Swelling and Photo-Expansion of Polyelectrolyte Thin Films

by

Oleh Tanchak

A thesis submitted to McGill University in partial fulfillment of the requirements for the degree of

Doctor of Philosophy

Department of Chemistry McGill University Montreal, Quebec Canada

© Oleh Tanchak

July 2006



Library and Archives Canada

Published Heritage Branch

395 Wellington Street Ottawa ON K1A 0N4 Canada Bibliothèque et Archives Canada

Direction du Patrimoine de l'édition

395, rue Wellington Ottawa ON K1A 0N4 Canada

> Your file Votre référence ISBN: 978-0-494-27846-8 Our file Notre référence ISBN: 978-0-494-27846-8

NOTICE:

The author has granted a nonexclusive license allowing Library and Archives Canada to reproduce, publish, archive, preserve, conserve, communicate to the public by telecommunication or on the Internet, loan, distribute and sell theses worldwide, for commercial or noncommercial purposes, in microform, paper, electronic and/or any other formats.

The author retains copyright ownership and moral rights in this thesis. Neither the thesis nor substantial extracts from it may be printed or otherwise reproduced without the author's permission.

AVIS:

L'auteur a accordé une licence non exclusive permettant à la Bibliothèque et Archives Canada de reproduire, publier, archiver, sauvegarder, conserver, transmettre au public par télécommunication ou par l'Internet, prêter, distribuer et vendre des thèses partout dans le monde, à des fins commerciales ou autres, sur support microforme, papier, électronique et/ou autres formats.

L'auteur conserve la propriété du droit d'auteur et des droits moraux qui protège cette thèse. Ni la thèse ni des extraits substantiels de celle-ci ne doivent être imprimés ou autrement reproduits sans son autorisation.

In compliance with the Canadian Privacy Act some supporting forms may have been removed from this thesis.

While these forms may be included in the document page count, their removal does not represent any loss of content from the thesis.



Conformément à la loi canadienne sur la protection de la vie privée, quelques formulaires secondaires ont été enlevés de cette thèse.

Bien que ces formulaires aient inclus dans la pagination, il n'y aura aucun contenu manquant.

Abstract

The swelling behavior of thin polyelectrolyte multilayers assembled from poly(allylamine hydrochloride) (PAH) and poly(acrylic acid) (PAA) under various pH and environmental conditions was characterized in real time by in situ single wavelength ellipsometry. Both the rates and extent of swelling were found to be independent of the solution environment, yet they depended strongly on the solution pH under which the layers were fabricated. The ambient humidity strongly influenced the rate of swelling, where a change by as little as 20% prior to swelling with bulk solution lead to a variation from seconds to tens of minutes to reach the final swollen thickness. Neutron reflectivity studies revealed that water is distributed asymmetrically within the multilayer, and preferentially localizes at the polymer surface, and explains the unusual effect of humidity on the swelling kinetics. The effect of solution pH and salt ions on the water distribution in the multilayer was also investigated by neutron reflectivity. Exposure to both pH and salt solutions increased water content in the film. These studies indicate that the water localizes asymmetrically in the film and predominantly segregates near the substrate when exposed to salt solutions and the distribution of salt ions also increases near the substrate region.

Finally, the light-induced expansion of thin films of polymers containing azobenzene chromophores and copolymers of PAA was characterized in real time by single wavelength ellipsometry. An initial expansion of the azo polymer films was found to be irreversible and with repeated irradiation cycles the expansion becomes reversible. Modulating either the pump beam power or the duration of irradiation gave control over the extent of the reversible expansion. This represents the first discovery of the photomechanical effect in azobenzene polymers, and in principle now allows these materials to be developed as reversible photo-actuation systems.

Résumé

L'éllipsométrie in situ en temps réel et à longueur d'onde fixe a été utilisé pour caractériser le gonflement des multicouches minces formées des polyélectrolytes de polyallylamine (PAH) et d'acide polyacrylique (PAA). Ces derniers ont été assemblés à différents pH et sous des conditions environnantes différentes. Il en a été déduit que la vitesse et le taux de gonflement sont tout deux indépendants de la solution environnante, mais dépendent fortement du pH des solutions utilisées dans la fabrication des couches. L'humidité ambiante a grandement influencée la vitesse de gonflement, puisqu'un changement d'humidité ambiante aussi faible que 20%, préalable au gonflement des films induit par une solution aqueuse, a conduit à une variation allant de quelques secondes à une dizaine de minutes pour atteindre un niveau de gonflement final. Les études de réflectivité des neutrons ont révélées que l'eau est distribuée asymétriquement à l'intérieur de la multicouche et localisée préférentiellement à la surface du polymère, ce qui explique l'effet inhabituel de l'humidité sur la cinétique du gonflement. L'effet du pH et des ions de sel sur la distribution de l'eau dans la multicouche a aussi été étudié par la réflectivité des neutrons. L'exposition des films aux conditions saline et de pH fait augmenter le contenu d'eau dans ces derniers. Ces études indiquent que l'eau est localisée asymétriquement dans le film et se confine de façon prédominante près du substrat lorsqu'il est exposé à des solutions salines. Par le fait même, la distribution des ions de sel augmente aussi dans la région située prés du substrat.

Finalement, l'éllipsométrie en temps réel et à longueur d'onde fixe a été utilisée pour caractériser l'expansion induite par la lumière des minces films de polymère composés de chromophores d'azobenzène et de copolymères de PAA. Une expansion initiale irréversible du film d'azo polymère a été observée lors d'une première irradiation, alors que la répétition des cycles d'irradiation a conduit à une expansion réversible des films. La modulation de la puissance de la pompe du faisceau ainsi que la durée d'irradiation ont permis de contrôler l'étendu de l'expansion réversible. Cette étude présente pour la première fois l'effet photo-mécanique des polymères d'azobenzène, ce qui en principe ouvre de nouvelles avenues dans le développement de systèmes de photo-actuation construits à partir de ces matériaux.

Forward

This dissertation is presented in the form of four original research papers which have been either published or submitted, each of which is presented as a chapter. Chapter 1 gives a comprehensive background of the field of study, and Chapters 2 through 5 contain original research results. Finally, a general conclusion and suggestions for future work are presented in Chapter 6.

Contributions of Authors

All of the papers were written by Oleh Tanchak. They were co-authored only with Professor Christopher Barrett as research advisor, unless stated otherwise. All of The research presented in this dissertation was initiated, performed, and critically analyzed only by the author; but with minor technical contributions of some co-authors as detailed below.

Chapter 2 describes the swelling dynamics of polyelectrolyte thin films. The work described in this chapter was completed solely by the author under the supervision of Professor Christopher Barrett, and published in *Chemistry of Materials* in 2004.

Chapters 3 and 4 describe investigations into the water and ion distributions both in vapor and bulk in polyelectrolyte multilayers using neutron reflectometry. The experiments in these chapters required technical assistance with the NRC Chalk River Neutron Scattering Laboratories. The sample preparation, neutron reflectivity measurements, and all data workup were completed by Oleh Tanchak, but some minor technical assistance for the 24hour/day neutron data collection was provided by Mr. Kevin G. Yager, under the supervision of Oleh Tanchak. Necessary instrumentation training at the C5 spectrometer was provided by Dr. Helmut Fritzsche and Dr. Thad Harroun at the Chalk River Laboratories. The fitting and interpretation of the data were completed solely by the author. Minor editorial advice for the final manuscript was provided by Dr. John Katsaras, Dr. Helmut Fritzsche, and Dr. Thad Harroun at NRC Chalk River, and by Professor Christopher Barrett. These results were written as papers entirely by Oleh Tanchak, one published in *Langmuir* in 2006, and the other currently under review in *Langmuir*.

Chapter 5 describes the photo-expansion of azobenzene containing polyelectrolyte thin films. The work described in this chapter was completed solely done by Oleh Tanchak under the supervision of Professor Christopher Barrett, and was published in *Macromolecules* in 2005.

I hereby give copyright clearance for the inclusion of the following papers, of which I am a co-author, in the Ph.D. dissertation of Oleh Tanchak, McGill University:

Tanchak, O. M.; Yager, K. G.; Fritzsche, H.; Harroun, T.; Katsaras, J.; Barrett, C. J. "Ion Distribution in Multilayers of Weak Polyelectrolytes: a Neutron Reflectivity Study" submitted to Langmuir July 2006, and under review.

Tanchak, O. M.; Yager, K. G.; Fritzsche, H.; Harroun, T.; Katsaras, J.; Barrett, C. J. "Water Distribution in Multilayers of Weak Polyelectrolytes" *Langmuir* 2006, 22, 5137-5143.

Tanchak, O. M.; Barrett, C. J. "Light-Induced Reversible Volume Changes in Thin Films of Azo Polymers: The Photomechanical Effect" *Macromolecules*. 2005, *38*, 10566-10570.

Tanchak, O. M.; Barrett, C. J. "Swelling Dynamics of Multilayer Films of Weak Polyelctrolytes" *Chemistry of Materials* 2004, *16*, 2734-2739.

Professor Christopher J. Barrett Department of Chemistry McGill University Quebec, Canada

06 28 Date

I hereby give copyright clearance for the inclusion of the following papers, of which I am a co-author, in the Ph.D. dissertation of Oleh Tanchak, McGill University.

Tanchak, O. M.; Yager, K. G.; Fritzsche, H.; Harroun, T.; Katsaras, J.; Barrett, C. J. "Ion Distribution in Multilayers of Weak Polyelectrolytes: a Neutron Reflectivity Study" submitted to Langmuir July 2006, and under review.

Tanchak, O. M.; Yager, K. G.; Fritzsche, H.; Harroun, T.; Katsaras, J.; Barrett, C. J. "Water Distribution in Multilayers of Weak Polyelectrolytes" *Langmuir* 2006, 22, 5137-5143.

July 27/2006

Date

Mr. Kevin G. Yager Department of Chemistry McGill University Quebec, Canada I herby give copyright clearance for the inclusion of the following papers, of which I am a co-author, in the dissertation of Oleh Tanchak.

Tanchak, O. M.; Yager, K. G.; Fritzsche, H.; Harroun, T.; Katsaras, J.; Barrett, C. J. "Ion Distribution in Multilayers of Weak Polyelectrolytes: a Neutron Reflectivity Study" (To be submitted)

Tanchak, O. M.; Yager, K. G.; Fritzsche, H.; Harroun, T.; Katsaras, J.; Barrett, C. J. "Water Distribution in Multilayers of Weak Polyelectrolytes" *Langmuir* **2006**, *22*, 5137-5143.

Jul - 20

Date

Dr. Helmut Fritzsche National Research Council Canada Canadian Neutron Beam Centre Chalk River Laboratories Ontario, Canada I herby give copyright clearance for the inclusion of the following papers, of which I am a co-author, in the Ph.D. dissertation of Oleh Tanchak, McGill University:

Tanchak, O. M.; Yager, K. G.; Fritzsche, H.; Harroun, T.; Katsaras, J.; Barrett, C. J. "Ion Distribution in Multilayers of Weak Polyelectrolytes: a Neutron Reflectivity Study" to be submitted to *Langmuir*.

Tanchak, O. M.; Yager, K. G.; Fritzsche, H.; Harroun, T.; Katsaras, J.; Barrett, C. J. "Water Distribution in Multilayers of Weak Polyelectrolytes" *Langmuir* **2006**, *22*, 5137-5143.

Dr. Jøhn Katsaras National Research Council Canada Canadian Neutron Beam Centre Chalk River Laboratories Ontario, Canada I herby give copyright clearance for the inclusion of the following papers, of which I am a co-author, in the Ph.D. dissertation of Oleh Tanchak, McGill University:

Tanchak, O. M.; Yager, K. G.; Fritzsche, H.; Harroun, T.; Katsaras, J.; Barrett, C. J. "Ion Distribution in Multilayers of Weak Polyelectrolytes: a Neutron Reflectivity Study" to be submitted to *Langmuir*.

Tanchak, O. M.; Yager, K. G.; Fritzsche, H.; Harroun, T.; Katsaras, J.; Barrett, C. J. "Water Distribution in Multilayers of Weak Polyelectrolytes" *Langmuir* **2006**, *22*, 5137-5143.

20 JULY 2006

Date

Dr. Thad Harroun National Research Council Canada Canadian Neutron Beam Centre Chalk River Laboratories Ontario, Canada

Acknowledgments

There are many people to whom I am truly grateful and indebted to. Their support and encouragement has immensely helped the completion of this work.

I want to thank my doctoral supervisor, Professor Christopher Barrett for the opportunity to do my research studies in his laboratory. I greatly appreciate all the support, encouragement, and the advice he provided me with over the years. The research freedom, experience, and challenging projects that he provided allowed me to grow as a scientist.

I am also very grateful to the members of the Barrett Research group. I am truly grateful to have had the honor to work with Kevin Yager, Emily Cranston and Rashida Smith, you guys provided with an intellectually stimulating work environment but above all, I appreciate your friendship and the support you have given me over the years. All of the members of the lab, both past and present, have made the whole experience very enjoyable. A special *merci beaucoup* to Annie Doris for all your help.

I would also like to acknowledge all the help I have received from the staff and faculty at the Otto Maas. In particularly, I would like to thank Mr. Fred Kluck and Mr. Rick Rossi who helped me out on numerous occasions in providing technical assistance. I would like to thank Dr. Wilczek for making my TA experience challenging yet enjoyable.

I was granted the opportunity to conduct research at the Chalk River laboratories and I would like to thank all of the staff for providing an amazing environment to work in. I am grateful to Dr. Helmut Fritzsche, Dr. Thad Harroun, and Dr. John Katsaras. Their hospitality and dedication to research made my stay at the facilities very enjoyable. I am grateful for all the people I met during my stay at McGill. In particular I would like to thank Mike, Jeff, Jake, Adil, Ian, Brian, Nicolas and Lawrence for helping me keep my sanity. I would like to also thank Andrew, Cezar, Will, and Vicki for all of the fun times we had together.

Irene, you are a truly amazing individual. You were always there when I needed you. Thank you for your patience and support through the rough times.

I consider myself very fortunate to have a wonderful family and I would like to thank them for their continuous understanding and support. Ivan, Taras and Myron, I appreciate your unconditional support and help. Mom, I thank you for all the sacrifices you have made over the years to make it possible for me to pursue my studies. Father, thank you for your patience and providing me with an environment that stimulated my scientific curiosity. I truly wish that you were here with us.

Introduction

1.1 INTRODUCTION TO POLYELECTROLYTES

Polyelectrolytes are a class of polymers where the monomer unit is ionizable. In the presence of a polar solvent, the ionizable groups are able to dissociate and give a charge to the polymer chain and take a counter ion from the solvent.¹ In solution, the charged polymers have many unique properties that largely govern their behavior upon adsorption to a surface.² Polyelectrolytes are classified as strong or weak depending on their ability to ionize in solution. If the degree of ionization is effectively independent of the solution pH, the polyelectrolyte is classified as strong. Conversely, if the charge fraction of the ionizable moieties can be modulated through the solution pH, the polyelectrolyte is termed as weak. Polyelectrolytes can either carry a positive charge (polycations) or a negative charge (polyanions). Examples of strong and weak polyelectrolytes are shown in Figure 1.1. Naturally occurring polyelectrolytes include DNA, RNA, and proteins.

The solution properties of polyelectrolytes are influenced by several factors such as solution pH, ionic strength, molecular weight, temperature, and the nature of the ions. For strong polyelectrolytes, the polymer configurations in dilute solutions are dominated by electrostatic interactions and ionic strength. While for weakly charged polyelectrolytes a combination of van der Waals, hydrogen bonding, and electrostatic interactions play a significant role in the dilute solution properties of the polymers. Polyelectrolytes have found use in a wide variety of industrial applications such as flocculants in water treatment processes, pharmaceuticals, and as thickening and gelling agents.³⁻⁵



PAH poly(allylamine hydrochloride

PAA poly(acrylic acid)



PDADMAC / P-DAC poly(diallyldimethylammonium chloride)

PEI polyethylenimine

30₃- Na

PSS poly(styrene sulfonate)

Figure 1.1 Examples of polyelectrolytes

1.2 POLYELECTROLYTE MULTILAYER FILMS

Thin organic films are of importance to many industrial and technological applications. For instance thin films are commonly used for membrane technologies, anticorrosion coatings, and antireflection. The ability to tailor chemical and mechanical film properties on the nanometer scale may lead to further technological advancements. Furthermore, the ability to produce thin films that are multifunctional, facile, robust, and defect-free over a large length scale is of great importance to industry and to the field of materials science.

The layer-by-layer (L-b-L) assembly method is a technique that allows for the formation of thin organic films. Iler first described the principle of this technique in the 1960s, where charged particles were assembled onto planar substrates.⁶ In the early 1990s, Decher and Hong extended the pioneering work began by Iler by introducing an electrostatic layer-by-layer self-assembly deposition technique for preparing polymerbased thin films that have many of the aforementioned desirable characteristics.^{7,8} This method is based on the alternating sequential adsorption of oppositely charged polymers from dilute solutions onto a substrate.^{7,9} The advantage of this technique over other thin film preparation methods such as spin coating and Langmuir-Blodgett, is the ability to produce highly tailored thin films with control over film architecture and the incorporation of functional groups within the structure of the film. The polyelectrolyte multilayer (PEM) thin films can be deposited on a variety of substrates with varying geometry and size. For instance, planar surfaces such as silicon, glass slides, quartz, mica, and metals have been successfully coated with PEMs. Small colloidal particles such as silica and polystyrene have also been used as substrates for multilayering. In addition, enzymes, prokaryotic and mammalian cells have been encapsulated with PEMs.¹⁰ The simplicity of the layer-by-layer technique makes it easy to modify the surface properties of the multilayer. Properties such as hydrophobicity and biocompatibility can be altered through the deposition of the last polyanion or polycation laver.^{11,12} Multilaver films are commonly prepared from aqueous solutions thus making this technique economically and environmentally appealing to industry. Potential applications of PEMs include their use as antireflection coatings,^{13,14} antifouling coatings,¹⁵ selective membranes,¹⁶ for chemical or biosensing¹⁷⁻¹⁹ and for drug

delivery.^{20,21} For many of these aqueous-based applications, knowledge of the *in situ* behavior and response to external stimuli is crucial for the understanding and development of applications. Furthermore, the swelling in water or other solvents is of fundamental importance and provides crucial information about the internal properties and the local hydration.

1.3 POLYELECTROLYTE ADSORPTION

1.3.1 POLYELECTROLYTES IN SOLUTION

In solution, polyelectrolytes are electroneutral, the charge balance is maintained by counterions. The configuration of the polyelectrolyte chains in solution is the result of Coulombic interactions between the charged moieties and screening of the charges by the counterions. In the dilute solution regime in a good solvent, polymer chains are isolated from each other, so uncharged chains can then be described by Gaussian statistics. However, polyelectrolyte chains are additionally governed by electrostatic interactions. If the degree of ionization along the chains increases, the polymer chains will then adopt a stretched conformation. The increase in the persistence length of the polymer chain is due to the electrostatic repulsion between the charged segments. If salt is added to the polyelectrolyte solution where the chains are fully charged, the coulombic interactions between the charged segments will be screened. This screening would cause a reduction in the persistence length of the polymer chain. The screening length is dependent on the ionic strength of the solution. The rigidity of the chain would therefore increase with increasing charge density and decreasing ionic strength. When polyelectrolytes are weakly charged in solution, the chains are not fully stretched due to the net reduction of the repulsive charges. The chain can then be best described as an electrostatic blob, where

the charged chain is divided into subunits of Gaussian electrostatic blobs. The size of each blob is given by the distance at which the interactions between neighboring blobs are on the order of K_BT .^{2,22} The electrostatic interaction within each blob is negligible and is unaffected by the presence of salt. The chain conformation within the blob can then be described as Gaussian. Therefore, changes in pH and salt concentration may produce considerable conformational changes through interfering with inter-monomer repulsion of the charges along the polymer chain.

1.3.2 ACID-BASE EQUILIBRIUM

Since the degree of ionization affects the size of the chains and ultimately the thin film properties, it is therefore important to discuss the acid base equilibrium of weak polyelectrolyte systems. Unlike strong polyelectrolytes, the degree of ionization in weak polyelectrolytes and hence the charge along the polymer chain is sensitive to small changes of the solution pH. The dependence of the degree of dissociation of weak polyelectrolytes on the solution pH can be described by the acid-base equilibrium. The dissociation of a weak acid in solution is given by

$$PolH_{aq} \iff Pol_{aq}^{-} + H_{aq}^{+}$$
(1.1)

where PoIH is the weakly acidic polyelectrolyte repeat unit. Titration with a base would give the fraction of PoIH and the fraction of the dissociated polyacid PoI⁻ + H⁺ at a particular solution pH. The dependence of the degree of dissociation of weak polyelectrolytes on solution pH can be approximated by its dissociation constants pK_a and pK_b . The degree of ionization of the functional groups on the polymer chain are dependent on the dissociation constants of the ionizable groups which in turn are pH dependent. The relationship between pH and pK_a for a weak acid is described by the Henderson-Hasselbalch equation.

$$pH = pK_a + \log \frac{\left[Pol^{-}\right]}{\left[PolH\right]}$$
(1.2)

As the pH approaches the pKa of the polyelectrolyte, there is a large change in the degree of dissociation of the ionizable groups. When the pH is equal to the pKa only 50% of the groups are protonated. With weak polyelectrolytes the charge density of the chains can be easily manipulated by adjusting the solution pH.

It is important to note that the local internal pH value of a polyelectrolyte chain as it approaches and adsorbs onto a multilayer might differ from the external solution value, so the local pH value therefore can control the dissociation constant. The p*Ka* value of a weak polyion can be shifted relative to the solution value because of the local electrostatic repulsion of the ionizable groups. The electrostatic environment may stabilize either the protonated or deprotonated forms of the polyelectrolyte chains. Measurements of the local p*Ka* shifts within multilayers have been recently achieved by incorporating pH-sensitive dyes²³ and through zeta potential measurements.²⁴ The p*Ka* shift of the polyelectrolyte can vary as much as 3 pH units when it is incorporated into a multilayer.²⁴

1.3.3 POLYELECTROLYTE ADSORPTION PROCESS

The adsorption of polyelectrolytes onto an oppositely charged surface is primarily driven by electrostatic interactions. The adsorption process is therefore dependent on the sign and magnitude of the charge density of the polyion, the underlying surface and the factors affecting them such as solution pH and ionic strength. There is much debate of whether the adsorption process is governed by kinetics or if the final structure is at a true thermodynamic equilibrium.⁹ Polyelectrolytes adsorbed to charged surfaces do not typically show reversibility. Harsh solution conditions such as extreme pH²⁵ and high salt concentrations²⁶ are required to weaken the electrostatic interaction between the adsorbed polyelectrolytes and the charged substrate.

The adsorption process is comprised of three main steps as shown schematically in Figure 1.2. The first step in the adsorption process involves the transport of the polymer chains from solution to the surface. The deposition of the polyelectrolyte chains is rapid, usually on the order of seconds to minutes.⁹ This step is diffusion-limited and depends on the configuration and hence the hydrodynamic radius of the polyelectrolyte chains.²⁷ If the solution pH is such to make the polyelectrolyte chains partially ionized, the smaller globular conformation of the chains leads to a faster adsorption rate.¹ Similarly, screening of the polyion charges by salt in strong polyeletrolytes leads to a smaller radius of gyration and results in rapid adsorption to the surface. However, at very high ionic strength the attractive interaction of the polyelectrolyte and the underlying surface are strongly screened. The adsorption process is no longer dominated by longrange electrostatic interactions but are driven by short-range attractive potentials.

During the second step the polymer chains begin to anchor to the surface, since many adsorption sites are available to the polymer chains. Although electrostatic interactions are responsible for the transport of polyelectrolyte chains to the surface, the primary driving force for chain attachment is entropy, not enthalpy.⁹ As the polymer chains begin to attach to the surface, counterions are liberated and exchange with the solvent. The liberation of counterions is entropically favourable, enthalpic contributions are less significant since the number of available ionic bonds in the system remains unchanged.²⁸



Figure 1.2 Polyelectrolyte adsorption process (a) diffusion of polymer to the surface (b) attachment to the surface (c) rearrangement of polymer chain

As more polyelectrolyte chains adsorb, the number of available binding sites of the surface decreases and the rate of adsorption becomes dependent on the attachment process. The rate of attachment of the polymer chains is further hindered due to the electrostatic repulsion between the adsorbed chains and the incoming chains from solution. Polyelectrolyte chains with a high linear charge density in low ionic strength solution will adopt a stretched conformation. Under these conditions, the interaction between the chains and the surface is strong, so the polyelectrolytes will lie flat with the segments existing primarily as trains leading to a thin layer with a thickness of a few Angstroms.²⁹ The system is charged-compensated when the charge associated with the adsorbed polyelectrolyte chains is equal to that of the surface.²⁷ However, the presence of loops and tails that extend away from the underlying surface lead to a net charge overcompensation. Charge overcompensation of the surface has been confirmed with zeta-potential measurements.^{30,31} The adsorption process stops due to the electrostatic repulsion of the attached polyelectrolyte. The charge overcompensation of the surface can

ultimately facilitate the adsorption of an oppositely charged polyelectrolyte. However, there is a critical charge density of the underlying surface below which the electrostatic interactions are too weak and the amount of polymer that adsorbs decreases.²⁷

In the final step of the adsorption process, the chains begin to rearrange on the surface.^{1,27} During this slow rearrangement stage the polymer chain segments are able to attain a configuration that is more thermodynamically favored. The molecular spreading process typically involves the unravelling of the polymer chains from their original globular conformation that contained a few attachment points. The chain then adopts a conformation with many segments attached to the underlying surface.³² Many factors influence the extent of the mobility of the polymer on the surface, such as electrostatic interactions between neighbouring chains for secondary attachment sites. However, segment mobility is limited by strong electrostatic interactions with the underlying surface and the overall conformation of the polymer chains mirrors what is observed in solution.^{33,34} The rearrangement of the adsorbed polymer is the rate limiting step of the adsorption process and the slow kinetics of this step is why polyelectrolyte adsorption is considered to be an irreversible process.

The solution properties have a large influence on layer properties. The variability of the solution pH affects the charge fraction in weak polyelectrolytes, similarly high ionic strength solutions can screen the electrostatic repulsion between charged links in strong polyelectrolytes. Polyelectrolyte chains with high charge density adopt a flat conformation on the oppositely charged substrate. Screening of the polyion charges in a strong polyelectrolyte solution leads to a smaller radius of gyration of the polymer chains. Consequently, adsorption of smaller coils will take place, which occupy a lower surface area per chain and leads to a larger layer thickness. This quantitatively explains the formation of thicker layers in the presence of salt in strong polyelectrolyte systems.^{29,35-37} At pH values where the polyelectrolyte charge density is low, the chains are not fully stretched and adopt a globular conformation. The resultant loopy structure leads to a thicker adsorbed layer. Additionally, more polymer chains are required to adsorb to compensate the surface charge.³⁸

1.4 LAYER-BY-LAYER ASSEMBLY

The basic principle of L-b-L involves the alternate deposition of cationic and anionic polymers onto a charged substrate, which leads to the formation of multilayer films. This technique used to make polyelectrolyte multilayer films can be classified as template assisted assembly.³⁹ The main driving force of this assembly method is electrostatics, and each deposition step involves the adsorption of an oppositely charged polyelectrolyte. The elegance of this technique allows for the assembly of thin films on a variety of substrates and geometries so long as the surface is solvent-accessible and that some sort of interaction exists between the substrate and the adsorbing species. After a few deposition steps with two or more polyelectrolyte species multilayer films are formed with highly interpenetrated layers (Figure 1.3).⁷



Figure 1.3 Schematic of the electrostatic layer-by-layer build-up of polyelectrolyte multilayers.

As previously mentioned, the formation of multilayer films involves electrostatic interaction, however, other types of interactions have been successfully used in the buildup of multilayer films. Such interactions include hydrogen bonding, covalent bonding, adsorption/drying cycles, charge transfer and specific recognition.⁴⁰⁻⁴⁵ The conformation of the adsorbing species and hence the overall architecture of the multilayer film is dependent on many interactions. It is therefore possible to control many of the film properties through these interactions. Material properties such as solution concentration, charge density, and molecular weight play a significant role in the final film properties. In addition to this, assembly parameters such as adsorption time, solvent type, rinsing protocol and drying procedure can also influence film properties. Furthermore, environmental conditions such as solution pH, ionic strength and temperature as well as ambient humidity can affect the chain conformation upon adsorption.⁴⁶ The dependence on temperature reflects the effect of the hydrophobic interaction between the polyelectrolyte chains.⁴⁷ The multilayer structure of the first few layers deposited are different from that of the last polyelectrolyte layer.³⁷ The nature of the substrate, surface roughness and the density of the charged groups play a significant role in the initial polymer adsorption process. However, the surface and bulk properties are largely unaffected by the underlying substrate. Since multilayer build-up involves the consecutive adsorption of the polyions, the influence of the substrate is typically lost after a few deposition cycles.

The versatility of the technique allows for the incorporation of charged compounds or nanoobjects into the multilayer through electrostatic interactions. Many different materials such as orientable chromophores,⁴⁸ quantum dots,⁴⁹ metals⁵⁰ and

carbon nanotubes⁵¹ have been successfully incorporated into multilayers. Given the large set of materials that can be incorporated into multilayer films, the L-b-L technique is well suited for the fabrication of complex surface coatings. Multilayer films are typically assembled using two oppositely charged linear polyelectrolytes. However, the technique is not limited by the configuration of the polymer; branched polymers,⁵² copolymers⁵³ and dendrimers^{54,55} can be incorporated into the multilayer.

1.4.1 FILM PREPARATION

The most common approach to produce thin films using the layer-by-layer assembly is solution dipping. Typically a hydrophilic substrate such as glass or Si (previously chemically treated) that has a non-zero surface charge is dipped into a bath containing a polyion. The concentration of the polyelectrolytes in solution is typically in the range of 10^{-3} to 10^{-1} M based on repeat units. For planar substrates, the complete adsorption of polyelectrolytes requires time scales of a few minutes.^{29,56-59} This is followed by successive immersion of the substrate into rinse baths (usually repeated two or more times). The rinsing process serves two purposes; first excess unabsorbed polyelectrolytes are removed and the rinse cycles help in stabilizing the weakly adsorbed polyelectrolyte. This process is repeated until the desired number of layers is obtained (Figure 1.4). The thickness of the films is controlled by the number of dipping cycles and by careful control of the pH and the ionic strength of the dipping solutions.

Polyelectrolyte multilayer build up is the result of the ionic interactions between the cationic and anionic groups of the polyelectrolyte that results in the formation of ionic cross–links that hold the multilayer together. Although charge neutrality is maintained within the polyelectrolyte film, charge reversal of the surface layer facilitates the adsorption of the next polyelectrolyte layer. This charge overcompensation of the previously adsorbed polyelectrolyte layer is the result of loops and tails that extend away



Figure 1.4 Schematic outline of the solution dipping method for the layer-by-layer assembly of films onto to planar substrates.

from the surface into solution. The electrostatic interaction is of a long-range character and extends beyond the layer thickness. The overall charge of the polymer segments must be of sufficient magnitude to allow the formation of a new layer of oppositely charged polyions. The extent to which the charge overcompensation occurs has a dependence on the degree of ionization of the polyelectrolyte.⁶⁰ The slow rearrangement of the previously adsorbed chains enables the diffusion of chain segments of the incoming layer into the inner regions of the PEM.⁶¹⁻⁶³ The ionic interactions of the positively and negatively charged segments lead to an irreversible charge complexation.^{64,65} Once the multilayer is formed the film is quite stable, with little chain diffusion in PEMs as indicated by neutron reflectivity studies. No differences are observed between the fresh sample and after one year of equilibration.⁷ Other methods of L-b-L assembly onto planar substrates include spin-coating^{66,67} and spray-assembly.⁶⁸ The assembly process for these techniques involves that same cycles as used in the solution dipping method. The advantage of these methods over solution dipping is that the amount of solution used is greatly reduced.⁶⁹

1.5 MONITORING MULTILAYER FILM GROWTH

Polyelectrolyte multilayer growth has been monitored either *in-situ* or *ex-situ* by following layer property changes with each deposition step or after the whole film has been formed. The techniques used are essentially the same used for other organic thin films. A common *ex-situ* method to monitor film growth on a planar substrate is UV-vis spectroscopy.^{9,70} Most materials that are used in the L-b-L assembly absorb in this wavelength region. A linear increase in absorbance with layer number is commonly observed.^{9,57,70,71} Other *ex-situ* methods used to monitor film growth are ellipsometry,^{9,29,31,57,70,72} X-ray^{7,56,73} and neutron reflectometry.³⁵ For monitoring film growth on colloidal particles elemental analysis and solid state NMR spectroscopy are typically used.⁷⁴⁻⁷⁶

While an *ex-situ* method of monitoring film buildup is generally straightforward, *in-situ* measurements are often more desirable since analysis can be done without interrupting deposition process. In some instances, depending on the sampling rate, *insitu* methods allow for monitoring kinetic processes such as adsorption and/or multilayer reorganization.^{62,77} The most common *in-situ* measurement methods include quartz crystal microbalance,^{70,78} surface plasmon resonance,⁷⁹ optical waveguide lightmode spectroscopy⁸⁰ and zeta potential.^{24,75,79} In addition, a number of *ex-situ* methods such as ellipsometry,⁸¹ atomic force microscopy,^{26,80} X-ray and neutron reflectometry^{62,82} have been adapted for monitoring multilayer growth. Although these *in-situ* techniques are used to monitor film growth, additional properties such as the swelling behavior,^{49,54,83} acid-base equilibria,²⁴ film morphology⁸⁴ and film stability³⁰ can be determined by these techniques. Structural properties of polyelectrolyte multilayers have been investigated with neutron reflectivity measurements,^{35,85} and small-angle X-ray reflectivity.⁸⁶

1.6 MULTILAYER GROWTH

For a large number of polyelectrolytes, the multilayer films grow linearly with the number of bilayers, that is, the amount of polyelectrolyte adsorbed (polycation and polyanion) in each deposition cycle is the same.^{70,87} However, in a number of cases the linear buildup typically does not occur for the initial layers and the layer thickness does not increase linearly for the first few bilayers. The nonlinearity in the film growth has been attributed to substrate effects such as interactions between the polyelectrolyte and the substrate surface that may lead to inhomogeneous surface coverage.^{17,31} Adsorption of flexible chains onto a hard substrate may result in stratification of polymer chains on the surface and lead a lower amount of polyelectrolyte adsorbed, whereas polyelectrolyte adsorption onto a rough surface with a previously adsorbed layer will result in an increase in roughness and an increase in layer thickness as each new layer is added.³⁵ After several layers are adsorbed, a stationary regime is reached where the film properties become independent of the substrate, the level of charge overcompensation becomes constant and the film growth becomes linear.

In some cases, anomalous adsorption is observed where no linear growth regime is ever reached. Pseudo-exponential growth of thickness and adsorbed amount is observed with each deposition step in polyelectrolyte systems that contain for example poly(L-glutamic acid)/poly(L-lysine),⁸⁰ and hyaluronic acid/poly(L-lysine).⁸⁸ Transitions from linear to exponential nonlinear growth have also been observed in polydiallydimethylammonium chloride/ poly-(styrenesulfonic acid) systems with increasing ionic strength of the dipping solution.⁸⁴ In these systems, more material gets adsorbed with increasing layer number and indicates that the layer structure is very dynamic.³⁶ The nonlinear growth has been correlated to an increased surface roughness with each adsorbing layer. The increase in surface roughness facilitates a larger surface area; more charged groups are available to complex with the incoming polyelectrolyte and results in a larger layer thickness with each deposition step.³⁶ A recent mechanism for exponential growth in these systems has been attributed to the diffusion of polyelectrolyte chains in and out of the film which results in a complete rearrangement of the multilayer with each new layer.⁸⁹ However, the anomalous growth behavior seen here is rare and is only observed in a few systems and therefore does not display the typical growth behavior of multilayer films.

During the multilayer buildup the internal bulk structure of the film is electroneutral or compensated whereas the outer layer is overcompensated and enables the adsorption of the next layer. Charge overcompensation and therefore reversal of the surface charge on polyelectrolyte adsorption is essential for multilayer assembly. The presence of small counterions renders the entire multilayer system neutral. In solution, polyelectrolytes contain counterions that are condensed along the polymer chain in order to balance the charge of the oppositely charged polymer segments.⁵⁷ As the polymer chain adsorbs onto an oppositely charged polyelectrolyte layer, ion-pairing between the charged segments is driven by the release of counterions and water exchange. Radiochemical labeling experiments indicate that the surface counterions are displaced during the adsorption of an oppositely charged polyelectrolyte layer.⁹⁰ In addition, the presence of added salt ions compete with charged polyelectrolyte-polyelectrolyte interaction. At high ion concentrations it is possible to displace all of the polymer from the surface. The multilayer buildup process is an ion exchange phenomenon and can therefore be best described as a competitive ion-pairing process.²⁹

There are two scenarios that describe how charge neutrality is maintained in the multilayer and is schematically shown in Figure 1.5.⁵⁷ In one case, intrinsic compensation, charge neutrality is fulfilled through the ionic linking of the positive polyelectrolyte and the complementary polymer. Alternatively, a fraction of these charges may not form ionic links with the underlying layer. In this case the charge balance of the system is maintained extrinsically by salt counterions originating from the bathing solutions used to assemble the film. Extrinsic and intrinsic charge compensation has been observed in polyelectrolyte multilayers. However, it is not possible for a multilayer to be solely comprised with extrinsic charge compensation, with the absence of ionic-linking the film would decompose back into solution.⁵⁷ Furthermore, it is not possible for the film to be dominated by intrinsic charge compensation, as this would lead to a well-defined stratified architecture. Polyelectrolyte multilayers have amorphous fuzzy layer

structures as determined by X-ray and neutron reflectivity. Typically, no Bragg peaks are observed because of high level of interdigitation of the adjacent layers.⁹¹



Figure 1.5 Polyelectrolyte multilayer, a) intrinsic and b) extrinsic charge compensation.

There is much controversy over the presence of counterions within the bulk interior of multilayers. Ion exchange experiments with radiochemical salts and neutron reflectivity studies indicate that no substantial amount of counterions is present within multilayers.^{57,92} Electrochemical experiments also indicate the absence of internal counterions in polyelectrolyte multilayers.⁹³ One view suggests that oppositely charged polyions intrinsically compensate each other; the excess counterions are displaced by the adsorption of the incoming polymer which is entropically favorable and removed by successive rinsing cycles.^{47,57} However, the surface contains excess polymer charge, which is inverted each time a new layer of polymer is added to the surface. Thus, counterions exist at or near the surface of a multilayer, to extrinsically compensate the surface and render the system electrically neutral.^{26,31,57} However, extrinsic compensation has been observed in systems assembled in salt solutions.⁹³⁻⁹⁵ In this case some of the polyelectrolyte ion pairs are disrupted by exchangeable salt ions which are able to penetrate into the film and are driven by an external chemical potential.⁹³ Post-assembly

exposure to salt solutions have been used to anneal multilayers, that result in a smoothing of the outer layer.⁹⁶ The presence of counterions have been reported in systems where the polyelectrolyte stoichiometry deviates from a 1:1 complexation.^{30,97,98} In addition, extrinsic ion pairs can be introduced into weak polyelectrolyte assemblies through varying the environmental pH of the solution.⁸¹ However, counterions have not been detected in large quantities within multilayers. Overall, successful multilayer buildup is driven by charge overcompensation of the film surface and the entropic gain through the release of counterions.

The current model for the composition of a multilayer is of the film-sub divided into three distinct regions (Figure 1.6).³⁷ It is known that the structure and physical properties of PEMs are dependent on the location within the multilayer film. For instance, diffusion rates are substantially different for polyelectrolyte layers near the surface than for those which comprise the bulk of the film.⁹⁹ Each zone in the proposed model differs in both the chemical and structural composition. Zone I is comprised of one or a few layers closest to the substrate, where the film properties are influenced by the nature of the substrate. The outer region of the film (zone III) is comprised of one or a few polyelectrolyte layers. In this diffuse region the surrounding solution environment or air influences the properties of the layers. The bulk region of the polyelectrolyte film designated as zone II, is sandwiched between zones I and III. In zone II the properties of the film are not influenced by either zones I and III. The three-zone model is only valid once a certain number of layers have been deposited. During the assembly process zone I is completed first and subsequently zone III will develop. Zones I and III will continually evolve before zone II is actually formed, as the deposition process continues until their



increasing number of layers

Figure 1.6 Schematic representation of the zone model for polyelectrolyte multilayer films. The interface between the zones is diffuse and is only schematically represented as sharp for clarity. Once all three zones are established only zone II grows with increasing number of layers.

final composition and thickness is obtained.³⁷ It is therefore probable that if an insufficient number of layers are added, zones I and III will not have reached their final composition and zone II will not be formed. As more layers are added, 1:1 complexes are formed between adjacent polyelectrolyte layers and zone II emerges. The addition of more polyelectrolyte layers leads to an increase of thickness in zone II. The structure and thickness of zones I and III remain relatively unchanged as more layers are added. As layers absorb to the outer surface of zone III, the number of layers in this zone will not increase. The diffuse layer at the interface between zones II and III far away from the surface will not be influenced by the presence of the additional layer in zone III and therefore becomes part of zone II. The addition of a layer to zone III simply moves the interface between zones II and III upward rather than increasing the thickness of the last zone.³⁷ This model is more suited to explain layer formation for simple and relatively

flexible polyion complexes that exhibit 1:1 stoichiometry. The situation becomes more complicated when the polyelectrolytes used in the layer-by-layer processes are not capable of forming a 1:1 stoichiometric complex. However, in most cases the stoichiometry does not deviate greatly from 1:1 complexation and the overall multilayer buildup process is believed to be similar.³⁷ In addition, this type of zonal model has also been observed in weak polyelectrolyte systems.¹⁰⁰

It should be noted that the transitions between the zones are gradual and not sharp. This is due to the amorphous nature of polyelectrolyte multilayer films that stems from the fuzziness of the interpenetration of polymer chains between the layers. It is therefore difficult to ascertain the exact location of the boundary between each zone, and the number of layers involved in each zone is dependent on a number of system parameters *i.e.* the nature of the substrate, the polyelectrolytes system, and the deposition conditions.³⁷ Besides film structure, the primary difference between each zone is the charge character. The bulk of the multilayer film (zone II) is generally comprised of polyelectrolyte layers in a 1:1 stoichiometry where the polymer segments are intrinsically compensated. Again the presence of counterions within multilayers as revealed by XPS,⁹⁵ neutron reflectometry,⁹² and radio-analytical techniques⁵⁷ is marginal or non-existent. However, zones I and III are both known to exhibit excess charge. In some instances, depending on charge density of the substrate and substrate roughness, counterions may be present in zone I. Polyelectrolytes that normally form 1:1 complexes in zone II may not be able to form intrinsic charge complexes with the substrate and the next polyelectrolyte layer. It is believed that the chain conformation during the adsorption process may hinder the development of a 1:1 charge compensation between the substrate and the adsorbed
polymer chains, so the excess charge would then be compensated extrinsically with counterions. However, in zone I counterions may or may not be present whereas counterions are thought to be ubiquitous to zone III. The addition of each new layer to zone III leads to charge overcompensation of the surface, so this extra charge must be neutralized by counterions. However, this does not mean that the excess charge is exclusively associated with the polymer chains of the last absorbed layer. As previously mentioned the polymer layers are highly interpenetrated, and it is therefore expected that the layers further away from the surface would also contribute to the surface charge excess. The fuzzy nature of the polyelectrolyte layers leads to a gradient of charge in zone III and in some instances zone I.³⁷ The gradient of charge in zone I is believed to be smaller than that of zone III or it might not exist at all. The gradient of charge in zone III extends from the interface of zone II and III and is maximal at the film surface.¹⁰¹ Whereas the charge in zone I is the greatest at the substrate and decays as zone II is approached. The differences in the charge state of each zone may contribute to the differences in their physicochemical behavior.³⁷

1.7 PROPERTIES OF WEAK POLYELECTROLYTE MULTILAYERS

The majority of work done on multilayer assemblies has involved strong polyelectrolytes or weak systems assembled under the appropriate pH conditions that render the chains fully charged. With these systems the polyelectrolyte chains tend to absorb in a flat conformation leading to the formation of very thin films.^{26,31,57} The use of salts to screen the repulsive charges on the chains has been used to control many physical properties of the multilayers, such as the layer thickness and morphology.^{35,84,96} However,

there are limitations to this approach, namely the small range of salt concentrations beyond which lead to film decomposition or solubility problems in the polyelectrolyte solutions.³¹ Unlike strong polyelectrolyte systems, the charge density of weak polyelectrolyte depends on the solution pH. The solution pH affects the conformation of the chains, which ultimately controls the conformation upon adsorption to a surface. The response of weak polyelectrolytes to their environmental pH has led to many dramatically different physicochemical properties and has been actively investigated by several research groups.^{14,72,81}

Pioneering work by Rubner and co-workers demonstrated that small changes in assembly pH can lead to a vast difference in the film properties of weak polyallylamine/poly(acrylic acid) (PAH/PAA) assemblies. The dry per-layer thickness can vary over an order of magnitude from ~5 to 80 Å as shown in Figure 1.7.^{38,72} The effect of solution pH on the charge fraction of the chains is similar to that of ionic strength, in so much as the reduction of intramolecular repulsion of the chain, which leads to a decrease in the chain stiffness. The charge density of PAH and PAA chains are dictated by their respective pK_b and pK_a values which are approximately 9.0 and 4.5.²⁴ For instance, molecularly flat films are formed when both the PAH and PAA chains are fully ionized at a neutral pH. The multilayer assemblies can be made to undergo a large thickness transition over a narrow pH range (less than 1 pH unit) if one of the polyelectrolytes is close to being fully charged by increasing or decreasing the solution pH from neutral. For instance, at an assembly pH 5.0, PAH is fully charged and PAA is close to being fully charged and the average incremental thickness of both absorbing species is greatly increased. Mayes and co-workers have developed a theoretical model

that explains this thickness transition.^{102,103} The pronounced thickness transition stems from the cooperative ionic linking of the polyelectrolyte chains that becomes flustered. The surface charge density of the adsorbing fully-charged polyelectrolyte drops below a



Figure 1.7 Average incremental per layer thickness and roughness contribution by PAA and PAH as a function of assembly solution pH.³⁸

critical value and the enthalpic energy required to keep the chain in an extended rod-like conformation is no longer able to overcome the entropic penalty of this conformation. As a result, the adsorbing chain adopts a globular structure with many loops and tails that yields very thick layers. Recently it has been observed that a similar thickness transition occurs with assemblies of PAA and PAH with strong polyelectrolytes. The transition occurs when the charge density of the weak polyelectrolyte is decreased from its fully charged state.¹⁰⁴ Another interesting thickness regime occurs in the pH range of ~2.5 to 4.5, where PAH is fully charged and PAA becomes more ionized with increasing pH. In this region, the relative amounts of PAA and PAH in the film can be varied widely depending on the assembly pH. Furthermore, such films are populated with unbound functional groups that can be used for many potential applications. In this pH region (2.5 to 4.5) the charge fraction of the adsorbing polyelectrolyte and the surface roughness of

the previously adsorbed layer are important parameters. The adsorbed amount of PAH is influenced by the charge fraction of the underlying layer, hence when the charge density of PAA is increased, more PAH is required to compensate the charge. The decrease in the adsorbed amount of PAA with increasing pH is due to the decrease of loops and tails as the chains become more ionized.^{38,72}

Variation of film morphology and surface roughness has been observed in weak polyelectrolyte systems.⁷² Through the control of assembly pH and salt concentration, PAH/PAA assemblies have been produced with surface morphologies that range from nearly featureless to vermiculate patterns.⁸¹ It is important to note that the surface roughness is largest when the assembly solutions of the polyions are near their pK_a and pK_b values.^{24,38} The dependence of the surface roughness on assembly pH also has a pronounced effect on the surface properties of the film. For example, Yoo *et al* have observed a large variation of the wettability of the water droplets on the film. The contact angle of the water droplets ranged from around zero to as high as 50°, and control over the degree of wettability was achieved through the assembly pH.^{38,72}

As previously mentioned, the assembly pH can greatly affect the dry film thickness. Multilayers are strongly hydrated, at ambient "dry" conditions PEMs contain a substantial amount of water (10-20%).^{35,105} The variability of the conformation of the polymer chains in the PEM also influences the degree of swelling that the films undergo when exposed to different pH environments.^{12,81} Typically, pH-induced swelling events are fully reversible, and a discontinuity occurs at either extreme pH or salt concentrations, which leads to film deconstruction. As expected, films assembled under highly charged conditions undergo a limited degree of swelling.⁸¹ This is primarily due to

a highly interpenetrated and ionically cross-linked film structure that inhibits an extensive expansion of the film when exposed to a solvent. Reducing the charge density of one or both polyions, however, would facilitate the formation of multilayer structures with many loops and tails that may provide an environment where a larger extent of swelling can be induced. In a special strong/weak PAH/PSS system, an extraordinary degree of swelling has been observed, where films swelled by more than 5 times their original thickness.^{106,107} It is believed that in this system the local pH and hydrophobic interactions lead to an increase in the extension of the polymer segments. It is also interesting to note that in this system the swelling is discontinuous in nature, as the film goes through a swelling/deswelling loop which is linked to a conformational memory of the PEM. Although the extent of swelling in some weak polyelectrolyte assemblies has been studied, the swelling dynamics and the factors that affect the rate of swelling have not been well studied.

1.8 INTRODUCTION TO AZOBENZENE

Azobenzene (azo) is a broad class of compounds that contain a characteristic (-N=N-) linkage joining two phenyl rings (Figure 1.8). The main property of this class of molecules is that they exhibit strong electronic absorption due to their highly conjugated π -system. Azobenzene compounds have many interesting properties; in particular they have the ability to undergo fully reversible photoisomerization from the thermally stable *trans* geometric isomer to a metastable *cis* form upon the absorption of photons. Much interest has been taken in their properties as chromophores, and in the incorporation of these systems into PEMs to serve as optically responsive materials. The absorption

spectrum of azobenzene is similar to that of carbonyl compounds and stilbenes (phenyl–C=C-phenyl).¹⁰⁸ Azobenzene molecules are relatively chemically stable and were originally used as dyes and colorants ¹⁰⁹ The absorption spectrum of azobenzene can be modified by the position of the ring substitution and may be tailored to lie anywhere from the ultraviolet to the visible-red region.



Figure 1.8 Azobenzene structure

Azobenzene can be divided into three spectral classes according to their $n \to \pi^*$ and $\pi \to \pi^*$ electronic transitions as described by Rau.¹¹⁰ These classes, which depend on the substituents on the phenyl rings are azobenzene-type molecules, aminoazobenzenetype molecules, and pseudo-stilbenes. The particular absorption spectra of each class lead to the observable colors yellow, orange, and red, respectively. Azobenzene-type molecules exhibit a low-lying $n \to \pi^*$ absorption band in the visible region and a strong $\pi \to \pi^*$ band in the UV region. Adding substituents to the ortho- or para-position of the phenyl rings can modify the absorption spectra of these materials. In particular, the addition of an electron donating group (such as $-NH_2$) leads to the aminoazobenzene class of azo-molecules. The aminoazobenzene-type molecules have absorption spectra where the $n \to \pi^*$ and $\pi \to \pi^*$ are in close proximity and may overlap. Finally, substituting azobenzene with an electron-donating and electron-withdrawing groups (such as an amino and NO₂, group) on the 4- and 4'-positions creates a push/pull electron effect due to the strongly asymmetric electron distribution. This substitution affects the transition bands, and leads to a reverse ordering absorption band. In this pseudo-stilbene class of azobenzene, the $\pi \rightarrow \pi^*$ transition is shifted to lower energy past the $n \rightarrow \pi^*$ towards the red. The variability in the λ_{max} of the different classes of azobenzene chromophores makes them particularly useful for a large number of applications. For instance, pseudo-stilbenes are very sensitive to their local environment and have been readily used as sensitive probes.¹¹¹⁻¹¹⁵

1.8.1 AZOBENZENE PHOTOCHEMISTRY

The optical isomerization of azobenzene is key to many interesting applications. The isomerization is completely reversible and is considered to be one of the cleanest photochemical reactions known.¹¹⁰ The photoisomerization event is depicted in Figure 1.9. For most azobenzenes, the molecule can be photochemically isomerized from *trans* to *cis* with high efficiency, using light with a wavelength anywhere within the broad *trans* absorption spectrum. During the photoinduced isomerization process, a geometric conversion between the *trans* to *cis* form occurs, which can be reconverted to the *trans* state either photochemically or thermally. The *trans* form of azobenzene is thermodynamically more stable then the *cis* form by about 50 kJ/mol.¹¹⁶ whereas the energy barrier to induce isomerization is approximately 200 kJ/mol.¹¹⁷ Therefore, under ambient light conditions the stable *trans* form will predominate and these systems can be considered to be all *trans*. Although the exact mechanism of the isomerization is still under debate, the process involves either the breaking of a single π bond followed by a rotation about the N–N bond, or inversion where the π bond remains intact.^{118,119} The

thermal relaxation to the more stable *trans* state is thought to occur through the rotation mechanism.¹²⁰ Alternatively, the conversion from *cis* to *trans* can be induced photochemically with a wavelength of light that overlaps with the corresponding *cis* absorption band. This geometrical change defines the shape and orientation of the azo-



Figure 1.9 The photoisomerization of the azobenzene molecule indicating the change in size and shape with light irradiation.

molecule. The isomerization produces a decrease in the distance between the phenyl rings from about 9.0 Å in the *trans* form to about 5.5 Å in the *cis* form.¹²¹ In addition, the *trans* form has a planar geometry, whereas the *cis* form adopts an out of plane configuration with the phenyl rings positioned at right angles of the C–N=N–C plane.¹²²

Many factors affect the kinetics of the isomerization events. In particular, the steady-state composition of azobenzene under illumination will depend on the irradiation intensity, the wavelength of the pump beam, temperature and the composition of the matrix (i.e. solution or free volume effects of a polymer). Typically, the conversion from *trans* to *cis* is achieved with timescales on the order of picoseconds.^{123,124} However, the

thermal reconversion from the *cis* to *trans* state is dictated by ring substitution and the local environment, with time scales ranging from milliseconds to hours. Under illumination with an appropriate wavelength of light, the azo-molecules will achieve a photostationary state. The photostationary state is in essence the *cis* concentration that results from the extent of the photochemical reaction. The final of photostationary *trans/cis* composition will depend on the competing effects of the rate of thermal relaxation to the *trans* state, the isomerization rate of the *trans* to *cis* conversion and depending on the system, the photochemically driven *cis* reconversion. The composition of the photostationary state is unique to each system and is dependent on the rate of thermal relaxation and the quantum yields for the two processes (Φ_{trans} and Φ_{cis}).¹²⁵

In some cases, such as in pseudo-stilbene systems, the absorption spectra of the two isomers overlap and a single wavelength can facilitate a rapid interconversion between the *trans* to *cis* and *cis* to *trans* configurations. This will lead to a mixed photostationary state and in the absence of illumination, the system will thermally convert back to the stable *trans* state. The rapid interconversion of the chromophores is believed to be the driving force behind some of the more interesting photo-induced motions and deformations of azo-polymer systems that can be used for nanopatterning.

1.8.2 AZOBENZENE MASS TRANSPORT AND PHOTO-INDUCED DEFORMATION

The isomerization of azobenzene and ultimately the geometric conversion from *trans* to *cis* have many unique properties. For instance, azobenzene systems have an

ability to photo-orient on the molecular scale when exposed to linearly polarized light. This allows birefringence to be written and erased with relative ease, which makes these systems important to many technological applications such as information storage and holography.^{126,127} Azobenzene molecules preferentially absorb polarized radiation along their long axis and through a statistical selection process, will order with their dipoles perpendicular to the polarization field. During irradiation with polarized light the azochromophores that have their dipoles aligned with the polarization direction will isomerize and reorient. If during the reorientation process the chromophores fall perpendicular to the polarization direction, the isomerization, and hence the reordering, will cease. The net result is an increase in the population of azo-molecules aligned perpendicular to the polarization direction and a photoinduced anisotropy of the film is achieved. The induced photo-orientation of the azo-polymers can be easily erased by heating the polymer past the glass transition temperature or through irradiation with circularly polarized light. The forces induced by the photoisomerization and the reversible photo switching process on single polymer chains have been investigated by AFM.^{128,129} Viscosity changes of azo-polymers in solution have also been investigated. It was found that irradiation of the solution leads to a net decrease in the viscosity and was attributed to the geometrical contraction of the polymer chains due to dipole-dipole interactions between the azo-chromophores.^{130,131} In addition, studies conducted with monolayers of azo-materials indicate that the larger *cis* conformation leads to a lateral expansion of the monolayer.¹³² The photoinduced geometric change of azo-containing monolayers has also led to the modification of the surface energy of thin films, where the water contact angle could be modulated with light.¹³³⁻¹³⁵

The most intriguing applications of azobenzene involve the photochemically induced deformation and the macroscopic mass transport of polymers. The photoisomerization characteristics of azobenzene have been used to produce surface modulations on thin films that contain azo-materials. A surface relief grating (SRG) can be produced experimentally by exposing the azo-polymer surface to an interference pattern of polarized light. The SRG arises from the large-scale mass transport of material.¹³⁶⁻¹³⁸ This mass transport is entirely light-driven and features can be inscribed even with modest irradiation power. The formation of SRGs requires an isomerization process (many trans-cis-trans cycles), and surface modulations will not form with other absorbing chromophores that do not undergo an isomerization process.^{139,140} This macroscopic motion is not limited to the azobenzene moieties, but also involves the movement of many polymer chains. Depending on the irradiation intensity, SRGs can be inscribed in a matter of seconds to minutes. The formation of SRGs is generally restricted to intermediate molecular weight polymers, and large molecular weight systems hinder polymer motion.¹⁴⁰ Typically, films doped with azo chromophores yield poor inscription patterns, and a more efficient SRG formation is achieved when the azo groups are attached to either the main chain or to side chains of the polymer systems.^{136,141}

It is important to note that mass transport can occur in azo-polymers that are in the glassy state. The SRGs that are inscribed onto the films are permanent although they can be erased by heating the film above the glass transition temperature.¹⁴² Another interesting feature of the mass transport in SRG formation is that the polymer chains move from regions of high light intensity to low light intensity. However, the mechanism of SRG formation is not well understood.¹³⁸ Several models that explain the formations of SRGs, based either on a gradient of electromagnetic energy density,¹⁴³ a pressure gradient caused by the difference in the volume of the *trans* and *cis* conformations,¹⁴⁰ or an anisotropic diffusion of the azobenzene chromophores,¹⁴⁴ have been proposed. None of the models, however, can fully explain all of the experimental results that are unique with SRG formation.

The macroscopic bending and unbending of free-standing films clearly demonstrates macroscopic motion induced by azo-photoisomerization.^{145,146} The bending direction in these liquid crystalline polymers can be selected by either orienting the chromophores with rubbing or with polarized light. The bending in these films occurs due to the absorption of the impinging light by the upper portions of the film which causes the film to contract. The interior of the film, which is not irradiated due to the strong absorption of the upper part of the film, does not contract. Similar effects have been investigated with thin films floating on water, where an expansion of a film was observed for amorphous materials and a contraction with liquid crystalline polymers.¹⁴⁷ An extension of the photo-induced deformation of azobenzene has been applied to the mechanical bending of a microcantilever coated with an azo-monolayer.¹⁴⁸

There is much interest in the incorporation of optically active azobenzene chromophores into polyelectrolyte assemblies.^{71,111,149-153} This of course takes advantage of the L-b-L assembly method and the photoresponsive properties of azobenzene. There are several approaches to incorporate azobenzene chromophores into PEMs. One approach involves the incorporation of a small ionic azobenzene dye during the assembly process.¹⁵⁴ Other systems are based on copolymers that are synthesized to contain repeat units of azo chromophores and polyelectrolyte groups.^{135,155} In some cases, azobenzene

can be incorporated into a pre-assembled PEM through a post-functionalization process.⁷¹ In all cases, photoinduced changes such as birefringence^{156,157} and the creation of surface patterns have been observed.^{158,159} These systems generally exhibit poor surface features when compared to non-polyelectrolyte azo systems.¹⁵⁸⁻¹⁶¹ There are essentially two opposing factors that affect SRG formation in PEMs. The electrostatic interactions enable the incorporation of azo chromophores into the system, which facilitate mass transport. However, the chain motion is restricted due to the ionic cross-linking in the PEM assembly and leads to inefficient SRG formation. Early attempts to produce SRGs in multilayer assemblies were hindered due to the high extent of ionic-linking. However, the use of weak polyelectrolyte systems with their tunable charge densities have overcome some of the inherent ionic-linking constraints of strong systems.⁷¹ Utilizing the electrostatic L-b-L method, the physicochemical properties of polyelectrolytes and the photoinduced properties of azobenzene may provide an avenue to produce novel materials.

1.9 THIN FILM CHARACTERIZATION

1.9.1 ELLIPSOMETRY

Ellipsometry is a technique that has been used for more than a century for the non-destructive analysis of the thickness and optical constants of thin films.^{162,163} The technique involves generating monochromatic light with a known polarization state that is specularly reflected from a planar surface at an oblique angle. The technique was termed ellipsometry since it involves the measurement and analysis of the ellipticity of polarization that is generated when the incident polarized light beam interacts with the sample. A typical ellipsometric experiment is shown in Figure 1.10.

Light with a well-defined polarization state is reflected from the surface at an angle of incidence Φ_0 relative to the surface normal. The trajectory of the beam lies in a plane normal to the surface of the sample, called plane of incidence (POI). The effect of the reflection depends on the polarization state of the incoming light and the incident angle. Typically oblique angles of incidence ($\Phi_0 > 0$) are used since the incident light



Figure 1.10 Reflection of a light beam from a surface in a typical ellipsometric experiment.

differs in its polarization state upon reflection. These changes are measured and quantified in an ellipsometric experiment. The difference in the polarization of light upon reflection from the sample is due to the interaction of polarization states of the electric field vector \vec{E} oscillating within the plane of incidence (*p*-polarization) and perpendicular to it (*s*-polarization). This change is related to the optical properties of the material, which in turn depend on physical properties (e.g. density) and chemical makeup. In isotropic materials, the *s* and *p* components of light are mutually orthogonal and do not interfere with each other and hence can be treated separately. The change in the polarization state upon reflection from a surface is defined by the ellipsometric angles Δ and Ψ . The change in the phase difference upon reflection is defined as

$$\Delta = \left(\delta_{rp} - \delta_{rs}\right) - \left(\delta_{ip} - \delta_{is}\right) \tag{1.3}$$

where $\delta_{rp} - \delta_{rs}$ and $\delta_{ip} - \delta_{is}$ are the phase differences of the *p* and *s* polarized light of the reflected and incident beams. In addition to a phase shift, the reflection will also induce a reduction in the amplitude of the parallel and perpendicular waves. The change in the ratio of the amplitude upon reflection for the *p* and *s* components can be described by the tangent of the of the angle Ψ

$$\tan \Psi = \frac{E_{rp} / E_{ip}}{E_{rs} / E_{is}}$$
(1.4)

When light impinges onto a film-covered substrate, the beam will undergo reflection and refraction at each interface. This will lead to multiple reflections as depicted in Figure 1.11. The resultant reflected beam is the infinite summation of these reflections, where each successive reflection into the ambient medium is smaller. The reflection properties of the sample are given by the corresponding reflection coefficients r_p and r_s that are described by the complex change in phase amplitudes of the reflected electric field E_r with respect to the incident beam E_i . The overall reflection coefficients are defined by

$$r_{p} = \frac{\left|E_{rp}\right|}{\left|E_{ip}\right|} e^{i\left(\delta_{rp} - \delta_{ip}\right)}$$
(1.5)

$$r_{s} = \frac{\left|E_{rs}\right|}{\left|E_{is}\right|} e^{i(\delta_{rs} - \delta_{is})} \tag{1.6}$$

The basic equation of ellipsometry then follows as

$$\rho = \frac{r_p}{r_s} = \tan \Psi e^{i\Delta} \tag{1.7}$$

36

The complex quantity $\rho = \frac{r_p}{r_s}$ is the ratio of the total reflection coefficients also known as

the Fresnel reflection coefficients. The quantity $\tan \Psi$ is the ratio of the magnitudes of the total reflection coefficients and hence a real number. Equation 1.1.7 relates the quantities Δ and Ψ with the reflectivity properties of the sample under investigation.



Figure 1.11 Incident and reflected light for two interfaces.

The total reflection coefficients r_p and r_s , and consequently ρ , are functions of the complex refractive index of the media (N₀), film (N₁), and substrate (N₂), the thickness of the film (L₁), the wavelength of light (λ), and the angle of incidence (Φ_0). For a one-layer sample consisting of two ideal atomically smooth, isotropic and abrupt interfaces, the total reflection coefficients are given by the Airy formula:

$$r_{p} = \frac{r_{01p} + r_{12p}e^{(-i2\beta)}}{1 + r_{01p}r_{12p}e^{(-i2\beta)}}$$
(1.8)

$$r_s = \frac{r_{01s} + r_{12s}e^{(-i2\beta)}}{1 + r_{01s}r_{12s}e^{(-i2\beta)}}$$
(1.9)

Where r_{01p} and r_{12p} are the Fresnel reflection coefficients at the interface between the medium/film and film/substrate for the p component, and r_{01s} and r_{12s} is for the s component of light. The phase change β occurs due to the multiple reflections the light

wave experiences as it transverses from the top of the film to the bottom of the film. Therefore, 2β is the phase difference between the part of the reflecting wave and the transmitted wave that has traversed the film twice. The film phase thickness is given by

$$\beta = 2\pi \left(\frac{L_1}{\lambda}\right) N_1 \cos \Phi_1 = 2\pi \left(\frac{L_1}{\lambda}\right) \sqrt{\left(N_1^2 - N_0^2 \sin^2 \Phi_0\right)}$$
(1.10)

If Snell's law is applied, the angle of light propagation within the film structure can be determined. The complex refractive index of the material is designated as

$$N = n - ik \tag{1.11}$$

where *n* is the refractive index and *k* is the extinction coefficient. Typically for most polyelectrolytes when analyzed in the visible region k=0 and the Fresnel coefficients (Equation 1.10), N_l and Φ_1 are real numbers. For absorbing films, *k* must be determined or when possible an appropriate wavelength outside the absorption maximum should be used.

For multiple films, the expression of equations 1.8 and 1.9 become more complicated due to the additional interfaces. However, these equations can be used in an iterative way, and often, a scattering matrix formalism is used to deduce the complex reflection coefficients.

Equations 1.7 to 1.10 can be used to predict Δ and Ψ if the thickness and refractive index are known, however the equations cannot be directly inverted. The equations can be inverted if the refractive index is known and then only thickness is calculated. For organic thin films <<100 Å, the refractive index or mass coverage is determined. If both thickness and refractive index are desired for films of >100 Å, an iterative approach is used where a fitting algorithm minimizes the difference between a

combination of optical constants that yields predicted Δ and Ψ values and the measured values.

The measured quantities Δ and Ψ are always correct assuming that the ellipsometer is properly aligned. Whether the calculated sample parameters such as thickness, refractive index and the extinction coefficient are correct is solely dependent on the assumed optical model for the system under investigation. The optical parameters can be determined accurately using ellipsometry if one assumes that the film is homogeneous and has a low surface roughness. Film roughness can distort experimental data from the predictions made on the basis of models assuming mathematically abrupt interfaces. However, ellipsometry is fairly immune to the effects of large surface inhomogeneity or roughness where such defects are greater than the wavelength of light. In this instance the macroscopic roughness scatters the reflected beam out of the specular beam. The loss in intensity does not affect the measurement greatly since ellipsometry measures the ratio of the s and p complex reflectance rather than the absolute reflectance. Samples with very large surface roughness can depolarize the reflected beam¹⁶⁴ and are very difficult to model accurately. The transfer of energy between the polarization states will depend on the topography of the surface roughness, angle of incidence and the wavelength. Ellipsometry is therefore not well suited to very rough samples. If homogenous roughness exists on a surface where the roughness is less than the wavelength of light, the depolarization effects are less noticeable. Data can often be analyzed by incorporating one or more intermediate layers in the optical model to simulate the surface roughness. Often the optical functions are approximated using effective medium approximations where the surface roughness is modeled as a layer

consisting of a mixture of the ambient media and the underlying layer. Scattering loss due to surface roughness is larger with shorter wavelengths than for longer wavelengths. It is therefore easier to model surface roughness using multi-wavelength spectroscopic ellipsometry.¹⁶⁵ Generally, it is difficult to model surface roughness using single wavelength ellipsometry and it is common practice to treat the film as a single film model.

Film anisotropy is also a challenge for ellipsometry. When a light beam passes through an isotropic medium into an anisotropic one, the *s* and *p* polarization components can be refracted through different angles. Ellipsometric measurements using different polarization states, angles of incidence, or surface orientations can give partial information on the complex amplitude reflection ratios in the x, y and z planes of the material. Treatment of the more difficult problem of anisotropic component materials is the subject of current research.¹⁶⁶⁻¹⁶⁸

Another ambiguity with ellipsometry is that both Δ and Ψ are periodic functions of film thickness, with the thickness period, L_0 , given by

$$L_{0} = \frac{\lambda}{2\sqrt{\left(N_{1}^{2} - N_{0}^{2}\sin\Phi_{0}\right)}} = \frac{2\pi L_{1}}{\beta}$$
(1.12)

Since the film thickness period is a function of wavelength, care must be given with single wavelength experiments to ensure that the proper film thickness is determined. Often, angle dependent measurements are performed since the periodicity is different at each angle.

1.9.2 NULL ELLIPSOMETRY

Null ellipsometry is one of the oldest ellipsometry configurations. The layout of this single wavelength configuration is shown in Figure 1.12. Another ellipsometry design configuration is the rotating analyzer type, where the intensity is recorded as a function of the analyzer setting and the unknown ellipsometric angles are worked out by Fourier analysis. This type of design has been successfully applied to multi-wavelength spectroscopic ellipsometry. Other designs include a polarization modulation ellipsometer, this configuration uses a variable phase retardation to determine the ellipsometric angles. The advantage of these types of ellispometric designs is that measurements can be made quickly. However, the null ellipsometry design is more robust, where the various nulling schemes can greatly reduce alignment errors. The main components of this system are a polarizer (P), compensator (C), sample (S), analyzer (A) and a detector (this configuration is known as a PCSA ellipsometer). With a nulling ellipsometer, the orientations of the polarizer, compensator, and analyzer are adjusted so that the intensity of the light reaching the detector is zero. There are many settings of the polarizer and compensator that can accomplish this. As will be shown later, the equations used to describe the polarization of light as it travels through the ellipsometer simplify considerably if the compensator is fixed at $\pm 45^{\circ}$. In this configuration the compensator (a quarter-wave plate) fixed at ±45° imparts a phase change and elliptically polarized light is produced incident on the sample. The compensator consists of a birefringent material cut to a thin plate. Optically the quarter-wave plate imposes a phase shift δ_c on the electric field component along the slow axis of the device, relative to the component along the orthogonal fast axis. Linearly polarized light oscillating parallel to either axis will remain linearly polarized. However, since the refractive indices are different for the



Figure 1.12 The PCSA nulling ellipsometer configuration.

fast and slow axes, a phase difference is introduced between the two components of an elliptically polarized beam, or a linearly polarized beam not aligned with the fast or slow axis. The light velocities along the fast and slow axes through the birefringent material vary inversely with the refractive index of that axis. This difference in the velocities gives rise to the phase difference when the beams recombine; the phase difference will be 90° for a quarter-wave plate. Another advantage of setting the quarter-wave plate to $\pm 45^{\circ}$ is that the amplitude of the *p* and *s* components of the light incident on the sample in the plane of incidence is always the same, independent of the polarizer setting, and these two incident polarizations only differ in phase. All polarization states of light can be produced with the fast axis of the quarter-wave plate set to $\pm 45^{\circ}$ with respect to the POI, through the rotation of the polarizer. In general, reflection of polarized light off a sample produces elliptically polarized light. The PCS combination can be made to produce linearly polarized light upon reflection from the sample by simply rotating the polarizer. The

analyzer (another polarizer element) is then oriented such that the linearly polarized light produced from the reflection from the surface is extinguished. The complex reflection coefficient is obtained by varying the azimuth positions of P and A for a fixed C until the signal is nulled (I = 0). The changes in polarization of light as it passes through a null ellipsometer can be described in an elegant manner using Jones vectors and matrices, a sound treatment that is shown by Azzam.¹⁶² The azimuth positions of the polarizer, analyzer and compensator are related to ρ as shown below

$$\rho = \frac{r_{\rho}}{r_s} = -\tan A \left[\frac{\tan C + \rho_c \tan(P - C)}{1 - \rho_c \tan C \tan(p - C)} \right] \text{ for } I = 0$$
(1.13)

where ρ_c is the complex transmittance ratio of the compensator,

$$\rho_c = \frac{t_s}{t_f} \equiv T_c e^{i\delta_c} \tag{1.14}$$

where t_s and t_f are the transmission coefficients for the electric field components along the slow and fast axes of the compensator respectively. Tc is the attenuation in amplitude relative to the orthogonal component parallel to its fast axis and δ_c is the phase shift. This equation can be further simplified if a quarter-wave plate is used as a compensator with the fast axis fixed at ±45°, where for an ideal quarter-wave plate ($\delta_c = -90^\circ$, $T_c = 1 \Rightarrow \rho_c =$ -i) and with equation 1.1.7 leads to

$$\rho = \frac{r_p}{r_s} = \tan \Psi e^{i\Delta} = \tan A_0 \exp\left[i2\left(P_0 + \frac{\pi}{4}\right)\right] \quad \text{if } C = -45^\circ \tag{1.15}$$

$$\rho = \frac{r_p}{r_s} = \tan \Psi e^{i\Delta} = -\tan A_0 \exp\left[-i2\left(P_0 - \frac{\pi}{4}\right)\right] \quad \text{if } C = 45^\circ$$

These equations link the azimuth null settings of the polarizer P_0 and the analyzer A_0 to the ellipsometric quantities Δ and Ψ in a straightforward manner, where $\Psi_0 = A_0$ and $\Delta = 2P_0 - 90^\circ$ when C = -45°. Once a null setting has been determined (P_0, A_0), the same holds true for another distinct set of nulling angles (P'_0, A'_0) through the rotation of the polarizer and analyzer

$$(P'_0, A'_0) = (P_0 + 90^\circ, 180 - A_0)$$
 if $I = 0$ for (P_0, A_0) (1.16)

By convention, restricting the angle of the quarter wave plate to -45° gives two distinguishable nulling polarizer-analyzer pairs of nulling angles denoted by (P_1, A_1) and (P_3, A_3) . These are referred to as null zones one and three. Similarly if the quarter-wave plate is set to $+45^{\circ}$ then pairs of nulling angles are denoted by (P_2, A_2) and (P_4, A_4) . The two nulls are designated as zones two and four. Among the different ellipsometer designs, the null configuration is one of the most robust and accurate. Measurements conducted by averaging the four zones give values of Δ and Ψ that are free of error due to misalignment of the components and sample imperfections. However, measuring by fourzone averaging is time consuming. Typically, automated null ellipsometers measure either in a single zone or by two-zone averaging.

1.9.3 OFF-NULL ELLIPSOMETRY

A limiting factor of null ellipsometry is the rather slow acquisition time due to the mechanical movement of the polarizer and analyzed to obtain null. With an automated null ellipsometry system, the typical acquisition time for a single Δ and Ψ data point is of the order of seconds. For fast transient events it may be impossible to obtain null conditions during measurement. A way to record fast kinetics with using a null ellipsometer in the PCSA configuration is to conduct off-null ellipsometry. This technique has been used to follow rapid adsorption of proteins and monitoring film

growth.¹⁶⁹⁻¹⁷¹ In an off-null experiment, the changes of the intensity are recorded during some surface process. The principle behind off-null ellipsometry is illustrated in Figure 1.13. The null positions of the polarizer P_0 and the analyzer A_0 of the sample are measured before the sample is perturbed. The position of the azimuth null settings are held constant during the experiment and the intensity I is recorded as a function of time. When the ambient medium changes abruptly at the start of an experiment, as in the case with swelling measurements, a predicted initial null position can be calculated using an appropriate model. The change in intensity ΔI is caused by variations of the sample during the experiment. Specifically, any change in the thickness or refractive index of the sample surface will result in an increased light intensity. When a stable final intensity is reached, the final null conditions are measured P_I and A_I .



Figure 1.13 Schematic illustration of the principle of off-null ellipsometry. For simplicity, only changes in the polarizer are shown. P_0 is the polarizer setting at null before the sample film is perturbed. P_1 is the polarizer setting at null after the sample is perturbed. ΔI is the change in intensity measured at a constant polarizer setting P_0 .

The light intensity I_t is a function of the initial null polarizer and analyzer azimuth positions and the time dependent null positions P_1 and A_1 , and is given by^{162,172}

$$I_{t} = I_{0} \sin^{2}(A_{1} - A_{0}) + \sin 2A_{0} \sin 2A_{1} \sin^{2}(P_{1} - P_{0})$$
(1.17)

where I_0 is an instrument-dependent normalization factor. As expected, the intensity will be zero if $P_I = P_0$ and $A_I = A_0$. The signal detected is a symmetric parabolic function of the polarizer off null azimuth deviation $(P_I - P_0)$, for any analyzer setting. By comparison, the signal detected for analyzer deviations $(A_I - A_0)$ is a parabolic function only when the polarizer is set at extinction. The change in the polarizer and analyzer settings from the null condition can be related to the ellipsometric quantities Δ and Ψ , if an appropriate model is used. Equation 1.1.17 simplifies for very thin films (<50 Å), in which case the change in the analyzer setting is negligible $(A_I \approx A_0)$ and I_t is related to changes in Δ only.

The advantage with operating in off-null mode is speed. However, off-null ellipsometry provides less information than conventional null ellipsometry since only one parameter *i.e.* intensity, is recorded. The technique is more suited for following changes of the sample properties such as thickness growth and changes in the optical properties of thin films.

1.9.4 NEUTRON REFLECTOMETRY

Neutron reflectometry is a well-established technique and can provide detailed information on the variation of the composition of a polymer film normal to the surface, with accuracy on a sub-nanometer length scale. Similar information may be obtained with X-ray reflectivity and to a lesser extent with ellipsometry. However, neutron reflectometry has many advantages over these techniques, namely the ability to tune the scattering contrast through isotopic modifying of the material or solvent, and small wavelength. Unlike X-rays, neutrons can easily penetrate most materials and as such, measurements can be made in liquid environments or through various sample containment cells. The relatively low energies of thermal neutrons used for reflectivity make the technique non-destructive. Although neutron reflectivity is a relatively old technique, its use in the study of polymers has only recently been explored.¹⁷³⁻¹⁷⁶ A full overview of the theory is beyond the scope of this thesis, but complete reviews can be found elsewhere.¹⁷⁷⁻¹⁸¹

Neutrons can be reflected from planar surfaces according to the usual laws of specular optics and can be considered as either particles or wave. The connection between the two descriptions is provided by the de Broglie relationship

$$\lambda = \frac{h}{m\nu}$$
, and $\nu = \frac{E}{h}$ (1.18)

where E is the energy of the neutron, m is the mass of the neutron, v is velocity and h is Plank's constant. The wavelengths (λ) of thermal neutrons are approximately 0.5 Å – 10 Å and are several orders of magnitude larger than the radius of the nucleus. The nucleus is effectively a point scatter and therefore a neutron scatters isotropically from the centre. The interaction between the neutron and the scattering centres (nuclei) can be approximated by

$$V_0 = \frac{h^2}{2\pi m} N_b$$
 (1.19)

where V_0 is the Fermi's pseudopotential to which the neutron is subjected and N_b is the scattering length density (SLD) defined as

47

$$N_{b} = \sum_{j} b_{j} n_{j} = \frac{\sum b_{j} D N_{A}}{M_{W}} = \sum \frac{b_{j}}{V}$$
(1.20)

 n_i is the number of nuclei per unit volume and b_i is the scattering length of nucleus j. For polymers, D is the bulk density, N_A is Avogadro's constant and M_W is the repeat unit molecular weight, which is used to obtain a unit volume V. The coherent scattering length b, or scattering amplitude, can be determined experimentally and cannot be calculated reliably in terms of fundamental constants. The scattering length is a measure of the strength of the neutron-nucleus interaction and is related to the scattering cross section σ by $\sigma = 4\pi b^2$. Nuclear interactions are typically spin dependent, neutrons carry spin (I = $\frac{1}{2}$ and as a result, the measured value of b is a superposition of the scattering lengths of all existing spin states. It is for this reason that the neutron scattering lengths can be both negative and positive, depending on the phase shifts the neutrons experience upon scattering from the nucleus. Unlike X-rays where the interaction is correlated with atomic number (electron density), the scattering length fluctuates as atomic number increases as shown in Figure 1.14.¹⁸² The neutron's interaction with a nucleus of an atom can vary from one isotope to another. For instance, hydrogen and deuterium, which both interact weakly with X-rays, have neutron scattering lengths that are substantially different: – 3.740×10^{-15} m and 6.674×10^{-15} m, respectively. This variation in SLD is useful in providing contrast through deuterating or labeling polymer layers, or by varying the scattering length of the medium. Furthermore, neutrons are sensitive to light elements such as hydrogen, which makes the technique particularly useful in the study of polymers.

The motion of the neutrons reflected from an interface, a planar boundary between air ($V_0 = 0$) and a uniform medium with a potential V_0 , depends only on the potential in the direction normal to the interface z. Upon reflection, the momentum and



Figure 1.14 The variation of neutron scattering length as a function of atomic weight.¹⁸²

energy of the neutron are usually conserved. It is therefore convenient to think in terms of the scattering vector \vec{q} , defined as the difference between the final and initial wave vector of the neutron $\vec{q} = \vec{k}_r - \vec{k}_i$. For elastic scattering, the length of the wave vectors remain constant ($\vec{k}_i = \vec{k}_r$). The momentum transfer perpendicular to the interface q_z , which is the projection of the wave vector along the *z* axis (as indicated in Figure 1.15) is given by the change in the neutron wave vector on reflection at the boundary

$$q_z = 2k_i = \frac{4\pi}{\lambda} \sin\theta_0 \tag{1.21}$$

For specular reflection, the incident angle θ_0 equals the reflected angle θ_r . In the reflectometry experiment the intensity of the neutrons scattered by the material is measured as a function of q_z and information about the sample can be obtained for

different length scales. For fixed wavelengths, the typical geometry involves the sample moving through an angle θ and the detector moving by 2θ .



Figure 1.15 Reflection from a beam on an interface between two media with refractive indices n_1 and n_2 . θ_r and θ_2 denote the angles of reflection and transmission, and the incident and reflective wave vectors, k_i and k_r , respectively. The momentum transfer vector q_z is defined as the difference in the wave vectors as given in the Figure.

As with light, total reflection of the neutron beam occurs if the refractive index of medium 1 (n_1) is larger than the other medium (n_2) . The incident beam is entirely reflected for angles smaller than the critical angle θ_c . Neutrons hardly interact with matter, so the neutron refractive index is always close to one. The refractive index for positive scattering (which includes most materials) is less than unity (for vacuum and air n = 1). The critical angle can be derived from Snell's law $n_1 \cos \theta_0 = n_2 \cos \theta_2$ with $\theta_2 = 0$. The index of refraction for neutrons is given by

$$n = 1 - \frac{\lambda^2}{2\pi} N_b + i\beta \tag{1.22}$$

The real component of refractive index describes the behavior of the transmission, and reflection, the imaginary part of the refractive index accounts for adsorption of neutrons by the material. For most materials $\beta \approx 0$, with only a few nuclei, such as cadmium, and boron, absorbing appreciably.

Since the neutron refractive indices of most materials are only slightly less than that of air, total external reflection is more commonly observed instead of the internal reflection experienced with light. Below the critical angle, the reflectivity (defined as the intensity ratio of the reflected to the incident neutrons as a function of q_z) is unity and the reflectivity profile does not contain any structural information about the layer. The presence of the totally reflected beam is of importance in reflectometry experiments, as it gives a means to determine the absolute value of the reflectivity. When the incident beam is at angles greater then θ_c the reflection does not disappear completely and as mentioned previously the reflectivity as a function of momentum transfer depends on the refractive index profile in the direction normal to the reflecting interface. For an ideal surface the expression for the reflectivity can be derived as¹⁸¹

$$R_{f} = r^{2} = \left[\frac{q_{z} - (q_{z}^{2} - q_{c}^{2})^{\frac{1}{2}}}{q_{z} + (q_{z}^{2} - q_{c}^{2})^{\frac{1}{2}}}\right]^{2}$$
(1.23)

where R_f is the Fresnel reflectivity, and q_c is the critical value of the momentum transfer for total reflection and is given by

$$q_c = \frac{4\pi}{\lambda} \sqrt{\left(1 - \cos^2 \theta_c\right)} = \sqrt{\left(16\pi\Delta N_b\right)}$$
(1.24)

 ΔN_b is the SLD difference of the incoming medium and sample, which provides scattering contrast. For measurements at values of q_z much larger than q_c the reflectivity can be approximated by

$$R_f \approx \frac{16\pi^2}{q_z^4} \Delta N_b^2 \tag{1.25}$$

which is the reflectivity in the kinematic approximation.¹⁸³ Equation 1.1.25 shows that the reflectivity above the critical angle decreases sharply with q_z . However, it is important to point out that Fresnel reflectivity does not depend on the sign of ΔN_b and gives no information about the phase. Therefore, more than one model may give the same reflectivity profile. A typical reflectivity curve for an organic layer on a silicon substrate is shown in Figure 1.16, along with the associated SLD profile of the sample. The modulations, or Kiessig fringes, of the curve are due to the constructive and destructive interference of the waves reflected from the different interfaces between the ambient media/polymer film and the polymer film/substrate. The occurrence of Kiessig fringes is an indication that the film is very smooth and homogeneous. From this feature, the thickness and the density of the layer can be estimated. The spacing of the maxima can be used to determine the film thickness $L \approx 2\pi/\Delta q$, provided that there is sufficient instrument resolution.

The equations used so far describe the reflectivity from infinitely sharp interfaces. In reality, the interfaces are not abruptly sharp, the material may have surface roughness or there might be a gradient in density due to the inter-diffusion between polymer and the surrounding medium or between consecutive layers of polymers. The reflectivity will fall off more rapidly if the interface is diffuse or if there is surface roughness. Specular reflectivity cannot distinguish between surface roughness and a diffuse interface. In either case, the Fresnel reflectivity can be modified with the exponential factor (Debye-Waller)^{181,184,185}

$$R = R_f \exp(-q_z^2 \sigma^2) \tag{1.26}$$

where σ is the variance of the Gaussian distribution describing the length of the layer imperfection.



Figure 1.16 a) Simulation of the reflectivity profile of a polymer film on a Si wafer substrate. b) Modeled profile of the characteristic density as a function of the thickness of the sample.

The evaluation of the SLD profile of the material is an inverse scattering problem. It is generally not possible to obtain SLD profiles by inversion of the measured reflectivity data. This is due to the lack of the neutron wave's phase information. The analysis of the reflectivity curves to obtain SLD profiles does not yield a unique solution. It is necessary to assume a realistic model and reject physically unreasonable SLD profiles. The parameters of the Fresnel model are refined to match the measured reflectivity. Typically this is done with the use of programs such as PARRATT32, which divide the profiles into boxes of constant density normal to the surface. The Parratt algorithm properly takes into account multiple reflections, dispersions and absorption corrections.¹⁸⁶ The SLD profile is modeled with ideal, flat layers, and roughness is introduced in order to describe the smooth transition of different densities between adjacent layers. The parameters that can be varied are the scattering length density of the boxes, the thickness of the boxes, and the width of the transitions between the boxes (σ interface roughness). Through iteration, the overall computed reflectivity is compared to the measured reflectivity through the minimization of an error function.

1.10 THESIS OBJECTIVES

The aim of this dissertation is to investigate the swelling properties of polyelectrolyte multilayers prepared from weak polyelectrolytes. Knowledge of the hydration properties of weak polyelectrolyte multilayer systems is of importance to the potential development of novel applications. Chapter 2 provides detailed study of the hydration properties and swelling mechanism of poly(acrylic acid) (PAA) and poly(allylamine hydrochloride) (PAH) multilayer films. The swelling properties were investigated *in-situ* under a variety of environmental conditions and the swelling rates were found to be strongly influenced by the pre-exposure to humid atmospheres. The anomalous effect of humidity on the swelling rate was investigated using neutron

reflectivity and is the focus of chapter 3. The ability to control the scattering length density of water allowed for the elucidation of the water association within the multilayer film. Additional neutron reflectometry studies probed the influence of pH and a salt solution on water distribution in the PAH/PAA films assembled with and without salt and is presented in chapter 4. The counterion distribution and the effect of the capping layer were also investigated for films assembled in the presence and in the absence of salt. Chapter 5 investigates the photo-induced expansion of thin films of poly-Disperse Red 1 acrylate (PDR1A) and copolymers containing PAA. The influence of film thickness, chromophore content and irradiation intensity on the photo-expansion properties of the films was examined. Finally, chapter 6 gives an overview of the general conclusions of this work and outlines some suggestions for future studies.

1.11 REFERENCES

- (1) Fleer, G. J.; Stuart, M. A. C.; Scheutjens, J. M. H. M.; Cosgrove, T.; Vincent, B. *Polymers at Interfaces*; Chapman & Hall: London, UK, 1993.
- (2) Barrat, J.-L.; Joanny, J.-F. Adv. Chem. Phys. 1996, 94, 1.
- (3) Jellinek, H. H. G.; Luh, M. D. J. Polym. Sci., Polym. Chem. Ed. 1969, 7, 2445.
- (4) Liu, Y.; Wang, S.; Hua, J. J. Appl. Polym. Sci. 2000, 76, 2093.
- (5) Schwoyer, W. L. K.; Editor. *Polyelectrolytes for Water and Wastewater Treatment*; CRC Press: Boca Raton, Fla., USA, 1981.
- (6) Iler, R. K.; Colloid, J. Interface Sci. 1966, 21, 569.
- (7) Decher, G. *Science* **1997**, *277*, 1232.
- (8) Decher, G.; Hong, J. D.; Schmitt, J. Thin Solid Films 1992, 210-211, Part 2, 831.
- (9) Bertrand, P.; Jonas, A.; Laschewsky, A.; Legras, R. *Macromol. Rapid Commun.* **2000**, *21*, 319.
- (10) Diaspro, A.; Silvano, D.; Krol, S.; Cavalleri, O.; Gliozzi, A. *Langmuir* **2002**, *18*, 5047.
- (11) Richert, L.; Lavalle, P.; Vautier, D.; Senger, B.; Stoltz, J. F.; Schaaf, P.; Voegel, J. C.; Picart, C. *Biomacromolecules* **2002**, *3*, 1170.
- (12) Mendelsohn, J. D.; Yang, S. Y.; Hiller, J. A.; Hochbaum, A. I.; Rubner, M. F. *Biomacromolecules* 2003, 4, 96.
- (13) Hattori, H. Adv. Mater. 2001, 13, 51.
- (14) Hiller, J. A.; Mendelsohn, J. D.; Rubner, M. F. Nature Materials 2002, 1, 59.
- (15) Muller, M.; Rieser, T.; Lunkwitz, K.; Meier-Haack, J. Macromol. Rapid Commun. 1999, 20, 607.
- (16) Balachandra, A. M.; Dai, J.; Bruening, M. L. Macromolecules 2002, 35, 3171.
- (17) Caruso, F.; Niikura, K.; Furlong, D. N.; Okahata, Y. Langmuir 1997, 13, 3427.
- (18) Lee, S.-H.; Kumar, J.; Tripathy, S. K. Langmuir 2000, 16, 10482.

- (19) Mueller, M.; Kessler, B.; Adler, H. J.; Lunkwitz, K. Macromol. Symp. 2004, 210, 157.
- (20) Qiu, X.; Donath, E.; Moehwald, H. Macromol. Mater. Eng. 2001, 286, 591.
- (21) Zhu, Y.; Shi, J.; Shen, W.; Dong, X.; Feng, J.; Ruan, M.; Li, Y. Angew. Chem., Int. Ed. 2005, 44, 5083.
- (22) De Gennes, P. G.; Pincus, P.; Velasco, R. M.; Brochard, F. Journal de Physique (Paris) 1976, 37, 1461.
- (23) Rmaile, H. H.; Schlenoff, J. B. Langmuir 2002, 18, 8263.
- (24) Burke, S. E.; Barrett, C. J. Langmuir 2003, 19, 3297.
- (25) Dubas, S. T.; Farhat, T. R.; Schlenoff, J. B. J. Am. Chem. Soc. 2001, 123, 5368.
- (26) Dubas, S. T.; Schlenoff, J. B. *Macromolecules* **2001**, *34*, 3736.
- (27) Hoogeveen, N. G.; Stuart, M. A. C.; Fleer, G. J. J. Colloid Interface Sci. 1996, 182, 133.
- (28) Ahrens, H.; Baltes, H.; Schmitt, J.; Moehwald, H.; Helm, C. A. *Macromolecules* 2001, *34*, 4504.
- (29) Dubas, S. T.; Schlenoff, J. B. *Macromolecules* **1999**, *32*, 8153.
- (30) Hoogeveen, N. G.; Stuart, M. A. C.; Fleer, G. J.; Boehmer, M. R. Langmuir 1996, 12, 3675.
- (31) Schlenoff, J. B.; Dubas, S. T. *Macromolecules* 2001, 34, 592.
- (32) Stuart, M. A. C.; Cosgrove, T.; Vincent, B. Adv. Colloid Interface Sci. 1986, 24, 143.
- (33) Beltran, S.; Hooper, H. H.; Blanch, H. W.; Prausnitz, J. M. *Macromolecules* **1991**, *24*, 3178.
- (34) Stuart, M. A. C.; Fleer, G. J. Annu. Rev. Mater. Sci. 1996, 26, 463.
- (35) Loesche, M.; Schmitt, J.; Decher, G.; Bouwman, W. G.; Kjaer, K. Macromolecules 1998, 31, 8893.
- (36) Ruths, J.; Essler, F.; Decher, G.; Riegler, H. Langmuir 2000, 16, 8871.
- (37) Ladam, G.; Schaad, P.; Voegel, J. C.; Schaaf, P.; Decher, G.; Cuisinier, F. Langmuir 2000, 16, 1249.
- (38) Shiratori, S. S.; Rubner, M. F. Macromolecules 2000, 33, 4213.
- (39) Decher, G. Comprehensive Supramolecular Chemistry 1996, 9, 507.
- (40) Sukhishvili, S. A.; Granick, S. J. Am. Chem. Soc. 2000, 122, 9550.
- (41) Hao, E.; Lian, T. Chem. Mater. 2000, 12, 3392.
- (42) Fang, M.; Kaschak, D. M.; Sutorik, A. C.; Mallouk, T. E. J. Am. Chem. Soc. **1997**, *119*, 12184.
- (43) Serizawa, T.; Hashiguchi, S.; Akashi, M. Langmuir 1999, 15, 5363.
- (44) Shimazaki, Y.; Mitsuishi, M.; Ito, S.; Yamamoto, M. Langmuir 1997, 13, 1385.
- (45) Cassier, T.; Lowack, K.; Decher, G. Supramol. Sci. 1998, 5, 309.
- (46) Tan, H. L.; McMurdo, M. J.; Pan, G.; Van Patten, P. G. Langmuir 2003, 19, 9311.
- (47) Buescher, K.; Graf, K.; Ahrens, H.; Helm, C. A. Langmuir 2002, 18, 3585.
- (48) Hong, J.-D.; Park, E.-S.; Park, A.-L. Langmuir 1999, 15, 6515.
- (49) Heflin, J. R.; Figura, C.; Marciu, D.; Liu, Y.; Claus, R. O. Appl. Phys. Lett. 1999, 74, 495.
- (50) Gittins, D. I.; Caruso, F. Adv. Mater. 2000, 12, 1947.
- (51) Rouse, J. H.; Lillehei, P. T. Nano Lett. 2003, 3, 59.
- (52) Laschewsky, A.; Wischerhoff, E.; Denzinger, S.; Ringsdorf, H.; Delcorte, A.; Bertrand, P. Chem. Eur. J. 1997, 3, 34.
- (53) Choi, J.; Rubner, M. F. J. Macromol. Sci., Pure Appl. Chem. 2001, A38, 1191.
- (54) Watanabe, S.; Regen, S. L. J. Am. Chem. Soc. 1994, 116, 8855.
- (55) Kim, B. Y.; Bruening, M. L. Langmuir 2003, 19, 94.
- (56) Lvov, Y.; Decher, G.; Moehwald, H. Langmuir 1993, 9, 481.
- (57) Schlenoff, J. B.; Ly, H.; Li, M. J. Am. Chem. Soc. 1998, 120, 7626.

- (58) Lvov, Y.; Ariga, K.; Onda, M.; Ichinose, I.; Kunitake, T. Colloids Surf., A 1999, 146, 337.
- (59) Kovacevic, D.; van der Burgh, S.; de Keizer, A.; Stuart, M. A. C. *Langmuir* **2002**, *18*, 5607.
- (60) Joanny, J.-F.; Castelnovo, M.; Netz, R. J. Phys.: Condens. Matter 2000, 12, A1.
- (61) Wang, L.; Schoenhoff, M.; Moehwald, H. J. Phys. Chem. B 2004, 108, 4767.
- (62) Plech, A.; Salditt, T.; Munster, C.; Peisl, J. J. Colloid Interface Sci. 2000, 223, 74.
- (63) Leporatti, S.; Gao, C.; Voigt, A.; Donath, E.; Moehwald, H. *Eur. Phys. J. E* **2001**, *5*, 13.
- (64) Arys, X.; Laschewsky, A.; Jonas, A. M. *Macromolecules* **2001**, *34*, 3318.
- (65) Schwarz, B.; Schonhoff, M. Colloids Surf., A 2002, 198-200, 293.
- (66) Lee, S.-S.; Hong, J.-D.; Kim, C. H.; Kim, K.; Koo, J. P.; Lee, K.-B. *Macromolecules* **2001**, *34*, 5358.
- (67) Chiarelli, P. A.; Johal, M. S.; Casson, J. L.; Roberts, J. B.; Robinson, J. M.; Wang, H.-L. *Adv. Mater.* **2001**, *13*, 1167.
- (68) Schlenoff, J. B.; Dubas, S. T.; Farhat, T. Langmuir 2000, 16, 9968.
- (69) Izquierdo, A.; Ono, S. S.; Voegel, J. C.; Schaaf, P.; Decher, G. Langmuir 2005, 21, 7558.
- (70) Schoeler, B.; Kumaraswamy, G.; Caruso, F. Macromolecules 2002, 35, 889.
- (71) Lee, S.-H.; Balasubramanian, S.; Kim, D. Y.; Viswanathan, N. K.; Bian, S.; Kumar, J.; Tripathy, S. K. *Macromolecules* **2000**, *33*, 6534.
- (72) Yoo, D.; Shiratori, S. S.; Rubner, M. F. *Macromolecules* 1998, 31, 4309.
- (73) Decher, G.; Lvov, Y.; Schmitt, J. Thin Solid Films 1994, 244, 772.
- (74) Rodriguez, L. N. J.; De Paul, S. M.; Barrett, C. J.; Reven, L.; Spiess, H. W. Adv. Mater. 2000, 12, 1934.
- (75) Smith, R. N.; Reven, L.; Barrett, C. J. *Macromolecules* 2003, 36, 1876.
- (76) Schwarz, B.; Schoenhoff, M. *Langmuir* **2002**, *18*, 2964.

- (77) Lowack, K.; Helm, C. A. *Macromolecules* **1998**, *31*, 823.
- (78) Lojou, E.; Bianco, P. *Langmuir* **2004**, *20*, 748.
- (79) Schwarz, S.; Nagel, J.; Jaeger, W. Macromol. Symp. 2004, 211, 201.
- (80) Lavalle, P.; Gergely, C.; Cuisinier, F. J. G.; Decher, G.; Schaaf, P.; Voegel, J. C.; Picart, C. *Macromolecules* **2002**, *35*, 4458.
- (81) Mendelsohn, J. D.; Barrett, C. J.; Chan, V. V.; Pal, A. J.; Mayes, A. M.; Rubner, M. F. *Langmuir* **2000**, *16*, 5017.
- (82) Steitz, R.; Leiner, V.; Siebrecht, R.; v. Klitzing, R. Colloids Surf., A 2000, 163, 63.
- (83) Tanchak, O. M.; Barrett, C. J. Chem. Mater. 2004, 16, 2734.
- (84) McAloney, R. A.; Sinyor, M.; Dudnik, V.; Goh, M. C. Langmuir 2001, 17, 6655.
- (85) Steitz, R.; Leiner, V.; Tauer, K.; Khrenov, V.; Klitzing, R. V. Appl. Phys. A: Mater. Sci. Process. 2002, 74, S519.
- (86) Glinel, K.; Laschewsky, A.; Jonas, A. M. Macromolecules 2001, 34, 5267.
- (87) Kolarik, L.; Furlong, D. N.; Joy, H.; Struijk, C.; Rowe, R. *Langmuir* **1999**, *15*, 8265.
- (88) Picart, C.; Lavalle, P.; Hubert, P.; Cuisinier, F. J. G.; Decher, G.; Schaaf, P.; Voegel, J. C. *Langmuir* 2001, 17, 7414.
- (89) Picart, C.; Mutterer, J.; Richert, L.; Luo, Y.; Prestwich, G. D.; Schaaf, P.; Voegel, J. C.; Lavalle, P. Proc. Natl. Acad. Sci. U. S. A. 2002, 99, 12531.
- (90) Schlenoff, J. B.; Li, M. Ber. Bunsen-Ges. Phys. Chem. 1996, 100, 943.
- (91) Schmitt, J.; Gruenewald, T.; Decher, G.; Pershan, P. S.; Kjaer, K.; Loesche, M. *Macromolecules* 1993, 26, 7058.
- (92) Korneev, D.; Lvov, Y.; Decher, G.; Schmitt, J.; Yaradaikin, S. Physica B: Condensed Matter 1995, 213-214, 954.
- (93) Farhat, T. R.; Schlenoff, J. B. Langmuir 2001, 17, 1184.
- (94) Jomaa, H. W.; Schlenoff, J. B. *Macromolecules* 2005, 38, 8473.

- Lourenco, J. M. C.; Ribeiro, P. A.; Botelho do Rego, A. M.; Fernandes, F. M. B.; Moutinho, A. M. C.; Raposo, M. Langmuir 2004, 20, 8103.
- (96) Dubas, S. T.; Schlenoff, J. B. *Langmuir* **2001**, *17*, 7725.
- (97) Caruso, F.; Lichtenfeld, H.; Donath, E.; Moehwald, H. Macromolecules 1999, 32, 2317.
- (98) Riegler, H.; Essler, F. Langmuir 2002, 18, 6694.
- (99) Klitzing, R.; Moehwald, H. *Macromolecules* **1996**, *29*, 6901.
- (100) Fujita, S.; Shiratori, S. Nanotechnology 2005, 16, 1821.
- (101) Klitzing, R.; Moehwald, H. Langmuir 1995, 11, 3554.
- (102) Park, S. Y.; Barrett, C. J.; Rubner, M. F.; Mayes, A. M. *Macromolecules* 2001, 34, 3384.
- (103) Park, S. Y.; Rubner, M. F.; Mayes, A. M. Langmuir 2002, 18, 9600.
- (104) Choi, J.; Rubner, M. F. Macromolecules 2005, 38, 116.
- (105) Farhat, T.; Yassin, G.; Dubas, S. T.; Schlenoff, J. B. Langmuir 1999, 15, 6621.
- (106) Hiller, J. A.; Rubner, M. F. Macromolecules 2003, 36, 4078.
- (107) Itano, K.; Choi, J.; Rubner, M. F. Macromolecules 2005, 38, 3450.
- (108) Patai, S.; Editor. The Chemistry of Functional Groups: The Chemistry of the Hydrazo, Azo, and Azoxy Groups, Pt. 1, 1975.
- (109) Zollinger, H. Color Chemistry: Syntheses, Properties and Applications of Organic Dyes and Pigments, 1987.
- (110) Rau, H. In *Photochemistry and Photophysics*; Rebek, J., Ed.; CRC Press: Boca Raton, FL, 1990; Vol. 2, pp 119.
- (111) Mermut, O.; Barrett, C. J. The Analyst 2001, 126, 1861.
- (112) Uznanski, P.; Pecherz, J. J. Appl. Polym. Sci. 2002, 86, 1459.
- (113) Naito, T.; Horie, K.; Mita, I. Polymer 1993, 34, 4140.
- (114) Norman, L. L.; Barrett, C. J. J. Phys. Chem. B 2002, 106, 8499.
- (115) Lamarre, L.; Sung, C. S. P. Macromolecules 1983, 16, 1729.

- (116) Mita, I.; Horie, K.; Hirao, K. Macromolecules 1989, 22, 558.
- (117) Monti, S.; Orlandi, G.; Palmieri, P. Chem. Phys. 1982, 71, 87.
- (118) Fujino, T.; Arzhantsev, S. Y.; Tahara, T. J. Phys. Chem. A 2001, 105, 8123.
- (119) Ho, C.-H.; Yang, K.-N.; Lee, S.-N. J. Polym. Sci., Part A: Polym. Chem. 2001, 39, 2296.
- (120) Xie, S.; Natansohn, A.; Rochon, P. Chem. Mater. 1993, 5, 403.
- (121) Ahluwalia, A.; Piolanti, R.; De Rossi, D.; Fissi, A. Langmuir 1997, 13, 5909.
- (122) Naito, T.; Horie, K.; Mita, I. Polymer Journal (Tokyo, Japan) 1991, 23, 809.
- (123) Kobayashi, T.; Degenkolb, E. O.; Rentzepis, P. M. J. Phys. Chem. 1979, 83, 2431.
- (124) Lednev, I. K.; Ye, T.-Q.; Hester, R. E.; Moore, J. N. J. Phys. Chem. 1996, 100, 13338.
- (125) Loucif-Saibi, R.; Nakatani, K.; Delaire, J. A.; Dumont, M.; Sekkat, Z. Chem. Mater. 1993, 5, 229.
- (126) Holme, N. C. R.; Ramanujam, P. S.; Hvilsted, S. Opt. Lett. 1996, 21, 902.
- (127) Viswanathan, N. K.; Balasubramanian, S.; Li, L.; Kumar, J.; Tripathy, S. K. J. *Phys. Chem. B* **1998**, *102*, 6064.
- (128) Hugel, T.; Holland Nolan, B.; Cattani, A.; Moroder, L.; Seitz, M.; Gaub Hermann, E. Science 2002, 296, 1103.
- (129) Holland, N. B.; Hugel, T.; Neuert, G.; Cattani-Scholz, A.; Renner, C.; Oesterhelt, D.; Moroder, L.; Seitz, M.; Gaub, H. E. *Macromolecules* 2003, 36, 2015.
- (130) Moniruzzaman, M.; Sabey, C. J.; Fernando, G. F. Macromolecules 2004, 37, 2572.
- (131) Kumar, G. S.; DePra, P.; Zhang, K.; Neckers, D. C. *Macromolecules* 1984, 17, 2463.
- (132) Higuchi, M.; Minoura, N.; Kinoshita, T. Colloid Polym. Sci. 1995, 273, 1022.

- (133) Siewierski, L. M.; Brittain, W. J.; Petrash, S.; Foster, M. D. Langmuir 1996, 12, 5838.
- (134) Delorme, N.; Bardeau, J. F.; Bulou, A.; Poncin-Epaillard, F. Langmuir 2005, 21, 12278.
- (135) Wu, L.; Tuo, X.; Cheng, H.; Chen, Z.; Wang, X. Macromolecules 2001, 34, 8005.
- (136) Kim, D. Y.; Tripathy, S. K.; Li, L.; Kumar, J. Appl. Phys. Lett. 1995, 66, 1166.
- (137) Rochon, P.; Batalla, E.; Natansohn, A. Appl. Phys. Lett. 1995, 66, 136.
- (138) Yager, K. G.; Barrett, C. J. Current Opinion in Solid State & Materials Science 2001, 5, 487.
- (139) Kim, D. Y.; Li, L.; Jiang, X. L.; Shivshankar, V.; Kumar, J.; Tripathy, S. K. *Macromolecules* **1995**, *28*, 8835.
- (140) Barrett, C. J.; Natansohn, A. L.; Rochon, P. L. J. Phys. Chem. 1996, 100, 8836.
- (141) Lee, T. S.; Kim, D. Y.; Jiang, X. L.; Li, L.; Kumar, J.; Tripathy, S. Macromol. *Chem. Phys.* **1997**, *198*, 2279.
- (142) Jiang, X. L.; Li, L.; Kumar, J.; Kim, D. Y.; Tripathy, S. K. Appl. Phys. Lett. **1998**, 72, 2502.
- (143) Viswanathan, N. K.; Balasubramanian, S.; Li, L.; Tripathy, S. K.; Kumar, J. Jpn. J. Appl. Phys., Part 1 1999, 38, 5928.
- (144) Lefin, P.; Fiorini, C.; Nunzi, J.-M. Opt. Mater. 1998, 9, 323.
- (145) Ikeda, T.; Nakano, M.; Yu, Y.; Tsutsumi, O.; Kanazawa, A. Adv Mater 2003, 15, 201.
- (146) Yu, Y.; Nakano, M.; Ikeda, T. Nature 2003, 425, 145.
- (147) Bublitz, D.; Helgert, M.; Fleck, B.; Wenke, L.; Hvilsted, S.; Ramanujam, P. S. *Appl. Phys. B: Lasers Opt.* **2000**, *70*, 863.
- (148) Ji, H.-F.; Feng, Y.; Xu, X.; Purushotham, V.; Thundat, T.; Brown, G. M. Chem. Commun. 2004, 2532.
- (149) Advincula, R. C.; Fells, E.; Park, M.-K. Chem. Mater. 2001, 13, 2870.

- (150) Ishikawa, J.; Baba, A.; Kaneko, F.; Shinbo, K.; Kato, K.; Advincula, R. C. Colloids Surf., A 2002, 198-200, 917.
- (151) Toutianoush, A.; Tieke, B. Macromol. Rapid Commun. 1998, 19, 591.
- (152) Balasubramanian, S.; Wang, X.; Wang, H. C.; Yang, K.; Kumar, J.; Tripathy, S. K.; Li, L. *Chem. Mater.* **1998**, *10*, 1554.
- (153) Van Cott, K. E.; Guzy, M.; Neyman, P.; Brands, C.; Heflin, J. R.; Gibson, H. W.; Davis, R. M. Angew. Chem., Int. Ed. 2002, 41, 3719.
- (154) Dragan, S.; Schwarz, S.; Eichhorn, K.-J.; Lunkwitz, K. Colloids Surf., A 2001, 195, 243.
- (155) Suzuki, I.; Sato, K.; Koga, M.; Chen, Q.; Anzai, J.-I. Mater. Sci. Eng., C 2003, C23, 579.
- (156) Bian, S.; He, J.-A.; Li, L.; Kumar, J.; Tripathy, S. K. Adv Mater 2000, 12, 1202.
- (157) dos Santos, D. S., Jr.; Bassi, A.; Rodrigues, J. J., Jr.; Misoguti, L.; Oliveira, O. N., Jr.; Mendonca, C. R. *Biomacromolecules* 2003, 4, 1502.
- (158) He, J.-A.; Bian, S.; Li, L.; Kumar, J.; Tripathy, S. K.; Samuelson, L. A. J. Phys. Chem. B 2000, 104, 10513.
- (159) He, J.-A.; Bian, S.; Li, L.; Kumar, J.; Tripathy, S. K.; Samuelson, L. A. Appl. *Phys. Lett.* **2000**, *76*, 3233.
- (160) Wang, X.; Balasubramanian, S.; Kumar, J.; Tripathy, S. K.; Li, L. Chem. Mater. **1998**, 10, 1546.
- (161) Wang, H.; He, Y.; Tuo, X.; Wang, X. Macromolecules 2004, 37, 135.
- (162) Azzam, R. M. A.; Bashara, N. M. *Ellipsometry and Polarized Light*; North-Holland: Amsterdam, Neth., 1977.
- (163) Tompkins, H. G.; Irene, E. A.; Editors. *Handbook of Ellipsometry*; William Andrew Inc.: Norwich, N. Y., 2005.
- (164) Pittal, S.; Snyder, P. G.; Ianno, N. J. Thin Solid Films 1993, 233, 286.
- (165) Aspnes, D. E.; Theeten, J. B.; Hottier, F. Phys. Rev. B: Condens. Matter Mater. Phys. 1979, 20, 3292.
- (166) Elman, J. F.; Greener, J.; Herzinger, C. M.; Johs, B. *Thin Solid Films* **1998**, *313-314*, 814.

- (167) Schubert, M. Phys. Rev. B: Condens. Matter 1996, 53, 4265.
- (168) Flueraru, C.; Schrader, S.; Motschmann, H.; Zauls, V. Thin Solid Films 2000, 379, 15.
- (169) Andree, H. A. M.; Hermens, W. T.; Willems, G. M. Colloids Surf., A 1993, 78, 133.
- (170) Nygren, H. Biophys. Chem. 1994, 52, 45.
- (171) Bae Young, M.; Oh, B.-K.; Lee, W.; Lee Won, H.; Choi, J.-W. Biosens. Bioelectron. 2004, 20, 895.
- (172) Archer, R. J. J. Opt. Soc. Am. 1962, 52, 970.
- (173) Russell, T. P.; Karim, A.; Mansour, A.; Felcher, G. P. *Macromolecules* 1988, 21, 1890.
- (174) Anastasiadis, S. H.; Russell, T. P.; Satija, S. K.; Majkrzak, C. F. Phys. Rev. Lett. 1989, 62, 1852.
- (175) Anastasiadis, S. H.; Russell, T. P.; Satija, S. K.; Majkrzak, C. F. J. Chem. Phys. 1990, 92, 5677.
- (176) Satija, S. K.; Majkrzak, C. F.; Russell, T. P.; Sinha, S. K.; Sirota, E. B.; Hughes, G. J. *Macromolecules* **1990**, *23*, 3860.
- (177) Daillant, J.; Gibaud, A. X-Ray and Neutron Reflectivity: Principles and Applications; Springer: Berlin, 1999.
- (178) Russell, T. P. Materials Science Reports 1990, 5, 171.
- (179) Penfold, J.; Thomas, R. K. J. Phys.: Condens. Matter 1990, 2, 1369.
- (180) Zhou, X.-L.; Chen, S.-H. Phys. Rep. 1995, 257, 223.
- (181) Dianoux, A., B., Lander, G. Editors, *Neutron Data Booklet*, 2 ed.; OPC Science: Philadelphia, PA, 2003.
- (182) Vogt, T. Encyclopedia of Applied Physics edited by George L. Trigg, 2003; Vol. 11.
- (183) Crowley, T. L.; Lee, E. M.; Simister, E. A.; Thomas, R. K.; Penfold, J.; Rennie, A. R. *Colloids Surf.* **1991**, *52*, 85.
- (184) Cowley, R. A.; Ryan, T. W. J. Phys. D: Appl. Phys. 1987, 20, 61.

- (185) Nevot, L.; Croce, P. Revue de Physique Appliquee 1980, 15, 761.
- (186) Parratt, L. G. Physical Review 1954, 95, 359.

Chapter 2

Swelling Dynamics of Multilayer Films of Weak Polyelectrolytes

2.1 INTRODUCTION

Polymer multilayers can be prepared by the sequential electrostatic adsorption of oppositely charged polyelectrolytes onto a substrate. Through control of various assembly parameters one can gain good control over the thickness, internal structure, and surface roughness of the multilayer.¹ Thin polyelectrolyte multilayer (PEM) films fabricated by this layer-by-layer (L-b-L) adsorption technique have been extensively studied, and have been demonstrated to have potential applications as sensors,^{2,3} membranes,⁴ drug delivery agents,⁵⁻⁷ and in some polyelectrolyte systems biocompatibility was observed.^{8,9} It is important to note that for many of these more interesting applications water transport plays a key role, and hence the conformation and behavior in an aqueous environment must be well understood for systems to be tailored and optimized. Some of the most interesting systems reported to date are PEMs of weak polyelectrolytes. Unlike strong polyelectrolytes that remain fully charged over a wide range of pH, the charge fraction of weak systems can be regulated with assembly pH, affording great control over many final film properties. Two of the most well studied weak polyelectrolytes are poly(acrylic acid) (PAA) and poly(allylamine hydrochloride) (PAH), which can exhibit many anomalous properties. For example, Shiratori and Rubner have found that PAH/PAA systems can undergo a large thickness transition depending on assembly conditions.¹⁰ Measuring the swelling in situ is key to the understanding of the structural and physical properties of multilayers in response to the local environmental in many applications. For instance, the swelling behavior of PEMs in air at different relative humidites has been used to Reprinted with permission from Chem. Mater. 2004, 16, 2734-2739. Copyright 2004 American Chemical Society. 67

determine a Flory-Huggins parameter for a fully charged PAH/PSS system and to suggest a mechanism for vapor water permeation.¹¹

When a thin polymer film is brought into contact with a penetrating liquid, the penetrant diffuses into the polymer matrix and the polymer swells. The solvent enters the polymer through pre-existing voids or through spaces that are formed by local segmental motion in the polymer network, which is followed by local relaxation of polymer segments. The swelling mechanism is then characterized by diffusion and relaxation times of the polymer. The process can be described as Fickian (case I) diffusion when the rate of permeant diffusion is much less than the polymer segment mobility. In this process there is a continuous concentration profile in the film and a steady transport of the penetrant.¹² When the rate of diffusion is much faster than the swelling-induced polymer relaxation, the diffusion process is classified as case II. Case II swelling is characterized by a sharp interface between the swollen polymer and unswollen polymer, that moves at a constant rate.¹² The diffusion process is termed super case II when a late-stage acceleration in the permeation rate occurs.¹²⁻¹⁵ Generally, with super case II swelling there is an induction period where a concentration profile has been established across the film. Super case II diffusion has been reported in polymer systems such as polystyrene swollen with *n*-hexane.¹⁴ Finally, anomalous or non-Fickain swelling is a combination of Fickian and case II swelling, and occurs when the rate of permeant diffusion and the rate of polymer relaxation are comparable.¹²

While swelling has been well studied in many hydrophobic polymer films, the kinetics and environmental factors that affect the swelling mechanism of PEMs in water have not been studied. In this paper, the swelling of PAH/PAA multilayers assembled under various conditions was studied as a function of various aqueous bath conditions by

in situ null- and off-null ellipsometery, to record swelling behavior in real time, and to determine the mechanism. The effect of humidity pre-exposure to the dry films on subsequent water transport through the multilayer films was also investigated, as this variable was found to be highly influential to the resulting swelling behavior.

2.2 EXPERIMENTAL SECTION

2.2.1 MATERIALS AND FILM ASSEMBLY

Poly(acrylic acid) ($MW = 90\ 000$) (PAA), Poly(allylamine hydrochloride) ($MW = 60\ 000$) (PAH) were obtained from Polysciences and Aldrich respectively, with structures detailed in Figure 2.1.



Figure 2.1 Structures of polyelectrolytes: PAA and PAH

Polyelectrolyte solutions of 10^{-2} M were prepared based on repeat unit molecular weight using 18.2 M Ω cm Millipore water. The pH of the polyelectrolyte solution was adjusted with HCl or NaOH, and solutions were then filtered though a 0.7 µm filter. Polished Si <100> silicon slides were cleaned in concentrated chromium (III) oxide/ sulfuric acid for 12 hours minimum and then first thoroughly rinsed with D.I. water and then rinsed with Millipore water. Multilayer films were fabricated based on the usual layer-by-layer technique using an automated dipper.^{10,16} The silicon substrate was first immersed into the PAH solution for 15 min. This was followed by a rinsing procedure, where the substrate was successively immersed into three rinse baths of Millipore water $(pH\sim 5.5-6.5)$ for 1, 2 and 2 min respectively. The substrate was then immersed into the oppositely charged polyanion (PAA) solution for 15 min, and followed by the same rinsing procedure to complete one bilayer. The process was repeated until the desired layer thickness was achieved (15, 25 and 60 bilayers for matched assembly pH 5.0, 3.5 and 6.5 respectively). After the films were assembled, excess water was removed with compressed air and then the films were oven dried under vacuum at 65 °C overnight. PAH/PAA films assembled at assembly pH= 6.5 were auto dipped with light agitation.

2.2.2 SWELLING EXPERIMENTS

The thickness and refractive index of the PAH/PAA films were measured using a Multiskop (Optrel, Germany) single wavelength (633 nm) null-ellipsometer at a fixed angle of 70° with respect to the normal. In situ measurements were conducted in a homebuilt liquid sample cell that has two fixed BK7 windows aligned perpendicular to the incident and reflected beam. Film thickness was measured dry, then swelling measurements were subsequently made by the addition of solution of pH = 4.0, 7.0, 8.0, 9.0 and 10.0 by adjusting the pH with HCl or NaOH and assumed an ambient refractive index for water of 1.332. The accuracy of the cell was tested through the non-swelling of a hydrophobic test film of polystyrene spin-coated onto Si wafer, to confirm that the instrument was correctly calibrated for the liquid cell. Ellipsometric measurements were performed first in air and then in solution. The error associated in the thickness and refractive index measurements were determined to be \pm 1% and \pm 0.2% respectively. For studies of the effect of salt on swelling, solutions of 1-6 mM NaCl were used. For the determination of the % swelling of the PAH/PAA film, 15 separate ellipsometric measurements were conducted in a 1.2 X 0.5 cm area around the center of the film. Experiments were preformed on multiple samples. The percent swelling is defined as:

$$\left(\frac{swollen \ thickness - dry \ thickness}{dry \ thickness}\right) \times 100\%$$
(2.1)

In cases where the swelling rate approached the timescale of sampling, off-null ellipsometry was used.^{17,18}

Controlled humidity environments for the dry films prior to measurement were established by using the equilibrium water vapor over saturated salt solutions.¹⁹ The PAH/PAA films were dried in cell with a dry nitrogen purge. After the film was dried the film was exposed to a constant purge of nitrogen at specific % humidity until equilibrium was reached. The film was then hydrated with water.

2.3 RESULTS AND DISCUSSION

2.3.1 EXTENT OF SWELLING

Polyelectrolyte multilayers consisting of (PAH/PAA), with PAA as the top capping layer, were assembled under different conditions as indicated in Table 2.1. In this study the layer number was varied to ensure similar film thickness was being compared between different assembly pH conditions. A typical swelling profile and corresponding refractive index change are shown in Figure 2.2; after the dry layer thickness was determined in air to be 1200 Å, water was added to the cell at time 0, and the thickness of the swelling film was recorded every ~2 s until saturation of 1440 Å is reached at ~ 2000

s. From this, an equilibrium swelling extent could be estimated as 20% by equation 2.1.

The validity of the final swollen thickness was verified through a simple conservation-of-

Assembly pH		Layer no.	Average dry thickness (Å)		
	3.5	50	1153		
	4.0	50	1325		
	5.0	20	668		
	5.0	26	1357		
	5.0	30	1739		
	6.5	120	402		

Table 2.1 Dependence of assembly conditions and layer number on the dry thickness.^a

^aThe average dry thickness was obtained at ~45% R.H. Errors associated with the average dry thickness are ~4%.

mass mixing approximation, to check that the refractive index measurement returned by the ellipsometer agreed with the corresponding water-dilution of the swollen polymer.



Figure 2.2 Typical swelling curve for assembly pH=3.5 (25 bilayers), when exposed to bath pH=4.0, showing swelling of 20% and a corresponding reduction in refractive index. Prior to solution exposure the film was equilibrated at ~45% R.H.

The final equilibrium swelling extent and reduced refractive index was within 1% of the calculated conservation-of-mass value. Equilibrium swelling extents for similar films constructed and measured in a range of pH solutions are presented in Figure 2.3.



Figure 2.3 The effect of assembly pH on the degree of swelling when exposed to various MilliQ bath pH. The symbols \diamond , \Box and \triangle , correspond to assembly pH= 3.5 (25 bilayers), assembly pH= 5.0 (15 bilayers), and assembly pH= 6.5 (60 bilayers) respectively. The films were equilibrated at ~45% R.H. prior to solution exposure.

Film assembled at pH= 3.5 (25 bilayers) exhibited only a modest extent of swelling (~20%) when immersed in solutions of pH= 4.0, 7.0, and 8.0 as shown in Figure 2.3. The films assembled at pH= 3.5 were not stable in water beyond pH= 8.0, as the original film thickness could not be recovered reversibly. The apparent low level of swelling of the pH= 3.5 assembled films may be due to the films being pre-swollen at ~45% relative humidity.

At an assembled pH of 5.0 (15 bilayers), the films swelled to a greater extent than those assembled at pH= 3.5. No great change in the extent of swelling was observed when the assembly pH= 5.0 films were exposed to bath pH of 4.0 to 9.0, in all cases the films swelled ~ 30%. However, the films swelled to ~ 56% when exposed to bath pH= 10.0. At pH=10.0, the free amine groups in PAH are less charged (~20% free NH₃⁺ groups) as compared to that of the assembly conditions, and the free carboxylic acid groups of the PAA are completely charged (100% COO⁻ groups).²⁰ At this solution pH, there would be a low amount of available ionic cross-links expected, and the increase in the repulsion of the negative charges of the free carboxylic acid groups on the PAA chains could facilitate a larger extent of swelling.

Films assembled at pH= 6.5 (60 bilayers) swelled to a greater extent than those assembled at pH= 3.5 and 5.0, however, this is may be an artifact of the greater preswollen thickness. The extent of swelling was ~ 40% upon exposure to a bath pH of 4.0. The films swelled to ~35% when immersed in bath pH= 7.0 and 10.0. Although one might expect an increase in swelling at pH= 10.0, the nature of the assembly condition might play a key role. The highly compact networked structure and lack of free amine and carboxylic acid groups, may impair greater swelling when exposed to bath pH= 10.0. In general the PAH/PAA system swells to the same extent (20 to 40%) regardless of the bath conditions used in this study, over a wide range of pH. It thus appears that the swelling properties of the polyelectrolyte multilayers are governed largely by the pH conditions under which they are assembled, and not by their pH environment.

2.3.2 DYNAMIC SWELLING AND KINETICS

The dynamic swelling behavior of the polyelectrolyte multilayer films was analyzed with the following equation: ²¹

$$\frac{M_l}{M_{\infty}} = kt^n \tag{2.2}$$

where M_t is the amount of water absorbed at time t, M_{∞} is the amount of solution absorbed at equilibrium, k is a characteristic constant dependent on the structure of the polymer network, and n is the exponent which describes the type of diffusion into the polymer. Equation 2.2 is valid only when the fraction of water (M_t / M_{∞}) uptake is less than 0.60.²¹ From the slopes and intercepts of $\ln(M_t / M_{\infty})$ versus ln t the constants n and k were calculated. A typical such fit is shown in Figure 2.4. From the evaluation of n the diffusion type for the system can be obtained. For a thin film, n = 0.5 implies Fickian diffusion, 0.5 < n < 1.0 indicates anomalous diffusion, n = 1.0 describes case II transport and when n > 1.0 the transport mechanism is super case II.^{12,21} For volume fractions greater than 60%, the swelling process was assumed to be dominated by the relaxation of the polymer network. The first-order sorption process was fit with the following equation:^{22,23}

$$\frac{M_t}{M_{\infty}} = 1 - A \exp(-k_2 t) \tag{2.3}$$

where A is a vertical scaling constant and k_2 is the relaxation constant. The preexponential factor and k_2 were calculated from the slopes and intercepts of the plot of



Figure 2.4 Swelling curve for assembly pH= 3.5 (25 bilayers), when exposed to MilliQ bath pH= 4.0. Prior to solution exposure the film was equilibrated at ~45% R.H. The solid line corresponds to a fit with equation 2.2 and the dashed line was fit with equation 2.3.

 $\ln(1-M_t/M_{\infty})$ versus time t. The evaluation of the constants n, k, k_2 and A at various film assembly conditions and solution pH were similarly determined, and are shown in Figures 2.5, 2.6 and in Table 2.2. From Figure 2.5 it is apparent that the transport mechanism is highly dependent on assembly pH. Films assembled at pH= 6.5 exhibited case II behaviour with $n \sim 1$ when exposed to bath pH= 4.0 and 7.0. Although the extent of swelling of assembly pH=6.5 films when exposed to bath pH=10.0 was recorded, the dynamics of the swelling was beyond the sampling rate of the off-null technique. The transport mechanism for assembly pH= 3.5 was determined to be super case II with $n \sim 3.2$ at solution pH= 4.0 and 7.0. With increasing solution pH, no significant change in the exponent was observed (nvaries from just 2.8 to 3.0).

Assembly pH= 5.0 films also appear to swell by a super case II process. When exposed to pH= 4.0, n was ~ 2.4. With increasing pH, n increased to approximately 3.2. At bath pH= 9.0 and 10.0, n decreased to ~2.0.

	Α			$k_2 (sec^{-1})$		
Bath pH	pH=3.5	pH=5.0	pH=6.5	pH=3.5	pH=5.0	pH=6.5
4.0	2E6	8E10	1.7	0.01	0.5	0.6
7.0	2E10	3E6	1.6	0.02	0.1	0.8
8.0	7E8	6E7		0.03	0.2	
9.0	1E5	2E5		0.04	0.2	
10.0		4E5			0.3	

Table 2.2 Assembly pH dependence on k_2 and A at various MilliQ bath pH.^{*a*}

^{*a*}Errors on k_2 are approximately 10%. The pre-exponential factor A is accurate to within an order of magnitude. Prior to solution exposure the films were equilibrated at ~45% R.H.

The dependence of swelling mechanism on assembly conditions is related to the amount of ionic-linking in the multilayer film. The films assembled at pH= 3.5 and 5.0 have a complex nature due to the 'loopy' structure of the multilayer. The availability of counter ions, free acid/base groups, increased water content and the highly entangled



Figure 2.5 The dependence of assembly pH on the transport mechanism at various MilliQ bath pH. The symbols \diamondsuit , \Box and \triangle , correspond to assembly pH= 3.5 (25 bilayers), assembly pH= 5.0 (15 bilayers) and assembly pH= 6.5 (60 bilayers) respectively. Errors associated with *n* are 14%. The films were equilibrated at ~45% R.H. prior to solution exposure.

structure can greatly influence chain dynamics that will affect transport mechanism and rates. Films assembled at pH= 3.5 have a highly convoluted internal structure and therefore probably this leads to the late stage exponential rate enhancement once the initial entanglements are overcome. Therefore the 'loopy' structure with fewer ionic-links of films assembled at pH= 3.5 might be expected to facilitate an enhanced relaxation controlled transport mechanism with the largest value of $n \sim 3.2$. Films assembled at pH= 5.0 also exhibited super case II transport. However, the mechanism is generally less relaxation controlled with a lower value of $n \sim 2.5$. At assembly pH= 6.5, the multilayer forms with a "zipper type" mechanism since both PAH and PAA are fully charged.¹⁰ The highly ionic-linked polymer network, free from these impeding considerations should be expected to exhibit an enhanced rate of permeation as observed, relative to a more diffusion controlled mechanism where $n \sim 1$, even though the process is still relaxation controlled.



Figure 2.6 Dependence of k on solution pH, for films assembled under various pH conditions. The symbols \diamond , \Box and \triangle , correspond to assembly pH= 3.5 (25 bilayers), assembly pH= 5.0 (15 bilayers), and assembly pH= 6.5 (60 bilayers) respectively. Errors associated with k are within an order of magnitude. Prior to solution exposure the films were equilibrated at ~45% R.H.

Assembly pH also has a significant effect on k, as time scales are many orders of magnitude different. As depicted in Figures 2.6 and 2.7, films assembled at pH= 6.5 undergo fast swelling with values of k in the range of 0.23 to 0.31 s⁻ⁿ when swelled with solutions of pH = 4.0 and 7.0. The swelling was completed within 5 s. Films assembled at pH= 5.0 underwent slower swelling; 60% sorption is generally complete in 40 s to 2 min. When exposed to solution pH= 4.0 the value of k is 1.4E-4 s⁻ⁿ, at a higher bath pH (7.0 and 8.0) k decreases to 1.9E-7 s⁻ⁿ and 3.6E-7 s⁻ⁿ respectively. At higher pH conditions of 9.0 and 10.0, k decreases to the same order of magnitude found when exposed to a bath pH of 4.0. Films assembled at pH= 3.5 have characteristic swelling times that are much slower than films assembled at pH = 6.5 and 5.0. Complete swelling generally takes approximately 5-30 min. The values of k increased to 3.2E-8 s⁻ⁿ at a bath pH of 9.0.



Figure 2.7 Swelling curves for different assembly pH values when exposed to bath pH= 4.0. pH= 3.5 (25 bilayers) \diamondsuit , pH= 5.0 (15 bilayers) \square , and pH= 6.5 (60 bilayers) \triangle . Prior to solution exposure the films were equilibrated at ~45% R.H. The time scales of maximum swelling are drastically different depending on assembly conditions (note the % swelling is plotted versus t^{0.5} for clarity)

The dependence on humidity to which the dry films were exposed prior to swelling on the onset of swelling is related to the amount of ionic-crosslinks and thus the amount of free carboxylic acid groups associated with PAA. As will be shown later, the dependence of k on humidity is most prevalent with films assembled at pH= 3.5. It is known that water clusters can form around the free carboxylic acid groups of PAA, and that the amount of water clusters associated with PAA is dependent on the humidity.²⁴ It may also be possible for water clusters to form around counterions within the multilayer. It is further known that for the PSS/PAH system water is a bad solvent for the system with $\chi \sim 0.91$.¹¹ It is not unrealistic to assume that the water/water association is much stronger than the association of water/polymer for PAH/PAA. The Flory-Huggins parameter for our systems was experimentally determined to be ~1.6 for films assembled at pH= 3.5. This strong association of water ($\chi > 0.5$) within the multilayer may inhibit the permeation of bulk liquid water through the film. Contact angle measurements for PAH/PAA systems indicated a hydrophilic surface,¹⁰ but it is still possible that the

internal polymer matrix is much more hydrophobic than the surface layer. Blockage of accessible microchannels in the film, through the formation of hydrogen bonded water clusters, or through hydrogen bonding interactions with entangled loops would lead to a longer time needed to establish a Fickian or case II front before the autocatalytic plastization of the film occurs resulting in super case II swelling. Therefore at a given humidity, films assembled at pH= 3.5 will take longer to reach maximum swelling than those assembled at pH= 5.0 and 6.5.

The first order relaxation process also appears to be strongly dependent on assembly conditions, as shown in Table 2.2. The relaxation process was substantially faster for films assembled at pH= 6.5 than those assembled at pH= 5.0 and 3.5. Films assembled at pH= 5.0 displayed a slower relaxation process than those assembled at pH= 6.5. The relaxation rate of the multilayers is also related to the amount of ionic-linking in the multilayer. The first order relaxation (k_2) is much faster with films assembled at pH= 6.5. The high degree of ionic-linking of the network would result in a high elastic restoring force.²⁵ Values of k_2 decrease as the ionic-linking of the multilayer network decreases, because the elastic restoring force decreases. The lowest values of k_2 were seen with films assembled at pH= 3.5 which have the lowest amount of ionic-linking groups.

Other factors that were investigated for their influence on the swelling dynamics were ionic strength of the solution, identity of the capping layer, and layer number. Only minor swelling changes were observed when assembly pH = 4.0 (25 bilayers) films were exposed to various salt concentrations up to a 6 mM NaCl solution, with only a ~5% increase in swelling seen when compared to that of pure unadjusted (pH 5.5 – 6.0) water. Similarly little dependence of the transport mechanism was observed on the nature of the capping layer for films assembled at pH= 3.5 (25 and 25.5 bilayers). The water transport

mechanism was super case II for both PAA and PAH capped multilayers, with similar dynamics. The effect of layer number was also studied for assembly pH= 5.0 films (10, 13 and 15 bilayers), with dry film thicknesses of approximately 670, 1360 and 1780 angstroms respectively. The extent of swelling in pure water for this thickness series was found to be $23 \pm 2\%$, $28 \pm 4\%$ and $29 \pm 3\%$ for 10, 13 and 15 bilayers respectively. The water transport mechanism was super case II for all the films, with $n \sim 1.5$, (10 bilayer) and $n \sim 1.8$ for the 13 and 15 bilayer films at ~45% R.H.. Values for *k* and k_2 were of the same order of magnitude and did not vary significantly. Overall, little dependence of the transport mechanism was seen with layer number.

2.3.3 THE EFFECT OF HUMIDITY ON SWELLING DYNAMICS

Ambient humidity levels (prior to swelling with bulk water) however, were observed to have a strong effect on the swelling dynamics of PAH/PAA films. The most pronounced effects are seen with films assembled at pH= 3.5 (compare Figure 2.4 and 2.8). The initial swelling behavior is super case II at both low and high humidity. At low and high humidity, the values of *n* are comparable: 3.2 and 3.3, respectively. However, the onset of swelling was orders of magnitude different, with the swelling process being completed in ~ 3 s when films were equilibrated at low humidity prior to solution swelling, as compared to 1800 s at high humidity. This behavior is also indicated by *k*, which was determined to be 2.5E-2 s⁻ⁿ and 3.8E-11 s⁻ⁿ when pre-equilibrated at ~20% and ~45% R.H. respectively, when swollen with pH=4.0 solution. A large difference in the relaxation process was also observed. At low humidity the k_2 was determined to be 7.2 s⁻¹ indicating a very fast relaxation. At high humidity the relaxation process was substantially slower and k_2 was found to be 0.017 s⁻¹. These trends were also seen at

higher bath pH's. One might naively expect that higher water vapor content in the film would plasticize the film and therefore increase the rate of swelling. However, the rate of swelling decreases with pre-exposure at high humidity. Previous investigations have shown that water adsorbed from a humid atmosphere into a hydrophobic polymer matrix



Figure 2.8 Swelling curve for assembly pH= 3.5, 25 bilayers when exposed to MilliQ bath pH= 4.0. Prior to solution exposure the film was equilibrated at ~20% R.H. The solid line corresponds to a fit with equation 2.2 and the dashed line was fit with equation 2.3.

(such as that under consideration here, with χ >0.5) forms tightly associated water clusters.²⁴ Furthermore, it has been suggested that the low mobility of these water clusters could explain lower diffusion rates at higher ambient humidity, at least with regard to sorption from the gas phase.¹² It is conceivable that a similar argument might apply here. At low humidity, the polymer network is free of bound water and as a result the first order relaxation is unhindered. At high humidity, the highly organized water within the polymer network would slow the dynamics.

2.4 CONCLUSIONS

PAA/PAH polyelectrolyte films swell in water to 20-50% of their dry thickness at 45% R.H., but at vastly different rates depending on the pH of their assembly. It has been demonstrated that the extent of swelling is largely independent of the environmental pH, salt concentration, and number of layers. It was found, however, that the assembly conditions of the polyelectrolyte multilayers strongly influence both swelling mechanism and kinetics. Our results suggest that the swelling mechanisms can be tuned through the assembly pH. Unexpectedly, it was found that ambient humidity strongly influences the rate of swelling. The time scales to reach maximum swelling varied from a few seconds to tens of minutes, depending on the pre-exposed humidity conditions. This anomalous swelling behavior should be considered by research groups who use polyelectrolyte multilayers for aqueous applications such as membrane coatings and drug delivery.

2.5 REFERENCES

- (1) Decher, G. Science 1997, 277, 1232.
- (2) Dai, J.; Jensen, A. W.; Mohanty, D. K.; Erndt, J.; Bruening, M. L. Langmuir **2001**, *17*, 931.
- (3) Lee, S.-H.; Kumar, J.; Tripathy, S. K. Langmuir 2000, 16, 10482.
- (4) Dai, J.; Balachandra, A. M.; Lee, J. I.; Bruening, M. L. *Macromolecules* 2002, 35, 3164.
- (5) Chung, A. J.; Rubner, M. F. Langmuir 2002, 18, 1176.
- (6) Shi, X.; Caruso, F. Langmuir 2001, 17, 2036.
- (7) Sukhorukov, G. B.; Antipov, A. A.; Voigt, A.; Donath, E.; Moehwald, H. *Macromol. Rapid Commun.* 2001, 22, 44.
- (8) Mendelsohn, J. D.; Yang, S. Y.; Hiller, J. A.; Hochbaum, A. I.; Rubner, M. F. Biomacromolecules 2003, 4, 96.

- (9) Diaspro, A.; Silvano, D.; Krol, S.; Cavalleri, O.; Gliozzi, A. Langmuir 2002, 18, 5047.
- (10) Shiratori, S. S.; Rubner, M. F. Macromolecules 2000, 33, 4213.
- (11) Kugler, R.; Schmitt, J.; Knoll, W. Macromol. Chem. Phys. 2002, 203, 413.
- (12) Naylor, T. Permeation Properties; Pergamon Press: New York, 1989; Vol. 2. p643.
- (13) Billovits, G. F.; Durning, C. J. Polymer 1988, 29, 1468.
- (14) Jacques, C. H. M.; Hopfenberg, H. B.; Stannett, V. In *Permeability Plastic Films and Coatings to Gases, Vapors, and Liquids*; Hopfenberg, H. B., Ed.; Plenum: New York, 1974; Vol. 6, p73.
- (15) Hopfenberg, H. B. J. Membr. Sci. 1978, 3, 215.
- (16) Yoo, D.; Shiratori, S. S.; Rubner, M. F. Macromolecules 1998, 31, 4309.
- (17) Archer, R. J. J. Opt. Soc. Am. 1962, 52, 970.
- (18) Azzam, R. M. A.; Bashara, N. M. *Ellipsometry and Polarized Light*; North-Holland, Amsterdam, 1977.
- (19) CRC Handbook of Chemistry and Physics; Weast, R. C., Ed.; Chemical Rubber Company: Cleveland, OH, 1970; p E-40.
- (20) Burke, S. E.; Barrett, C. J. Langmuir 2003, 19, 3297.
- (21) Ritger, P. L.; Peppas, N. A. J. Controlled Release 1987, 5, 37.
- (22) Enscore, D. J.; Hopfenberg, H. B.; Stannett, V. T. Polymer 1977, 18, 793.
- (23) Berens, A. R.; Hopfenberg, H. B. Polymer 1978, 19, 489.
- (24) Chang, M.-J.; Myerson, A. S.; Kwei, T. K. J. Appl. Polym. Sci. 1997, 66, 279.
- (25) Mermut, O.; Lefebvre, J.; Gray, D. G.; Barrett, C. J. *Macromolecules* **2003**, *36*, 8819.

Chapter 3

Water Distribution in Multilayers of Weak Polyelectrolytes

Chapter 2 described an extensive investigation of the swelling dynamics of thin polyelectrolyte multilayers assembled with poly(acrylic acid) (PAA) and poly(allylamine hydrochloride) (PAH) when exposed to various pH conditions. Using single wavelength ellipsometry, it was determined that the extent of swelling was largely independent of the solution environment that the films were exposed to once assembled. The transport mechanism was non-Fickian and the swelling rates were significantly affected by the initial assembly conditions. We observed swelling rates that varied by more than 3 orders of magnitude depending on the pH of the assembly of the layers and surprisingly on the pre-exposure humidity levels. The effect humidity had on the swelling rates is more prevalent with films that have a higher content of free carboxylic acid groups. In fact, times to reach equilibrium swelling ranged from seconds to tens of minutes for the same films assembled at a pH of 3.5, with only a modest change in the ambient humidity (~20 % R.H. change) prior to measurement. The strong effect of ambient humidity on the rate of swelling is presumably due to the formation of water clusters that associate with the free acid groups in the film. The water clusters essentially block accessible microchannels in the film and impede the diffusion of water into the sub-region of the multilayer. In this chapter neutron reflectometry was used to probe the fine structure and water distribution in the film when exposed to water vapor and bulk water. The investigation was done on PAH/PAA films (assembled at pH= 3.5 where the humidity effect is more pronounced) in order to gain further insight to the unusual and strong effect

Reprinted with permission from *Langmuir* **2006**, *22*, 5137-5143. Copyright 2006 American Chemical Society. 85 of humidity on the swelling kinetics. The manipulation of the scattering length of the solvent (water), allowed for the unambiguous determination of the water distribution in the multilayer.

3.1 INTRODUCTION

Polyelectrolyte multilayers (PEMs) prepared by sequentially dipping a charged substrate into solutions of oppositely charged polyelectrolytes are of interest in many material applications due to their novel properties. Film thickness and surface properties can be controlled in weak polyelectrolyte systems through the regulation of the pH and the ionic strength of the solution, through the control of the solution's screening length and the average charge, which modifies the polymer conformation during adsorption.¹ The ease of thin film assembly and the ability to introduce functional groups into the multilayers makes PEMs suitable for applications such as sensors,²⁻⁴ separation membranes,⁵⁻⁷ and drug delivery vehicles.^{4,8-11} However, the ionic character of the internal cross-link points and free acid/base groups makes their interaction with water complex. Recently it has been found that PEM pre-exposure to various humidity environments can greatly influence bulk water uptake, where the rate of swelling could be varied by three orders of magnitude based on the relative humidity prior to exposure to bulk water.¹² Films pre-exposed to high humidity required a longer time to reach saturation when swollen with bulk water. This observation is counter-intuitive since one might expect that pre-exposure to high levels of water vapor could plasticize the multilayer and accelerate the rate of swelling. The sensitivity of PEMs to water vapor content may be attributed to structural changes in the film and/or water organization

86

within the film, and knowledge of the hydration properties and the water distribution within the PEM is of great importance to many applications.

Studies on the build-up of PEMs have shown that fully charged PEM systems composed of polystyrenesulfonate/polyallylamine can be subdivided into three regions of gradual transitions.¹³ The first region is typically composed of a few dense layers that are influenced by the underlying substrate. The second bulk zone consists of polyanion/polycation layers of 1:1 stoichiometry, and the third outer region contains a few layers that are charge overcompensated, which enables adsorption of further layers. Neutron reflectivity studies have proven to be a powerful method to characterize the internal structure of PEM in terms of their polymer density and water content,^{14,15} and it has been shown that the internal structure of the PEM layers are highly interpenetrated and that initially deposited layers are thinner than the bulk.^{14,15} Other studies have shown that a density gradient of the polyelectrolyte chains occurs within PEMs when exposed to D₂O.¹⁶ Neutron reflectivity studies have also been used to determine Flory-Huggins interaction parameters.¹⁷ However, these previous studies did not elucidate the water distribution within the multilayer. In this paper, we provide a direct measurement of water association inside weak poly(acrylic acid) and poly(allylamine hydrochloride) (PAA/PAH) PEMs. The water distribution in PAA/PAH assembled films was measured when exposed to water both as vapor, and in the bulk, using neutron reflectivity. These experiments give insight into the sensitivity of the swelling dynamics with water vapor of the multilayers, and to understanding the water distribution within the film, which could aid in further technological applications of these films. The determination of the water distribution within the films was achieved by varying the effective scattering length density (SLD) of a solvent mixture to equal zero. This ability to control the SLD of the

solvent is unique to neutron reflectivity, since one can select among chemically identical isotopes that have different neutron scattering lengths. Although controlling the SLD of the environment is commonly employed in studies with biological systems, this technique has not been commonly used in the study of multilayer films. The ability to tune the solvent scattering properties (by controlling hydrogen to deuterium mix) without affecting chemical properties has enabled water distributions to be examined in detail.

3.2 EXPERIMENTAL SECTION

3.2.1 MATERIALS AND FILM ASSEMBLY

Poly(acrylic acid) ($MW = 90\ 000$) (PAA), and poly(allylamine hydrochloride) ($MW = 60\ 000$) (PAH) were obtained from Polysciences and Aldrich respectively. Polyelectrolyte solutions of 10^{-2} M (concentration based on monomer unit) were prepared in 18.2 M Ω · cm Millipore water. Multilayer films were fabricated according to the usual layer-by-layer technique using an automated dipper.^{18,19} Polished Si (100) silicon wafers (~100 mm diameter and ~6 mm thick) purchased from Wafer World Inc. were used as substrates and were cleaned in concentrated chromium (III) oxide/sulfuric acid for at least 12 hours. The films were then first thoroughly rinsed with D.I. water and then rinsed with Millipore water. The pH of the polyelectrolyte solution was adjusted with HCl to a pH of 3.5 for both the polycation and polyanion solutions. An alternating series of polycation and polyanion layers was deposited by immersing the wafers for 15 min into the polyelectrolyte solutions. Between each adsorption step, the wafer was successively immersed into three rinse baths of Millipore water for 1, 2, and 2 min respectively. The process was repeated until the desired layer thickness of ~800 Å was achieved (18 bilayers). After the films were assembled, excess water was removed under a stream of compressed nitrogen. The assembled films were then oven dried under vacuum at 65 °C overnight. The films were then stored under vacuum until placed into the environmental sample chamber for measurement.

3.2.2 NEUTRON REFLECTOMETRY AND DATA ANALYSIS

The reflectivity experiments were performed at the Chalk River Laboratories (National Research Council Canada) on the C5 spectrometer at a neutron wavelength of 2.37 Å. Measurements were preformed in the specular reflection mode and the momentum transfer $q_z = (4\pi/\lambda) \sin \theta$, was varied by scanning in the q_z range of 0.006 Å⁻¹ to 0.08 $Å^{-1}$. The collimation slits were varied throughout the scan to ensure that the illuminated sample area remains the same and defines the instrument resolution at $\Delta q_z/q_z$ = 0.045. The background scattering was measured off-specularly with a fixed angular displacement of the sample of -1° for the humidity cell and -0.15° for the liquid cell. Measurements were performed in three q_z regions: $q_z = 0.08$ Å⁻¹ to 0.048 Å⁻¹, $q_z = 0.052$ Å⁻¹ to 0.018 Å⁻¹ and $q_z = 0.022$ Å⁻¹ to 0.006 Å⁻¹. The overlaps between the three regions are used to match up the intensities in the separate regions. The data was normalized by the incident beam intensity to account for variations due to slit widths. The count time in the high q_z regions (0.08 Å⁻¹ to 0.018 Å⁻¹) was increased in order to maintain a proper count statistics throughout the entire scan. The samples were placed into an environmental chamber where the humidity, temperature, and solvent conditions can be controlled. The properties of this sample cell and its ability to precisely maintain constant humidity has been fully characterized previosuly.²⁰ The sample stage was maintained at

25 °C for all experiments. For dry scans the PAH/PAA films were kept dry in the cell with a nitrogen purge. Controlled humidity environments for films prior to measurement and while in the sample cell were established by using the equilibrium water vapor over saturated salt solutions.²¹ The samples were allowed to equilibrate for a minimum of 12 hours in the humidity chamber prior to any measurements. Bulk water and humidity swelling studies were carried out using 100% D₂O. Dried films were obtained by placing the sample under vacuum for 16 hours at 65 °C, and purged with nitrogen while in the sample cell, after the films had been H-D exchange equilibrated by exposure to D_2O vapor before drying. To deconvolute the contributions from the swollen PEM matrix and from water uptake within the film, swelling experiments were also conducted using a water/solvent mixture of 92:8 H₂O:D₂O. This solvent mixture has a net scattering length density of zero, and hence only the PEM matrix contributes to scattering. The water distribution within the film was then obtained by simply subtracting the SLD profile from the original (100% D₂O) scattering curve. Although water and deuterium oxide have slightly different kinetic properties, they possess largely similar thermodynamic properties and the chemical potentials can be assumed to be equivalent.¹⁷ In the case where bulk water with a solvent mixture of $92:8 H_2O:D_2O$ was used, the lack of a critical edge required the reflectivity curve to be normalized with the corresponding 100% D₂O normalization factor. The scattering length density profiles of the films were fitted with Parratt's dynamic approach,²² using the Parratt32 fitting software (provide by HMI). The instrumental resolution was included when fitting the reflectivity curves. The silicon oxide thickness and roughness was fitted from neutron reflectivity curves on bare Si wafers of the same batch as those used as substrates for multilayering. Details of the fit parameters are provided as supporting information. Errors on the structural parameters

were determined by varying the fit parameter based on a 10% increase of χ^2 , and Patterson analysis of reflectivity data was also carried-out.²³ Patterson analysis of the reflectivity data however was limited by the fact that the experiments were only conducted to $q_z = 0.08$ Å⁻¹, and resolution limitations made it difficult to assess the sharpness at the polymer surface independently from this fit. The correlation distances of the interface using this analysis however were similar to the SLD profile interface estimates obtained from the fits using Parratt32, and support well our interpretation by the primary fitting method and analysis presented here.

3.3 RESULTS AND DISCUSSION

Figures 3.1 and 3.2 show the raw neutron reflectivity data of PAH/PAA samples, and best fits to a four-slab model in which the properties of the Si substrate were kept constant. The spectra contain numerous Kiessig oscillations to $q_z = 0.08$ Å⁻¹ suggesting that the films are of uniform thickness, which can be determined by $2\pi/\Delta q_z$, where Δq_z is the distance between two successive fringes. A simple one-box or two-box model of the polymer film was insufficient in producing reasonable fits to the data especially for the cases where the samples were hydrated. In the case of the humidity-swollen films, a low-SLD outer layer was added to account for chain extension into the ambient environment.

In the case of dry films, additional narrow boxes at the polymer/substrate and the polymer/environment interfaces were required to obtain best fits, and one large slab was used to model the bulk interior of the multilayer. Fits obtained for the bulk water experiments could be fit by subdividing the film bulk into three sub-regions of slightly changing SLD.



Figure 3.1 Neutron reflectivity data (error bars are within the size of the symbols) and fit (solid continuous line) for assembly pH= 3.5 PAA/PAH multilayer film a) in the dry state, b) exposed to 11% R.H with a 100% D₂O content. The corresponding SLD profile of the model is shown in the inset.

The resulting SLD profile however was found to contain step features that were artifacts of the fitting method. A gradient model was then used instead, where the bulk interior of the multilayer was modeled using a sigmoidal function. The resulting fit was as good as the four-box model, and produced a similar SLD profile. All parameters (film/substrate roughness, internal roughness, film/air roughness and the SLD of the polymer slabs) were free to evolve except for the SLD of the substrate and oxide, and produced physically reasonable fits. In the resulting SLD profiles of the multilayer films,



Figure 3.2 Neutron reflectivity data (error bars are within the size of the symbols) and fit (solid continuous line) for assembly pH= 3.5 PAA/PAH multilayer film a) exposed to 11% R.H. with a solvent vapor mix of 92:8 (H₂O:D₂O), b) exposed to 43% R.H. with a 100% D₂O content. The corresponding SLD profile of the model is shown in the inset.

we have chosen to define z = 0 as the silicon/oxide film interface, and the multilayer film can be described well using a three-region model of nominal thickness 794±15 Å (determined from the midpoint of the diffuse polymer-air interface). The SLD profile indicates that the free surface was quite diffuse, and that the bulk of the film is best described by a smooth and flat profile. The absence of oscillations in the profile shows that the bulk multilayer structure is evidently highly interpenetrated, consistent with
previous investigations.^{14,15} The spike seen at z = 0 is attributed to the high SLD (3.475×10⁻⁶ Å⁻²) of the SiO₂ layer. However, the film-substrate interface appears to have a measurably higher SLD than the film bulk. This increased SLD near the substrate interface is likely due to higher density of polymer material, which is consistent with other literature suggestions. Conceivably, the increased SLD could also be due to a localization of counterions, but to account for the increased SLD near the substrate (1.5×10⁻⁶ Å⁻², as compared to 0.7×10^{-6} Å⁻² in the film bulk) would require, for example, ~6 Na⁺ ions per PAA group. The films studied were assembled at pH=3.5, and under these conditions PAH is fully charged and PAA is partiality ionized (~ 76 %).^{14,20} Given that only ~25% of the PAA groups are available for bonding to counterions (the rest form ionic crosslinks), it does not seem reasonable to suggest that the increased SLD is due to counterions alone.

The films assembled at pH=3.5 can be viewed as a mesh of many voids in which water molecules absorb. The incorporation of deuterium oxide vapor into the film, which has a large positive scattering (SLD = $6.4 \times 10^{-6} \text{ Å}^{-2}$) leads to an increase of the SLD of the multilayer as seen in Figures 3.1 b) and 3.2 b). A single-slab model could not describe films swollen in a humid atmosphere, and an internal asymmetry in the film was necessary in order to reproduce the experimental reflectivity profiles. However, it is difficult to determine whether the contribution to the SLD profile is due to film swelling or sorption of D₂O vapor. To determine the SLD profile of the polyelectrolyte multilayer at 11% R.H., a vapor solvent mixture of 92:8 H₂O:D₂O was used. When the multilayer was exposed to this environment only the film contributes to scattering, since this solvent mixture has an effective scattering length density of zero. The resulting SLD profile is shown in Figure 3.2 a), and is very similar to that of polymer in the dry state (Figure 3.1

a), indicating that the multilayer does not swell to an appreciable extent. As inferred from the dry and 11% R.H. (92:8 H₂O:D₂O) SLD profiles, the extent of H/D exchange in the film was negligible even when exposed to 100% D₂O vapor. It is plausible that at this low humidity the osmotic stress is insufficient to induce film swelling. The low water fraction in the film (and hence low extent of swelling) limits the amount of exchangeable water available to the film. The SLD profile of water within the film was then deconvoluted from the contributions due to film and water in the original 11% R.H. $(100\% D_2O)$ scattering curve, and is shown in Figure 3.3. It is clear that the water distribution within the multilayer is asymmetrical; the water vapor is strongly localized at the film-air interface and does not penetrate to the substrate. Ellipsometry studies on films of similar thickness exposed to 11% R.H. have shown a ~1.15% increase in thickness. Defining the absolute thickness of the sample is nontrivial due to the fuzzy interface resulting from the polyelectrolyte's loops and tails which extend into the humid environment. For this reason, we chose to determine the film thickness at the midpoint of the bulk polymer-air interface. For the profile of the 11% R.H. (100% D₂O) film, the thickness was observed to have increased by $0.45\pm0.03\%$. In contrast, the thickness determined with ellipsometry was modeled as a single slab and did not take into account the internal density gradient of water vapor, nor does it accurately interpret the diffuse surface. These factors may lead to an inaccurate determination of the optical properties of the film by this technique, but the extent of swelling using the two techniques is still quite similar however. Neutron Experiments also show that exposures to 43% R.H. (100% D_2O) leads to a 4.98±0.03 % increase in thickness (834±16 Å), as indicated in Figure 3.2 b). There was sufficient osmotic stress induced on the polymer network to expand to a greater extent than when exposed to 11 % relative humidity. The polymer/air

interface is sharp, as seen in the SLD profile and is an indication that water is localized preferentially at the surface. Ellipsometry studies on films exposed to 43% R.H. have shown a \sim 4.2 % increase in thickness, which is consistent with the neutron reflectivity results presented here.



Figure 3.3 SLD profile of the neutron reflectivity data for a multilayer film exposed at 11% R.H.. The open symbols corresponds to the model at 11% R.H. (100% D_2O) the dashed line corresponds to the SLD profile at 11% R.H. (92:8 solvent mix of $H_2O:D_2O$) and the black solid line is the difference of the SLD profiles and indicates the water distribution within the film.

The asymmetrical water distribution in the PEM and the relatively sharp boundary at the polymer-air interface may contain clues of the strong effect of water vapor adsorption on the swelling kinetics with bulk water. For instance, bulk water swelling studies on multilayers assembled at pH=3.5 required \sim 3 s to reach equilibrium when the film was pre-exposed to an environment of 20% R.H., whereas when the film was equilibrated at 45% relative humidity, \sim 1800 s were required to reach maximum swelling.¹² Water molecules are likely in constant motion, but hydrophobic interactions

of the PAH and PAA polymer backbone may well force the water molecules into a more rigid organized cluster of hydrogen-bonded molecules, whereas the free carboxylic acid groups of the PAA would participate in hydrogen-bonding network.²⁴ This effect serves to increase the structural organization of water, and thus decreases the entropy of the water molecules in the clusters. The relatively sharp interface (Figure 3.3) strongly suggests that water is segregated at the film-vapor interface. As shown in the supporting information (Figure 3.1S) the fit is sensitive to the bulk interfacial roughness. An increase in the surface roughness of only 5 Å is sufficient to cause a substantial deviation from the fit, indicating the requirement for the sharp interface. Water localization at the film-air interface might also be ascribed to surface tension effects, however, this is not likely the case as will be shown later.

The asymmetrical water distribution cannot be explained with a simple diffusion model where water penetrates in a passive manner through the pores of the PEM. Our results support the notion that the outer layers are more diffuse than the interior of the multilayer^{10,25} as indicated by the SLD profile of the dry film (Figure 3.1a) and indeed more water vapor is associated with the outer layer (Figure 3.3), which is consistent with previous investigations.^{13,16,26} However, a simple percolation model would predict a constant water distribution through the bulk region of the film that extends to the substrate, which is not the case as our results clearly indicate that the water vapor does not penetrate to the substrate and is distributed asymmetrically throughout the film. Furthermore, this model would fail to explain the water localization at the polymer-air interface. The water gradient that forms in the film can be explained through kinetic arguments though. Essentially, water adsorbs at the free surface of the film and blocks accessible microchannels in the film, thereby inhibiting further diffusion of the vapor. If

this were strictly a surface phenomenon the water distribution within the film would eventually saturate and have a uniform profile throughout the film. However, ellipsometry studies on PEMs of similar thickness exposed to 11% R.H. indicate that the exposure times used in these experiments is sufficient for the film to reach saturation. Furthermore, a partial scan ($q_z = 0.022 \text{ Å}^{-1}$ to 0.006 Å⁻¹) was taken ~ 11 hours prior to the full scan. The partial and full scans overlap each other, indicating that the film was equilibrated. Insufficient exposure time would have resulted in an observable shift in the critical edge to higher q_z . If the drying process, after exposure to D₂O vapor, was not uniform or incomplete, an observable asymmetry in the film SLD would have also been observed in the 11% R.H. (92:8 solvent mix of H₂O:D₂O) experiment (due to the higher scattering contrast of deuterium). We must stress that the resultant profiles represent the multilayers at equilibrium and are not merely a snapshot of the diffusion process or isotopic exchange. It is therefore more likely that water clusters would form a gradient throughout the film, which would further restrict the motion of water vapor and establish a chemical gradient through the film. As the vapor front moves through the film, the formation of water clusters would impede the diffusion of more water into the microchannels of the sub-phase, resulting in less water being available to the underlying layers. This is clearly shown in the SLD water profile within the film, where vapor does not penetrate to the substrate-polymer interface. Swelling studies with bulk water suggest that the interior of the PEM is less restrictive than the outer surface layers. Upon exposure to bulk water the film gradually expands, but only to a modest extent. After a relatively long induction period which is dependent on the pre-exposure humidity, the rate of swelling abruptly increases until eventually a constant rate of swelling is established. PEM swelling dynamics support the idea of a gradient of water clusters

through the film, where water is found to preferentially localize at the PEM surface. This asymmetric water distribution may also be due to the formation of a pK_a gradient in the film during assembly, characterized previously.²⁰ As layers are added, the apparent pK_a of the PAA shifts to lower values, where the surface layers are more ionized than those within the film. The free carboxylic acid groups at the surface of the film would therefore associate with the water clusters through hydrogen bonding, which results in a higher concentration of water near the surface. The degree of ionization decreases on approach to the substrate, as fewer carboxylic acid groups are available to aid in the formation of water clusters and a gradient in the water distribution results. In either case, these effects are more pronounced at higher humidity and leads to a longer time scale for the diffusion, but the osmotic stress is larger and the polymer network expands. It is therefore conceivable that the diffusion of bulk water would be hindered through the blockage of accessible microchannels in the film, through the formation of hydrogen-bonded water clusters, and this effect would lead to longer time scales required to reach saturation with increasing humidity. More importantly, the gradient of water clustering would explain the long induction time required to establish a late stage acceleration in swelling due to autocatalytic plastization of the film as observed in kinetic studies.

The SLD values produced from the fits of the reflectivity curves for PEM films are consistent with those reported previously in the literature.^{15,17,27} The physical density and corresponding water fraction distribution in the PEM are shown in Figure 3.4, where the density profiles were calculated using an association stoichiometry of PAA to PAH, with the PAA ionized to ~76%. This percent ionization is based upon literature reports of the effective pKa of PAA chains in PAA/PAH multilayers (where an apparent pKa = 3 was observed),²⁸ and is consistent with FTIR measurements of PAA ionization in multilayers.¹⁸ The association of counterions was omitted in the calculations since it was



Figure 3.4 Film density and water distribution for a multilayer film exposed at 11% R.H. The open symbols correspond to the film density and the dashed line corresponds to the water fraction distribution within the film.

extent of exchange in the films appeared negligible, and assumed then to be zero for the fitting. Based on this, the average physical density of the bulk interior of the PEM was determined to be 0.8 ± 0.1 g·cm⁻³, which is reasonable considering that under the assembly conditions the PEM forms a loose structure and is consistent with measurements on PAH/PSS multilayers, where densities of ~0.8–1.1 g/cm³ were deduced.^{15,26,29,30} As indicated, the polymer-air interface is diffuse whereas at the substrate interface the multilayer is more dense than in the bulk. This densification is presumably due to substrate effects during the assembly of the few first layers. The water density associated to the diffuse outer layer is ~40% of that of bulk water, whereas the water content ranged from 30–20% in the bulk of the film.

The distribution of bulk water was also studied. Neutron reflectivity data, fits, and the corresponding SLD profiles of the PEM exposed to pure D₂O and to the solvent mixture of 92:8 H₂O:D₂O are shown in Figure 3.5. When exposed to bulk water the SLD profiles reveals that the multilayer film swells considerably to 1071 ± 13 Å, with an extent of swelling of $34.87\pm0.03\%$, which is consistent with other reports in the literature which range from ~20% to 40%.^{15,27}

The profile of water within the film was again deconvoluted from the contributions due to film (92:8 H₂O:D₂O) and water in the original 100% D₂O scattering curve as shown in Figure 3.6. The resultant water distribution in films swollen with bulk solvent is again asymmetric. Here again, a relatively sharp film-ambient interface is observed, and water is preferentially found to localize at the film surface, only partially penetrating to the substrate. This implies that surface tension effects are not responsible for the water localization at the surface; the relatively sharp interface is present even though the film was exposed to bulk water, which is consistent with the formation of water clusters. The physical density and water fraction distribution in the PEM when exposed to bulk water is shown in Figure 3.7. The density profile of the PEM was calculated in a similar manner as the 11 % R.H. case with an assumed association stoichiometry of PAA (~76% ionized) to PAH. However, when complete D/H exchange was assumed the overall density of the PEM was higher than the case when exposed to water vapor. Since the mass density of the film is conserved, the resultant bulk interior density of the film should be 0.59 ± 0.02 g·cm⁻³ when swollen to an extent of ~35 %. It is known that the kinetics of H₂O to D₂O exchange is faster than D₂O to H₂O exchange due to the lower zero point energy of the D-O bond. It is therefore conceivable that inefficient isotopic substitution (D to H) occurred in the PEM film due to insufficient

solvent exposure time. However, the film SLD for the bulk 92:8 $H_2O:D_2O$ shows no asymmetry and suggests that the exchange event has occurred uniformly in the film. The



Figure 3.5 Neutron reflectivity data (error bars are within the size of the symbols) and fit (solid continuous line) for a multilayer film a) exposed to 100% bulk D_2O and b) exposed to bulk water with a solvent mix of 92:8 (H₂O:D₂O). The corresponding SLD profile of the model is shown in the inset.

reflectivity data for the bulk 92:8 H₂O:D₂O experiment was analyzed using data from regions two and three ($q_z = 0.052 \text{ Å}^{-1}$ to 0.018 Å⁻¹ and $q_z = 0.022 \text{ Å}^{-1}$ to 0.006 Å⁻¹) (~ 5.5 hours after the scan in region 1, $q_z = 0.08 \text{ Å}^{-1}$ to 0.048 Å⁻¹). Fits obtained using the truncated data sets (region two, and regions two and three) gave similar profiles to that obtained using all the three scan regions. The bulk SLD of the film was virtually unchanged and suggests that the exchange process was complete. Analysis of the spacing of the Kiessig fringes from the three regions also indicates that the timescale used in the experiment was sufficient for the exchange process. If the SLD of the film were changing in time, the position of the Kiessig fringes would be changing during scanning, leading to an apparent modification of the fringe shape. The fact that the Kiessig spacing does not change over the measured q_z range indicates that the SLD of the film was constant during the measurement. We can therefore state with confidence that the resultant SLD profile is not due to a kinetic D to H exchange process (kinetic isotope effect), and represents the film at equilibrium. To account for the problem of inefficient D/H exchange, the H/D ratio was calculated based on the assumed physical density and the inferred SLD profile of the film. The extent of the H/D exchange was thus determined to be ~59 %. Here



Figure 3.6 SLD profile of the neutron reflectivity data for a multilayer film exposed to bulk water. The open symbols corresponds to the model with 100% D_2O the dashed line corresponds to the SLD profile with the solvent mix of 92:8 $H_2O:D_2O$ and the black solid line is the difference of the SLD profiles that indicates the water distribution within the film.

again the polymer-water interface is diffuse whereas the multilayer is more dense at the polymer/substrate interface than in the bulk. It is difficult to know with any certainty the extent of H/D exchange with respect to the 100% D₂O bulk water experiment. The extent of deuteration in the film could range from 100% to 41% (the corresponding water fraction distributions are shown in Figure 3.7). In either case, the overall water distribution in the film is asymmetrical, similar to the case of exposure to 11 % R.H.. The difference between the two is a decrease of ~8% in the water fraction within the film in the case where exchange is 100%. The water fraction associated with the diffuse outer layer is ~54% and the water content in the bulk of the film ranges from 45-35%. The water content near the polymer/substrate interface is much lower (~18%) than the bulk



Figure 3.7 Film density and water distribution for a multilayer film exposed to bulk water. The open symbols correspond to the film density, the dashed line corresponds to the water fraction distribution within the film with the extent of deuteration calculated to 41% and the solid line corresponds to the water fraction distribution within the film with the extent of deuteration calculated to 100%.

interior of the film. The overall water fraction in the film is higher due to the increase of osmotic stress on the polymer network.

Although there is sufficient osmotic stress to induce expansion of the PEM network, water clusters may still be forming within the film. Similar arguments as in the case of sorption from the gas phase could be applied to the case of swelling with bulk water, however, the effect is not as pronounced as in the case of vapor sorption. In this instance, water would permeate quickly through the film since the PEM was swollen from the dry state. As the solvent front moves through the film, the water molecules would associate with the free carboxylic acid groups as well as induce hydrophobic interactions between the polyelectrolyte chains, leading to the formation of a gradient of water clusters that is preferentially localized at the surface. In principle, this would inhibit water from penetrating to the substrate, since the accessible microchannels deep within the film would be blocked.

3.4 CONCLUSIONS

Neutron reflectivity experiments have provided some the fine details of film swelling and water localization in thin PAH/PAA multilayer films assembled at a pH of 3.5. In particular, the ability to tune solvent scattering properties (by controlling hydrogen to deuterium mix) without affecting chemical properties has enabled water distributions to be examined in detail. It is now apparent that water localizes asymmetrically within multilayer systems in both the gas phase and when swollen with bulk water. In either case, water segregates predominantly at the diffuse free surface. The localization of water at the polymer-air interface can be used to explain anomalous swelling kinetics, where time scales to reach maximum swelling varied from a few seconds to tens of minutes, depending on the pre-exposed humidity conditions of these novel materials.

3.5 REFERENCES

- (1) Decher, G. *Science* **1997**, *277*, 1232.
- (2) Lee, S.-H.; Kumar, J.; Tripathy, S. K. Langmuir 2000, 16, 10482.
- (3) Dai, J.; Jensen, A. W.; Mohanty, D. K.; Erndt, J.; Bruening, M. L. *Langmuir* **2001**, *17*, 931.
- (4) Zhai, L.; Nolte, A. J.; Cohen, R. E.; Rubner, M. F. *Macromolecules* **2004**, *37*, 6113.
- (5) Dai, J.; Balachandra, A. M.; Lee, J. I.; Bruening, M. L. Macromolecules 2002, 35, 3164.
- (6) Jin, W.; Toutianoush, A.; Tieke, B. *Langmuir* **2003**, *19*, 2550.
- (7) Miller, M. D.; Bruening, M. L. *Langmuir* **2004**, *20*, 11545.
- (8) Shi, X.; Caruso, F. *Langmuir* **2001**, *17*, 2036.
- (9) Sukhorukov, G. B.; Antipov, A. A.; Voigt, A.; Donath, E.; Mohwald, H. *Macromol. Rapid Commun.* **2001**, *22*, 44.
- (10) Chung, A. J.; Rubner, M. F. Langmuir 2002, 18, 1176.
- (11) Nolan, C. M.; Serpe, M. J.; Lyon, L. A. Biomacromolecules 2004, 5, 1940.
- (12) Tanchak, O. M.; Barrett, C. J. Chem. Mater. 2004, 16, 2734.
- (13) Ladam, G.; Schaad, P.; Voegel, J. C.; Schaaf, P.; Decher, G.; Cuisinier, F. *Langmuir* **2000**, *16*, 1249.
- (14) Schmitt, J.; Gruenewald, T.; Decher, G.; Pershan, P. S.; Kjaer, K.; Loesche, M. *Macromolecules* **1993**, *26*, 7058.
- (15) Loesche, M.; Schmitt, J.; Decher, G.; Bouwman, W. G.; Kjaer, K. *Macromolecules* **1998**, *31*, 8893.
- (16) Steitz, R.; Leiner, V.; Siebrecht, R.; Klitzing, R. Colloids Surf., A 2000, 163, 63.

- (17) Kugler, R.; Schmitt, J.; Knoll, W. Macromol. Chem. Phys. 2002, 203, 413.
- (18) Shiratori, S. S.; Rubner, M. F. *Macromolecules* **2000**, *33*, 4213.
- (19) Yoo, D.; Shiratori, S. S.; Rubner, M. F. *Macromolecules* **1998**, *31*, 4309.
- (20) Harroun, T. A.; Fritzsche, H.; Watson, M. J.; Yager, K. G.; Tanchak, O. M.; Barrett, C. J.; Katsaras, J. *Rev. Sci. Instrum.* **2005**, *76*, 065101.
- (21) Lide, D. R. CRC Handbook of Chemistry and Physics, 83rd Edition, 2002.
- (22) Parratt, L. G. *Physical Review* **1954**, *95*, 359.
- (23) Crowley, T. L.; Lee, E. M.; Simister, E. A.; Thomas, R. K. *Physica B* 1991, *173*, 143.
- (24) Israelachvili, J. N. Intermolecular and Surface Forces: With Applications to Colloidal and Biological Systems, 1985.
- (25) Wong, J. E.; Rehfeldt, F.; Haenni, P.; Tanaka, M.; Klitzing, R. v. *Macromolecules* **2004**, *37*, 7285.
- (26) Plech, A.; Salditt, T.; Munster, C.; Peisl, J. J. Colloid Interface Sci. 2000, 223, 74.
- (27) Glinel, K.; Prevot, M.; Krustev, R.; Sukhorukov, G. B.; Jonas, A. M.; Moehwald, H. *Langmuir* **2004**, *20*, 4898.
- (28) Burke, S. E.; Barrett, C. J. Langmuir 2003, 19, 3297.
- (29) Tarabia, M.; Hong, H.; Davidov, D.; Kirstein, S.; Steitz, R.; Neumann, R.; Avny, Y. J. Appl. Phys. **1998**, 83, 725.
- (30) Steitz, R.; Leiner, V.; Tauer, K.; Khrenov, V.; Klitzing, R. V. Appl. Phys. A: Mater. Sci. Process. 2002, 74, S519.



Figure 3.1S Neutron reflectivity data and fit for assembly pH= 3.5 PAA/PAH multilayer film exposed to 11% R.H. with a 100% D₂O content. Variation of the bulk interface roughness +5 Å, +10 Å, -5 Å and a one-box model are shown.

Table 1S Structure parameter of dry PAH/PAA film. Errors are calculated based on a 10% increase in χ^2 , box 1 is the SLD at the polymer/environment interface, $\sigma_{f/e}$ signifies the roughness at the surface, and $\sigma_{f/s}$ is the roughness at the film/substrate interface.

Film Thickness (Å)	SLD, ρ (10 ⁻⁶ Å ⁻²)										
	Box 1	$\sigma_{f/e}(Å)$	Box 2	σ _{int 2} (Å)	Box 3	σ _{int 3} (Å)	Box 4	σ _{f/s} (Å)			
80+694+26+17±15	0.3±0.1	16±17	0.82±0.09	81±32	1.5±0.17	28±7	1.9±0.2	8±9			

Table 2S Structure parameter of PAH/PAA film exposed to 11% R.H. with a 100% D₂O content. Errors are calculated based on a 10% increase in χ^2 , box 1 is the SLD at the polymer/environment interface, $\sigma_{f/e}$ signifies the roughness at the surface, and $\sigma_{f/s}$ is the roughness at the film/substrate interface.

Film Thickness (Å)						SLD, ρ (10 ⁻⁶ Å ⁻²)						
· · · · · · · · · · · · · · · · · · ·	Box 1	σ _{f/e}	Box 2	σ _{int 2}	Box 3	σ _{int 3}	Box 4	σ _{int 4} (Å)	Box 5	σ _{int 5}	Box 6	σ _{f/s}
70+40+346+335+99+13±16	0.12±0.04	(A) 14±18	0.42±0.04	(A) 11±9	3.75±0.03	(A) 8±4	2.9±0.1	111±34	2.53±0.07	(A) 98±5	1.4±0.2	(A) 12±7

Table 3S Structure parameter of PAH/PAA film exposed to 11% R.H. with a solvent vapor mix of 92:8 (H₂O:D₂O). Errors are calculated based on a 10% increase in χ^2 , box 1 is the SLD at the polymer/environment interface, $\sigma_{f/e}$ signifies the roughness at the surface, and $\sigma_{f/s}$ is the roughness at the film/substrate interface.

Film Thickness, (Å)		SLD, $ ho$ (10 ⁻⁶ Å ⁻²)									
104+641+48+27±18	Box 1	σ _{f/e} (Å)	Box 2	σ _{int 2} (Å)	Box 3	σ _{int 3} (Å)	Box 4	σ _{f/s} (Å)			
	0.3±0.1	20±18	0.8±0.1	79±32	1.2±0.1	26±13	1.9±0.1	9±8			

Table 4S Structure parameter of PAH/PAA film exposed to 43 % R.H. with a 100% D₂O content. Errors are calculated based on a 10% increase in χ^2 , box 1 is the SLD at the polymer/environment interface, $\sigma_{f/e}$ signifies the roughness at the surface, and $\sigma_{f/s}$ is the roughness at the film/substrate interface.

Film Thickness, (Å)	SLD, <i>ρ</i> (10 ⁻⁶ Å ⁻²)											
	Box 1	σ _{f/e}	Box 2	σ _{int 2}	Box 3	σ _{int 3}	Box 4	σ _{int 4} (Å)	Box 5	σ _{int 5} (Å)	Box 6	σ _{f/s}
70+31+362+337+117+14±19	0.07±0.03	(A) 14±16	0.47±0.06	(A) 14±11	3.77±0.02	(A) 8±3	2.8±0.1	123±14	2.55±0.05	102±43	1.4±0.2	(A) 12±7

Table 5S Structure parameter of PAH/PAA film exposed to bulk D₂O. Errors are calculated based on a 10% increase in χ^2 , box 1 is the SLD at the polymer/environment interface, $\sigma_{f/e}$ signifies the roughness at the surface, and $\sigma_{f/s}$ is the roughness at the film/substrate interface. The bulk asymmetry in the interior of the multilayer (790 Å) was modeled using a sigmoidal function (equation 1S), parameters A and B were held constant and correspond to the SLDs at the substrate/film interface and the free surface respectively.

Film Thickness, (Å)	SLD, <i>ρ</i> (1	0 ⁻⁶ Å ⁻²)					
	σ _{f/e} (Å)	Box 1	σ _{int 1} (Å)	Box 2	σ _{f/s} (Å)	С	D
250+790+20±13	7±5	3.8±0.2	20	2.9±0.2	9±17	430±231	120±71

$$f(z) = A + \frac{B}{1 + e^{-\left(\frac{z-C}{D}\right)}}$$
(1S)

110

Table 6S Structure parameter of PAH/PAA film exposed to bulk water with a solvent mix of 92:8 (H₂O:D₂O). Errors are calculated based on a 10% increase in χ^2 , box 1 is the SLD at the polymer/environment interface, $\sigma_{f/e}$ signifies the roughness at the surface, and $\sigma_{f/s}$ is the roughness at the film/substrate interface.

Film Thickness, (Å)	SLD, ρ (10 ⁻⁶ Å ⁻²)								
174+826+74+32±5	Box 1	σ _{f/e} (Å)	Box 2	σ _{int 2} (Å)	Box 3	σ _{int 3} (Å)	Box 4	σ _{f/s} (Å)	
	0.60±0.04	50±15	0.89±0.03	10±9	1.15±0.03	17±3	1.76±0.07	14±2	

Chapter 4

Ion Distribution in Multilayers of Weak Polyelectrolytes: A Neutron Reflectivity Study

The previous chapter described the water distribution within the weak polyelectrolyte system when exposed to an environment of controlled humidity and to bulk water. The water distribution in the film was found to be asymmetric and to preferentially localize at the free surface of the film in both the gas phase and in solution. The segregation of water at the polymer-air interface and the asymmetric water distribution can be used to explain the anomalous kinetics reported in chapter 2. This supports the notion of water structuring that impedes the diffusion of bulk water into the sub-phase of the film. The focus of this chapter was to investigate the effect of pH and salt on the water distribution within the film. Neutron reflectivity was used to probe the water and counterion distribution in films that were exposed to salt solutions and in those assembled with salt. As previously done in chapter 3, the scattering properties of solvent were adjusted in order to deconvolute the water distribution in the film. Furthermore, the scattering properties of the salt ions provided a way to resolve their distribution in the polyelectrolyte multilayer films.

4.1 INTRODUCTION

The electrostatic interaction between two oppositely charged polyelectrolyte chains is the main driving force for the formation of polyelectrolytes multilayers (PEMs). The alternating adsorption of two oppositely charged polyelectrolytes onto a substrate using the layer-by-layer (L-b-L) technique can produce thin multilayer films with well-

defined composition, thickness and surface properties.¹ With weak polyelectrolyte systems, the degree of ionization of both polymer systems (polyacid and polybase) can be regulated by varying the solution pH and allows for further control of the film properties.² The ability of the L-b-L method to form thin films that are structurally diverse has attracted intense interest for building novel systems with many potential applications including sensors,³⁻⁵ optical devices,^{5,6} separation membranes,⁷⁻⁹ and drug delivery vehicles.¹⁰⁻¹³

The ability to predict the behavior and response of these systems under various conditions such as exposure to water, pH, and the influence of salt on the microstructure of the film is of fundamental importance. Knowledge of the internal properties of the PEMs may give insight to further fine-tune film properties in order to produce novel materials. However, the interaction of water with polyelectrolyte thin films is of crucial importance, and is complex. Recently it has been found that water distribution within weak polyelectrolyte thin films is asymmetric and localizes preferentially at the polymer surface when films were swollen using both humid air and bulk water.¹⁴ The determination of the water profile in these PEMs helped to explain the anomalous swelling kinetics previously observed in these systems.¹⁵ However, the effect of pH and counterions on the water distribution in polyelectrolyte multilayers has not been fully elucidated, and reported experimental results are contradictory on the role of salt and counterions in the formation of PEMs.¹⁶⁻¹⁹ Recently neutron reflectometry studies on poly[5-(2-trifluoromethyl-1,1,1-trifluoro-2-hydroxypropyl)-2-norbornene] spin cast polyelectrolyte films have indicated a depletion of the counterion near the substrate of the film and an enrichment near the free surface of the film.²⁰ Although these experiments revealed the distribution of base counterions within the film, the study was not performed

114

with a multilayer system. In this paper, we provide a direct measurement of the water association and counterion distribution inside weak poly(acrylic acid) and poly(allylamine hydrochloride) (PAA/PAH) PEMs, when treated post-assembly with varying solution pH and salt conditions. The water distribution and counterion distribution in PAA/PAH assembled films was measured when exposed to salt solution both *in situ* and dried using specular neutron reflectivity. Using a null solvent, which was achieved by tuning the scattering length density (SLD) of a solvent mixture (92:8 H₂O:D₂O) to zero, the water and salt ion distribution within the film was determined. These experiments give insight into the understanding of the distribution of salt ions in the film, which could aid in developing further technological applications.

4.2 EXPERIMENTAL SECTION

4.2.1 MATERIALS AND FILM ASSEMBLY

Poly(allylaminehydrochloride) ($MW = 60\ 000$) (PAH) was purchased from Aldrich. Poly(acrylic acid) ($MW = 90\ 000$) (PAA), was obtained from Polysciences as a 25% aqueous solution. The polyelectrolytes were used as received without further purification. Polyelectrolyte solutions of 10^{-2} M (concentration based on monomer unit) were prepared in 18.2 M Ω ·cm Millipore water. Multilayer films were fabricated according to the usual protocol using an automated dipper.^{2,14,21} Polished Si (100) silicon wafers (~100 mm diameter and ~6 mm thick) purchased from Wafer World Inc. were used as substrates. The wafers were cleaned in concentrated chromium (III) oxide/sulfuric acid for at least 12 hours and then thoroughly rinsed with D.I. and Millipore water. The solution pH of the polyelectrolytes was adjusted to 3.5 using HCl. The substrates were then alternately immersed into the polyelectrolyte baths for 15 minutes. Between each deposition step, the films were successively immersed into three rinse baths of Millipore water for 1, 2, and 2 min respectively. The process was repeated until the desired number of layers was deposited (18 bilayers). For the capping layer study an additional PAH layer was added for a total of 18.5 bilayers. In the case of salt-assembled films, 0.2M NaCl solutions in Millipore water were used for the polyelectrolyte solutions and the rinse baths, a total of 9 bilayers were deposited. After the films were assembled, excess water was removed under a stream of compressed nitrogen. For salt-assembled films, the surface was quickly rinsed with Millipore water in order to remove excess salt on the film. The assembled films were then dried under vacuum at 65 °C overnight. The films were then stored under vacuum until placed into the environmental sample chamber for measurement.

4.2.2 NEUTRON REFLECTOMETRY AND DATA ANALYSIS

Neutron reflectivity experiments were performed at the Chalk River Laboratories Canada (National Research Council Canada) on the C5 spectrometer. Measurements were performed in the specular reflection mode, as a function of the momentum transfer $q_z =$ $(4\pi/\lambda) \sin \theta$, in the range of q_z range of 0.006 Å⁻¹ to 0.08 Å⁻¹, where λ is the fixed incident neutron wavelength of 2.37 Å. Measurements were performed in three q_z regions: $q_z = 0.08$ Å⁻¹ to 0.048 Å⁻¹, $q_z = 0.052$ Å⁻¹ to 0.018 Å⁻¹ and $q_z = 0.022$ Å⁻¹ to 0.006 Å⁻¹. The resolution of the measurements was varied in discrete steps by changing collimation and exit slit widths at several scattering angles, and the count times were adjusted so that proper count statistics were maintained throughout the entire scan, with a typical (full-width half-maximum) resolution of $\Delta q_z/q_z = 0.045$. The background

scattering was measured off-specularly with a fixed angular displacement of the sample of -1° for the dry measurements and -0.15° for the liquid cell. The overlap between the regions was used to match up the absolute reflected intensities in the three separate regions and the data was normalized by the incident beam intensity to account for the variations due to the changing slit widths. The samples were placed into an environmental chamber where the temperature and solvent conditions could be controlled.²² The sample stage was maintained at 25 °C for all experiments and for dry scans the films were kept dry in the cell with a nitrogen purge. Bulk water swelling studies were carried out using 100% D₂O, the pD of the solutions was adjusted with either NaOD or DCl. To deconvolute the contributions of the swollen PEM matrix and counterions from water uptake within the film, swelling experiments were also conducted using a null solvent (a mixture of 92:8 H₂O:D₂O). This solvent mixture has a net scattering length density of zero, and therefore only the PEM matrix and/or the counterions contribute to neutron scattering intensity. The water or counterion distribution within the film was then obtained by simply subtracting the SLD profile from the original (100% D_2O) scattering curve. In the case of the null solvent experiments, the lack of a critical edge required the reflectivity curve to be normalized with the corresponding 100% D₂O normalization factor. Various salt (NaCl, LiCl and KCl) solutions were prepared in either D_2O or null solvent. The films were exposed to the salt or pD solutions for a minimum of 7 hours. The scattering length density profiles of the films were fitted with Parratt's dynamic approach,²³ using the Parratt32 fitting software (provided by HMI) and the instrumental resolution was included when fitting the reflectivity curves. The silicon oxide thickness and roughness were fitted from neutron reflectivity curves on bare Si wafers of the same batch as those used as substrates for

multilayering. A simple one-box or two-box model of the polymer film was insufficient in producing reasonable fits to the data especially for the cases where the samples were swollen or with dry film that had been exposed to salt solutions. A three or four-box model was used to fit the reflectivity curves, where single thin slabs were used to model polymer/substrate and polymer/environment interfaces. A larger slab was used to model the bulk interior of the multilayer. All parameters (film/substrate roughness, internal roughness, film/air roughness and the SLD of the polymer slabs) were free to evolve except for the SLD of the substrate and oxide. In the resulting SLD profiles of the multilayer films, we have chosen to define z = 0 as the silicon/oxide film interface.

4.3 RESULTS AND DISCUSSION

Polyelectrolyte films containing PAH/PAA were assembled at pH = 3.5 with and without 0.2M NaCl, and the effect of exposure to pH, salt conditions, and capping layer were investigated. The films were then scanned to $q_z = 0.08$ Å⁻¹ in the environmental chamber. Firstly, the effect of the pD of the solution was investigated. Figure 4.1 shows the raw neutron reflectivity data and model fits of PAH/PAA samples that were exposed to solutions of varying pD (3.0, 6.3, 7.0, and 8.0) in 100% D₂O. The SLD profile necessary for a good fit of the sample immersed in pure D₂O (pD = 6.3) is not uniform throughout the film, but instead is strongly asymmetric, increasing from the substrate interface to the free surface. This non-uniform and increasing SLD profile is also apparent when the film is immersed in pD = 7.0 solution, but is not apparent when the film is immersed in pD = 4.0 solutions, where the SLD is essentially uniform throughout the swollen film. This trend is illustrated more clearly in Figure 4.2a where the film thickness has been normalized. Although the films were assembled under the

same pH conditions, deviations such as temperature, humidity, and pH can lead to slight variation in the thickness of the films as seen in Figure 4.1 and Figure 4.1S (for dry films). To provide an estimate of the amount of D_2O incorporated in the film, the area



Figure 4.1 Neutron reflectivity data (error bars are within the size of the symbols) and fit (solid continuous lines) for PAA/PAH films assembled at pH = 3.5 exposed to D_2O at a) (pD = 6.3), b) pD = 7.0, c) exposed to pD = 8.0, and d) exposed to pD = 3.0. The model fit for corresponding SLD profiles of the film are shown in each inset. The corresponding dry reflectivity data and SLD profiles are shown in the supplemental section (Figure 4.1S).

under the swollen profile was integrated and the corresponding dry SLD area was subtracted and normalized, as shown in Figure 4.2b. As evident in Figures 4.2a and 4.2b, in addition to the strong asymmetry in the SLD profile for the sample in pD = 6.3, there is

also less D_2O incorporated into this film compared to the others. As the pD of the solution is increased from pD = 6.3, the SLD profiles become more uniform, and a greater content of D_2O is observed in the film. When the film was exposed to a low pD



Figure 4.2 a) SLD profiles of the films normalized to the same thickness, under solution conditions of: pD = 6.3 (dashed line), pD = 7.0 (\Box), pD = 8.0 (solid line), and pD = 3.0 (\diamond). b) Normalized SLD area of the pD series (swollen SLD area – dry SLD area)/dry SLD area.

value of 3.0, the bulk SLD again becomes more uniform, and more D_2O also appears to have penetrated the film relative to the pD = 6.3 system. The increase in the D₂O content in the films with a pD value higher or lower than 6.3 can be attributed to the effect of the strong pD change imposed on the ionizable PAA and PAH groups, relative to the pH ~5.5-6.5 conditions that are experienced by the films during all of the rinsing steps during assembly and preparation. At higher pD values, the free carboxylic acid groups on the PAA chains become more charged (to near 100% COO⁻ groups at pD = 8.0),²⁴ whereas the free amine groups of PAH become less charged. This results in a self- repulsion of the polyelectrolyte chains that enhances the porous structure of the film which leads to a greater D₂O content in the film, and to greater permeability towards the substrate. Similarly, when the film was exposed to a lower pD value (3.0) the amine groups of the PAH chains become fully charged, while the charge fraction on the PAA chains decreases, leading to a similar charge inequality, and similar behavior in water. This also may lead to a more diffuse film structure that can facilitate an enhanced permeability of D₂O toward the substrate. It may be also possible that the increased amount of ionic groups present in the film after exposure to the pD solutions could enhance water uptake where each additional ionic group provides a site for water to cluster. It is important to note that the films expanded to the same extent when exposed to the pD solutions, which is consistent with previous studies of swelling vs pH.¹⁵

The effect of varying ionic strength was then investigated. Enhanced water permeability towards the substrate was also seen in this salt study, where Figure 4.3 shows the neutron reflectivity data and model fits of PAH/PAA samples that were exposed to solutions of varying NaCl concentrations (0.0 M, 0.1 M, and 0.2 M) in D₂O. The SLD profile of water within the film was then deconvoluted by subtracting the contribution of the swollen film (null solvent swelling experiments as shown in Figure 4.2S) and water (100% D₂O), and is shown again normalized to thickness in Figure 4.4. The water distribution within the multilayer is again strongly non-uniform when the film is exposed to low ionic strength water, and the water appears predominantly localized at the film-ambient interface and does not completely penetrate towards the substrate, in agreement with previous studies.¹⁴



Figure 4.3 Neutron reflectivity data (symbols) and model fits (lines) for PAA/PAH multilayer films assembled at pH = 3.5, and exposed to D_2O with ionic strength of: a) no added salt, b) 0.1 M NaCl, and c) 0.2 M NaCl. The corresponding SLD profile of the model fits are shown in the insets. The corresponding reflectivity data and SLD profiles for the 92:8 (H₂O:D₂O) null solvent reference experiments are shown in the supplemental section (Figure 4.2S).



Figure 4.4 Water distribution in PAA/PAH multilayer films assembly pH = 3.5, exposed to D_2O no salt added (dashed line), exposed to 0.1 M NaCl (open symbols), and exposed to 0.2 M NaCl (solid line).

The water fraction associated with the outer layer is ~ 54%, while in the bulk region of the film the water content ranges from ~45–35%. When the film was exposed to a solution of 0.1 M NaCl now however, the water fraction in the bulk region of the film became more uniform, near ~50%, while the water fraction associated with the outer layer is ~60%. There is also an apparent decrease in water content near the substrate interface, but the overall water content in the film clearly has increased when compared to the salt-free case. When the film was exposed to a 0.2 M NaCl solution, the overall water content in the film increased even more substantially, and now with an increasing water profile from the free surface towards the substrate that ranges from ~45%-50%, to ~56% observed near the substrate. The increase in the water content in the film when exposed to salt solutions can be attributed to a screening effect. As the ionic strength of the solution increases, shielding of the charges on the polyelectrolyte chains in the multilayer increases, and a decrease in the electrostatic interaction between the chains results. The

decrease in the electrostatic interaction between the chains leads to the formation of a more diffuse film structure that enhances the permeation of salt ions (used to extrinsically compensate for the free charges) and additional waters of hydration into the film as observed. At higher salt concentrations the mobility of the polymer chains is enhanced due to the freeing up of the ionic sticker groups. The polyelectrolyte segments associated with the salt counterions are more hydrophilic and therefore more water will be associated with the polymer chains.²⁵

The reflectivity data, model fits, and SLD profiles for a dry film before and after sequential exposure to salt solutions of 0.2 M LiCl and 0.2 M KCl are shown in Figures 4.5 and 4.6. As evident in the SLD profile after exposure to the salt solutions, an increase in the SLD is seen near the substrate and the bulk region of the film. This suggests that salt ions preferentially localize near the substrate. Using the inferred molecular volume and the scattering length of KCl, the amount of ions present per repeat unit can be calculated by subtracting the underlying SLD of the dry film prior to exposure to the salt solution from the SLD of the film (dry) that was exposed to the salt solution. The amount of KCl ions per repeat unit was calculated to be 0.77 at a distance of 300 Å from the substrate and 1.53 at a distance of 100 Å from the substrate. The amount of ions in the film increases near the substrate and is consistent with the notion that the water fraction distribution and hence the amount of ions in the film increase dramatically near the substrate as previously shown (Figure 4.4). The decrease in the SLD profile near the free surface of the film after exposure to the salt solutions indicates that there is some material loss or rearrangement of the polymer chains. These relatively harsh conditions of high salt that the film was subjected to may have contributed to the decrease in the SLD near the free surface.



Figure 4.5 Neutron reflectivity data (error bars are within the size of the symbols) and model fit (line) for PAA/PAH multilayer films assembled at pH = 3.5 measured in the dry state, but after exposure to 0.2 M LiCl and 0.2 M KCl 100% D₂O solutions. The reflectivity data and fit for the dry film prior to exposure to the salt solutions can be found in the supplemental section (Figure 4.1S c).



Figure 4.6 SLD profiles of PAA/PAH multilayer films assembled at pH = 3.5 in the dry state prior to exposure to salt solutions (solid line) and then after exposure to 0.2 M LiCl and 0.2 M KCl 100% D₂O solutions (dashed line).

It is also possible that the apparent decrease in the dry SLD profile near the surface could be due to the presence of lithium ions that associate with the free COO⁻ groups that are present in the PAA capping layer. Lithium ions have a negative scattering length (-1.9 fm) whereas potassium has a large positive scattering length (3.67 fm). It is possible that the potassium ions have not completely exchanged with the lithium ions near the film surface and hence results in the apparent lower SLD profile near the surface. In addition a non-stoichiometric exchange of ions would have to occur, with more lithium ions associated with Cl⁻ in that region. However, incomplete and non- stoichiometric exchange of ions is not likely the case as suggested by null solvent experiments (solvent mix of 92:8 (H₂O:D₂O)), presented in Figure 4.7 and Figure 4.8. Here the SLD profile



Figure 4.7 Neutron reflectivity data (symbols) and model fits (lines) for PAA/PAH multilayer films assembled at pH = 3.5 and exposed to a) a solution of 0.2 M KCl with a solvent mix of 92:8 (H₂O:D₂O), and b) a solution of 0.2 M LiCl with a solvent mix of 92:8 (H₂O:D₂O). The data are offset for clarity.

for the 0.2 M KCl is higher in the bulk region due to the positive scattering length of potassium. The overall SLD is lower in the case of 0.2 M LiCl since lithium has a negative scattering length. The amount of ion per repeat unit (potassium ions that displaced the lithium ions) can be calculated from this using the inferred molecular



Figure 4.8 SLD profiles of multilayer films exposed to a solution of 0.2 M LiCl with a solvent mix of 92:8 ($H_2O:D_2O$) (solid line) and exposed to a solution of 0.2 M KCl with a solvent mix of 92:8 ($H_2O:D_2O$) (dashed line).

volume (based on the dry salt-free SLD of the film), the scattering length difference of potassium and lithium (5.57 fm) and by subtracting the SLD profile of LiCl from KCl. The amount of exchangeable cations per repeat unit was determined to be 1.32 at a distance of 100 Å. In the bulk region of the film (700 Å from the substrate) the amount of ions per repeat unit was calculated to be 0.48. However, as seen in the SLD profile for the film exposed to 0.2 M LiCl (Figure 4.8) with a solvent mix of 92:8 (H₂O:D₂O), the SLD is higher near the free surface, and this would suggest that a low amount of lithium ions are present at this interface. The decrease in the SLD at the free surface in the dry film (Figure 4.6) has not been observed in the other films studied without prior pD treatment,

so it is therefore more likely that the decrease is caused by material loss or rearrangement of the polymer chains due to the previous pD treatments.

Figure 4.9 shows the dry neutron reflectivity data and fits of PAH/PAA samples that were exposed to salt solutions of 0.2 M NaCl and 0.2 M LiCl in null solvent (92:8 ($H_2O:D_2O$)), the resulting SLD profiles are shown in Figure 4.10. The SLD profile of the



Figure 4.9 Neutron reflectivity data and fit (solid continuous line) for multilayer films a) in the dry state prior to exposure to 0.2 M NaCl and 0.2 M LiCl salt solutions and b) in the dry state after exposure to solutions of 0.2 M NaCl and 0.2 M LiCl with a solvent mix of 92:8 ($H_2O:D_2O$). The data are offset for clarity.

dry film after exposure to the salt solutions reveals a higher density near the substrate. The higher SLD here indicates that salt ions (LiCl) preferentially localize near the substrate. This is consistent with the notion that the water fraction and the amount of salt ions that are able to diffuse into the film greater near the substrate (Figure 4.4). The enhanced permeability near the substrate leads to the observed increase in the SLD of the dry film after exposure to the salt solutions. Assuming 100% displacement of NaCl by LiCl and that the chains are 100% hydrogenated, the amount of LiCl ions per repeat unit

100 Å from the substrate was determined to be 1.81, whereas a much lower amount (0.08) of salt ions are found in the bulk region.



Figure 4.10 SLD profiles of multilayer film in the dry state prior to exposure to salt solutions (solid black line) and after exposure to solutions of 0.2 M NaCl and 0.2 M LiCl with a solvent mix of 92:8 ($H_2O:D_2O$) (dashed line).

The effect of the cation type on the water distribution in the film was also investigated. Figure 4.11 shows the reflectivity data, fits, and profiles for a film exposed to 0.1 M LiCl and 0.1 M NaCl in 100% D_2O and null solvent. The water distribution in the multilayer film that was exposed to salt solutions containing LiCl and NaCl is shown in Figure 4.12, calculated by subtracting the null solvent profile of the swollen film from the corresponding D_2O profile. The resulting profiles suggest that the water distribution in the film is similar, within experimental uncertainties, regardless of what type of salt was used. Therefore, the water distribution in the multilayer film does not appear to be affected by the type of salt ions used at a concentration of 0.1 M.


Figure 4.11 Neutron reflectivity data (error bars are within the size of the symbols) and fit (solid continuous line) for a multilayer film a) exposed to a solution of 0.1 M LiCl 100% D₂O and b) exposed to a solution of 0.1 M LiCl with a solvent mix of 92:8 (H₂O:D₂O). The corresponding SLD profile of the model is shown in the inset. For the corresponding data and fits for 0.1 M NaCl 100% D₂O and 92:8 (H₂O:D₂O) refer to Figure 4.3b), and Figure 4.2S b) respectively.

The extent of diffusion of salt ions into and out of a PAA/PAH multilayer film was also studied, as a function of the identity of the polymer at the free surface (the capping layer). Figure 4.13 shows the neutron reflectivity data of a film capped with PAH in the dry state before exposure to a salt solution, after exposure to a salt solution of 0.1 M LiCl in a null solvent, and again after exposure to water. The corresponding SLD profiles are shown in



Figure 4.12 Difference in the SLD profiles of the neutron reflectivity data for a multilayer film exposed to 0.1 M NaCl and 0.1 M LiCl solutions (100% D_2O and 92:8 (H₂O:D₂O). The difference of the SLD profiles indicates the water distribution within the film. The solid line corresponds to the water distribution in the film when exposed to a solution of 0.1 M NaCl. The open symbols indicate the water distribution in the film when exposed to a solution of 0.1 M LiCl.

Figure 4.14. Exposure to a 0.1 M LiCl solution resulted in an overall increase in the SLD profile with a large increase in the SLD near the substrate. This increase in the SLD near the substrate suggests that salt ions preferentially localize near the substrate, as previously discussed, and as observed in the other profiles. The distribution of the LiCl ions in the film as a function of film thickness however is shown in Figure 4.15 (solid line). The number of salt ions per Å³ was estimated with the difference between the dry SLD profile after exposure to a 0.1 M LiCl solution, and the underlying SLD profile for a dry film exposed to a salt solution. As previously stated, there is a higher concentration of salt ions near the substrate, as well as a pronounced increase in the SLD near the free surface of the film. As will be discussed later, the increase in the SLD near the free surface of the film may be due to a capping layer effect. The number of ions per repeat unit was calculated to be 2.0 at a distance of 100 Å from the substrate. This amount was

determined by the usual manner described here (subtracting the original underlying dry SLD profile from the dry LiCl profile, using the inferred molecular volume from the dry



Figure 4.13 Neutron reflectivity data (error bars are within the size of the symbols) and fit (line) a PAA/PAH multilayer film (PAH capped) a) in the dry state prior to exposure to a salt solution b) in the dry state after exposure to a solution of 0.1 M LiCl with a solvent mix of 92:8 (H₂O:D₂O) and c) in the dry state after exposure to H₂O. The data are offset for clarity.



Figure 4.14 SLD profile for a dry multilayer film (PAH capped). The solid line is the SLD profile of the film prior to exposure to a salt solution. The dashed line is the SLD profile of the film that was dried after exposure to a 0.1 M LiCl solution and the open symbols is the dry SLD profile of the film after it was exposed to water.



Figure 4.15 Ion distribution in a dry multilayer film (PAH capped). The solid line represents the ion distribution (LiCl) through the multilayer film. The diffusion of LiCl ions from the film into MilliQ water is represented by the dashed line

profile and the scattering length of LiCl). In the bulk region of the film (700 Å from the substrate) the number of ions per repeat unit was determined to be 1.13. After exposure to water the SLD profile decreased, which suggests that LiCl ions diffused out of the film into solution. However, the extent of the salt ion diffusion out of the film was not 100% as indicated by the slightly higher SLD in the bulk region of the film relative to the original dry film SLD. In addition, the diffusion of the salt ions out of the film did not affect the SLD near the substrate and suggests that the affinity of the salt ions to the polymer chains in this region of the film is strong. The diffusion of LiCl ions from the film is shown in Figure 4.15 (dashed line) as inferred by the difference between the SLD profiles of the dry film after exposure to a 0.1M LiCl solution and water. This clearly indicates that the diffusion of the salt ions primarily occurs in the bulk and outer region of the polyelectrolyte multilayer film. The number of ions that have diffused out of the film in the bulk region (700 Å from the substrate) was determined to be 0.77 per segment, which corresponds to a depletion of $\sim 68\%$.

The effect of the identity of the capping layer is evident in Figure 4.16, where the film assembled with an additional layer (PAH capped). The resulting SLD profile under null solvent conditions where only the polymer and salt ions contribute to the reflectivity data reveals an increase in the SLD near the substrate. This increase in the SLD profile



Figure 4.16 a) Neutron reflectivity data (error bars are within the size of the symbols) and fit (solid continuous line) for a multilayer film (PAH capped) exposed to a solution of 0.1 M LiCl with a solvent mixture of 92:8 ($H_2O:D_2O$), b) the corresponding SLD profile.

near the substrate indicates that more ions are present which is consistent with previous arguments presented in this discussion. However, there is an increase in the SLD near the free surface of the film which is also apparent in the dry profile (Figures 4.14 and 4.15).

It is possible that this increase in the SLD near the free surface is due to the association of CI^{-} ions with the free amine groups of the PAH layer capping layer. Chloride has a very large scattering length (9.58 fm), in comparison to lithium (-1.9 fm) and sodium (3.63 fm), and can be easily differentiated at the surface of the film. It is therefore conceivable that the relatively low scattering length of the cations used in this study would not be easily differentiated near the free surface of the PAA capped films.

In a case where ions of type A are then replaced by ions of type B, there are four scenarios to consider. Firstly, there is the simple assumption that the type A salt ions, for instance Na⁺ and Cl⁻ can displace the other type B salt ions (Li⁺ and Cl⁻) in the film. Secondly, there is the possibility that there is an incomplete exchange of the type B salt ions and some residual type A salt ions that remain in the film. The third scenario is that the multilayer film has a different affinity for different types of salts, i.e. the film may have a greater affinity for type A ions versus type B ions. Finally, there is the possibility of a non-stoichiometric inclusion in the film, where one type of counterion (either the positive or negative species) will preferentially associate in the multilayer film. The experimental evidence shown here suggests that scenario two is unlikely, since ion exchange was seen with the multilayer system irrespective of what order of salt solutions were used. The third possibility is also unlikely since the water distribution in the film is apparently unaffected by the type of cation used, however, the degree of diffusion is affected by salt concentration. Calculating an inferred swollen SLD from a dry film (prior to salt solution exposure, Figure 4.14) gives values in the bulk region that are much higher $6.7 \times 10^{-7} \text{ Å}^{-2}$ than those obtained experimentally when exposed to salt solutions (Figure 4.16, SLD = $5.2 \times 10^{-6} \text{ Å}^{-2}$). For this to be possible there would have to be more Li⁺ incorporated into the bulk of the multilayer. The SLD value in the bulk region of the

film is lower than for the films assembled without a PAH capping layer. It is therefore more likely that there is a non-stoichiometric diffusion that occurs. Under the assembly conditions, PAH is fully charged and PAA is partially charged. It is therefore possible that as the salt ions diffuse into the film, more lithium ions will associate with the free carboxylic acid groups in the film. This would lead to the apparent decrease in the SLD in the bulk region of the film. Previous studies on this system suggest that the film is more dense near the substrate than in the bulk region of the film.¹⁴ It is well known that the film morphology near the substrate can be quite different than the bulk, so it is not at all inconceivable that substrate effects may induce the film to form a stoichiometry close to 1:1 near the substrate. This type of film structure, mimicking a strong polyelectrolyte multilayer, might facilitate a stoichiometry of counterions with a ratio of more Cl⁻ that extrinsically compensates the charges then in the bulk region. This would explain the increase in the SLD near the substrate relative to the bulk region of the film; whereas the increase at the diffuse surface is due to the presence of Cl⁻ ions.

The distribution of ions in films assembled in the presence of salt was also investigated. Figure 4.17 shows the dry neutron reflectivity data and fits for an assembly pH = 3.5 PAA/PAH multilayer film assembled with 0.2 M NaCl before and after exposure to a solution of 0.2 M LiCl in pure D₂O. The overall SLD of the dry film assembled with 0.2 M NaCl (Figure 4.18) is greater than those that were not assembled in the presence of salt. This increase in the SLD is due to the high scattering length of Cl⁻ (9.58 fm) and Na⁺ (3.63 fm) ions that extrinsically compensate the multilayer film. Furthermore, the region near the substrate of the film has a higher SLD than the bulk region and suggests that salt ions preferentially localize near the substrate of the film.



Figure 4.17 a) Neutron reflectivity data (error bars are within the size of the symbols) and fit (solid continuous line) for assembly pH = 3.5 PAA/PAH multilayer film assembled with 0.2 M NaCl. a) dry film prior to exposure to salt solutions, b) dry film after exposure to 0.2 M NaCl and 0.2 M LiCl 100% D₂O content. The data are offset for clarity.



Figure 4.18 SLD profile for a dry assembly pH = 3.5 PAA/PAH multilayer film assembled with 0.2 M NaCl. The solid line is the SLD profile of the film prior to exposure to a salt solution. The open symbol is the SLD profile of the film that was dried after exposure to a 0.2 M NaCl and 0.2 M LiCl solution.

This was also observed with films that were assembled salt-free where the film was exposed to salt solutions post assembly and suggests that this phenomenon of salt localization near the substrate is inherent to the polyelectrolyte system investigated. After exposure to a solution of 0.2 M LiCl in pure D_2O , the dry SLD of the film decreased in the bulk and near the substrate regions of the film. This suggests that the sodium ions that were originally incorporated into the multilayer have been displaced by the lithium ions. The amount of Na⁺ displaced by Li⁺ ions per repeat unit was determined to be 1.02 in the bulk region of the film (500 Å from the substrate) and 2.28 near the substrate (100 Å from the substrate).

4.4 CONCLUSIONS

Neutron reflectivity experiments have provided a means to examine the water and counterion distribution in weak polyelectrolyte multilayer films. It is evident that exposing the films to a pH above or below that of the rinse bath results in an enhancement of water permeation. An increase in water penetration into the films was also observed with films exposed to salt solutions. The water content in the film increases with increasing salt concentration. It is apparent that the water localizes asymmetrically in the film, and predominantly segregates near the substrate, which is contrary to the distribution seen with salt-free solutions. This water localization and hence the increased salt content near the substrate region of the film manifests itself in the dry film profiles, where an increase of the salt ions near the substrate region is observed. The capping layer strongly influences the ion distribution in the film, however, an enhanced ion content is still observed near the substrate. Films assembled with salt also exhibited an increased salt ion content near the substrate. This suggests that the pronounced increase of the counterions near the substrate as observed in films exposed to salt solutions is an inherent property of the PEM system investigated.

4.5 REFERENCES

- (1) Decher, G. Science **1997**, 277, 1232.
- (2) Shiratori, S. S.; Rubner, M. F. *Macromolecules* **2000**, *33*, 4213.
- (3) Lee, S.-H.; Kumar, J.; Tripathy, S. K. *Langmuir* **2000**, *16*, 10482.
- (4) Dai, J.; Jensen, A. W.; Mohanty, D. K.; Erndt, J.; Bruening, M. L. *Langmuir* **2001**, *17*, 931.
- (5) Zhai, L.; Nolte, A. J.; Cohen, R. E.; Rubner, M. F. *Macromolecules* **2004**, *37*, 6113.
- (6) Nolte, A. J.; Rubner, M. F.; Cohen, R. E. *Langmuir* **2004**, *20*, 3304.
- (7) Dai, J.; Balachandra, A. M.; Lee, J. I.; Bruening, M. L. *Macromolecules* 2002, 35, 3164.
- (8) Jin, W.; Toutianoush, A.; Tieke, B. Langmuir 2003, 19, 2550.
- (9) Miller, M. D.; Bruening, M. L. *Langmuir* **2004**, *20*, 11545.
- (10) Shi, X.; Caruso, F. Langmuir 2001, 17, 2036.
- (11) Sukhorukov, G. B.; Antipov, A. A.; Voigt, A.; Donath, E.; Moehwald, H. *Macromol. Rapid Commun.* **2001**, *22*, 44.
- (12) Chung, A. J.; Rubner, M. F. Langmuir 2002, 18, 1176.
- (13) Nolan, C., M.; Serpe, M., J.; Lyon, L. A. Biomacromolecules 2004, 5, 1940.
- (14) Tanchak, O. M.; Yager, K. G.; Fritzsche, H.; Harroun, T.; Katsaras, J.; Barrett, C. J. Langmuir 2006, 22, 5137.
- (15) Tanchak, O. M.; Barrett, C. J. Chem. Mater. 2004, 16, 2734.
- (16) Schmitt, J.; Gruenewald, T.; Decher, G.; Pershan, P. S.; Kjaer, K.; Loesche, M. *Macromolecules* **1993**, *26*, 7058.

- (17) Fery, A.; Schoeler, B.; Cassagneau, T.; Caruso, F. Langmuir 2001, 17, 3779.
- (18) Laurent, D.; Schlenoff, J. B. Langmuir 1997, 13, 1552.
- (19) Riegler, H.; Essler, F. Langmuir 2002, 18, 6694.
- (20) Prabhu, V. M.; Vogt, B. D.; Wu, W.; Douglas, J. F.; Lin, E. K.; Satija, S. K.; Goldfarb, D. L.; Ito, H. *Langmuir* **2005**, *21*, 6647.
- (21) Yoo, D.; Shiratori, S. S.; Rubner, M. F. Macromolecules 1998, 31, 4309.
- (22) Harroun, T. A.; Fritzsche, H.; Watson, M. J.; Yager, K. G.; Tanchak, O. M.; Barrett, C. J.; Katsaras, J. *Rev. Sci. Instrum.* **2005**, *76*, 065101/1.
- (23) Parratt, L. G. Physical Review 1954, 95, 359.
- (24) Burke, S. E.; Barrett, C. J. Langmuir 2003, 19, 3297.
- (25) Dubas, S. T.; Schlenoff, J. B. Langmuir 2001, 17, 7725.

4.6 SUPPLEMENTAL SECTION



Figure 4.1S Neutron reflectivity data (error bars are within the size of the symbols) and fit (solid continuous line) for dry multilayer films used in the pD series (Figures 4.1 and 4.2). a) prior to being exposed to bulk D_2O with a pD of 5.5, b) prior to being exposed to bulk D_2O with a pD of 7.0, and c) prior to being exposed to bulk D_2O with a pD of 3.0 and 8.0. The corresponding SLD profile of the model is shown in the inset.



Figure 4.2S Neutron reflectivity data (error bars are within the size of the symbols) and fit (solid continuous line) for a multilayer film a) exposed to bulk water with a solvent mix of 92:8 ($H_2O:D_2O$), b) exposed to a solution of 0.1 M NaCl with a solvent mix of 92:8 ($H_2O:D_2O$), and c) exposed to a solution of 0.2 M NaCl with a solvent mix of 92:8 ($H_2O:D_2O$). The corresponding SLD profile of the model is shown in the inset.

Chapter 5

Light-Induced Reversible Volume Changes in Thin Films of Azo Polymers: The Photo-Mechanical Effect

In the preceding chapters, the swelling kinetics, water and counterion distribution was investigated for the PAH/PAA multilayer system. It was found that the water distribution in the film was highly affected by solution pH and salt content. From these extensive investigations, a thorough understanding of the response of these systems to external stimuli was obtained. In this chapter, we explore the photochemically induced expansion of thin polymer films that contain the azobenzene chromophore and polyelectrolytes. This fundamental study on the photomechanical effect was conducted on poly-Disperse Red 1 acrylate (PDR1A) and copolymers containing the polyelectrolyte acrylic acid. Factors such as azobenzene content, film thickness, and isomerization power were investigated. This study gives insight to the formation of surface relief gratings and supports an isomerization pressure mechanism. In addition, these studies may help in the development of novel biocompatible photo-responsive materials that utilize the L-b-L technique, the hydration properties of polyelectrolytes and the photochemical properties of azobenzene.

5.1 INTRODUCTION

Thin films of azobenzene (azo) containing polymers have many potential applications as photoactive materials for micropatterning,¹ reversible optical storage,^{2,3} and as sensors,⁴⁻⁷ based on the light-activated interconversion between the two geometrical isomers. The photochemical *trans* to *cis* isomerization and the thermal or

Reprinted with permission from *Macromolecules* 2005, *38*, 10566-10570. Copyright 2005 American Chemical Society. 143

photochemical back conversion to the energetically favoured trans isomer are wellstudied phenomena.^{8,9} The photo-induced *trans-cis* isomerization generally takes picoseconds to milliseconds to complete in solution,^{10,11} while the thermal relaxation from cis to trans is a slower process that requires tens of seconds to many hours depending on the chromophore,¹² and the nature of the polymer backbone.^{13,14} Although the photochemical trans-to-cis isomerization of azobenzene has been well studied for nearly fifty years,¹⁵ many interesting questions concerning the behavior of polymeric azo systems remain unanswered. For example, spin-cast films of azo polymers have been found to produce surface relief gratings (SRGs) when exposed to interfering laser irradiation,¹⁶⁻¹⁸ whereby the polymer moves across a surface in response to light of certain polarizations. The mechanism of the mass transport well below T_g is still unresolved, but it has been suggested that the formation of SRGs is possibly due to a photo-expansion effect.^{19,20} Recently, similar interest has been given to the photo-deformation properties of other azo thin films, such as studies with free films of azo-polyester which have shown macroscopic deformation upon irradiation with low power circularly polarized light for both amorphous or liquid crystalline polymers.²¹ Lastly, Ikeda and co-workers have also demonstrated a light-induced bending of free standing liquid-crystal network azo films, whereby light impinging on the surface causes the material to bend and curl along the polarization director, relaxing back to flat when the *cis* to *trans* back isomerization is activated at a different weavelength.^{22,23} Despite some similarities to previous observations of photochemically induced free volume changes in azo films measured by ellipsometry,²⁴ or by total attenuated reflection,^{25,26} no current explanation for a mechanical force at the molecular level exists for the phenomena of both SRG photoinscription and LC film curling. In addition to any fundamental insight to be gained from a detailed study of this effect, an understanding of the photo-expansion behavior of these azo polymer systems might provide development of some interesting applications based on this piezoelectric-like response, such as photo-actuation or artificial muscles. In this paper, we use null-ellipsometry to confirm a photo-mechanical response in azo polymers directly for the first time, and then characterize this photo-mechanical effect for thin films poly-Disperse Red 1 acrylate (PDR1A) and copolymers of acrylic acid (AA) with varying dye content, under various irradiation conditions and film thicknesses. In addition to providing a thorough characterization of the photo-mechanical effect for development of future photo-mechanical materials, this work also allows insight into the previously unresolved mechanisms of light-activated material response, such as LC film bending, and the mass transport effect of SRG formation.

5.2 EXPERIMENTAL SECTION

5.2.1 MATERIALS

A co-polymer series of poly-Disperse Red 1 acrylate (PDR1A) and acrylic acid (AA) as shown in Figure 5.1, was synthesised by free radical polymerization.²⁷ Thin films of PDR1A and co-polymers were prepared by spin-coating (1300 RPM) from solutions made from distilled tetrahydrofuran onto polished <100> silicon wafers. The films were annealed under vacuum for 8 hours at 110°C.



Figure 5.1 Chemical structure of poly(DR1A-co-AA) where n = 1, 0.35 and 0.05

5.2.2 PHOTO-EXPANSION

The thickness and refractive index changes of the azo-films were measured using a Multiskop single wavelength (633 nm) null-ellipsometer (Optrel, Germany) at a fixed angle of incidence (70°). Although the He-Ne laser of the measuring beam is far from the absorption maximum of PDR1A, the power was attenuated by a 2.0 O.D. filter to further minimize any induced photo-orientation during the measurements. The irradiation (pump) beam at $\lambda = 514$ nm was obtained from an Ar⁺ ion laser. The beam was expanded to a diameter of 5.0 mm with a series of lenses in order to ensure that the probe beam crosssection (2.3 mm) was completely irradiated. The pump beam was arranged to be incident normal to the plane of the film and so that the pump beam coincides with the rotational axis of the goniometer. The pump beam was circularized with a quarter wave-plate to ensure that no in-plane photo-alignment of the azo-chromophore occurred. The power of the pump beam (0.7-215 mW/cm^2) was varied by attenuation with neutral density absorbance filters.

5.3 RESULTS AND DISCUSSION

Isomerization was induced in amorphous films of the azo copolymers by brief irradiation with the pump beam, and the corresponding change in film thickness was measured. The *trans-cis* conversion is depicted in Figure 5.2, as well as a schematic representation of the resulting photo-expansion response. As depicted, the isomerization of the initially all *trans* state azo film leads to an initial irreversible expansion of the film when irradiated to the *cis*-rich photostationary state. Following the thermal *cis-trans*



Figure 5.2 An illustration of photochemical induced *trans* to *cis* isomerization of azobenzene and a schematic representation of the photo-expansion effect in poly(DR1A-co-AA) thin films where the thickness d' > d'' > d.

relaxation the film contracts, and upon further irradiation the film expands again, this time reversibly. A typical photo-expansion cycle profile of PDR1A is shown in Figures 5.3 and 5.4.



Figure 5.3 Typical initial expansion and relaxation curve for 100 mol % PDR1A with a 30s pump beam irradiation at 514 nm with a beam intensity of 207 mW/cm², showing a saturation of thickness increase in the first pump cycle, and a relaxation in the dark.

Upon irradiation for 30 seconds with circularly polarized light, an initial increase in film thickness of 3% was observed, with a corresponding decrease in refractive index, but this increase in thickness was not observed to be fully reversible on relaxation. Subsequent photo-expansion is reversible however, as presented in Figure 5.4, along with the associated decrease in refractive index observed during the irradiation cycle. This refractive index decrease does not mirror the thickness increase exactly, because the irradiated material now contains a mixture of *cis* and *trans* isomers which possess different refractive indices. The time-scales required to reach saturation of the initial expansion are on the order of many tens of seconds to many tens of minutes depending on pump beam power. These time scales are significantly longer than the photochemically induced *trans-cis* isomerization of the azo-polymer in pump-relaxation experiments which typically require under a few seconds to reach saturation. At low power, the expansion grows over time more slowly, but eventually reaches the same extent of expansion obtained at high power. Since the saturation time depends on irradiation power, there is strong suggestion that it is the *trans-cis* cycling that drives the expansion of the film.



Figure 5.4 Typical reversible expansion and relaxation curve for 100 mol % PDR1A, with three 30s pump cycles irradiated at 514 nm with a beam intensity of 207 mW/cm² a) indicating the % maximum and % reversible expansion for the first three pump cycles b) corresponding refractive index change.

Azo isomerization alone has been shown to be on the order of microseconds or faster, and has a high quantum yield, so in principle a brief irradiation of this timescale should be sufficient to cause expansion in the film. Irradiations of one second duration at a power of $\sim 200 \text{mW/cm}^2$ were observed to induce a measurable photo-mechanical

response, though less than saturation, and the effect achieves more then 90% of its saturation of thickness change after 10 seconds of exposure. Although most of the characterization shown here used 30 second exposures to reach saturation, azo polymers exhibit sufficient response on shorter time scales to act as photo-induced actuators for some applications. Following a ten-minute period where the azo-polymer was allowed to thermally relax with *cis-trans* thermal isomerization, the film was then irradiated again and expanded to an extent of 1.3% relative to the relaxation thickness. With repeated irradiation cycles, the extent of photo-induced expansion remained constant with a reversible expansion of $\sim 1.3\%$. To ensure that upon isomerization the pump beam did not induce a significant orientation of the chromophores and hence the corresponding birefringence be misinterpreted as thickness change, studies were also conducted with an integrating sphere. This served to completely depolarize the pump beam, but the same expansion profiles with refractive index conserved were observed. This indicated that the azo-polymer chromophores remained unoriented when irradiated with circularly polarized light and thus did not interfere with ellipsometeric measurements, which assume an isotropic sample. Furthermore, birefringence was not observed in irradiated regions, measured through usual techniques.⁹

The initial non-reversible expansion of the film is due to a rapid *trans-cis* cycling that occurs during isomerization. Although 100 mol % PDR1A has a T_g of approximately 95 °C, the rapid *trans-cis-trans* cycling likely also has a softening effect on the film, enhancing the photo-mechanical effect. Recently, Mechau et al. have shown a small change in the elasticity of an azo-film due to a photo-induced mechanical softening effect.^{28,29} The relatively long times required to reach maximum thickness imply that azo chromophores would undergo a large number of these *trans-cis-trans* cycles. It is

proposed that this *trans-cis-trans* cycling requires an increase in the free volume of the polymer matrix, because of the change in shape requirements between the trans and cis geometries, the local movement of the azo moieties, and the concomitant segmental motion of the polymer chains. These effects result in the observed increase in thickness and a reduction in the refractive index of the film, and when the pump beam was turned off, the film thermally relaxed as expected. The original film thickness however was not fully recovered after the first cycle, suggesting that the some of the photochemically induced free volume increase remains trapped in the polymer matrix. Similar findings were observed in azo-PMMA systems using a quartz crystal microbalance, where some of the free volume change induced by *trans-cis* isomerization was captured irreversibly in the film.⁴ In our materials however, when the film was heated above T_g in an attempt to recover the initial pre-irradiation film thickness, the resulting thickness after heatingcooling was 3.5% thinner than initial. This decrease in the irradiated film thickness above T_g may be due to a more efficient molecular packing achieved through the isomer cycling, or also to the formation of density gradients in the film, as reported previously.³⁰⁻³² It is clear however that the thermal *cis-trans* relaxation alone is not as effective in re-packing the polymer chains to their initial density as is heating the film above the glass transition temperature.

With repeated irradiation cycles the film expanded reversibly. After the first irradiation cycle, the free volume of the polymer matrix has reorganized and increased to its maximum, and the subsequent reversible expansion appears simply as an elastomeric response of the polymer matrix to light, through rapid *trans-cis-trans* cycling on irradiation. When the pump beam is turned off, the film undergoes *cis-trans* relaxation and the matrix deforms back reversibly. The timescale of this mechanical relaxation is at

least an order of magnitude slower than the thermal *cis-trans* relaxation rate, suggesting that a slow material relaxation dominates after the chromophores have reverted back to the *trans* form in the dark. The relaxation profiles were fit to a first order decay and rate constants were found to be independent of the pump beam power, with a mean value of $0.006 \pm 0.001 \text{ s}^{-1}$, while typical *cis-trans* relaxation rate constants for PDR1A were measured to be approximately 0.24 s^{-1} .¹⁴ This would suggest that the reversible relaxation component is largely regulated by the polymer matrix, and is not by the thermal relaxation of the *cis* fraction.

Similar photo-expansion measurements were then conducted varying the azo chromophore content of the polymer, the intensity of the pump beam, and the film thickness. The thickness dependence of PDR1A on the extent of expansion is shown in Figure 5.5. As depicted, the overall extent of thickness increase for the homopolymer and the 35 mol % copolymer is 10 Å in thin films (of ~ 250 Å). As the film thickness is increased the overall extent of expansion and saturates at ~23 Å in the thicker films in the range of ~ 1200-1500 Å. The 5 mol % PDR1A showed no discernable change in film thickness when irradiated. The similar extent of expansion for the homopolymer and the 35 mol % PDR1A-co-AA as well as the zero extent of expansion of the 5 mol % PDR1Aco-AA can be attributed to the volume fraction of the azo moieties in the matrix. Even though the mol fractions appear quite different, the 35 mol % PDR1A occupies a volume fraction of ~ 70 % azo in the material which provided a similar extent of expansion to that of the homopolymer, regardless of film thickness. However, the 5 mol % PDR1A copolymer has a volume fraction of only ~ 20 %, and appears to be below a critical azo threshold to efficiently facilitate the movement of polymer backbone and hence no thickness increase in the film was observed. This dependence on the azo content is nonlinear and suggests that a critical minimum concentration is required for a cooperative motion of the azo molecules to induce deformation of polymer matrix.



Figure 5.5 Thickness study for 100%, 35% and 5 mol % copolymers irradiated at 514 nm (210 mW/cm^2) . a) The maximum extent of thickness increase obtained during irradiation, and b) 30 s isomerization cycles following a 10 min relaxation showing % maximum and reversible expansion b). The closed symbols \bullet , \blacktriangle and \blacklozenge correspond to the maximum expansion of the first cycle for 100, 35 and 5 mol % PDR1A respectively. The open symbols correspond to the reversible expansion.

The homopolymer and the 35 mol % PDR1A-co-AA both exhibited a decrease in the extent of relative expansion as film thickness is increased for both the maximum (from 4-1.5%) and reversible components (from 1.5-0.5%) as shown in Figure 5.5 b). The 100 mol% and 35 mol% PDR1A-co-AA films both had a similar relative extent of expansion over the thickness range studied. The apparent decrease in the relative extent of expansion with increasing film thickness of the 100 mol% and 35 mol% PDR1A-coAA polymers is likely due to the extinction of the incoming pump beam near the free surface of the highly-absorbing films. The molar absorptivity of the homopolymer was determined to be $\sim 4.3 \ \mu m^{-1}$ at 514 nm, which implies that for a film that is $\sim 1500 \ \text{Å}$ thick, only $\sim 30 \ \%$ of the incident light will reach the substrate, whereas in a thin film of 250 Å more than 80% of the light will reach the bottom of the film. Therefore, thicker films expand to a lesser relative extent than thinner films due to a lower effective irradiation intensity near the substrate than at the exposed surface, which also implies that this observed expansion is in fact in the form of a gradient through the film, normal to the incident light.

The extent of reversible expansion of 100 mol % PDR1A versus the irradiation power is presented in Figure 5.6. At low pump beam power (0.7 mW/cm²) the film expanded to ~ 0.1% reversible and saturated to ~ 1.2 % at ~90 mW/cm². Above an irradiation intensity of ~90 mW/cm² the extent of reversible photo-expansion appears constant. At low irradiation power, a measurable but smaller change in expansion can be induced, as the chromophores would be expected to suffer a reduction in the number of azo groups able to isomerize. This is due to the dominance of the thermal *cis-trans* conversion at low power, which reduces the *cis* population in the photostationary state, and results in a low extent of expansion. At higher irradiation intensities the *trans-cistrans* isomerization process would be expected to become more efficient and hence the film expands to a greater extent, also as observed. Thus the reversible component can be attributed to the geometrical changes of the azo molecules during the irradiation and is dependent on the *cis* fraction in the film, whereas the irreversible expansion is dependent only on the *trans-cis-trans* cycling to induce a free volume change in the film. This behavior is comparable to that of the thickness dependence study, where a reduction in intensity occurs when the pump laser passes through the highly absorbing film.



Figure 5.6 Pump laser power dependence on the extent of reversible expansion for a 220 Å, 100 mol % PDR1A irradiated at 514 nm.

This demonstration of a photo-mechanical effect that varies with irradiation intensity and azo content implies that this is a phenomenon general to all thin films of azobenzene polymers above a certain azo content. This study also suggests that previously observed light-induced mechanical changes (such as SRG formation) are probably due to this photo-mechanical effect, including a previously postulated rationalization of an isomerization pressure mechanism for SRG formation.^{18,19} This proposed mechanism relies on the formation of a free volume pocket around the azo molecules, which results in a mechanical pressure exerted on neighbouring polymer chains in regions of high light intensity. The pressure gradient that is formed by a corresponding interfering light gradient then drives plastic flow of the polymer to regions of low light intensity, and requires only a few % expansion with light for this to occur, similar to the range of the effect measured here directly.^{19,20} The photo-mechanical effect

could now be considered sufficient to drive a pressure type mechanism in the formation of SRGs, and other light-driven mechanical systems fashioned with azo polymers.

5.4 CONCLUSIONS

A photo-mechanical effect was observed in thin films of azo polymers, whereby light produces a reversible increase in thickness, and corresponding decrease in refractive index. The initial photo-expansion of PDR1A films is not fully reversible, but subsequent irradiation cycles exhibit a completely reversible expansion over many cycles. We have demonstrated that the relative extent of expansion of PDR1-co-AA copolymers can be controlled through film thickness, and by varying the pump beam intensity or duration. The response of the polymer matrix appears to govern the relaxation rate of the polymers in the dark, and not the thermal back isomerization. Low power irradiation is sufficient in producing a photo-mechanical response in the azo films and in principle these polymers could be developed as photo-induced actuators. This photo-mechanical effect appears to be of sufficient magnitude to explain some previously observed light-activated mechanical changes in similar materials, such as a pressure type mechanism being responsible for the formation of SRGs in azo films.

5.5 REFERENCES

- (1) Noel, S.; Batalla, E.; Rochon, P. J Mater Res 1996, 11, 865.
- Dhanabalan, A.; Dos Santos Jr., D. S.; Mendonça, C. R.; Misoguti, L.; Balogh, D. T.; Giacometti, J. A.; Zilio, S. C.; Oliveira Jr., O. N. Langmuir 1999, 15, 4560.
- (3) Hagen, R.; Bieringer, T. Adv. Mater. 2001, 13, 1805.

- (4) Srikhirin, T.; Laschitsch, A.; Neher, D.; Johannsmann, D. Appl. Phys. Lett. 2000, 77, 963.
- (5) Bredenbeck, J.; Helbing, J.; Behrendt, R.; Renner, C.; Moroder, L.; Wachtveitl, J.; Hamm, P. J. Phys. Chem. B 2003, 107, 8654.
- (6) Uznanski, P.; Pecherz, J. J. Appl. Polym. Sci. 2002, 86, 1459.
- (7) Kleideiter, G.; Sekkat, Z.; Kreiter, M.; Lechner, M. D.; Knoll, W. J. Mol. Struct. **2000**, *521*, 167.
- (8) Natansohn, A.; Rochon, P. Adv. Mater. 1999, 11, 1387.
- (9) Natansohn, A.; Rochon, P. Chem. Rev. 2002, 102, 4139.
- (10) Kobayashi, T.; Degenkolb, E. O.; Rentzepis, P. M. J. Phys. Chem. 1979, 83, 2431.
- (11) Lednev, I. K.; Ye, T.-Q.; Hester, R. E.; Moore, J. N. J. Phys. Chem. 1996, 100, 13338.
- (12) Rau, H. In *Photochemistry and Photophysics*; Rebek, J., Ed.; CRC Press: Boca Raton, FL, 1990; Vol. 2, pp 119-141.
- (13) Paik, C. S.; Morawetz, H. Macromolecules 1972, 5, 171.
- (14) Barrett, C.; Natansohn, A.; Rochon, P. Chem. Mater. 1995, 7, 899.
- (15) Birnbaum, P. P.; Style, D. W. G. Trans. Faraday Soc. 1954, 50, 1192.
- (16) Rochon, P.; Batalla, E.; Natansohn, A. Appl. Phys. Lett. 1995, 66, 136.
- (17) Kim, D. Y.; Tripathy, S. K.; Li, L.; Kumar, J. Appl. Phys. Lett. 1995, 66, 1166.
- (18) Yager, K. G.; Barrett, C. J. Curr. Opin. Solid State Mater. Sci. 2001, 5, 487.
- (19) Barrett, C. J.; Natansohn, A. L.; Rochon, P. L. J. Phys. Chem. 1996, 100, 8836.
- (20) Barrett, C. J.; Rochon, P. L.; Natansohn, A. L. J. Chem. Phys. 1998, 109, 1505.
- (21) Bublitz, D.; Helgert, M.; Fleck, B.; Wenke, L.; Hvilsted, S.; Ramanujam, P. S. *Appl. Phys. B: Lasers Opt.* **2000**, *70*, 863.
- (22) Ikeda, T.; Nakano, M.; Yu, Y.; Tsutsumi, O.; Kanazawa, A. Adv. Mater. 2003, 15, 201.
- (23) Yu, Y.; Nakano, M.; Ikeda, T. *Nature* **2003**, *425*, 145.

- (24) Shi, Y.; Steier, W. H.; Yu, L.; Chen, M.; Dalton, L. R. Appl. Phys. Lett. 1991, 58, 1131.
- (25) Sekkat, Z.; Morichere, D.; Dumont, M.; Loucif-Saibi, R.; Delaire, J. A. J. Appl. *Phys.* **1992**, *71*, 1543.
- (26) Ivanov, M.; Todorov, T.; Nikolova, L.; Tomova, N.; Dragostinova, V. Appl. Phys. Lett. **1995**, 66, 2174.
- (27) Ahmad, N.; Barrett, C. J. In Polym. Mater. Sci. Eng., 2001; Vol. 85, p 607.
- (28) Mechau, N.; Neher, D.; Borger, V.; Menzel, H.; Urayama, K. Appl. Phys. Lett. 2002, 81, 4715.
- (29) Mechau, N.; Saphiannikova, M.; Neher, D. Macromolecules 2005, 38, 3894.
- (30) Pietsch, U.; Rochon, P.; Natansohn, A. Adv. Mater. 2000, 12, 1129.
- (31) Geue, T.; Henneberg, O.; Grenzer, J.; Pietsch, U.; Natansohn, A.; Rochon, P.; Finkelstein, K. Coll. Surf. A 2002, 198-200, 31.
- (32) Geue, T. M.; Saphiannikova, M. G.; Henneberg, O.; Pietsch, U.; Rochon, P. L.; Natansohn, A. L. J. Appl. Phys. 2003, 93, 3161.

Conclusions, Contributions to Original Knowledge, and Suggestions for Future Work

6.1 CONCLUSIONS AND CONTRIBUTIONS TO ORIGINAL KNOWLEDGE

Weak polyelectrolyte multilayer systems have many potential applications in membrane separations, drug delivery, and biocompatible surface preparations. Many of the film properties can be controlled by manipulating the charge fraction on the polymer chain. In all of these applications, knowledge of the *in-situ* conformation, swelling extent, and dynamics are crucial. The primary focus of this dissertation is the study of the structural and physical properties of polyelectrolyte multilayers perturbed from ambient conditions to a natural hydrated state, characterized through non-destructive techniques such as ellipsometry and neutron reflectivity. A comprehensive study of the swelling behavior of poly(acrylic acid) (PAA) and poly(allylamine hydrochloride) (PAH) multilayer films is given in chapter 2. The swelling dynamics was investigated in real time by *in-situ* single wavelength null-ellipsometry under a variety of environmental conditions. The swelling rates varied widely (3 to 1800 seconds) depending on the assembly pH of the layers, and on the humidity level that the films were pre-exposed prior to measurement. A reflectivity based off-null ellipsometry technique was implemented to study short time-scale swelling events. The swelling rates for films assembled at a pH of 3.5 were strongly influenced by pre-exposure to humid atmospheres. This was the first comprehensive study to report the unusual effect of humidity on the swelling rates in polyelectrolyte multilayer assemblies. The swelling mechanism was found to be non-Fickian and the swelling rates were predominantly

independent of the bath pH the films were exposed to. The unusual effect of humidity on the swelling rate was investigated further and is reported in chapter 3. Neutron reflectivity experiments were conducted on the PAH/PAA system in the dry sate, after exposure to a variety of relative humidities and to bulk water. By adjusting the scattering length density (SLD) of the solvent (vapor or bulk water) to zero, we were able to resolve the SLD profile of the hydrated PEM without any contributions from the solvent. The films were also exposed to 100% D₂O (vapor and bulk water), from which we were able for the first time to deconvolute the water profile in the PEM. This study revealed that the water distribution in the multilayers is asymmetric where there is higher concentration at the outer part of the film. The study also revealed that the boundary at the polymer/solvent interface is relatively sharp. Both the asymmetric distribution of water vapor within the PEM and the sharp interface suggest that water structures through the film. This water structuring through the film blocks the accessible microchannels in the film and leads to the unusual swelling kinetics observed at higher humidities. In addition, neutron reflectometry was used to probe the influence of pH and salt solutions on water distribution in the PAH/PAA films and this is described in chapter 4. Films were assembled in the presence and in the absence of salt. By taking advantage of the variation of scattering length of the salt ions used, the counterion distribution in the PEMs was determined. The effect of the capping layer on the counterion distribution was also investigated. An enhanced permeation of water into the film was observed when exposed to a pH above or below that of water used to rinse the films during the assembly process. Exposure to salt solutions also increased the water content in the films where the water distributes asymmetrically towards the substrate. A higher salt ion content was observed near the substrate in films assembled in the presence of salt as well as in the cases where films were assembled in the absence of salt but subsequently exposed to salt solutions. The capping layer was found to strongly influence the counterion distribution, in this case a pronounced increase of the salt ion was observed near the substrate and at the polymer/liquid interface. These studies fully characterize the response of the weak PAH/PAA system to external stimuli.

Another goal of this thesis is the study of photo-responsive azobenzene chromophores in polyelectrolyte systems. These studies are key in the development of many technologies as reversible photo-mechanical materials. The photo-expansion of spin-cast thin films of azobenzene containing poly-Disperse Red 1 acrylate (PDR1A) and copolymers containing PAA were characterized for the first time by null-ellipsometry and is presented in chapter 5. The photochemical expansion of the film was found to have an irreversible component during initial isomerization and a reversible component upon subsequent irradiation cycles. The extent of the irreversible expansion, which was found to be dependent on the film thickness, ranged from 1.5% to 4% and 0.6% to 1.6% for the reversible expansion. In addition, the extent of the reversible expansion can be controlled by either varying the duration of the irradiation or by modulating the power. The study provides insight to the formation of surface relief gratings and the short time scales required to induce a mechanical response of the film suggest that the material is suitable for a variety of potential applications such as photo-actuation.

6.2 SUGGESTIONS FOR FUTURE WORK

The polyelectrolyte system studied in this dissertation has some unusual sorption properties. Some industrial applications may require non-aqueous solvents used in processing thin films. It would be of interest to see how this PEM system would interact with other non-aqueous solvents. Experiments using organic solvents in the vapor phase may also provide a further understanding of the structure of the films in response to hydrophobic solvents. Such studies could lead to new systems that can potentially be used as nonspecific chemical sensors.

Another area of research that can be explored is the effect of temperature on the extent of swelling or deswelling in the PEMs. It is probable that these materials may exhibit a lower critical solution temperature (LCST) phase transition, where changes in the film morphology and permeability can be thermally switched. This may lead to applications such as drug delivery vehicles, where the molecule of interest can be loaded into the PEM system and subsequently released under thermal stimulus.

With conventional neutron reflectometry experiments only the reflected intensity is recorded as a function of momentum transfer. It is known that due to the lack of the phase information, analysis of the reflectivity curves is consistent with more than one SLD profile. To circumvent this, an emerging technique, which provides contrast variation using polarized neutrons and a ferromagnetic reference layer could aid future studies on PEM systems.^{1,2} Contrast variation is based on measurements for neutrons polarized in the spin up and in the spin down states and yields a different SLD in each polarization state. The advantage of using polarized neutron beams in conjunction with the ferromagnetic reference layer is that it is possible to obtain both the specular reflection amplitude and the phase angle. Knowledge of the phase angle allows for the unambiguous determination of the SLD profile of the film.

The incorporation of photo-switchable azo chromophores into PEM systems offers a host to a wide array of applications including sensors and actuators. However, the interaction of water, solvents, and temperature on the photo-physical and mechanical properties are complex and require further investigation. Azobenzene is sensitive to its local environment and therefore is responsive to the polyelectrolyte matrix. Studies can be conducted on the effect of humidity on the photo-physical properties of the system such as the photostationary state (quantum yields), surface energy (contact angle) and biocompatibility. The photoexpansion is modest for the systems studied although it may be sufficient to induce changes in surface properties upon irradiation such as roughness, and wettability. Light-induced hydrophobic surfaces may lead to applications requiring easily switched wetting behavior, such as in microfluidics. The changes in surface roughness and wettability may also resolve some of the problems of laminar flow in these devices. Laminar flow may be disrupted photo-chemically using azo polymers and allow for proper mixing of the analytes. Furthermore the facile and robust L-b-L technique makes it stable for coating the thin capillaries of the device. Other properties such as photoinduced surface wettability and biocompatibility changes can also be investigated as a function of relative humidity.

6.3 REFERENCES

- (1) Schreyer, A.; Majkrzak, C. F.; Berk, N. F.; Grull, H.; Han, C. C. J. Phys. Chem. Solids 1999, 60, 1045.
- (2) Grull, H.; Schreyer, A.; Berk, N. F.; Majkrzak, C. F.; Han, C. C. *Europhys. Lett.* **2000**, *50*, 107.