \theta_{phi}, \) and \( \tau_f \) for the forward surface rearrangement calculated from fitting the time dependent goniometric contact angle data at various temperatures using Equation (8-2). The averaged set of individual data with the effects of evaporation removed and the corresponding fitted results can be found in the Supplemental Information (Figure 8-10).

<table>
<thead>
<tr>
<th>Temperature (°C)</th>
<th>( \theta_{phob} ) (deg)</th>
<th>( \theta_{phi} ) (deg)</th>
<th>( \tau_f ) (sec)</th>
</tr>
</thead>
<tbody>
<tr>
<td>10</td>
<td>110 ± 3</td>
<td>69 ± 13</td>
<td>79 ± 19</td>
</tr>
<tr>
<td>20</td>
<td>111 ± 8</td>
<td>67 ± 8</td>
<td>54 ± 18</td>
</tr>
<tr>
<td>30</td>
<td>110 ± 7</td>
<td>60 ± 14</td>
<td>34 ± 5</td>
</tr>
<tr>
<td>40</td>
<td>105 ± 16</td>
<td>66 ± 12</td>
<td>14 ± 1</td>
</tr>
</tbody>
</table>

Table 8-1 shows clearly that the time constant characterizing surface reconstruction in the PEG-functionalized PVA/PAA multilayer films decreases with increasing temperature, while \( \theta_{phob} \) and \( \theta_{phi} \) remain nearly constant. The temperature dependence of the surface rearrangement rate was assumed to follow an Arrhenius form:

\[
\tau_f^{-1} = A_f \exp\left(-E_{a,f}/RT\right)
\]

where \( A_f \) is the Arrhenius pre-exponential factor, \( E_{a,f} \) is the activation energy associated with the forward rearrangement mechanism, \( R \) is the ideal gas constant, and \( T \) is the absolute temperature. A semi-logarithmic plot of the time constant versus reciprocal temperature is presented in Figure 3b, and shows good agreement with Equation (8-3) over the range of temperatures studied here. An Arrhenius activation energy of \( E_{a,f} = 40.5 \) kJ/mol was obtained from the best fit slope of the plot which is similar to the value (39.0 kJ/mol) reported for transient contact angle data obtained on a poly(methyl methacrylate) film. The relatively low value of the activation energy results from the enhanced segmental motion that
is possible at the interface as well as the effects of water plasticizing the film. These activation energies are consistent with segmental motion of polymer chains in environments with large free volumes, such as the high temperature asymptotic limit of the Williams-Landel-Ferry formalism (17.2 kJ/mol),\textsuperscript{155} and with the values associated with \( \beta \)-relaxation processes in bulk polymers (~59-66 kJ/mol for PVA).\textsuperscript{156}

### 8.3 Modeling the Kinetics of Surface Rearrangement in Dynamic Tensiometry

Dynamic tensiometry allows for a more complete characterization of the wetting behavior of switchable surfaces, including the investigation of both the forward and reverse rearrangement. The first immersion into water of the PEG-functionalized PVA/PAA surface in a dynamic tensiometer probes the forward surface rearrangement through the measurement of an apparent velocity-dependence in the advancing contact angle of the air-equilibrated surface, as shown schematically in Figure 8-4a. During emersion (i.e., as the sample is removed from the liquid) the receding contact angle of water on the reconfigured surface is measured. As the sample is re-exposed to air the surface rearranges back towards the original dry state. Upon the second and all subsequent immersions, the rate of this reverse rearrangement will be probed, because the contact line is now moving over locations on the surface that are in various degrees of rearrangement back to the original state.

The extent of surface rearrangement in the PEG-functionalized PVA/PAA multilayer film is manifest in the advancing water contact angle of the surface. In a goniometric system the time evolution of the advancing water contact angle on the surface is observed; in the case of tensiometry, a single velocity-dependent advancing water contact angle is observed where the deflection of the liquid meniscus (i.e., the contact angle) reaches a steady state configuration as the three-phase contact line advances across the surface. If the selected rate of immersion, \( \nu \), is much faster than the rearrangement kinetics, then the high advancing water contact angle associated with the initial hydrophobic state is expected to dominate the tensiometric measurements. Conversely, very slow immersion will produce tensiometric data that approach the asymptotic hydrophilic behavior that was observed in goniometric experiments at long times.
Figure 8-4 a. Schematic of the PEG-functionalized PVA/PAA multilayer film undergoing surface reconstruction during the first tensiometric immersion in water. Hydrophobic moieties are represented by acetate groups and hydrophilic groups, such as PEG and carboxylic acid groups, are represented by hydroxyl groups; b. Force trace for the first immersion of the PEG-functionalized PVA/PAA multilayer film into water at 30 °C occurring at three different rates. Solid red (----), dashed green (-----), and dotted blue (-----) lines correspond to instrument speeds of 1.0 mm/s, 0.1 mm/s, and 0.01 mm/s, respectively; c. Force trace for first immersion of the same surface into water at 10 °C. Colored lines correspond to the same rates as in (b). The values of $\alpha_j$ are 186, 18.6, and 1.86 for the three instrument speeds of 1.0 mm/s, 0.1 mm/s, and 0.01 mm/s, respectively.

To quantify the qualitative descriptions of “slow” and “fast” we compare the time scale associated with molecular rearrangement $\tau_f$ with the characteristic time scale at which the liquid meniscus advances across the surface during the immersion process $\tau_c = \ell_{cap}/V$, where $\ell_{cap}$ is the capillary length of the liquid. The resulting dimensionless ratio of time scales for the forward rearrangement is given by
\[
\alpha_f = \frac{\tau_f}{\ell_{\text{cap}}/V} = \frac{\tau_f}{\ell_{\text{cap}}}
\]  

(8-4)

In the limit \( \alpha_f \ll 1 \) we expect surface rearrangement to be fast so that the advancing contact angle is small and the surface appears hydrophilic. If \( \alpha_f \gg 1 \) the meniscus advances very rapidly compared to the rearrangement rate and the surface will appear hydrophobic. Equation (8-2) models the advancing contact angle of the reconfiguring surface as a function of elapsed rearrangement time. If we evaluate this equation after a characteristic elapsed time of \( t_c = \ell_{\text{cap}}/V \) we obtain the following expression:

\[
\frac{\cos \theta(t_c) - \cos \theta_{\text{phil}}}{\cos \theta_{\text{phob}} - \cos \theta_{\text{phil}}} = \exp\left(-\frac{\ell_{\text{cap}}/V}{\tau_f}\right) = \exp\left(-1/\alpha_f\right)
\]  

(8-5)

A transition from a high contact angle regime \( \left( \theta \approx \theta_{\text{phob}} \right) \) to a rearrangement-dominated, low contact angle regime \( \left( \theta \approx \theta_{\text{phil}} \right) \) is expected as the magnitude of the dimensionless group \( \alpha_f \) passes through unity.

Similarly, the reverse rearrangement can also be modeled as a first-order thermally-activated rate process with the additional consideration of the evaporation of bulk water from the surface of the previously immersed and swollen multilayer film. For simplicity, we assume that the reverse rearrangement does not begin until the excess water evaporates from the surface of the film (i.e., after a delay time \( t_d \)). Therefore, the following first-order model with time delay is used to describe the reverse surface rearrangement:

\[
\frac{\cos \theta(t) - \cos \theta_{\text{a,f}}}{\cos \theta_{\text{rec}} - \cos \theta_{\text{a,f}}} = H(t - t_d) \exp(-\left(t - t_d\right)/\tau_r)
\]  

(8-6)

where \( \theta_{\text{rec}} \) is the receding water contact angle, \( \theta_{\text{a,f}} \) is the advancing water contact angle observed in the tensiometric system during the forward rearrangement (i.e., Equation (8-5) evaluated at \( t_c \) or \( \alpha_f = \tau_f/\tau_c \)), \( H \) is the Heaviside unit step function, and \( \tau_r \) is the characteristic time constant of the
reverse rearrangement. The elapsed time that the surface material at a given position on the sample is out of the probe liquid and exposed to air can be expressed in terms of instrument parameters as
t = 2x/V + 2 s ≈ 2x/V, where x is the immersion depth (starting at x = 0) and the additional 2 seconds results from the instrument idle time between emersion and immersion.

8.4 Effects of Rate and Temperature
As mentioned above, probing the surface of the PEG-functionalized PVA/PAA multilayer film over increasingly greater velocities at a given temperature should result in higher measured advancing water contact angles during the first immersion of the sample, because the material near the meniscus will have had less time to rearrange relative to the time scale $t_{cap}/V$ of contact line advancement. This behavior, increasing $\theta_{adv}$ with increasing $\alpha_r$, was observed clearly in our experiments, shown in Figure 8-4b. The contact angle is extracted from the force measurements by fitting Equation (8-1) to the data. As a result, $\cos \theta$ is directly related to the value of the measured force $F_0$ when the fit over the linear portion of the data is extrapolated to $x = 0$. Positive values of $F_0$ correspond to wetting contact angles ($\theta < 90^\circ$) and negative values to nonwetting contact angles ($\theta > 90^\circ$). $\alpha_r$ was determined by fitting all of the measured force data with Equation (8-1) using Equations (8-3), (8-5), and (8-6) to determine the time-varying value of the contact angle.

In addition to varying the rate of immersion/emersion, $r/t_{cap}$, the temperature of the fluid was also varied in the tensiometry experiments to further characterize the kinetics of the surface rearrangement phenomena. Experiments were carried out at four temperatures (40 °C, 30 °C, 20 °C, and 10 °C) and three speeds (1.0 mm/s, 0.1 mm/s, and 0.01 mm/s). The force traces for the first immersion at 10 °C at the three experimental speeds are shown in Figure 8-4c. Unlike the results seen in the 30 °C data of Figure 8-4b, at 10 °C the results of the three experiments nearly coincide and the advancing contact angle of 120 ± 7° that is extracted from the data is close to the initial hydrophobic state value of 111 ± 4° obtained via
goniometry. Thus at 10 °C the rate of the forward rearrangement is significantly slower than the rate of contact line advancement (i.e., \( \alpha_f > 1 \)), even at the lowest experimental velocity of \( 10^{-2} \) mm/s.

**Figure 8-5** Dynamic tensiometry measurements for switchable PEG-functionalized PVA/PAA multilayer films probed with water. Three rates and four water temperatures were examined. Solid red (---), dashed green (---), and dotted blue (---) lines correspond to first, second, and third tensiometric cycles, respectively. The values of the dimensionless parameter \( \alpha_f \) (defined in equation 4) are given for each condition with \( \tau_f \), computed from subsequent model fitting. The delay time for drying \( \tau_f \) mentioned in the text is evident for the re-immersion traces at the lower temperatures and two lower speeds.
The full set of rate- and temperature-dependent immersion and emersion tensiometry data is shown in Figure 8-5. As expected, upon immersing at the highest speed (right most column of plots in Figure 8-5) the initial advancement into water yields a high initial contact angle ($F_0 < 0$) throughout the first immersion. After exposure to water, the contact line recedes with a low receding contact angle ($F_0 > 0$) over the rearranged surface. Subsequent immersion/emersion cycles show only the low contact angle, rearrangement-dominated regime, because the surface does not have time to revert back to the hydrophobic state at the high immersion/emersion speed (i.e., the analogous dimensionless parameter for the reverse surface rearrangement is $\alpha, \gg 1$). Experiments carried out at a speed that is an order of magnitude lower (middle column of plots in Figure 8-5) show that the initial advancement of the meniscus still proceeds with a high advancing contact angle and after exposure to water the contact line recedes with a low receding contact angle. However, upon a second advancement into water, the advancing contact angle exhibits transient behavior as the surface rearranges back to its initial hydrophobic state. At this instrument speed the sample is exposed to air for a sufficient period of time that the reverse surface rearrangement (from the hydrophilic to the hydrophobic state) occurs within the time scale of the experiment (i.e., $\alpha, -1$). This behavior is repeated in subsequent cycles, which highlights the complete reversibility of this surface switching phenomena. Finally, immersing at the slowest speed ($V = 0.01 \text{ mm/s}$), the advancing force traces indicate that the surface is hydrophilic ($F_0 > 0$) for temperatures $T \geq 20 ^\circ \text{C}$. The rate of surface reconfiguration is fast ($\alpha_f < 1$) compared to the translation rate of the meniscus. Subsequent immersions again show recovery towards $\theta \rightarrow \theta_{\alpha,f}$ introduced in Equation (8-6) since the surface has sufficient time out of the water to undergo the reverse rearrangement.

The effect of temperature on the surface rearrangement can be clearly seen in the lowest immersion/emersion speed (0.01 mm/s) data taken at 10 °C and 20 °C. At 20 °C the surface appears hydrophilic even during the first immersion with a low contact angle and positive force intercept, $F_0$; however, at 10 °C the surface rearrangement has slowed enough ($\tau_f^{10\text{°C}} > \tau_f^{20\text{°C}}$) that the initial immersion
now occurs faster than the time scale of rearrangement \( (i.e., a_f > 1) \) and the surface appears hydrophobic with a high advancing contact angle. Likewise, the effect of temperature on the reverse rearrangement (from the hydrophilic to the hydrophobic regime) can be observed in the intermediate rate \( (0.1 \text{ mm/s}) \) results. The recovery to the hydrophobic state (observed during the second immersion) occurs more rapidly at 40 °C than at 10 °C. The higher temperature increases the rate of surface rearrangement and allows for faster restoration of the hydrophobic state.

8.5 Model and Kinetic Parameters for Surface Rearrangement

The measured force data was fitted with equation (8-1) using equations (8-3), (8-5), and (8-6) to calculate the time-varying value of the contact angle \( \theta(t) \). When the tensiometer changes directions there is a small transition region where the contact line pins as the contact angle moves from the advancing value to the receding value or \textit{vice versa}. The contact angle in this region was modelled by solving the Young-Laplace equation for our systems geometry.\cite{15} The resulting model for the tensiometric force data contains eight parameters, for which the fitted values are summarized with their goniometric equivalents in Table 8-2.
Table 8-2 Parameters for the fitting of experimental goniometric and tensiometric data to the kinetic models given in equation (8-2) and equations (8-3)-(8-5).

<table>
<thead>
<tr>
<th>Variable</th>
<th>Units</th>
<th>Goniometry</th>
<th>Tensiometry</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\theta_{phob}$</td>
<td>degrees</td>
<td>109$^a$</td>
<td>125</td>
</tr>
<tr>
<td>$\theta_{phob}$</td>
<td>degrees</td>
<td>66$^a$</td>
<td>53</td>
</tr>
<tr>
<td>$\log_{10} A_f$</td>
<td>-</td>
<td>5.5</td>
<td>4.7</td>
</tr>
<tr>
<td>$E_{a,f}$</td>
<td>kJ/mol</td>
<td>40.5</td>
<td>40.1</td>
</tr>
<tr>
<td>$\theta_{rec}$</td>
<td>degrees</td>
<td>16</td>
<td>25</td>
</tr>
<tr>
<td>$t_d$</td>
<td>seconds</td>
<td>- $^b$</td>
<td>151</td>
</tr>
<tr>
<td>$\log_{10} A_r$</td>
<td>- $^b$</td>
<td>-</td>
<td>1.15</td>
</tr>
<tr>
<td>$E_{a,r}$</td>
<td>kJ/mol</td>
<td>- $^b$</td>
<td>18.5</td>
</tr>
</tbody>
</table>

$^a$ Values are averaged from the contact angles obtained for different temperatures (Table 8-1)

$^b$ $t_d$, $\log_{10} A_r$, and $E_{a,r}$ are not available because goniometry can only probe the forward surface rearrangement.

Figure 8-6 Comparison of the predicted values and measurements for the tensiometric force of PEG-functionalized PVA/PAA multilayer films probed with water at 0.01 mm/s during immersion and emersion. Solid red (−−−), dashed green (−−−−), and dotted blue (−−−−−−) lines correspond to first, second, and third tensiometric cycles, respectively. The values of $\alpha$, for each condition are shown in the figure.
Table 8-2 shows that good agreement between the Arrhenius parameters can be obtained from the two experimental methods (goniometry and tensiometry) for the forward surface rearrangement. The activation energy of this process arises from the segmental motion of hydrophobic and hydrophilic moieties at the interface between the PEG-functionalized PVA/PAA multilayer film and liquid water.

The value for the advancing water contact angle in the hydrophobic regime ($\theta_{\text{phob}}$) obtained from tensiometry is slightly higher than the value obtained from goniometry, which is due to the inherent experimental difficulties in obtaining this value with a goniometer. The surface immediately begins to rearrange when contacted with water and as a result several seconds elapse between placing the drop, the decay of all internal motion, and starting the contact angle measurement in a goniometric system. Tensiometry avoids this issue by immersing the sample into a reservoir of the probe liquid at a slow fixed speed and the tensile force on the surface is measured in real time. The advancing water contact angle is then obtained from regression of Equation (8-1) to the linear portion of the immersion force traces.
Figure 8-7 Comparison of the predicted values and measurements for the tensiometric force of PEG-functionalized PVA/PAA multilayer films probed with water at 20 °C. Solid red (---), dashed green (--.), and dotted blue (-----) lines correspond to first, second, and third tensiometric cycles, respectively. The values of $\alpha_f$ for each condition are shown in the figure.

The force traces produced from the dynamic model with the fitted parameters from Table 8-2 are shown with the corresponding experimental data in Figure 8-6 and Figure 8-7 for selected temperatures and rates. The complete set of model results plotted in a form analogous to Figure 8-5 can be found in the Supplemental Information (Figure 8-11) with their corresponding $\alpha_f$ values.

In general, good agreement is observed between the model and the data. In Figure 8-6 the initial advancing contact angle is in agreement with the data, and the fitted activation energy of 40.1 kJ/mol captures the temperature dependence of the rearrangement process. The effect of immersion speed is clearly illustrated by Figure 8-7. At low wetting speeds ($\alpha \lesssim O(1)$) the surface rearranges as it is exposed to water and the surface appears hydrophilic (i.e., $F_0 > 0$). However, at high immersion speeds ($\alpha >> 1$) the surface appears strongly hydrophobic. The onset and duration of the reverse rearrangement is also well predicted by the model for both varying rate and temperature; however, the shape of the force trace
during the reverse rearrangement associated with the second and third immersion cycles does not fully agree with the experimental data. The small deviations are most likely a result of some surface rearrangement taking place as the excess water dries from the exposed sample surface, which the model does not account for. The parameter values for the model characterizing the reverse rearrangement are also expected to be less accurate than the corresponding forward rearrangement parameters, because the air temperature and humidity (i.e., the ambient environment in which the reverse rearrangement occurred) was not rigorously controlled. As a result, the surface temperature of the multilayer film during the reverse rearrangement is not necessarily the same as the temperature of the probe liquid. IR thermal imaging of the films during the tensiometer experiment (Figure 8-12 in the Supplemental Information), show that at low temperatures (10 °C) the multilayer film is at the liquid temperature during the reverse rearrangement; however, at higher temperatures (40 °C) the multilayer film rapidly cools as a result of evaporation of the water during rearrangement with most of the process occurring at ambient temperatures (~ 22 °C).

8.6 Conclusion
PEG-functionalized PVA/PAA multilayer films exhibit a transient and reversible contact angle behavior as a result of thermally-activated surface reconstruction. Contact angle goniometry was used to measure and analyze the time evolution of advancing water contact angles over a range of temperatures and a temperature-dependent characteristic time constant ($r_f$) for the forward surface reconstruction (from hydrophobic to hydrophilic) was subsequently extracted. Furthermore, an Arrhenius relationship was used to determine the activation energy ($E_{a,f} = 40.5$ kJ/mol) of the surface reconstruction process from the goniometric data. Utilizing dynamic tensiometry the kinetics of the surface rearrangement could be probed in more detail by immersing (and subsequently withdrawing) glass substrates coated with the multilayer film into (and out of) a reservoir of water at various speeds ranging from 0.01 mm/s to 1 mm/s and over a range of temperatures from 10°C to 40°C. Modeling the forward and reverse surface reconstruction with a first-order rate equation, the activation energies for both of these processes can be
determined. The value obtained for the forward surface rearrangement ($E_{a,f} = 40.1$ kJ/mol) agrees well
with the goniometric results. The dynamics of this reversible surface switching process could be
understood in terms of a single dimensionless grouping $\alpha = \tau_f V / \ell_{WP}$ that represents a ratio of the time
scale for molecular rearrangement ($\tau_f$) to a characteristic tensiometric time scale for the advancement of
the solid-liquid-air interface ($\ell_{WP} / V$). The experimental measurements and first order model both show
that the wettability characteristics of this switchable surface transition from strongly hydrophobic (with a
high advancing contact angle at high speeds or low temperatures) to strongly hydrophilic (dominated by
surface rearrangements and low contact angles at low speeds or high temperatures) as this dimensionless
group is reduced below $\alpha \sim O(1)$. This dimensionless group thus plays the same role in dynamic
tensiometry as the Deborah number in rheological problems$^{157}$ and characterizes the interplay between the
rate of the surface rearrangement process and the observation period. It will be interesting to see how
well this idea can be used to understand, quantify and compare the dynamical responses of the wide range
of other switchable and reconfigurable surfaces that are currently being developed.

8.7 Materials and Methods

**Materials:** Poly(vinyl alcohol) (PVA, $M_w = 131$ kDa, PDI = 1.50, 87-89% hydrolyzed, Sigma-Aldrich),
poly(acrylic acid) (PAA, $M_w = 225$ kDa, 20% aqueous solution, Sigma-Aldrich), glutaraldehyde solution
(Grade II, 25% in $H_2O$, Sigma-Aldrich), 2-butanone (MEK, 99+% A.C.S. reagent, Sigma-Aldrich),
diiodomethane (Sigma-Aldrich), hexadecane (Sigma-Aldrich), poly(glycidyl methacrylate) (PGMA, $M_w$
$= 25$ kDa, 10% solution in MEK, Polysciences), and poly(ethylene glycol methyl ether) (PEG, $M_w = 5$
kDa, Sigma-Aldrich) were used as received. Standard soda lime glass microscope slides and phosphate
buffered saline (PBS) were obtained from VWR. Deionized water (DI, 18.2 M$\Omega$-cm, MilliQ) was used in
all aqueous polymer solutions and rinsing procedures.

**Fabrication of PEG-functionalized PVA/PAA multilayer film:** The glass substrates were first
degreased by sonication in a 4% ($v/v$) solution of Micro-90 (International Products Co.) for 15 min,
subsequently sonicated twice in DI water for 15 min, and then dried with compressed air. They were treated with oxygen plasma (PDC-32G, Harrick Scientific Products, Inc.) for 2 min at 150 mTorr and then PGMA anchoring chemistry was applied using previously described protocols to covalently bond the first layer of PVA to the substrate. Hydrogen bonded PVA/PAA films were produced via Layer-by-Layer (LL) assembly using a Stratosequence VI spin dipper (Nanostrata Inc.) controlled using StratoSmart v6.2 software. The LL assembly process employed dipping times of 10 min for each polymer solution, followed by three rinses of 2, 1, and 1 min. The concentration of the PVA and PAA solutions was 1 mg/mL and the pH of these solutions and the rinse water were adjusted to pH 2.0 with 0.1 M HCl. The assembled PVA/PAA multilayer films (consisting of 30 bilayers) were then thermally cross-linked at 140 °C for 5 min in vacuum to impart pH-stability, and these stabilized films were subsequently immersed in 10 mg/mL PEG solution (pH 2.0) for 20 min. The PEG-functionalized PVA/PAA multilayer films were prepared by soaking in 0.13% (w/w) glutaraldehyde in PBS at 30 °C for 10 min, rinsing with DI water, and drying with compressed air.

**Film Characterization:** Transient goniometric water contact angle measurements were performed using a ramé-hart model 590 goniometer after vertically dispensing sessile droplets of deionized water \((y=72.8 \text{ mN/m})\) on various coatings. Advancing water contact angles were measured as deionized water was supplied via a syringe. Transient water contact angle measurement commenced immediately after the water drop was advanced to a volume of approximately 10 μL. Measurements were taken over three or more different locations on each LL film, and the reported uncertainties are standard deviations associated with the measurement of these contact angle values. The reversibility of surface rearrangement was demonstrated by immersing the initially dry sample into deionized water for 10 min, and then measuring advancing water contact angles on the hydrated film (immediately after the sample was removed from the water) as well as in a dry state (after drying in ambient lab conditions, 22 ± 1 °C and 40 ± 10% RH, for 15 min). The temperature-dependence of the advancing and receding contact angles was quantified using an environmental chamber (ramé-hart, P/N 100-07) with water circulation. Water drops
were placed on the surface after the sample had been pre-equilibrated in the environmental chamber at the specified test temperature for at least 10 min. Contact angle measurements with other probe fluids (specifically the nonpolar liquids diiodomethane and hexadecane) were performed in the same manner. Tensiometric force measurements were made using a DCAT 11 (DataPhysics Instruments) tensiometer. The samples were probed at velocities ranging from $0.01 \leq V \leq 1$ mm/s and temperatures ranging from $10-40$ °C with a sampling frequency of 50 Hz and total immersion depths of $x \leq 25$ mm.

8.8 Supplemental Information

![Graphs](image)

**Figure 8-8** a. Advancing and receding contact angle of diiodomethane (DM) and hexadecane (HD) on PEG-functionalized PVA/PAA multilayer film. b. Transient contact angle measurements probed with DM and HD for PEG-functionalized PVA/PAA multilayer film.
Figure 8-9 Time dependence of the contact angle with water in $\cos \theta$ for PEG-functionalized PVA/PAA multilayer film at room temperature ($22 \pm 1^\circ C$) with the effects of evaporation removed. Open boxes, circles, and triangles represent individual data points averaged every 10 sec while the bold line represents the model fit.

Figure 8-10 Time dependence of the contact angle with water $\theta$ for PEG-functionalized PVA/PAA multilayer film at a. $T = 10^\circ C$, b. $T = 20^\circ C$, c. $T = 30^\circ C$, d. $T = 40^\circ C$ with the effects of evaporation removed. Open boxes, circles, and triangles represent individual data points averaged every 10 sec while the bold line represents the model fit.
Figure 8-11 The complete set of model results plotted analogous to Figure 5.
Figure 8-12 IR thermal imaging of the films during the tensiometer experiment.
9. DESIGNING ZWITTER-WETTABLE SURFACES

This was a comprehensive collaborative project among various research groups where the effect of surface wettability and diffusivity of water molecules in thin films on condensation of water molecules from the vapor phase was explored in detail. Both authors, Lee, H. and Gilbert, J. B. equally contributed to this work. Both Lee, H., and Gilbert, J.B. conceived the idea and designed the experiments. Lee, H. performed the film fabrication, wetting characterization and analysis, scanning electron microscopy, profilometry measurement, and antifogging performance tests. Gilbert J.B. performed the depth-profiling x-ray spectroscopy measurement and analysis, and performed the fabrication of polymer patches. Dr. Angile, F.E. and Dr. Lee, D. from University of Pennsylvania conducted the permeability measurement using QCM-D and analyzed the data. Yang, R. from Karen K. Gleason’s group provided the PPFDA coating using iCVD technique. Reproduced in part from a publication to be submitted as this thesis was being published.

9.1 Introduction

Control of water condensation from vapor on a surface is critical for a broad range of applications including heat-transfer, fog-harvesting, and high-performance optical devices. As a result, significant attention has been devoted to study the effect of surface chemistry, and roughness on water condensation over the past few decades. Many interesting new phenomenon such as jumping-droplets during coalescence, and low-volatility liquid impregnated surfaces with enhanced heat transfer has been discovered and expanded potential applications by engineering surfaces with optimal surface roughness and surface wetting characteristics.

For example, in the area of controlling water condensation for optically clear antifogging coatings, smooth hydrophilic or nano-textured superhydrophilic coatings were found to significantly reduce light scattering by facilitating film-like condensation. While many of these coatings perform satisfactorily in specifically defined condensing environments, these hydrophilic surfaces (i) may exhibit frost formation or excess and non-uniform water condensation under aggressive fogging conditions,
which results in poor optical performance of the coating, and (ii) may have reduced durability due to fouling by contaminants.

To overcome the limitations of the currently accepted hydrophilic antifogging method new insights into the design of antifogging materials are needed. Recent developments by us and others have presented possible solutions by reporting surfaces that can be both antifogging and hydrophobic. These counter-intuitive surfaces consist of polymeric networks of hydrophilic as well as hydrophobic moieties that can imbibe a considerable amount of water molecules from the vapor phase directly into the hydrogel-like film while the surface maintains a hydrophobic appearance. We recently defined these surfaces as zwitter-wettable surfaces, due to the capability to simultaneously absorb molecular water from the environment while exhibiting hydrophobic character to water droplets. It was also shown that incorporating hydrophilic poly(ethylene glycol)(PEG) segments resulted in antifogging coatings with frost-resisting capabilities. The presence of PEG increased the nonfreezing water capacity of the thin film due to its strong hydrogen bonding capability. While the major focus of these studies was to achieve antifogging coatings that perform well in very harsh conditions (below the freezing point of water), the detailed explanation correlating the abnormally high water contact angles (60-70°, or even as high as 110°) and the antifogging performance was rather limited. Furthermore, the experimental complexity of these individual systems restricted their thorough characterization which limited our understanding of the underlying mechanism.

In our previous work, we have shown that smooth hydrophilic antifogging surfaces result in a sheet of water on the surface and thus additional droplets form an effective water contact angle of 0°. Yet with zwitter-wettable surfaces, a water droplet on top of a film containing condensed water still exhibited a water contact angle above 90°, indicating that the water molecules in the vapor phase were directly imbibing into the film. Therefore, we hypothesized that in addition to roughness and surface chemistry, a third factor, the capability of the film to transport molecular water to the underlying reservoir must be
considered in the design of antifogging coatings. Thus, it was anticipated that a hydrophilic reservoir capped with a thin hydrophobic layer with high molecular water permeability could limit the nucleation and growth of water droplets on the surface during condensation and thus produce a hydrophobic and antifogging surface.

9.2 Fabrication of Zwitter-Wettable Surfaces

![Diagram of Zwitter-Wettable Surfaces]

- Hydrophilic surface
- Zwitter-wettable surface
- PPFDA coated (CHI/Nafion)
- PPFDA only

The diagram illustrates the fabrication process, showing the effects of hydrophilic and PPFDA coatings on the wettability of surfaces.
Figure 9-1 (a) Structures of the polymers described in this paper. Polycations and polyanions are labeled with parenthesis (+), (-), respectively. (b) Water advancing contact angle of the samples tested. (c) Photographs taken immediately after transfer to ambient lab conditions (22 ± 1 °C, 40 ± 10% RH) from a -1°C refrigerator (1 hr). Only the hydrophilic surface and zwitter-wettable surface resisted fog formation. (d) Schematic representation of hydrophilic surface with sessile drop and during condensation. (e) Schematic representation of zwitter-wettable surface with sessile drop and during condensation.

To test this hypothesis, the layer-by-layer (LbL) self-assembly technique was chosen to assemble various coatings with heterostructured architecture. For the base platform, hydrophilic polysaccharides (chitosan (CHI) as the polycation (+) and carboxymethyl cellulose (CMC) as the polyanion (-) as shown in Figure 9-1a) were LbL assembled electrostatically to create a hydrophilic antifogging coating as reported earlier. As shown in Figure 9-1b, 30- bilayers of CHI/CMC on a glass substrate has a water advancing contact angle of ~20°. Then the surface wetting characteristics of this 30- bilayer hydrophilic antifogging surface was altered to become hydrophobic with either 3- bilayers of (CHI/Nafion) by LbL technique or chemical vapor deposited (CVD) with poly(perfluorodecyl acrylate) (PPFDA). 3- bilayers of CHI/Nafion increased the water advancing contact angle up to ~110° and the PPFDA coating enhanced the water advancing contact angle to ~125°. The number of 3- bilayers was chosen because fewer bilayers would exhibit transient contact angle behavior due to surface rearrangement which complicates the analysis. All samples chosen for our analysis do not exhibit significant contact angle changes with time (Supplemental Information Figure 9-5).

As shown in Figure 9-1c, photographs were taken immediately after transfer to ambient lab conditions (22 ± 1 °C, 40 ± 10% RH) from a -1°C refrigerator (1 hr) and only the hydrophilic surface and the CHI/Nafion coated hydrophilic surface resisted fog formation. It has been reported earlier that the hydrophilic CHI/CMC coating remains optically clear during condensation due to their superior water-absorbing characteristics that form a uniform, non-light-scattering film of water on the surface as shown in Figure 9-1d. However, when this same surface was subsequently coated with hydrophobic CHI/Nafion, this coating exhibited a zwitter-wettable behavior where water molecules in the vapor phase directly imbibed into the film, while the surface remains hydrophobic to water droplets as shown in Figure 9-1e.
Yet, when the same hydrophilic surface was coated with PPFDA, the film exhibited fog formation. As revealed in Table 9-1, film thickness change after subsequent assembly are similar in its extent (69 nm and 62 nm, respectively) and the water advancing contact angles are both well above 90°. Two control samples where (CHI/Nafion)₃₀ and PPFDA are solely coated on a glass substrate also exhibited fog formation even though the surface wetting characteristics resemble the zwitter-wettable (CHI/Nafion)₃ coated hydrophilic surface. These results clearly indicate that the surface wetting characteristic does not solely determine whether a surface will fog and that the presence of the underlying hydrophilic “reservoir” is indeed critical.

Table 9-1 The thickness of the multilayer films used in this work.

<table>
<thead>
<tr>
<th></th>
<th>(CHI/CMC)₃₀</th>
<th>(CHI/CMC)₃₀</th>
<th>(CHI/CMC)₃₀</th>
<th>(CHI/Nafion)₃₀</th>
<th>PPFDA</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>(CHI/Nafion)₃</td>
<td></td>
<td>(CHI/Nafion)₃</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>615 ± 16 nm</td>
<td>684 ± 5 nm</td>
<td>677 ± 1 nm</td>
<td>18 ± 3 nm</td>
<td>72 ± 2 nm</td>
</tr>
<tr>
<td></td>
<td>(+ 69 nm)ᵃ</td>
<td>(+ 62 nm)ᵇ</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

ᵃFilm thickness change after assembling a capping layer.
Figure 9-2 (a) Schematic diagram of the polymer patch fabrication process. (b) Scanning electron microscopy (SEM) image of the polymer patch. Scale bar is 50 μm. Outlet image shows the enlarged SEM image and the average carbon and fluorine signal obtained from energy dispersive X-ray spectrometry (EDS). (c) Optical microscopy image of the polymer patch after exposure to humid air. (d) ESEM images of the condensation of water vapor on a polymer patch. Water droplets start to form on the off-patch areas and at the edges of the patches.

Previously, Varanasi et al., demonstrated that spatial control in the condensation of water molecules from the vapor phase can be achieved by patterning a surface with significant contrast in local intrinsic wettability to preferentially guide water molecules to nucleate and grow on the hydrophilic regions. To demonstrate the unique capability of our zwitter-wettable films to spatially control condensation of water molecules from the vapor phase, patterned films with zwitter-wettable characteristics were fabricated (Figure 9-2a). First, patches of the hydrophilic (CHI/CMC) reservoir (10-bilayers) were fabricated using
lift-off photolithography. 14, 165 10- bilayers were chosen because higher numbers of bilayers would result in incomplete patterning during the fabrication process. Then, the hydrophobic thin film (CHI/Nafion) (3-bilayers) was deposited, resulting in a surface with uniform (CHI/Nafion) over both the small patches of (CHI/CMC) as well as the off-patch areas. The uniform fluorine EDS signal (Figure 9-2b) confirms the consistent coverage of the Nafion, while the non-uniform carbon signal shows the presence of the underlying hydrophilic reservoir ((CHI/CMC)) in the patch area. When the patterned film is exposed to progressively higher water vapor pressure (Figure 2c and 2d) the water condensation is spatially controlled. Initially the water condenses in the hydrophilic reservoir of the patch, changing the refractive index and thus the color of the patch, however minimal droplets are seen on the surface (Figure 9-2c). As the water vapor pressure increases, progressively larger droplets start to form on the interstitial fogging areas, while no droplets are seen on the patch areas with zwitter-wettable characteristics. The capability to spatially control the condensation of water through patterning of the hydrophilic reservoir, while still presenting a uniform hydrophobic surface is indeed unique to zwitter-wettable surfaces.

In addition, contact angle measurements were performed on the (CHI/Nafion), coated hydrophilic reservoir using both high and low surface tension nonpolar liquids, diiodomethane (γLV = 50. 8 mN/m) and hexadecane(γLV = 27.5 mN/m) to further investigate the uniqueness of this zwitter-wettable surface. These results are shown in Supplemental Information Figure 9-6. Both liquids exhibited reasonably high advancing contact angles with low contact angle hysteresis indicating that surface exhibits a Teflon-like behavior to nonpolar liquids. Unlike typical hydrophilic surfaces where low surface tension liquids would completely spread, organic contaminants could be removed relatively easily due to the weak retention force offered by the hydrophobic capping layer.
9.3 Axial Composition Analysis Using Depth-Profiling XPS

Figure 9-3 (a) Schematic of depth-profiling x-ray photoelectron spectroscopy (XPS) used to acquire atomic concentration profile and molar ratio profile of various samples tested. Here, atomic concentration of (CHI/Nafion)₃ coated hydrophilic surface is shown as an example. (b) Molar ratio of hydrophilic surface ((CHI/CMC)₃) with depth in the film. (c) Molar ratio of (CHI/Nafion)₃ coated hydrophilic surface with depth in the film. (d) Molar ratio of PPFDA coated hydrophilic surface with depth in the film.

To investigate the origin of the (CHI/Nafion)₃ coated hydrophilic reservoirs favoring direct imbibing of water molecules into the film, the axial chemical composition analysis was performed. C₆₀ cluster-ion depth profiling X-ray Photoelectron Spectroscopy (XPS) was used to study the chemical composition with depth on various coatings with heterostructured architecture. Previously our group showed that this technique can provide atomic concentration information as well as the chemical state of polymer thin films with a resolution around 15nm. This capability was only recently enabled by the development of cluster-ion C₆₀ etching which is much less damaging to polymers than the single-ion etching methods commonly used. As shown in Figure 9-3a the depth profiling process uses iterative C₆₀⁺ etching and XPS acquisition to acquire an atomic concentration profile with depth. This atomic concentration with
depth can be further analyzed using a mass balance to determine the molar repeat ratio of the various polymers with depth, allowing for the analysis of polymer interlayer diffusion. From Figure 9-3b it is clear that there is a 2:1 CHI:CMC molar ratio in the hydrophilic reservoir and that this ratio is effectively maintained when the reservoir is coated with either the (CHI/Nafion)$_3$ (Figure 9-3c) or the PPFDA film (Figure 9-3d). Due to the lack of interlayer diffusion, it is clear that the different antifogging performance can be attributed to the characteristics of the thin capping layer alone.

9.4 Permeability Measurements Using QCM-D

![Diagram](image)

Figure 9-4 (a) Diffusivity (D) of water vapor in hydrophilic reservoir and (CHI/Nafion)$_3$ coated hydrophilic reservoir (b) Solubility of water vapor in hydrophilic reservoir and (CHI/Nafion)$_3$ coated hydrophilic reservoir. (c) Schematic representation of the effect of the ability of thin hydrophobic capping layer to transport water molecules: For low diffusivity capping layer, water molecules nucleate and grow on the surface while for high diffusivity capping layer, water molecules in the vapor phase prefer to directly imbibe into the underlying hydrophilic reservoir.

With the insight gained from the depth-profiling XPS study, the ability of thin hydrophobic capping layer to transport water molecules were investigated by permeability measurements using quartz crystal microbalance with dissipation monitoring (QCM-D). It has been previously demonstrated that QCM-D enables real-time measurements of water vapor uptake by a thin film with high precision and provides quantitative information on water diffusivity (D), and solubility (S).167 Briefly, quartz crystals coated with various films are introduced into a chamber where the changes in the frequency and dissipation are monitored upon exposure to a steam of humidified nitrogen and fitted using the Voigt viscoelastic model to predict the increase in thickness under humidified nitrogen. Then, the diffusivity (D) of water vapor in the film is determined by using Fickian diffusion model fitting and the solubility (S) by calculating the
change in mass between dry nitrogen and wet nitrogen. Detailed method of measurement and assumptions used for one-dimensional diffusion of water molecules can be found in the Supporting Information.

As shown in Figure 9-4a and b, the diffusivity ($D$), solubility ($S$) were measured for the following samples: (1) (CHI/CMC)$_3$ hydrophilic reservoir and (2) (CHI/Nafion)$_3$ coated hydrophilic. Comparing the hydrophilic reservoir alone to the hydrophilic reservoir coated with (CHI/Nafion)$_3$, both the diffusivity ($D$) and the solubility ($S$) were similar in their values. However, a hydrophobic capping layer that reduces the capability of the film to transport water molecules would thus favor nucleation on the surface which is indeed the case for PPDFA coated hydrophilic reservoir. This phenomenon is schematically shown in the top of Figure 9-4c. Since the diffusivity and solubility of the hydrophilic reservoir did not change when coated with the (CHI/Nafion) capping layer this indicates that a (CHI/Nafion) capping layer does not hinder water transport to the underlying hydrophilic reservoir. However, the (CHI/Nafion) layer without a reservoir does not have sufficient capacity to absorb water and eventually fogs after being saturated with water during condensation, agreeing with the antifogging test results in Figure 9-1c.

Previously, it has been reported$^{128}$ that a hydrophilic surface ($\theta \sim 25^\circ$) nucleates tens of orders of magnitude faster than a hydrophobic surface ($\theta \sim 110^\circ$) at a typical saturation ratio of $\frac{P}{P_\infty} = 1.7$. This allows water nucleation and subsequent growth to preferentially occur on more hydrophilic regions. In our zwitter-wettable surface, on the other hand, the surface is hydrophobic while highly diffusive to water molecules. Thus, the antifogging capability of the surface is further enabled since surface hydrophobicity retards nucleation and growth, while the CHI/Nafion capping layer allows facile diffusion of water molecules to the hydrophilic reservoir. This unique combination allows a zwitter-wettable surface to be hydrophobic and also antifogging.

Simple but careful design of this model system allowed the previous complex network of hydrophilic and hydrophobic moieties to be decoupled into a heterostructured film consisting of hydrophilic reservoir and a hydrophobic capping layer. While surface chemistry and roughness were the main factors
for controlling water condensation until now, a third factor, the capability of the film to transport water molecules needs to be considered. Furthermore, no surface rearrangement in our model zwitter-wettable surface allowed the film to exhibit truly hydrophobic behavior to water droplets unlike the previously studied zwitter-wettable system\textsuperscript{99,107} where the film exhibited a hydrophobic to hydrophilic transition when contacted with water.

Enabled by the experimental techniques to determine diffusivity (D) and solubility (S) via QCM-D, the design considerations discussed in this work can be further expanded to fabricate optimal hydrophilic reservoirs and hydrophobic capping layers depending on the application requirements. Furthermore earlier observations such as a critical film thickness requirement for hydrophilic antifogging coatings\textsuperscript{15} can be clarified in detail with respect to diffusivity (D) and solubility (S). In addition, optimal material selection for a specific condensation environment, governed by initial substrate temperature, and exposing environment (relative humidity, and temperature), can be further fine-tuned allowing additional physicochemical properties such as enhanced mechanical durability or frost-resisting capabilities to be taken into account while designing future zwitter-wettable surfaces.

9.5 Conclusions

In summary, we showed that when a thin hydrophobic layer with sufficient permeability is assembled on top of a hydrophilic reservoir, antifogging coatings with zwitter-wettable characteristics can be prepared. Enabled by depth profiling XPS and QCM-D, the required film properties were detailed for the design of future zwitter-wettable surfaces. Future work incorporating new surface chemistry and roughness may further extend zwitter-wettable surfaces to enable the fabrication superhydrophobic antifogging surfaces. Additionally we believe further applications of directed condensation of molecules from the vapor phase include water separation and purification.

9.6 Materials and Methods

Layer-by-Layer Assembly of the Polymer Thin Films: Sequential adsorption of polymer layers were performed using a StratoSequence VI spin dipper (nanoStrata Inc.), controlled by StratoSmart v6.2
software, at 80 rpm. The concentrations of chitosan (CHI, low molecular weight), carboxymethylcellulose (CMC, Mw = 250 000 g/mole) and Nafion dispersion (Alfa Aesar, 5% (w/w) in water and 1-propanol) in the dipping solutions were 1 mg/mL, 1 mg/mL and 0.25 % (w/w) respectively. For chitosan, 0.3 %(v/v) acetic acid was added prior to dissolving the polymer and was filtered with 200 μm pore filter (VWR) after stirring overnight. Distilled water (>18 MΩ·m, Millipore Milli-Q™) water (DI water) was used in formulating the solution and in all rinsing procedures. The dipping time in the CHI, CMC, and Nafion solutions were each 10 min followed by three sequential rinse steps (of 2, 1, and 1 min). All solutions and their respective rinse solutions were adjusted to pH 4.0 with either NaOH or HCl respectively.

Glass substrates were first degreased by sonication in a 4% (v/v) solution of Micro-90 cleaner (International Products Co.) for 15 min, subsequently sonicated twice in DI water for 15 min. The substrates were blow-dried with dry air and treated for 2 min with oxygen plasma (PDC-32G, Harrick Scientific Products, Inc.) at 150 mTorr before the LbL assembly.

Contact Angle Measurements: Transient contact angle measurements as well as advancing and receding contact angles of probe liquids on various samples were performed using a Ramé-Hart model 590 goniometer, by dispensing liquid droplets of volume V ~ 10 μL.

Preparation of Poly(perfluorodecyl diacrylate) (PPFDA) Coating Using Initiated Chemical Vapor Deposition (iCVD): iCVD polymerization of perfluorodecyl diacrylate (PFDA) (97%, Aldrich) was conducted similar as previously described. Briefly, the peroxide initiator, TBPO (98%, Aldrich), was delivered into the reactor through a mass flow controller (MKS Instruments) at a constant flow rate of 3.2 sccm. PFDA was vaporized in a glass jar that was heated to 80 °C. The flow rates were controlled using needle valves and kept constant at 0.2 and 0.6 sccm. The filaments were resistively heated to 230 °C using a DC power supply (Sorensen), and the temperature was measured by a K-type thermocouple (Omega Engineering). The sample stage was backcooled at 30 °C using a recirculating chiller/heater (Neslab RTE-7). The working pressure was maintained at 200 mTorr using a throttle valve (MKS Instruments).
The reactor was covered with a quartz top (2.5 cm) that allows in-situ thickness monitoring by interferometry with a 633 nm HeNe laser source (JDS Uniphase). Final thickness of the polymer deposited on the hydrophilic surface corresponds to ~65 nm.

**Permeability Measurements Using QCM-D:** Gold-coated QCM-sensors (Q-Sense Inc.) are cleaned with UV/ozone treatment for 10 min, then immersed in 2% (v/v) Sodium Deodecyl Sulfate (SDS) for 30 min in room temperature, rinsed with DI water, and finally blown dry with compressed air. Also, another UV/ozone treatment was done for 10 min before the baseline measurement. The baseline frequency and dissipation are first recorded with a blank crystal under dry nitrogen and calibrated to zero for the sorption measurements. All the multilayer films are then formed on the crystals through the similar procedure used for glass substrate. Here, gold crystals were immobilized on a plastic microscope slide (P11011P) in between two grooves made with a razor blade. The film on the back side of crystal is carefully removed using 1.0 M NaOH with a cotton swab and then rinsed thoroughly with DI water. After the multilayer coated sensors are loaded in the QCM chamber (E4 QCM-D unit (Q-Sense Inc.)), the frequency and dissipation shifts are monitored at varying humidity conditions.

The measured frequency and dissipation are fitted using the Voigt viscoelastic model incorporated in Q-Sense analysis software (QTools) to predict the increase in film thickness under wet nitrogen (~95% RH) due to the absorption and diffusion of water in the film similar to previously described procedure.\(^\text{167}\)

Average density of chitosan, carboxymethyl cellulose and Nafion was used to determine the film thickness from QCM-D measurements.

The diffusivity (D) of water vapor in the film is determined from the plot of the thickness change versus time under wet nitrogen (~95% RH) using a numerical model for one-dimensional diffusion of water into a thin film as shown previously.\(^\text{167}\)
\[
\frac{m_{t}-m_{\infty}}{m_{\infty}-m_{0}} = 1 - \sum_{n=0}^{\infty} \frac{8}{(2n+1)^{2}\pi^{2}} \exp \left[ -\frac{D(2n+1)^{2}\pi^{2}t}{l^{2}} \right]
\]  
(9-1)

where \(m_{\infty}, m_{t}, \text{and } m_{0}\) are the mass of the thin film and water at time = \(\infty\), \(t\), and 0, respectively. \(t\) and \(l\) are the time and thickness of the film, respectively. Since the film mass is linearly proportional to the thickness, above equation can be simplified to,

\[
-\frac{1}{\pi^{2}} \ln \left[ \frac{(m_{\infty}-m_{t})\pi^{2}}{8(m_{\infty}-m_{0})} \right] = \frac{D}{l^{2}} \frac{t}{l^{2}}
\]  
(9-2)

where the slope can be used to determine the diffusivity \((D)\). The solubility \((S)\) of water vapor in the film is simply determined by calculating the change in the mass of the film between under dry nitrogen and wet nitrogen, \(m_{\infty} - m_{0}\). The water permeability \((P)\) can be subsequently be determined by the following relationship: \(P = D \cdot S\). Also, the effect of water adsorption on blank QCM crystals have been corrected as reported earlier.167

For this measurement, a humidified stream is introduced at 10 cm\(^{3}\) (STP) min\(^{-1}\), with the corresponding mass transfer analog Biot number to be in the order of \(10^{4}\), indicating that the water-vapor transport process is diffusion-limited. It is known that the lateral diffusion is much faster than the normal diffusion through the film168 and thus our measurement will be dominated by one-dimensional diffusion of water normal to the film and the film swelling occurs dominantly in one dimension.

**Scanning Electron Microscopy (SEM) Measurements:** Scanning electron microscopy micrographs were obtained using a JEOL 6010LA in back scattered electron shadow image mode (BES) operated at an accelerating voltage of 10 kV. Energy dispersive X-ray spectrometry (EDS) was performed as well to perform elemental analysis of the Zwitter-wettable patch sample. Environmental scanning electron microscope (ESEM, Zeiss Evo 55) was used to investigate the nucleation and condensation phenomena in situ.

**Depth Profiling X-ray Photoelectron Spectroscopy:** Chemical composition of the surface was characterized using a PHI Versaprobe II X-ray photoelectron spectrometer with a scanning...
monochromated Al source (1486.6 eV, 50W, spot size 200 µm). Depth profiling was accomplished using the instrument's C$_{60}^+$ ion source. The takeoff angle between the sample surface and analyzer was 45° and the X-ray beam collected C1s, O1s, F1s, N1s and Si2p elemental information while rastering over a 200 µm x 350 µm area. Detailed XPS acquisition parameters are in the table below. Sputtering occurred in 1 minute intervals while the sample was moved using concentric Zalar rotation at 1 rpm. The C$_{60}^+$ source was operated at 10 kV and 10 nA and rastered over a 3x3 mm area at an angle 70° to the surface normal. Atomic composition was determined based on photoelectron peak areas and the relative sensitivity factors provided in PHI's Multipak processing software. All data were background subtracted, smoothed using a five point quadratic Savitzky-Golay (S-G) algorithm and charge-corrected so that the carbon-carbon bond has a binding energy of 285.0 eV. The surface of the glass substrate was defined as the point at which the atomic concentration of silicon reached 5% in the depth profiling data. The molar ratio profile was calculated via an oxygen mass balance. To minimize experimental bias, pure films of chitosan, CMC, Nafion and PPFDA were analyzed via Depth Profiling XPS as the basis for the effective molecular repeats.

Table 9-2 Detailed XPS Depth Profiling Conditions

<table>
<thead>
<tr>
<th>Element</th>
<th>Binding Energy (eV)</th>
<th>Pass Energy (eV)</th>
<th>Data Spacing (eV)</th>
<th>Sweeps</th>
</tr>
</thead>
<tbody>
<tr>
<td>C1s</td>
<td>280-298</td>
<td>117.4</td>
<td>0.5</td>
<td>2</td>
</tr>
<tr>
<td>O1s</td>
<td>526-538</td>
<td>117.4</td>
<td>0.5</td>
<td>2</td>
</tr>
<tr>
<td>Si2p</td>
<td>95-107</td>
<td>117.4</td>
<td>1.0</td>
<td>1</td>
</tr>
<tr>
<td>F1s</td>
<td>682-695</td>
<td>117.4</td>
<td>0.5</td>
<td>2</td>
</tr>
<tr>
<td>N1s</td>
<td>393-405</td>
<td>117.4</td>
<td>0.5</td>
<td>2</td>
</tr>
</tbody>
</table>

**Zwitter-wettable Patch Fabrication:** Patch fabrication was based on a photolithographic lift off procedure. Briefly, the slides were cleaned with 2% (v/v) solution of Micro-90 cleaner (International Products Co.), 1M NaOH and then rinsed with water. Next, the photoresist was spin coated onto the surface and developed as previously described. After deposition of the uniform hydrophilic layer via layer by layer processing, the film was patterned by dissolving the remaining photoresist in sonicating
acetone for 10 seconds, leaving behind patches of hydrophilic (CHI/CMC). Finally the hydrophobic
(CHI/Nafion) film was deposited uniformly over the surface via layer by layer processing.

9.7 Supplemental Information

![Graph](image)

Figure 9-5 (a) Water contact angle evolution over time for (CHI/CMC)30 subsequently coated with
1-, 2-, and 3- bilayers of (CHI/Nafion) by LbL technique. (b) Water contact angle evolution over
time for various samples tested in this work.

The linear decrease in water contact angle can be attributed to evaporation of water from the static drop
over the elapsed time of the experiment.107

![Graph](image)

Figure 9-6 Advancing and receding contact angle of water, diiodomethylene, and hexadecane on
(CHI/Nafion), coated hydrophilic reservoir.
9.8 Preliminary Work for Future Studies

9.8.1 The Effect of Additional (CHI/Nafion) Bilayers on Hydrophilic Reservoir ((CHI/CMC)_30)

It was demonstrated earlier in this chapter that when a thin hydrophobic layer with sufficient diffusivity is assembled on top of a hydrophilic reservoir, antifogging coatings with zwitter-wettable characteristics can be prepared. In this study, more number of (CHI/Nafion) bilayers was assembled on top of hydrophilic reservoir to study the effect of thickness in detail.

First, additional film thickness increase was measured via profilometry after various number of (CHI/Nafion) bilayers were assembled on top of hydrophilic reservoir. As shown in Figure 9-7, while drastic increase in film thickness is observed in the initial few bilayers, the change in film thickness starts to plateau with increase in number of bilayers, becoming almost negligible (or even slight reduction) after 20- bilayers.

![Figure 9-7 Film thickness change after assembling various number of (CHI/Nafion) bilayers.](image)

Previously, 3- bilayers of (CHI/Nafion) was chosen as a model system for zwitter-wettable surface because as shown in Figure 9-5a, fewer bilayers would exhibit transient contact angle behavior due to surface rearrangement which complicates the analysis. Thus, it was initially presumed that further assembly of (CHI/Nafion) bilayers would remain the water contact angle to be non-transient but only
increase in its film thickness. However, as shown in Figure 9-8, increasing the number of (CHI/Nafion) bilayers resulted in this transient contact angle behavior to reappear.

Figure 9-8 Water contact angle evolution over time for hydrophilic reservoir \((\text{CHI/CMC})_{30}\) capped with (CHI/Nafion) layers.

In order to study the transient water contact angle behavior more in depth, a drop shape analysis was applied as shown in Figure 9-9. While the volume change with time is similar (small, 10-20% decreases in volume can be anticipated due to evaporation of water from the droplets) regardless of how many bilayers are on top, spreading was significant for the 10-, 20-, 30- bilayer films, indicating that the surface reconstructs from a high initial to a lower final water contact angle for these films.
Figure 9-9 (a) Water droplet volume evolution over time (600 s) for hydrophilic reservoir \(((\text{CHI/CMC})_{30})\) capped with various numbers of \((\text{CHI/Nafion})\) bilayers expressed as \(\Delta V/V_0\) where \(\Delta V=V-V_0\) and \(V_0\) is the initial water droplet volume at \(t=0\). (b) Wetted surface area evolution over time (600 s) for hydrophilic reservoir \(((\text{CHI/CMC})_{30})\) capped with various numbers of \((\text{CHI/Nafion})\) bilayers expressed as \(\Delta S/S_0\) where \(\Delta S=S-S_0\) and \(S_0\) is the initial wetted surface area at \(t=0\).

Next, we acquired the atomic concentration profile of these films using depth-profiling x-ray photoelectron spectroscopy (XPS) as shown in Figure 9-10. The black dotted line corresponds to the dry film thickness of the hydrophilic reservoir before the subsequent assembly of \((\text{CHI/Nafion})\) layer. From the atomic concentration with depth provided, it is apparent that the ratio of carbon and oxygen is effectively maintained in the hydrophilic reservoir regardless of the number of \((\text{CHI/Nafion})\) bilayers deposited. Similar to our previous analysis conclusion, there is no significant interlayer diffusion and the resulting antifogging performance can be attributed solely to the characteristics of the capping layer alone.
Figure 9-10 (a) Atomic concentration profile of (CHI/Nafion)$_{10}$ coated hydrophilic reservoir. (b) Atomic concentration profile of (CHI/Nafion)$_{20}$ coated hydrophilic reservoir. (c) Atomic concentration profile of (CHI/Nafion)$_{30}$ coated hydrophilic reservoir.

Also, photographs were taken immediately after transfer to ambient lab conditions (24 °C, 60 % RH) from a -1°C refrigerator (1 hr).

![Figure 9-11](image)

Figure 9-11 Photographs taken immediately after transfer to ambient lab conditions (24 °C, 60 % RH) from a -1°C refrigerator (1 hr).

As shown in Figure 9-11, hydrophilic reservoir coated with more than 10- bilayers of (CHI/Nafion) all resisted fog formation even though the capping layer thickness was thicker than the 3- bilayer (CHI/Nafion) tested earlier. The additional film thickness increase for 3- bilayer (CHI/Nafion) was 69 nm while 10-, 20-, 30- bilayer of (CHI/Nafion) was 89 ± 3, 152 ± 3, and 148 ± 3 nm, respectively.

Although further investigation is necessary to fully understand the unexpected growth behavior and the transient contact angle behavior that reappears after a certain number of bilayers, the above results suggest that as long as the hydrophobic capping layer has sufficient capacity to transport water molecule to the underlying hydrophilic reservoir at a specific condensation environment, the thickness of the capping layer does not significantly matter. The next interesting path would be to perform permeability measurements to further validate this hypothesis.
9.8.2 PEG- Functionalized PVA/PAA Multilayer Films with Various Capping Layers

It has been demonstrated earlier in this thesis that PEG-functionalized PVA/PAA multilayer film exhibits zwitter-wettable behavior as well as significantly enhanced anti-fog and frost-resistant behavior. However, when in contact with water, these films exhibit a hydrophobic to hydrophilic transition behavior due to surface reconstruction. Based on the design framework on zwitter-wettable surfaces, it is anticipated that modifying PEG-functionalized PVA/PAA multilayer films with a suitably designed hydrophobic capping layer would result in a truly hydrophobic behavior without compensation of its frost-resisting capabilities.

To test this hypothesis, various capping layers were assembled on top of PEG-functionalized PVA/PAA multilayer films. First, 1-, 2-, 3- bilayers of (CHI/Nafion) and 3- bilayers of (CHI/CMC) were assembled on top of PEG-functionalized PVA/PAA multilayer films using LbL self-assembly. As shown in Table 9-3 below, reduction in film thicknesses were observed when subsequently assembled with either (CHI/CMC) or (CHI/Nafion).

Table 9-3 The film thickness change after assembling a capping layer.

<table>
<thead>
<tr>
<th></th>
<th>+(CHI/CMC)₃</th>
<th>+(CHI/Nafion)₁</th>
<th>+(CHI/Nafion)₂</th>
<th>+(CHI/Nafion)₃</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Before</strong></td>
<td>1395 ± 33 nm</td>
<td>1644 ± 11 nm</td>
<td>1625 ± 11 nm</td>
<td>1643 ± 36 nm</td>
</tr>
<tr>
<td><strong>After</strong></td>
<td>1302 ± 23 nm</td>
<td>1580 ± 8 nm</td>
<td>1561 ± 15 nm</td>
<td>1608 ± 10 nm</td>
</tr>
<tr>
<td><strong>Net Change</strong></td>
<td>-94 nm</td>
<td>-63 nm</td>
<td>-65 nm</td>
<td>-35 nm</td>
</tr>
</tbody>
</table>

Then, the contact angles on these films were probed with water as shown in Figure 9-12. Non-transient water contact angle behavior was observed even with 1- bilayer of (CHI/Nafion). For the film coated with 3- bilayers of (CHI/CMC), water advancing contact angle reduced close to ~80° which is similar in value to the poly(vinyl acetate) coating demonstrated earlier in Figure 7-11 (θ_{adv} = 75 ± 2°).
Figure 9-12 Water contact angle evolution over time for PEG-functionalized PVA/PAA multilayer films subsequently coated with various capping layers.

Next, a simple anti-frost experiment was conducted by incubating the above samples in -20°C freezer for 1 hr and transferring to ambient lab conditions (22 ± 1 °C, 40 ± 10 % RH). As shown in Figure 9-13, photographs were taken immediately after transfer and all the films subsequently coated with capping layers exhibited frost formation regardless of the type and number of bilayers assembled. However, it is noteworthy to mention that even though these samples exhibited frost formation, all were antifogging in milder challenges.
Figure 9-13 Photographs taken immediately after transfer to ambient lab conditions (22 ± 1 °C, 40 ± 10 % RH) from a -20°C freezer (1 hr). (a) PEG-functionalized PVA/PAA multilayer film subsequently coated with 3- bilayer of (CHI/CMC). (b) PEG-functionalized PVA/PAA multilayer film subsequently coated with 1-, 2-, and 3- bilayers of (CHI/Nafion).

To rule out the effect of assembly pH on frost-resistant behavior, control experiment was performed as shown in Figure 9-14. Here, PEG-functionalized PVA/PAA multilayer films were exposed to pH 4.0 DI water for 1.5 hr which is equivalent to the amount of time needed for 3- bilayers of LbL assembly. As shown in Figure 9-14, no frost formation was observed indicating that the exposure to the assembly pH did not alter the properties of the PEG-functionalized PVA/PAA multilayer film. Also, no significant change in film thickness was observed after the exposure.

Figure 9-14 Photographs taken immediately after transfer to ambient lab conditions (22 ± 1 °C, 40 ± 10 % RH) from a -20°C freezer (1 hr). Both the control and the sample exposed to assembly pH for 1.5 hr resisted frost formation.

To investigate the chemical composition of the (CHI/Nafion), coated PEG-functionalized PVA/PAA multilayer film, depth-profiling XPS was used.
Figure 9-15 (a) N\textsubscript{\text{1s}}, and F\textsubscript{\text{1s}}, signal of (CHI/Nafion)\textsubscript{3} coated (CHI/CMC)\textsubscript{30} multilayer film and (CHI/Nafion)\textsubscript{3} coated PEG-functionalized PVA/PAA multilayer film focused on the top 200 nm. (b) Carbon spectra with depth for (CHI/Nafion)\textsubscript{3} coated PEG-functionalized PVA/PAA multilayer film.

As shown from Figure 9-15a, the N\textsubscript{\text{1s}}, and F\textsubscript{\text{1s}}, signal comparison between (CHI/Nafion)\textsubscript{3} coated (CHI/CMC)\textsubscript{30} multilayer film and (CHI/Nafion)\textsubscript{3} coated PEG-functionalized PVA/PAA multilayer film revealed that N\textsubscript{\text{1s}}, and F\textsubscript{\text{1s}}, signals are only present on the surface and partially on the first layer below for (CHI/Nafion)\textsubscript{3} coated PEG-functionalized PVA/PAA multilayer film. Here, N\textsubscript{\text{1s}}, signal is attributed to amine groups in chitosan while F\textsubscript{\text{1s}}, signal is from the fluorinated moieties in Nafion. This indicates that there is no evidence of chitosan or Nafion diffusion into the PEG-functionalized PVA/PAA multilayer film and only a very thin (CHI/Nafion) layer less than 20 nm is present at the surface.

Also the carbon spectra with depth in Figure 9-15b shows that the surface has a peak at 292 eV which is attributed to C-F bond in Nafion and no shift in COOH peak (289 eV) or in PEO/PAA peak (286.5 eV) is observed beyond the first layer. This indicates that there is no evidence of significant exchange of PVA, PEO, or PAA out of the film upon subsequent assembly of (CHI/Nafion).

These preliminary data suggests that capping PEG-functionalized PVA/PAA multilayer film with 1- to 3- bilayers of (CHI/Nafion) does indeed inhibit the surface rearrangement and have truly hydrophobic behavior but sacrifices its anti-frosting capability. Also, no sign of significant interlayer diffusion was observed with depth-profiling XPS study. From the diffusivity study discussed earlier in this chapter, it is
possible that this thin hydrophobic layer slightly reduces the diffusivity of the overall system and has
some extent of solubility. Thus, it is hypothesized that frost formation is either due to formation of water
clusters in non-bound state within this thin capping layer or oversaturation of the hydrophobic layer due
to reduction in diffusivity and subsequent nucleation and growth on the surface. In order verify this
hypothesis, fluorosilane treatment was performed. Careful deposition of fluorosilane monolayer was
anticipated to allow high diffusivity but minimal solubility to resist frost formation.

A quick fluorosilane treatment using $1H,1H,2H,2H$-perfluorododecyltrichlorosilane was conducted on
PEG-functionalized PVA/PAA multilayer film via the previously described procedure with the exception
that no external heat was applied that might alter the crosslinking density in PVA/PAA multilayer films.
As shown in Figure 9-16a, fluorosilane treatment indeed worked on a soda lime glass without heating,
enhancing the water contact angle to expected values ($\theta_{\text{adv}} = 108 \pm 4^\circ$, $\theta_{\text{rec}} = 94 \pm 2^\circ$). However, for PEG-
functionalized PVA/PAA multilayer films, $1H,1H,2H,2H$-perfluorododecyltrichlorosilane produced a
translucent layer on the surface that was easily removed by rinsing with DI water as shown in Figure
9-16b. After rinsing with DI water, the film became transparent again and exhibited the same transient
water contact angle behavior observed in untreated PEG-functionalized PVA/PAA film. Trichlorosilanes
are known for their tendency to polymerize themselves on surfaces in certain conditions. Thus, the next
interesting but simple thing to try out would be to use monochlorosilanes.

![Figure 9-16](image-url)

**Figure 9-16** (a) Photograph of a water droplet placed on top of fluorosilane treated soda lime glass.
(b) Photograph of a PEG-functionalized PVA/PAA multilayer film after fluorosilane treatment and
showing how easily it can be removed by placing a water droplet on the surface.
10. SUMMARY AND FUTURE WORK

10.1 Thesis Summary

In this thesis, hydrogen-bonded layer-by-layer (LbL) assembly consisting of poly(vinyl alcohol)(PVA) was studied from a fundamental perspective and applied in various applications. We started with a brief chapter introducing hydrogen-bonding interactions as the primary driving force for the LbL assembly and compared to the typical electrostatically assembled systems. Motivating with the advantages of incorporating PVA into multilayer film, the parameters which gives us control over the physicochemical properties of these hydrogen-bonded multilayer films were then discussed, namely the type of interacting polymer pairs, molecular weight, and the assembly pH. Additional parameter specific to PVA, degree of hydrolysis (DH) was readily adopted from previous literatures as a new design parameter for PVA based hydrogen-bonded LbL assembly.

Systematic study on how various assembly parameters influence water insoluble complex formation and subsequently on multilayer film formulation was discussed next. Weak polyacids such as poly(acrylic acid) (PAA) and poly(methacrylic acid)(PMAA) was chosen as the complementary hydrogen-acceptor polymer for this study. It was found that multilayer films containing PVA and PAA could be successfully assembled only by using high molecular weight partially hydrolyzed PVA and low pH solutions. By comparing films with those containing PMAA, it was shown that the extent of PVA hydrolysis becomes significant only when weak hydrogen bonding pairs such as PVA and PAA were used. Also, the effect of DH of PVA and type of weak polyacid on pH-stability of the resulting film was investigated in detail. We then discussed the opportunity offered by the abundance of free hydroxyl and carboxylic acids in the multilayer film which allows enhanced pH-stability by thermal and chemical methods as well as numerous opportunities for post-assembly functionalization.

We also extended this work to include biologically relevant molecules such as tannic acid (TA) which exhibited enhanced pH-stability without further crosslinking due to high pKₐ value of TA. Again, conformal thin film consisting of PVA and TA were created by systematically varying the assembly pH,
molecular weight, and DH of PVA. Due to the self-associating behavior of TA depending on the concentration and pH of the medium, varying the DH of complementary polymer PVA resulted in opposite trend in growth behavior which was verified via both profilometry and quartz crystal microbalance with dissipation (QCM-D).

Having successfully incorporated PVA into a hydrogen-bonded multilayer, we explored the advantages of hydrogen-bonding LbL structures enabling assembly of multiple stacks with differing composition and properties. Careful design of polymer pairs and stacking order yielded complex hydrogen-bonded heterostructured architectures that sequentially dissolve with increase in local pH condition as well as PVA based multifunctional freestanding film with tunable film thickness.

The second half of this thesis consisted of developing optically transparent antifogging coatings that perform well in very harsh conditions (below the freezing point of water) and providing a design consideration for optimal antifogging coating for a specific condensation environment governed by the initial substrate temperature, and the exposing environment (relative humidity, and temperature). We started with developing an experimental protocol that enables quantitative analysis of antifogging performance via real-time monitoring of transmission levels as well as image distortion. Having the protocol to quantify the antifogging performance, we moved on to test various coatings with different surface wetting characteristics. We demonstrated that unlike typical hydrophilic nor hydrophobic surfaces, PVA/PAA multilayers exhibit a zwitter-wettable behavior, whereby the multilayer film exhibits a facile, rapid absorption of molecular-level water into a film from the gas phase while simultaneously exhibiting very high contact angles for macroscopic liquid drops of water placed on the surface of the same film. Additional functionalization of this nano-blended PVA/PAA multilayer with PEG segments produced a significantly enhanced antifog and even frost-resistant behavior which was due to the increase in the nonfreezing water capacity of the multilayer film.
The investigation of high water advancing contact angle and transient water contact angle behavior of PEG-functionalized PVA/PAA multilayers led to a separate work where the wetting characteristics were further characterized with dynamic tensiometry. We have shown that the time-dependent wetting behavior of these coatings results from the transient surface rearrangement of hydrophilic functional groups towards the surface in response to exposure to a liquid water environment. By using a simple first-order thermally-activated model, the kinetics of surface rearrangement was explored in detail by utilizing dynamic tensiometry where a single dimensionless parameter was proposed that represents a ratio of the time scale for molecular rearrangement to a characteristic tensiometric time scale.

Finally, a model system was designed to study the zwitter-wettable phenomenon in more detail. The complex network of hydrophilic and hydrophobic moieties was decoupled into a heterostructured film consisting of hydrophilic reservoir and a hydrophobic capping layer. Enabled by the thorough characterization of the films using a quartz crystal microbalance with dissipation monitoring (QCM-D) and depth-profiling X-ray photoelectron spectroscopy (XPS), we found that the retarded nucleation of water droplets on hydrophobic surfaces and the facile diffusion of water molecules impart antifogging coatings with zwitter-wettable characteristics.

10.2 Future Research Directions

The introduction of the PVA based multilayer system represents a new, stable, and quite versatile platform for applications ranging from biological to optical. In particular, we have shown the specific application of optically transparent antifogging in this thesis. Nevertheless, this platform can be further expanded to exploit its advantage in biofunctionalization capabilities. We have shown that PVA/PAA multilayer film is stable in physiological condition and has the free carboxylic acid groups and hydroxyls group in the film suitable for further chemistry to be applied. Thus, variety of target molecules can be applied making this system a versatile platform for biological applications. Such applications may include covalently binding single strand DNA and using this as a platform for complementary DNA strand detection or selectively functionalizing with biotin or antibodies for bioassay development.
Our work on anti-frosting coatings also suggests interesting future experiments. In particular, the deposition of these PEG-functionalized PVA/PAA multilayer films on a rough transparent surface with appropriately designed geometry would allow creating anti-frosting superhydrophobic surfaces. However, as demonstrated in this thesis, PEG-functionalized PVA/PAA multilayer films exhibits a hydrophobic to hydrophilic transition when contacted with water. With the insight gained from the design framework on zwitter-wettable surfaces, modifying this surface with a suitably designed hydrophobic capping layer might result in this film to exhibit truly hydrophobic behavior to water droplets and thus non-transient superhydrophobic behavior on a rough surface.

Our collaborative work on the diffusivity measurements using QCM-D also leaves interesting future experiments. Enabled by the experimental techniques to determine diffusivity and solubility via QCM-D, the design considerations discussed in this thesis can be further expanded to fabricate optimal hydrophilic reservoirs depending on the application requirements. Earlier observations such as a critical film thickness requirement for hydrophilic antifogging coatings can be clarified in detail with respect to diffusivity and solubility. In addition, optimal material selection for a specific condensation environment can be further fine-tuned allowing additional physicochemical properties such as enhanced mechanical durability or frost-resisting capabilities to be taken into account for designing functional zwitter-wettable surfaces. For example, in conjunction with thermal analysis (which allows to determine how efficient a specific molecule are capable of suppressing freezing point of water), the type of molecules to functionalize with, their molecular weight, and extent of functionalization can be further optimized to achieve optimal anti-frosting coating for desired application.

It would also be interesting to determine how PEG hydrogel behaves under the conditions we tested in this thesis. This leaves a number of open questions. Further investigations should focus on whether surface hydrophobicity is necessary even if the non-freezing capacity is so high. Not only the effect of surface wettability but also systematically varying the crosslinking density of these PEG gels and
studying with all the characterization techniques mentioned in this thesis might provide further understanding of what we know so far.
11. CITATIONS


149. Dettre, R. H.; Johnson, R. E., Contact Angle Hysteresis. In Contact Angle, Wettability, and Adhesion, American Chemical Society: 1964; Vol. 43, pp 136-144.


