Organic Self-Assembled Films for Nonlinear Optics: Film Structure, Composition and Kinetics of Film Formation

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ABSTRACT

Organic materials exhibiting second-order non-linear optical (NLO) properties are a key to the development of advanced electro-optic (EO) modulators used in fiber-optic communications system. This work addresses the fabrication and characterization of organic materials with NLO properties using a self-assembly approach by alternately dipping a charged substrate into positively and negatively charged polymers to build up layer-by-layer (LbL) films.

The effect of solution pH on the formation of LbL films fabricated using the polycation poly(allylamine hydrochloride) (PAH) and the polyanion poly{1-[p-(3’-carboxy-4’-hydroxyphenylazo)benzenesulfonamido]-1,2-ethandiyl} (PCBS) was studied using a quartz crystal microbalance with dissipation (QCM-D) monitoring, ellipsometry, absorbance, and second harmonic generation (SHG) measurements. PCBS has an azo-benzene chromophore side group that, when sufficiently oriented, results in measurable SHG. Films of PAH/PCBS fabricated at neutral pH where both PAH and PCBS are highly charged led to thin bilayers, ~1 nm, with a 1:1 molar ratio of PCBS:PAH. This molar ratio was found to be important for long-range polar ordering of PCBS in these films. Increasing the rate of convection was found to reduce the time required for complete adsorption of the polyion. This can have a significant impact on fabrication of films with high bilayer numbers.

A variation of the above technique, which involves adsorbing one of the constituents electrostatically and another covalently, was studied using PAH and a reactive dye, Procion Brown (PB), which has a significantly higher hyperpolarizability than PCBS. It was found that a high pH, ~10.5, was important for achieving covalent attachment of the PB to the underlying PAH films. This resulted in much higher SHG
intensities compared to when PB was deposited pH at 8.5-9.5 where the attachment of PB was due to a combination of electrostatic and covalent interactions. QCM-D results for PAH/PB films revealed the presence of a high percentage of unreacted amine groups in the underlying PAH film. A rate constant value for PB attachment step to the underlying PAH was also calculated.

To enhance the SHG intensity of these films, silver nanoprisms were synthesized and deposited onto films using physisorption. An enhancement in the SHG intensity was observed for both PAH/PCBS and PAH/PB films.
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Chapter 1 Introduction

1.1 Motivation

Electro-optic (EO) modulators convert electrical signals to optical signals and thus play an important role in today’s telecommunication network. With an increase in internet traffic worldwide, faster and cheaper EO modulators are needed. The schematic of an electro-optic modulator based on a Mach-Zehnder interferometer\(^1\) is shown in Figure 1.1-1. In this schematic, the unmodulated light enters the device and can be modulated by applying a voltage. A change in voltage across the section with NLO material causes a change in refractive index which causes a phase shift in the optical signals passing through it which leads to light modulation.

![Figure 1.1-1 Schematic of an electro-optic modulator based on Mach-Zehnder interferometer. The unmodulated light enters the device from the left and splits into two beams one of which passes through a section covered with nonlinear optical (NLO) material. A change in voltage across the section with NLO material causes a change in refractive index which causes a phase shift in the optical signals passing through it which leads to light modulation.](image)

State-of-the-art EO modulators employ inorganic crystalline materials such as lithium niobate in the optical waveguide. However, these materials are very expensive to fabricate due to difficulties in fabrication and processing techniques. Organic waveguides offer significant advantages over lithium niobate such as lower cost, much higher data transmission rates, and ease of fabrication. In organic waveguides, highly polarizable chromophores (dye molecules) must be oriented in a polymer film and that orientation
must be maintained for years for effective device operation. Figure 1.1-2 shows a cross-section of Mach-Zehnder interferometer based on organic films.

**Figure 1.1-2** The above figure shows cross-section of Mach-Zehnder interferometer which is covered with organic NLO material. The chromophores should have a net orientation for this material to exhibit nonlinear optical (NLO) properties and this net orientation should be maintained for years for effective operation of this device.

In organic films the second order nonlinear susceptibility of a NLO film, $\chi^{(2)}$ is directly proportional to the chromophore density and hyperpolarizability as given by the equation:

$$\chi^{(2)} = NF\beta\langle \cos^3 \theta \rangle$$

in which $N$ is the chromophore density, $F$ is the local field factor, $\beta$ is the hyperpolarizability and $\theta$ is the orientation angle of the chromophores. Rational design thus involves choosing a chromophore with a suitably high $\beta$ and incorporating it into a film with high density $N$, and low tilt angle $\theta$.

The EO coefficient of organic films, $r_{33}$ is related to $\chi^{(2)}$ by the following relation,

$$\chi^{(2)} = -\frac{n^4 r_{33}}{2}$$
in which $\chi^{(2)}$ is given by equation (1) and $n$ is the refractive index of the material. Application of a voltage, $E$ across NLO material changes the refractive index of the material given by the equation. 

$$
n = n_0 \left( 1 - \frac{1}{2} n_0^2 r_{33} E \right)
$$

(3)

in which $n_0$ is the refractive index of the material in the absence of any electric field. From Equation 3, higher the $r_{33}$, the higher is the sensitivity of $n$ with the applied electric field, $E$ leading to a better modulation. Thus, the rational design of an electro-optic modulators thus involves a material with high EO coefficient, $r_{33}$.

Based on the above equations, the main requirements of a good NLO organic film are:

- High $\chi^{(2)}$ value or high EO coefficient, $r_{33}$, which is directly proportional to $\chi^{(2)}$.
- The thickness of the organic films should be $\sim$ 1064 nm which is the principal wavelength of communication optical signals.
- These materials should exhibit very high thermal and temporal stability. Typically a long term thermal stability of the order of days for operating temperatures as high as 125°C and short term thermal stability for temperatures approaching 200°C for device fabrication. \(^3\)
- NLO organic films should be optically homogeneous to minimize the scattering losses.
- The processing time to make these films should be of the order of minutes to hours.
- These films should not have a high absorption coefficient at the communication wavelength and at half the communication wavelength. This is to minimize losses due to absorption and second harmonic generation (SHG).

There are three major approaches to make organic EO modulators.

1. Poled (Guest/Host) Polymers
2. Layer-by-layer Self-Assembly
3. Ionically Self-Assembled Multilayer (ISAM)

Each of these is briefly discussed next:

**1.1.1 Poled (Guest/Host) Polymers**

Poled (Guest/Host) polymer films have been intensively studied and consist of an NLO active chromophore (Guest) embedded in a polymer complex (Host). The system is then heated above the glass transition temperature, $T_g$, and an electric field is applied to align the chromophores. The matrix is then quenched to room temperature thus locking the alignment of the chromophores. At present, the lifetime of EO modulators made of poled polymer films is only a few months due to thermally driven disorientation making them impractical for EO modulator applications. A schematic representation of this technique is shown in Figure 1.1-3.

Single and trifunctional dendritic chromophores were synthesized and doped into amorphous polycarbonate samples to study the electro-optic properties of the resulting material. The observed EO coefficients was measured to be 69.6 pm/V. This value is quite high when compared to commercially used EO modulator, lithium niobate, which has an EO coefficient of 32 pm/V. However, these EO coefficients dropped to 16.3 pm/V after cooling in the presence of electric field.
1.1.2 Layer-By-Layer Self-Assembly Technique

A second approach to make organic EO modulators involves layer-by-layer self-assembly technique for fabricating organic thin films by regioselective reaction between two different compounds or by covalently binding two different compounds or via triple hydrogen bonds.6-9 This has been studied extensively by Mark and co-workers.7-9
Long processing times mentioned below and very small thickness of the bilayers are some of the drawbacks of this process. This technique will be discussed in detail in Chapter 2. Siloxane based self-assembly for an electro-optic modulator\textsuperscript{8} was used and polar films consisting of 40 alternating chromophore and capping layers was achieved. The thickness of each bilayer was 3.26 nm and it took approximately 40 minutes to deposit each bilayer. Temporal stability and high reaction time to make these films are some of the drawbacks of this technique.

1.1.3 ISAM approach

The third technique which is the focus of this research involves Ionically self-assembled multilayer (ISAM) films made with polyelectrolytes. ISAM films made with two azobenzene chromophore side groups exhibit remarkable second order nonlinear optical (NLO) susceptibilities and also have unprecedented NLO stability for periods of over two years and at temperatures as high as 150°C.\textsuperscript{10} This temporal and thermal stability far surpasses that reported for all other approaches for making organic EO modulators.

The original ISAM technique was developed by Decher et al..\textsuperscript{11} It has a number of applications in different fields such as integrated molecular optics, electronics, and biosensors.\textsuperscript{12} The ISAM method involves alternate adsorption of polycations and polyanions (or negatively charged chromophores) on a charged surface. The adsorption of a charged polymer on an oppositely charged surface leads to the charge reversal which facilitates the adsorption of next charged polymer. This ISAM process is shown in Figure 1.1-4.

A variation of the ISAM process using films made with a reactive dye such as Procion Brown (PB) is shown in Figure 1.1-5. In this process, PB is attached covalently to the underlying layer of PAH and PAH is electrostatically adsorbed to the underlying layer of PB. The covalent attachment of PB to the underlying layer of PAH aligns the chromophore which gives a net orientation to the chromophores in the bulk material. By
using this technique, chromophores with high hyperpolarizability can be incorporated in ISAM films resulting in films with high $\chi^{(2)}$ or, $r_{33}$.

![Diagram of ISAM film formation process](image)

Figure 1.1-4 Schematic of ISAM film formation process. A negatively charged substrate is dipped into a positively charged polymer which leads to a charge reversal and facilitates the adsorption of negatively charged polymer. This leads to the formation of a bilayer and this process could be continued for any number of bilayers.
Some of the outstanding problems with making ISAM films for practical EO modulator are listed below. These form the basis for the research objectives of this thesis which are described at the end of this chapter.

1. A principal problem in making a practical EO modulator using ISAM films is that the current ISAM process is much too slow. An EO modulator film must be an optically homogeneous waveguide at least 1 micron thick since fiber optic communications typically employ light with a wavelength of ~1000 nm. The ISAM films are formed one bilayer at a time and the bilayer thickness is approximately 1 nm; so an ISAM film for an EO modulator requires the deposition of 1000 bilayers. It takes almost 10 minutes to deposit each bilayer which means that an EO modulator film would require 7 days of continuous fabrication, a period that is too long to be practical. Thus, it is important to dramatically reduce the film fabrication times. It is significant that relatively little is fundamentally known about the kinetics of ISAM film formation. Thus, there is a need to understand what factors most critically affect the time required for film deposition such as convective flow effects, the concentrations...
of polyelectrolytes, ionic strength, pH, and solvent composition in order to have a practical method for making an organic EO modulator waveguide.

There is a general lack of understanding of the kinetics of ISAM film formation process. There is relatively little literature on the kinetics of polymer deposition on surfaces in layer-by-layer fashion using in-situ surface sensitive techniques such as QCM, SPR, reflectometry, ellipsometry. Also, not much is known about some of the mechanical properties of these films such as viscoelasticity and shear modulus.

To understand the kinetics of ISAM film formation, a quartz crystal microbalance (QCM) was used. QCM is an ultra-sensitive mass sensor consisting of a piezoelectric quartz crystal sandwiched between a pair of electrodes. When the electrodes are connected to an oscillator and an AC voltage is applied over the electrodes the quartz crystal starts to oscillate at its resonant frequency due to the piezoelectric effect. If a rigid layer is evenly deposited on one or both sides of the electrodes the resonant frequency will decrease proportionally to the mass of the absorbed layer according to the Sauerbrey equation.13

2. There is still much that is not understood about how ISAM film processing conditions such as pH, concentration of polymers, ionic concentration, dipping time and rinsing time affect the fabrication of optically homogeneous ISAM films, specifically the composition of ISAM films and the chromophore orientation. This could help to make thick organic films for practical organic materials with acceptably low scattering losses.

3. ISAM films exhibit relatively low electro-optic coefficient values (r33 of 14 pm/V for ISAM films14 compared to 30 pm/V for lithium niobate). Thus, there is a need to enhance performance including the need for novel chromophores with high polarizability and the use of surface plasmon effects to increase the electro-optic coefficients of these organic materials.
Surface plasmons are electromagnetic modes that travel along the interface between a metal and a dielectric.\textsuperscript{15-17} This electric field has a maximum value at the interface and decays exponentially into the dielectric over a distance comparable to the wavelength.\textsuperscript{16} Gold and silver nanoparticles are most commonly used to exhibit surface plasmon effects by subjecting them to an external electric field. Therefore, incorporating these nanoparticles into ISAM films might increase the second-order susceptibility by providing a very high local electric field. The intensity of the electric field emitted by surface plasmons are very sensitive to the geometry of the nanoparticles\textsuperscript{18, 19} as well as any coupling to nearby structures.\textsuperscript{20, 21} Surface enhanced Raman spectroscopy (SERS) is based on the same technique to increase the signal from Raman spectroscopy using surface plasmon effects. Today, SERS is a well established technique; however, plasmonic enhancement to increase the NLO properties of organic material involves great challenge to incorporate gold and silver nanoparticles into organic films such that these materials lack global inversion center.

\textbf{1.2 Research Objectives}

The following are the research objectives for the thesis. This research specifically aims to study the fundamental physical chemistry that underlies the alternate adsorption of polymer films that leads to the formation of ISAM layers. These research objectives constitute several sub-goals towards achieving the ultimate goal of making a proto-type electro-optic modulator.

1. Study the formation of thick ISAM films needed for practical electro-optic modulators using:
   (a) conventional dipping techniques
   (b) a custom-built deposition device with potential for minimizing fabrication time

2. Understand the parameters affecting the formation of ISAM films at the molecular level. This includes studies of:
   (a) the structure and composition of polymer-polymer ISAM films
(b) the structure and composition of LbL films comprised of a hybrid polyelectrolyte-reactive dye system
(c) kinetics of film formation including a mass transfer model to understand deposition kinetics

3. Exploring the effects of surface plasmons to enhance the electro-optic coefficient of NLO material by incorporating silver nanoparticles in the ISAM films.

Each of these objectives is discussed in detail below.

**Objective 1(a)** is aimed at fabricating and characterizing thick films exhibiting second order NLO properties for practical electro-optic modulator devices. For this study, the positively charged polycation used was poly(allylamine hydrochloride) (PAH) and the negatively charged polyanion used was poly{1-[p-(3’-carboxy-4’-hydroxyphenylazo)benzenesulfonamido]-1,2-ethanediyl} (PCBS). The PAH/PCBS films are fabricated using two automatic dipping processes and characterized by experimental techniques such as absorbance measurements, ellipsometry, second harmonic generation (SHG) measurements, atomic force microscopy (AFM), and chromophore tilt angle measurements.

**Objective 1(b)** concerns the design and testing of a device to scale up the layer-by-layer deposition process. This study is aimed at fabricating a flow-cell device to deposit layer-by-layer films on top of a substrate. This can potentially help to scale up the layer-by-layer process.

**Objective 2(a)** employs a quartz crystal microbalance (QCM) as a tool for probing the structure and composition of films made with PAH/PCBS. The experiments involved in-situ deposition of the polycation PAH followed by rinsing to remove excess PAH and then deposition of polyanion/dye PCBS followed by rinsing to remove excess PCBS. This procedure was repeated up to 10-15 bilayers (one bilayer consists of a layer of PAH and a layer of PCBS). The change in frequency per bilayer was observed to vary linearly
with increasing number of bilayers. Also, the data obtained was fit using the Voigt model to measure thickness, chromophore density, and water content of the films. The thickness values measured by QCM were compared with thickness measurements from ellipsometry to get an estimate of percentage of water of hydration in these films.

**Objective 2(b)** concerns a study of the effect of pH on the structure and NLO properties of PAH/Procion Brown (PB) dye films. The pH affects both the reactivity of the cationic PAH film with the PB dye and also the conformation of attached PAH chains, a possibly important factor that might affect dye composition and orientation. To accomplish this, experiments were systematically performed; in one set of experiments, the pH of PAH was varied systematically and in the second set of experiments, the pH of PB was varied systematically.

**Objective 2(c)** concerns a study of the kinetics of deposition of the polymer/polymer ISAM and the modified ISAM reactive dye systems. Based on the geometry of the QCM flow cell, a mass transfer theory was developed to estimate a value of mass transfer coefficient. This model was used to study the effect of convection on deposition kinetics of both PAH/PCBS and PAH/PB LbL films.

**Objective 3** concerns an exploration of the use of surface plasmons to enhance SHG effects. This study is aimed at understanding the interactions between the surface plasmon generated by metallic nanoparticles and ISAM films. For this particular study, the metallic particles used were silver nanoparticles triangular in shape. They were incorporated into ISAM films by physisorption to study the enhancement in SHG of these ISAM films.

**1.3 Thesis Outline**

**Chapter 2. Literature Review**

Chapter 2 provides a detailed literature review on nonlinear optics which results in second harmonic generation (SHG) and electro-optic (EO) effects. This is followed by
various techniques such as poled polymers, layer-by-layer self-assembly and ISAM process by which organic films exhibiting nonlinear optical phenomena can be fabricated. It then reviews the effect of deposition conditions such as solution pH, ionic strength, effect of solvent quality on the properties of ISAM films. Mass transfer theories based on the stagnation flow geometry and capillary flow conditions are also reviewed to understand the kinetics of ISAM film formation process. A review of the literature concerning the Quartz Crystal Microbalance (QCM) is also presented which explains the uses of this technique and its limitations. Finally, a literature review on the synthesis of silver nanoprisms is presented.


Chapter 3 addresses the research objective #1(a) mentioned in the previous section. This chapter discusses thick films approaching 1μm in thickness was fabricated by alternately depositing PAH and PCBS on a glass substrate. Linear increase in thickness up to 740 nm was achieved while depositing PAH/PCBS films using ISAM technique while maintaining a linear increase in absorbance and a quadratic increase in second harmonic generation (SHG).22

Chapter 4. A study of film structure and adsorption kinetics of polyelectrolyte multilayer films: effect of pH and polymer concentration

Chapter 3 addresses the research objective #2(a) mentioned in the previous section. It discusses the experimental technique to use the QCM as a tool to study the adsorption of polymer films on silica surface. Uptake in mass by the QCM is reflected by a decrease in frequency, Δf of the QCM and the two are linearly proportional to each other. A linear decrease in frequency was observed with increasing number of bilayers confirming the homogeneous formation of ISAM films. The composition of these films was also obtained by comparing the Δf for PAH versus that of PCBS. The data obtained with the QCM was fit into a Voigt model to obtain the thicknesses of these adsorbed films. The wet thickness values measured by QCM were compared with dry thickness
measurements from ellipsometry to get an estimate of percentage of water of hydration in these films.

**Chapter 5. A Study of Film Formation and Adsorption Kinetics of Polymer/Polymer and Polymer/Dye Films Using QCM**

Chapter 5 addresses research objective #2(c). It discusses the derivation of the mass transfer coefficient, $k_t$ based on the geometry of the QCM flow cell. The $k_t$ of PCBS adsorption step was estimated both theoretically and experimentally as a function of fluid flow rate. For the PB attachment step, a rate constant for the covalent reaction between PB and underlying PAH was calculated.

**Chapter 6. Thick film device based on a flow-cell**

This chapter addresses research objective #1(b); a flow cell device was built to alternately flow the polymer/dye solutions and DI water over a glass substrate. The optical properties of the LbL films fabricated using this device were compared with the optical properties obtained using a conventional dipping device.

**Chapter 7. Effect of pH on the Optical Properties of Hybrid PAH/PB Layer-by-Layer Films**

This chapter addresses research objective #2(b). In this study, the pH of PAH was varied systematically keeping the pH of PB constant. In second set of experiments, pH of PB was varied systematically keeping the pH of PAH constant. This study is aimed at finding the optimum pH conditions for the ISAM deposition process to increase the pot-life of the PB solution.

**Chapter 8. Enhancement of Second Harmonic Generation (SHG) Intensity by Incorporating Silver Nanoprism in Layer-by-Layer Films**

This chapter addresses research objective #3. Silver nanoprism was synthesized using the photochemical synthesis procedure described in the literature. They were physisorbed on top of a PAH terminated PAH/PCBS and PAH/PB LbL films. To study
the SHG enhancement, SHG measurements were taken on bare LbL films and compared with those of LbL films coated with silver nanoprisms.

Chapter 9. Conclusions and Future Work

This chapter summarizes the most significant findings and it also states the future work planned for this project.

1.4 References:


Chapter 2 Literature Review

2.1 Introduction to nonlinear optics

In linear optics, an optical wave traveling through an optical medium can be described by a linear wave equation. Due to this assumption, two harmonic waves in the medium obey the principle of superposition. These waves travel without distortion which can be either due to the medium itself or as a result of the mutual interference of the waves. However, when the light intensity becomes high, linear optics is not enough to describe the situation. With the advent of more intense and coherent light made available by the laser, it is found that optical properties of the medium, such as refractive index, become a function of the intensity of the light. When two or more light waves interfere within the medium, the principle of superposition no longer holds. The light waves interact with one another and with the medium. These nonlinear phenomena require an extension of the linear theory that allows for a nonlinear response of optical materials to the electromagnetic radiation.

Electromagnetic waves create a complex of interactions with the charged particles of the medium when they pass through the medium. The charged particles in the medium experience forces due to the electric field of the waves, motion of the charges and by the magnetic field of the waves. In response to these oscillating fields, the charges themselves oscillate and act as radiators of secondary electromagnetic waves. These oscillations lead to the generation of electric dipole moments, which in turn contribute to the total internal field. Therefore, to determine the net field at some point, the fields of both the source waves and the charged oscillations must be taken into account.

Nonlinear phenomena are due to the inability of the dipoles in the optical medium to respond in a linear fashion to the alternating electric field associated with the light beam. The inner-core electrons are tightly bound to the massive atomic nuclei. Thus the loosely bound outer electrons are primarily responsible for the polarization of the optical medium when subjected to an external electric field. When the oscillations of these
electrons in response to the external field are small, the polarization is proportional to the applied electric field. However, when the intensity of the light or the electric field increases, this proportionality begins to fail. This excites the nonlinear behavior in the optical medium. Another way of exciting nonlinear behavior without using high intensity light is to choose the exciting optical frequency near a resonant frequency of the oscillating dipoles. This technique is widely used in nonlinear spectroscopy and is known as resonance enhancement.1

In recent years, nonlinear optical properties in organic and polymer systems have attracted considerable interest because of their applications in various electronic components like electro-optic modulators which are explained in the next section. The π-electron excitations occurring on the individual molecules or polymer chains are the basic reason for the observed nonlinear optical behavior. To understand the nature of optical nonlinearity, one needs to start from the following Maxwell’s equations:

\[
\nabla \times E = -\frac{1}{c} \frac{\partial B}{\partial t} \tag{1}
\]

\[
\nabla \times B = \frac{1}{c} \frac{\partial E}{\partial t} + \frac{4\pi}{c} j \tag{2}
\]

\[
\nabla \cdot E = 4\pi \rho \tag{3}
\]

\[
\nabla \cdot B = 0 \tag{4}
\]

in which,  
\[E(r,t) = \text{electric field}\]  
\[B(r,t) = \text{magnetic field}\]  
\[\rho = \text{charge density}\]  
\[j = \text{current density}\]
The relation between the charge density, $\rho$ and the current density, $j$ can be easily derived from the Maxwell’s equation as,
\[
\rho = \rho_0 - \nabla \cdot P
\]  
\[
j = j_0 + \frac{\partial P}{\partial t}
\]
in which $\rho_0$ and $j_0$ are the free electric charge and current densities respectively. The electric dipole moment per unit volume is denoted by $P$. In a free medium, there is no free electric charge and current which implies that,
\[
\rho_0 = 0
\]
\[
j_0 = 0
\]
Equation (3) can then be written as,
\[
\nabla \cdot E + 4\pi \nabla \cdot P = 0
\]  
Equation (1) and equation (2) combine to give,
\[
\nabla^2 E - \nabla (\nabla \cdot E) - \frac{\partial^2 E}{c^2 \partial t^2} - \frac{4\pi}{c^2} \frac{\partial^2 P}{\partial t^2} = 0
\]
The relation between $P$ and $E$ can be written as,
\[
P(\omega) = \chi^{(0)} + \chi^{(1)} (-\omega, \omega) E_j(\omega) + \chi^{(2)} (-\omega, \omega_1, \omega_2) E_j(\omega_1) E_k(\omega_2) + ...
\]
in which,
\[
\omega = \omega_1 + \omega_2 + \omega_3 + \omega_4 + ....
\]
\[
\chi^{(0)} = \text{permanent zero-order susceptibility}
\]
\[
\chi^{(1)} = \text{linear susceptibility, often called the polarizability}
\]
All the higher order $\chi^{(n)}(n > 1)$ are the nonlinear optical susceptibilities of the medium.

2.1.1 Second Harmonic Generation

Second harmonic generation (SHG) results from the second-order term in Equation (9).
\[
P^{(2)} = \chi^{(2)} (-\omega, \omega_1, \omega_2) E_j(\omega_1) E_k(\omega_2)
\]
In the above equation, the second-order polarization term is proportional to the square of the electric field. Figure 2.1-1 shows the illustration of polarization as a
function of the electric field for the linear case and the deviation from the linearity due to the higher-order term.

![Figure 2.1-1 Schematic of linear and typical nonlinear response of polarization P to an applied electric field E.](image)

It is an important point to note that the even-order nonlinear susceptibilities only exist in non-centrosymmetric media. In centrosymmetric media, all of the susceptibility tensors are invariant under spatial inversion. The polarization vector, \( P \) and applied field, \( E \) are all polar vectors which do not change sign under spatial inversion operation. This can be inferred directly from equation (9). Let us pick the even-order nonlinear susceptibility and rewrite equation (9) in the following form,

\[
P_i^{(2n)}(\omega) = \chi_{jk...2n}^{2n}(-\omega, \omega_1, \omega_2, \omega_3, \ldots, \omega_{2n})E(\omega_1)E(\omega_2)\ldots E(\omega_{2n})
\]

Under spatial inversion it becomes,

\[
-P_i^{(2n)}(\omega) = \chi_{jk...2n}^{2n}(-\omega, \omega_1, \omega_2, \omega_3, \ldots, \omega_{2n})[-E(\omega_1)][-E(\omega_2)]\ldots [-E(\omega_{2n})]
\]

\[
= (-1)^{2n} \chi_{jk...2n}^{2n}(-\omega, \omega_1, \omega_2, \omega_3, \ldots, \omega_{2n})E(\omega_1)E(\omega_2)\ldots E(\omega_{2n})
\]

\[
= \chi_{jk...2n}^{2n}(-\omega, \omega_1, \omega_2, \omega_3, \ldots, \omega_{2n})E(\omega_1)E(\omega_2)\ldots E(\omega_{2n})
\]

\[
= P_i^{(2n)}(\omega)
\]
This is possible only if \( \chi^{2n}_{ijk\ldots2n}(\omega_1,\omega_2,\omega_3,\ldots,\omega_{2n}) = 0 \). Hence, even order susceptibility is equal to zero in centrosymmetric media. This is true for all even-order susceptibilities.

Quartz crystals and many other crystals as well, do not possess this inversion symmetry. These crystals therefore manifest second harmonic generation.

If the applied field is of the form, \( E = E_0 \cos \omega t \), then the second order polarizability can be written as,

\[
P^{(2)} = \chi^{(2)}_{ijk} E_0^2 \cos^2 \omega t = \chi^{(2)}_{ijk} E_0^2 \left[ \frac{1}{2} (1 + \cos 2\omega t) \right]
\]

The second-order polarization \( P^{(2)} \) consists of two terms as seen in the above equation. The first term is a constant or DC component of the applied optical field. This term is often referred to as optical rectification. The second term in the above equation consists of a term of twice the frequency of the applied optical field. Thus, an optical material exhibiting second-order polarization generates an electromagnetic radiation of frequency twice that of the incident beam.

2.1.2 Electro-optic effect (Pockel’s effect)

The basic equation describing nonlinear behavior was given by equation (9). When an electric field, \( E \) is applied to an electro-optic device, the refractive index varies as given by the equation,

\[
\frac{1}{n^2} = \frac{1}{n_0^2} + rE + RE^2
\]

in which \( r, R \) are the linear and quadratic electro-optic coefficients respectively and \( E \) is the applied DC electric field.

The Pockel’s effect results from the linear term in Equation (13), which upon rearrangement (after ignoring the nonlinear terms) gives the refractive index as a function of applied DC electric field,
This is the basis for electro-optic (EO) modulators which encode electrical signals onto fiber optic transmissions. They have been under development for several years because of their need in high-speed, low drive voltage fiber optic communication links, for high capacity local area networks (LANs), for video transmission, for radiofrequency (and microwave to millimeter wave) distribution and for ultrafast information processing such as analog-to-digital conversion. The voltage required to vary the output from a maximum value to zero is called half-wave voltage \( V_{\pi} \) and for a Mach-Zehnder interferometer architecture (shown in Figure 2.1-2), \( V_{\pi} \) is related to the electro-optic coefficient, \( r \) as, \(^4\)

\[
V_{\pi} = \frac{\lambda h}{n^3 r L \Gamma}
\]  

(15)

Improving the performance of electro-optic modulators depends on decreasing the halfwave voltage, \( V_{\pi} \) because the EO modulator gain is inversely proportional to \( V_{\pi}^2 \) in which \( \lambda \) is the optical wavelength, \( h \) is the gap between electrodes, \( n \) is the index of refraction, \( r \) is the electro-optic coefficient, \( L \) is the interaction length and \( \Gamma \) is the modal overlap integral.

---

Figure 2.1-2 Schematic of an electro-optic modulator based on Mach-Zehnder interferometer. The unmodulated light enters the device from one end and splits into two beams one of which passes through a section covered with nonlinear optical material. A change in voltage across the section with NLO material causes a change in refractive index which causes a phase shift in the optical signals passing through it which leads to light modulation.
Low values of $V_\pi$ can be achieved by adjusting one or several parameters in Equation 15. However, many factors such as reducing gap distance, $h$, or increasing interaction length, $L$, are limited by optical insertion loss and modulation frequency requirements.\textsuperscript{4} For organic electro-optic modulators, the most effective approach for low $V_\pi$ is to increase the EO coefficient $r$, which is directly proportional to the second order nonlinear susceptibility, $\chi^{(2)}$, as given by the equation,

$$\chi^{(2)} = -\frac{n^4r}{2}$$

in which $n$ is the refractive index of the material defined by Equation (14), $r$ is the electro-optic coefficient of the material.

The second order nonlinear susceptibility is directly proportional to the chromophore density and hyperpolarizability as given by the equation,\textsuperscript{5}

$$\chi^{(2)} = N F \beta \langle \cos^3 \theta \rangle$$

in which $N$ is the chromophore density, $F$ is the local field factor, $\beta$ is the hyperpolarizability and $\theta$ is the orientation angle of the chromophores (see Figure 1.1-2).

![Cross-section of Mach-Zehnder interferometer](image)

**Figure 2.1-3** Cross-section of Mach-Zehnder interferometer which is covered with organic NLO material. The chromophores should have a net orientation for this material to exhibit nonlinear optical (NLO) properties and this net orientation should be maintained for years for effective operation of this device.
There are several requirements for a practical, organic, electro-optic modulator film, including: (1) the absorbance of the chromophores should be minimal in the wavelength range in which it operates, (2) film $\chi^{(2)}$ should exhibit no significant loss upon heating needed for device integration; typically a long term thermal stability for operating temperatures as high as 125°C and short term stability for temperatures approaching 200°C, (3) the film thickness needs to be $\geq 1$ μm in order to sustain waveguiding at wavelengths typically used in optical fibers for telecommunications, (4) polar ordering of the chromophores should be maintained over this film thickness, and (5) films should be compositionally and hence optically homogeneous to minimize losses due to scattering.

### 2.2 Organic NLO films

#### 2.2.1 Introduction

State-of-the-art EO modulators employ inorganic crystalline materials such as lithium niobate in the optical waveguide. However, these materials are very expensive to fabricate due to difficulties in fabrication and processing techniques. Organic waveguides offer significant advantages over lithium niobate (LiNbO$_3$) such as lower cost, much higher data transmission rates, and ease of fabrication. In organic waveguides, highly polarizable chromophores (dye molecules) must be oriented in a polymer film and that orientation must be maintained for years for effective device operation. Table 2.2-1 below shows a comparison of inorganic NLO material LiNbO$_3$ and organic NLO material fabricated using poled polymer technique discussed in next section. ²
### Table 2.2-1 Comparison of inorganic and organic EO modulators

<table>
<thead>
<tr>
<th>Physical / Device Property</th>
<th>LiNbO$_3$</th>
<th>Poled Polymers</th>
</tr>
</thead>
<tbody>
<tr>
<td>Electro-Optic Coefficients(pm/V)</td>
<td>32</td>
<td>10-50</td>
</tr>
<tr>
<td>Dielectric Constant</td>
<td>28</td>
<td>4</td>
</tr>
<tr>
<td>Fabrication and Processing</td>
<td>Difficult</td>
<td>Simple</td>
</tr>
<tr>
<td>Demonstrated Bandwidth</td>
<td>40</td>
<td>&gt;100</td>
</tr>
<tr>
<td>Device Lifetime</td>
<td>Years</td>
<td>Months</td>
</tr>
</tbody>
</table>

The different techniques to make organic NLO films are discussed below.

### 2.2.2 Poled (Guest/Host) Polymer Films

Electric field poling of polymer complex (Host) to align the chromophores (Guest) is the most intensively studied technique to make organic and polymeric nonlinear (NLO) materials for electro-optic modulators. A poled (Guest/Host) polymer film consists of a NLO active chromophore (Guest) embedded in a polymer complex (Host). The system is then heated above the glass transition temperature and a strong electric field (~ $10^5 - 10^6$ V/m) is applied to align the chromophores. This technique was first described by Meredith et al.$^6$ and was first used in electro-optic modulators by Singer et al.$^7$ who employed a nonlinear optic dopant molecule azo dye disperse red 1 (4-[N-ethyl-N-(2-hydroxyethyl)]amino-4’-nitroazobenzene) in a polymer matrix made of poly (methylmethacrylate) (PMMA). Thin films (~4 μm) of the azo dye in PMMA were prepared by spin coating onto indium tin oxide (ITO) coated glass. To orient the chromophores in the solid solution of azo dye and the polymer, the temperature of the solid solution was raised above the glass transition temperature ($T_g \sim 100^\circ$C) and an intense electric field of 0.2 – 0.6 MV cm$^{-1}$ was applied, thereby partially aligning the nonlinear optical molecules. The film was then cooled to room temperature, resulting in a system whose nonlinear optic molecules are aligned within the polymer matrix. The second harmonic coefficient was found to be $6 \pm 1.3 \times 10^{-9}$ esu experimentally. They also developed a thermodynamic model based on non-interacting molecular dipoles to describe the poling process and found the results to be consistent with experimental results.
Since then, with the synthesis of newer and better chromophores, this area saw a significant growth.\textsuperscript{8-10} Single and trifunctional dendritic chromophores were synthesized and doped into amorphous polycarbonate samples to study the electro-optic properties of the resulting material.\textsuperscript{8} Two samples were prepared by mixing single-functional dendritic chromophores with amorphous polycarbonate (APC) and by mixing trifunctional dendritic chromophores with APC in cyclopentanone/cyclohexanone (1:1). To study the EO effects, thin films were fabricated (thickness 2.2 - 2.5 µm) on ITO precoated glass and 100 nm gold films were deposited on top of the organic thin film to fabricate the sandwiched sample. After that, the sample was heated and a high-electric field was applied to align the chromophores. They measured EO coefficients and found a large variation with temperature. The observed EO coefficients was measured to be 69.6 pm/V and 29.8 pm/V for sample 1 and sample 2 respectively at about 130\textdegree C and 150\textdegree C for sample 1 and sample 2 respectively. These values are quite high when compared lithium niobate, which has an EO coefficient of 32 pm/V. However, these EO coefficients for sample 1 and sample 2 came down to 16.3 pm/V and 24.7 pm/V respectively after cooling in the presence of an electric field.

Some of the outstanding issues with making a practical EO modulator from this technique are incompatibility of chromophores with the polymer, low life-time of EO modulators made by poled polymer technique due to chromophore’s alignment instability and poor mechanical strength.

2.2.3 Layer-By-Layer Self-Assembly

Organic thin films for nonlinear optical materials can also be prepared by regioselective reaction between two different compounds.\textsuperscript{11} Marks et al. carried out a regioselective alkylation of 1-(4-pyridyl)-2-[5-(dicyanomethanide) thien-2-yl] ethylene sodium salt by a covalently surface-bound benzyl halide, producing a polar-ordered zwitterionic thin film. The nonlinear optical properties of the films produced by the above reaction were measured using SHG and it was found that the average tilt angle of the chromophore was \( \sim 46^\circ \) and a \( \chi^{(2)} \) of 5 x \( 10^{-8} \) esu at a fundamental wavelength of 1064 nm as compared to 200 x \( 10^{-9} \) esu for lithium niobate. The environmental stability of self-
assembled films produced by this technique was found to be much less than LB films (Y-
type, 30 layers) and spin coated films.

In another study of siloxane-based self-assembly for electro-optic modulators,12
polar films consisting of 40 alternating chromophore and capping layers was achieved.
The thickness of each bilayer was 3.26 nm and it took approximately 40 minutes to
deposit each bilayer. An organic thin film for electro-optic application was also
fabricated using vapor-phase self-assembly via triple hydrogen bond.13

The methods to make self-assembled organic thin films for electro-optic
modulators show promising values of $\chi^{(2)}$ and electro-optic coefficients. However, the
environmental stability11 as well as long time duration12 to make these films pose a great practical problem to make a commercial product out of this technique.

2.2.4 Ionically Self-Assembled Multilayer (ISAM) Films

This technique was pioneered by Decher et al.14, 15 and involves the alternate adsorption of polycations and polyanions on charged surfaces which leads to the formation of ionically self-assembled multilayer (ISAM) films, also commonly referred to as layer-by-layer (LbL) films. When a polyelectrolyte adsorbs onto an oppositely charged surface, charge reversal on the surface typically occurs; this facilitates the adsorption of the next layer of oppositely charged polymer. In principle, films with an arbitrary number of bilayers can be fabricated in this fashion. Figure 2.2-2 shows the schematic of ISAM process which shows a glass slide dipped alternately into positively and negatively charged polymers. Deionized (DI) water is used in between the deposition steps to rinse off the excess polymer.

For materials exhibiting NLO effects, polar ordering of the chromophores can be studied using second harmonic generation (SHG) measurements. The second harmonic intensity should increase quadratically with the film thickness if polar order is maintained and the film thickness is much less than the coherence length (typically on the order of 10 μm.). The properties of these films such as thickness, absorbance, and square root of
SHG intensity have been found to increase linearly with the number of bilayers. Some studies have also reported exponential or less than exponential increase in the properties of these films. 16-18 For layer-by-layer films formed via electrostatic and hydrogen bonding effects, polar ordering depends on several factors, including the chemistry and architecture of the component polymers. In one study, complexation between a cationic cyclodextrin derivative and a polyanion with an azobenzene side group led to quadratic growth of SHG for films up to 30 bilayers thick but not beyond that. 16 Non-quadratic growth of SHG was found for films consisting of up to 10 bilayers made with a cationic polyionene containing an azobenzene side group and poly(vinyl sulfate). 17 Similar results were reported for films consisting of up to 6 bilayers made with a quaternary polyamine and the anionic azobenzene-containing polymer that is the focus of the present work. 18 Another study showed a linear increase in absorbance up to at least 80 bilayers; however, the SHG failed to show quadratic scaling above 50 bilayers. 19 The effect of polycation type – branched poly(ethyleneimine) and linear poly(diallyldimethylammonium chloride) – on the orientation of the azo group in polycation/PCBS LbL films was studied using absorbance measurements, although NLO effects were not probed. 20 A lyotropic, cationic polyionene and strong polyanions were used to make highly ordered films consisting of up to 50 bilayers, but SHG was not studied. 21 In most of these studies where film thickness was measured, it was found that the film thickness and chromophore content – the latter characterized by absorbance measurements – scaled linearly with the bilayer number. While this linear scaling is not required for chromophore ordering that gives rise to significant values of $\chi^{(2)}$, linear scaling is necessary to yield films with a uniform value of $\chi^{(2)}$ throughout the film which would be desirable for an optical waveguide in an electro-optic modulator.

The properties of these films (such as thickness, absorbance etc.) have been found to be dependent on properties of the polyelectrolyte solutions such as pH22-25 and ionic strength26 which makes it easier to manipulate the properties of these films at the molecular level. For weak polyelectrolytes, the fractional charge on the polyon depends on the pH of the solution. When the polymer is highly charged, chains tend to adsorb in flat, train-like conformations whereas, when the polymer is relatively uncharged, chains
adsorb with thick and loop-like conformations due to decreased repulsion between the chains.\textsuperscript{22, 23, 27, 28} This is shown schematically in Figure 2.2-1.

Figure 2.2-1. Alternate adsorption of (a) highly charged polymer, (b) uncharged polymer on a substrate.

Due to this ease of fabrication of these films and the ability to tune the properties of these films at the molecular level, the ISAM technique has many potential applications in fields such as integrated molecular optics, electronics, and biosensors.\textsuperscript{29-32}

Figure 2.2-2. Schematic of ISAM film formation process. A negatively charged substrate is dipped into a positively charged polymer which leads to a charge reversal and facilitates the adsorption of negatively charged polymer. This leads to the formation of a bilayer and this process could be continued for any number of bilayers.
A variation of the above ISAM process involves incorporating a NLO active dye chromophore in these films by means of covalent bonding.\textsuperscript{17, 33-35} To better orient the chromophores in these films, a modification of the above technique which involves depositing one of the constituents electrostatically and then attaching the other constituent covalently to the underlying polymer or dye film is used to fabricate these films, referred as “hybrid LbL” films.\textsuperscript{34-36} One adsorption step in this process is electrostatic in nature whereas the other step involves a covalent attachment. The covalent attachment of the dye to the underlying layer of polymer helps to align the chromophores in one direction, thereby decreasing the tilt angle and increasing the $\chi^{(2)}$. The pH of the solution affects the ionization of the adsorbed polyelectrolyte which affects the properties of the LbL films.\textsuperscript{22, 23, 27, 32, 34, 37} The effect of varying pH on hybrid LbL films made using PAH and procion red dye (PR) was studied by Van Cott et al.\textsuperscript{34} When the pH of PAH was held constant at 4.5, and the pH of PR was increased from 7.0 and 10.5, absorbance per bilayer and $\chi^{(2)}$ increased which was due to the combined increase in chromophore density and increased covalent-coupling efficiency which increases the molecular ordering of PR molecules. At pH 7.0, PR is be incorporated in the films by a combination of electrostatic, hydrogen bonding and covalent coupling; whereas, at pH 10.5, covalent reaction between PAH and PR was favored and, therefore, a high degree of ordering was observed which led to an increase in $\chi^{(2)}$. The properties of hybrid LbL films are also affected by the ionic strength of the solution. Heflin et al. studied the effect of the ionic strength of PB solution on the properties of hybrid LbL films at a fixed pH of 10.5.\textsuperscript{35} PB has higher polarizability, $\beta$, than PR and resulted in films with $\chi^{(2)}$ values three times higher.\textsuperscript{34} The $\chi^{(2)}_{zzz}$ values of the hybrid LbL films peaked at 0.5 M NaCl salt concentration in the PB solution. The increase in ionic strength led to a decrease in the Debye length so that the charged chromophores could pack more closely, leading to an increase in $\chi^{(2)}_{zzz}$. Although the effect of ionic strength on the properties of the hybrid LbL films was studied in detail, the effect of pH was not studied. The pH of the PB solution affects the rate of hydrolysis of
PB in solution which makes the PB moieties unreactive in the solution and affects its pot life.  

A very interesting feature of these ISAM films is their excellent thermal and temporal stability, an important factor for EO modulator applications and one that has been a significant limitation for commercialization of organic EO modulator materials. In the previous work by Heflin et al., ISAM films made with PAH and an azobenzene-containing polyanion, PS-119, exhibited complete recovery in $\chi^{(2)}$ after the films were heated at 150° C for 15 hours and then cooled to room temperature. 38, 39 These films have shown no measurable loss in $\chi^{(2)}$ upon storage under atmospheric conditions at room temperature for 10 years.

Many groups report low degree of internal organization, a nonlinear increase in absorbance with increasing bilayer numbers, exponential increase in thickness and a non-quadratic increase in SHG of these films. 16-18, 21 These effects have been attributed to possible irregular deposition of polycation dye on the surface, creating an irregular surface with dangling polymer loops and tails in which the next polion can penetrate leading to a rougher surface and resulting in nonlinear growth of these multilayers 17. Also, the effect of processing conditions such as substrate preparation, rinsing time in between deposition steps and properties of polymer and dye solutions such as pH and ionic strength can lead to nonlinear growth of these ISAM films. The effect of solution properties such as ionic strength and pH on films formation are discussed below.

**2.2.4.1 Effect of Salt concentration on the deposition**

The effect of ionic strength or salt concentration on the adsorption of polyelectrolytes has been studied. 26, 40, 41 For a solution containing symmetrically monovalent salt such as NaCl, the Debye length i.e. the length over which the electrostatic repulsive forces exists is given by the relation,

$$\kappa^{-1} = \frac{0.304}{\sqrt{c}}, \text{ in nm}$$

(18)
in which \( c \) is the effective ionic concentration in moles/liter (M). From the above equation, it can be seen that as the ionic concentration increases, the Debye length decreases. Because of this, the molecules can be packed more closely with increasing ionic strength and therefore polymer chains would tend to adsorb in loops and tails at higher ionic strength and therefore higher mass of polymer or charged chromophore can be adsorbed by increasing the effective ionic concentration. This is shown schematically in Figure 2.2-3. The effective ionic concentration can be increased by adding salt such as NaCl or by increasing the concentration of polyelectrolyte.

![At low salt concentration](image1.png)  ![At high salt concentration](image2.png)

**Figure 2.2-3 Effect of salt concentration on the conformation of adsorbed polymers.**

This is consistent with the experimental results seen by Dubas et al.\(^\text{42}\) with the film thickness value reaching the maximum at a salt concentration of 0.3 M. They also observed that the ISAM films start to decompose at salt concentration greater than 0.6 M. In another study by the same group\(^\text{26}\), they studied the swelling behavior of adsorbed films upon exposure to solutions of different salt concentrations. By use of in-situ atomic force microscopy, polyelectrolyte multilayers were shown to swell on exposure to solutions containing salt. The quasilinear swelling response, used to estimate swelling coefficients and equilibria, exhibits orders of magnitude of difference, depending on the pair of polyelectrolytes constituting the multilayer. The surface roughness of as-made multilayers was observed to decrease significantly upon annealing in salt solutions.

### 2.2.4.2 Effect of pH

An extensive study was done by group of Barrett et al. on the effect of pH on properties of ISAM films\(^\text{22, 23}\). In one of their studies done using PAH and poly(acrylic
acid) (PAA), they found that the local apparent dissociation constant of polyelectrolytes adsorbed on the films could be quite different from that of solutions.\textsuperscript{22} In the other study done by Barrett et al.\textsuperscript{23} they used PAH as the polycation and P-Azo (Poly\{1-[4-(3-carboxy-4-hydroxyphenylazo)-benzenesulfonamido]-1,2ethandiyl\}) as the polyanion to study the affect of pH on the thickness of the multilayers formed and the growth of multilayers was studied as a function of time and concentration. They found a 20-fold increase in the optical absorbance when the solution pH was increased from 3 to 10. Using PAH and PAA polyelectrolytes, bilayers with thicknesses ranging from less than 1 nm to 12 nm have been prepared at different pH conditions\textsuperscript{27}.

A study of effect of pH on ISAM films made using PAH and Procion Red dye (PR) was done by Van Cott et al.\textsuperscript{34} They studied set of four different pH conditions. The pH values of the dipping solution determine the ionization state of the amine moieties on PAH, which affects both the conformation of the polymer upon adsorption and its subsequent reactivity with PR dye. In the first set of experiments, the pH of PAH was kept constant at 4.5 and the pH of PR was 7.0 and 10.5. In the second set of experiments, the pH of PAH was 7.0 and the pH of PR was 7.0 and 10.5. They found that the pH value of the PR solution had a significant affect on the amount of chromophore incorporated in the film as well as on the values of $\chi^{(2)}$ and $(I_{2\omega})^{1/2}$ per bilayer. When the pH of PAH was held constant at 4.5, and the pH of PR was increased from 7.0 and 10.5, they found an increase in the amount of PR deposited per bilayer and an increase in $(I_{2\omega})^{1/2}$ per bilayer which is consistent with the increased covalent-coupling efficiency. They found that increasing the pH of PR increases the molecular ordering of PR molecules thus increasing the $\chi^{(2)}$. At low pH (7.0) of PR, PR may be incorporated in the films by a combination of electrostatic, hydrogen bonding and covalent coupling; whereas, at high pH (10.5) of PR, covalent reaction between PAH and PR is favored and therefore, a high degree of ordering is observed which leads to an increase in $\chi^{(2)}$.

Thus, by manipulating the pH of the solution of weak polyelectrolytes, one has a good molecular control over the formation of ISAM films.
2.3 Mass transfer models

This section gives a review of mass transfer models used to study the kinetics of adsorption of polymers on a substrate. Two types of geometries, stagnation flow and shear flow, are reviewed below. A review for polyelectrolyte adsorption kinetics study is also presented.

2.3.1 Stagnation Flow

The adsorption of a polymer on a substrate in stagnation point has been studied in detail by Dijt et al. as originally discussed extensively by Dabros and Van de Ven. Dijt et al. studied the kinetics of adsorption of poly(ethylene oxide) (PEO) from water onto silica using stagnation point geometry, as shown in Figure 2.3-1, using a reflectometry technique. It was considered that the rate of adsorption of small molecules is determined by three processes: (1) transport towards the surface and/or (2) attachment to the interface and/or (3) re-conformation at the surface. To access the role of each of the three contributions, the kinetics of adsorption were studied under well defined hydrodynamic conditions. A typical experimental set up used by Dijt et al. is described in Figure 2.3-1.

![Figure 2.3-1](image)

Figure 2.3-1 Schematic representation of stagnation point flow experimental set-up.
The Peclet number characterizes the significance of convection effects relative to diffusion in the mass transport to the surface. For spherical particles of radius, \( R \), and a diffusion coefficient \( D \), the Peclet number is defined as,

\[
Pe = \frac{2a^3 \nu \bar{\alpha} Re}{R^3 D}
\]

(19)

in which \( \nu \) is the kinematic viscosity, \( \bar{\alpha} \) is a dimensionless streaming intensity parameter, \( R \) is the radius of the inlet tube and \( Re \) is the Reynolds number given by,

\[
Re = \frac{UR}{\nu}
\]

(20)

in which \( U \) is the mean fluid velocity at the end of the inlet tube. For most polymers \( Pe \) is very small, typically of the order of \( 10^{-8} \).

Dabros and Van de Ven expressed the flux \( J \) of particles towards the surface (per unit area) as:

\[
J = \frac{Dc}{\alpha} Sh
\]

(21)

where, \( c \) is the polymer concentration and the Sherwood number \( Sh \) is a complex function of the Peclet number. In the limit of very small \( Pe \), this function takes the simple form

\[
Sh = 0.616 Pe^{1/3}
\]

(22)

Combining equations (1), (3) and (4) an expression for \( J \) is written as:

\[
J = 0.776 \nu^{1/3} R^{-1} D^{2/3} \left( \bar{\alpha} Re \right)^{1/3} c
\]

(23)

The above equation assumes that the concentration of the polymer at the surface is zero. Also, any specific interactions between particle and surface are assumed to be negligible. \( \bar{\alpha} \) is the dimensionless flow intensity parameter which is a function of Reynolds number \( Re \).

From equation 23, the mass transfer coefficient can be written as,

\[
k_j = 0.776 \nu^{1/3} R^{-1} D^{2/3} \left( \bar{\alpha} Re \right)^{1/3}
\]

(24)

Thus using equation (24), the mass transfer rate can be estimated for the stagnation flow. Using equation (23), they compared the calculated mass transfer rate towards the surface with the observed adsorption rate of PEO. The results for PEO
adsorption on silica surface were shown. The initial adsorption rate \((d\Gamma/dt)_{t=0}\) was estimated. This observed initial slope was then compared with the theoretical value obtained from equation (5). A good agreement between the observed values of mass transfer rate and theoretical values was seen and the adsorption was found to be mass transfer limited.

2.3.2 Shear Flow

In another study done by Dijt et al., a capillary flow geometry was used to study the adsorption and desorption of PEO on glass by studying the hydrodynamic thickness of the adsorbed interfacial layer. They used hydrodynamic thickness instead of adsorbed mass to probe the molecules adsorbed in form of tails. Those molecules adsorbed in form of tails were not completely accounted for merely by the adsorbed amount; however, they were determined almost completely by the hydrodynamic thickness. Therefore, hydrodynamic thickness can be used as a probe of the tails, whereas the adsorbed amount cannot be used as such. They used measurement of streaming potential in glass capillaries to obtain the hydrodynamic thickness under well defined hydrodynamic conditions. This method can be used to study the adsorption of uncharged polymer as a function of time.

Both for adsorption and desorption the steady-state rate of mass transfer in a capillary is given by the equation of Leveque. The flux \(J\) of the polymer can be written as:

\[
J = 0.885 \left( \frac{D^2 v_m}{R z} \right)^{3/5} (c_b - c_s)
\]

In this equation \(v_m\) is the mean fluid velocity, \(D\) is the diffusion constant of the polymer, \(R\) is the radius of the capillary tube; \(c_b\) and \(c_s\) are the concentrations of the bulk and in the subsurface region respectively and \(z\) is the lateral distance downstream from the capillary entrance. Both \(c_b\) and \(c_s\) are assumed to be independent of \(z\). For adsorption \(c_b > c_s\) and \(J > 0\), whereas in desorption \(c_b < c_s\) and \(J < 0\).
This theory can be used to estimate the mass transfer coefficient \( k_t \) as a function of Reynolds number and the diffusion coefficient \( D \). The mass transfer coefficient as a function of Reynolds number from equation (25) can be written as:

\[
\frac{k_t}{\nu} = 0.885 \left( \frac{D^2 \nu \text{Re}}{R^2} \right)^{1/3}, \text{ in m/s}
\]  

(26)

Excellent quantitative agreement was found between the predicted and observed \( \delta \) as a function of time.

### 2.3.3 Theory of polyelectrolyte adsorption

The kinetics of polyelectrolyte adsorption were studied theoretically by Cohen Stuart et al.\(^{28}\). Their model is based on the assumption that a polyelectrolyte encounters a barrier in its motion towards an adsorbing surface and the height of the barrier, which is of electrostatic origin, is calculated with a self-consistent-field (SCF) model. It was found that the salt concentration greatly affects the height of the barrier with high salt concentration needed to reach the equilibrium in adsorption.

According to the theory proposed by Cohen Stuart et al., the polyelectrolyte adsorption on the surface meets two main types of resistances: the resistance due to transport (convection and diffusion) effects and the resistance due to the electrostatic barrier.

The resistance due to transport effects is based on the impinging-jet geometry\(^{43}\) discussed above and is given as,

\[
J = 0.776 \left( \frac{V \alpha}{r} \right)^{1/3} \left( \frac{D}{r} \right)^{1/3}
\]

(27)

in which \( V \) is the fluid velocity, \( \alpha \) a dimensionless streaming intensity parameter, \( r \) is the radius of the inlet tube and \( D \) is the diffusion coefficient of the polymer.

The resistance due to electrostatic barrier is given by the equation below expressed from Kramer’s theory as done by Semenov et al.\(^{47}\)

\[
R^e(\theta) = \int_0^\infty e^{-\frac{\theta}{kT}} \frac{u(\Omega \sigma)}{D} \, dz
\]

(28)
in which \( D \) is the diffusion coefficient of the charged chromophore, \( u(T,z) \) is the potential energy felt by an adsorbing molecule which is at a distance \( z \) from where it first touches the surface, \( kT \) has its usual meaning.

If it is assumed that the electrostatic potential energy to be constant over a Debye length \( (\kappa^{-1}) \) and to drop to zero at \( \kappa^{-1} \), then the energy barrier is easily computed as:

\[
R^e(\theta) = \frac{e^{u(T)} k \kappa^{-1}}{D}
\]

(29)

The overall kinetics equation for this case is given by,

\[
R_{total} \frac{d\Gamma}{dt} = R_{total} \Gamma_m \frac{d\theta}{dt} = c_b - c_s
\]

(30)

in which \( \Gamma_m \) is the maximum surface coverage in mg/m\(^2\), \( \theta \) is fraction of surface covered, \( c_b \) is the bulk concentration and \( c_s \) is the subsurface concentration and \( R_{total} = R_t + R^e(\theta) \).

2.4 Introduction to QCM

2.4.1 Introduction

The quartz crystal microbalance (QCM) is an ultra-sensitive mass sensor which consists of a piezoelectric quartz crystal sandwiched between a pair of electrodes. Crystals which acquire charge when compressed, twisted or distorted are said to be piezoelectric. Due to the piezoelectric properties and crystalline orientation of the quartz, the application of voltage between these electrodes results in shear deformation of the crystal. Therefore, when the electrodes are connected to an oscillator and an AC voltage is applied over the electrodes the quartz crystal starts to oscillate at its resonant frequency due to the piezoelectric effect.

The piezo-electric effect of the quartz crystal started to gain attention as early as the beginning of 20\(^{th}\) century. The use of quartz crystals for all kinds of frequency controlled applications started in 1934 when AT-cut quartz crystal was introduced. At that time it was known that a change in mass of these crystals caused a frequency shift. However, these understandings were based only on qualitative basis. In 1959, Sauerbrey
49 published a paper that showed that the frequency shift of the quartz crystal resonator is directly proportional to the added mass. This was the first breakthrough towards the quantitative way to measure very small mass changes. It was found that this analysis is valid if the frequency decrease due to loading is approximately 2% of the unloaded frequency or the fundamental resonant frequency. In other words, the QCM becomes inaccurate for masses greater than about 2% of the crystal mass50. Beyond that range, the relation between the frequency decrease and the mass loading is non-linear.

If a rigid layer is evenly deposited on one or both sides of the electrodes the resonant frequency will decrease proportionally to the mass of the absorbed layer according to Sauerbrey equation49:

\[
\Delta f_m = -\frac{2 \times f_0^2 \times \Delta m}{A \times \sqrt{\rho_q \mu_q}}
\]  

(31)

in which
\[
\Delta f_m = \text{measured frequency shift}
\]
\[
f_0 = \text{fundamental frequency of the crystal}
\]
\[
\Delta m = \text{mass change per unit area}
\]
\[
A = \text{piezo-electrically active area}
\]
\[
\rho_q = \text{density of quartz, } 2.648 \text{ g/cm}^3
\]
\[
\mu_q = \text{shear modulus of quartz, } 2.947 \times 10^{10} \text{ Pa}
\]

It should be noted that the above equation (31) is not valid if the deposited mass is: a) not rigidly deposited on the electrode surface b) slips on the surface c) not evenly deposited on the surface of the electrodes. In short the Sauerbrey equation is valid only for uniform, rigid, thin-film deposits. Due to this reason QCM was for many years just regarded as a gas-phase mass detector. In the beginning of 1980’s, it was realized that a quartz crystal can be excited to a stable oscillation when it was completely immersed in the liquid. In this case the oscillation frequency depends also on the density and viscosity of the liquid in contact with the crystal. Much of the work in this regard is by Kanazawa
and coworkers. According to Kanazawa\textsuperscript{51}, the change in the resonant frequency of the QCM taken from air into liquid is proportional to the square root of the product of the liquid density and the liquid viscosity. It is given by the following relationship:

\[
\Delta f_{\text{aqueous}} = -\left[\frac{n f_0^{3/2}}{(\pi \mu q \rho_q)^{3/2}}\right] (\rho_L \eta_L)^{1/2}
\]  

(32)

in which

\( n \) = number of faces of the QCM in contact with the liquid

\( \rho_L \) = density of the bulk liquid

\( \eta_L \) = viscosity of the bulk liquid

The frequency shift predicted by equation (32) is found to be in reasonable agreement with the experimental data obtained by Advincula and coworkers\textsuperscript{3}. The above equation can be used to predict the change in frequency due to difference in the solution viscosity and density. Even a small amount of change in the solution properties can have significant affect on the QCM response. Using Equation (32), a 10\% change in the viscosity of solution (keeping the density constant) corresponds to a change in approx. 37.3 Hz which corresponds to an equivalent mass deposition of 6.6 mg/m\textsuperscript{2} using Sauerbrey equation\textsuperscript{49}. Thus, the viscosity effects can be very large and can lead to significant error if not properly accounted for.

In addition to the measurement of change in fundamental frequency of quartz crystal upon mass loading, certain high-end QCM measure changes in higher harmonics and corresponding changes in dissipation of the film. This technique is widely known as QCM-D technique. The higher harmonic together with its corresponding dissipation constant can then be modeled using Voigt model to estimate the film thickness, viscoelasticity and shear modulus of the adsorbed films. Thus, a QCM-D sensor provides two major advantages as compared to a QCM sensor that measures frequency only. First, it provides quantitative information about the viscoelastic properties of soft films such as biofilms and polymers. Second, it provides information by which adsorbed mass can be accurately determined even in cases where the Sauerbrey relation is not valid\textsuperscript{52}.  

41
QCM has been used by many researchers to study polymer adsorption on different surfaces, in biological area to study the adsorption of protein, antibody, enzymes, DNA, cells etc., to study the hydration of polymers or swelling of polymeric surfaces. The availability of a number of different surfaces such as metals, metal oxides, polymeric surfaces, hydroxyapatite and other custom surfaces had made QCM a popular tool among the research community. This is one of the biggest advantages of using QCM over other adsorption study technique such as, surface plasmon resonance (SPR). However, on the negative side, since QCM is based on piezoelectric effect, it is very sensitive to vibrations which could result due to number of conditions including change in pressure in the flow through cell. The QCM crystal is also sensitive to changes in temperature and fluid properties as discussed above using Equation (2). In fact, this sensitivity of QCM to fluid viscosity has led some research groups to use QCM to measure changes in viscosity of solutions. Moreover, QCM measures the mass of everything deposited on its surface including the water of hydration in the films deposited on the surface. This adds to the complexity where just dry mass of the film is desired; however, this becomes an added advantage where swelling behavior of surfaces are being studied. To understand the results obtained from QCM, there needs to be an understanding as to what might be causing the observed change in frequency and try to separate the frequency change from undesired and desired effects.

Different harmonics of QCM-D have different penetration depth or decay length of the shear wave that is radiated into the contacting fluid and it is given by,

\[ \delta = \left( \frac{2\eta}{\omega \rho} \right)^{1/2} \]

in which \( \eta \) is the fluid viscosity, \( \omega = 2\pi f \), \( f \) is the oscillation frequency and \( \rho \) is the fluid density. Thus, for water at 20°C, for 1st harmonic the decay length of this shear wave is 252 nm, whereas for 3rd harmonic, it’s 145 nm. This implies that at lower harmonics, more of the liquid region is being sampled, whereas at higher harmonics, the region closer to the surface is getting sampled. Thus, QCM sensitivity to surface mass can be emphasized over liquid sensitivity by operating at higher harmonics. Operating
the QCM at higher harmonics can therefore help in getting better experimental data where adsorption of thin films such as polymer adsorption on the surfaces are being studied; however, for QCM studies where changes in viscosity of fluid in contact is of importance, it might be good to operate the QCM at lower harmonic. The decay length as a function of harmonic is shown in Figure 2.4-1. At the 1\textsuperscript{st} harmonic, the shear wave has a decay length of approx. 250 nm which means that it samples the fluid properties in addition to sampling the adsorbed film properties. At higher harmonics, the shear wave has much smaller decay length, which would mean that higher harmonics sample more of film properties than fluid properties.

![Figure 2.4-1: Decay length as a function of harmonic. As the harmonic increases, the decay length decreases as a result of equation (3).](image)

In liquid phase QCM measurements, water may couple with the adsorbed polymer layers, thereby increasing the mass of the films. The amount of water coupled has been shown to vary significantly, depending on the nature of the film, with mass uptake estimations between a factor of 1.5 and 4 times larger than the dry mass\textsuperscript{52}. The QCM-D technique could be very helpful in measurements taken in liquid phase, since it can give direct information on the water content of the probed film when combined with optical measurements. Hook et al.\textsuperscript{55} studied the adsorption of protein on titanium oxide surfaces using three different techniques: ellipsometry (ELM), optical waveguide lightmode
spectroscopy (OWLS) and quartz crystal microbalance/dissipation technique (QCM-D). They found that ELM and OWLS technique in most cases give the most consistent and comparable results whereas, the QCM-D technique gives a higher value in terms of mass as compared to the above two optical techniques and the primary reason for higher mass uptake values from QCM are attributed to coupled water.

2.4.2 Applications of QCM

The QCM has been widely used as a biosensor,\textsuperscript{56-66} to study the adsorption of proteins,\textsuperscript{55, 67} to study adsorption of inorganic material such as nanoparticles,\textsuperscript{68, 69} for measuring thin film growth in deposition and sputtering process,\textsuperscript{70} to measure changes in viscosity,\textsuperscript{53} and to study polyelectrolyte adsorption.\textsuperscript{20, 71-78}

2.4.3 Previous Studies on polyelectrolyte adsorption using QCM

Lvov et al. studied the adsorption kinetics and the effect of rinsing in between adsorption cycles of poly(allylamine hydrochloride) (PAH) and poly(styrenesulfonate) (PSS) using a QCM in-situ.\textsuperscript{72} They observed a 10-20 minutes time for the adsorption to reach complete saturation of polyelectrolytes on the underlying surface in aqueous phase. They also observed a much higher decrease in frequency than expected even after attributing almost 50 - 60 % of that frequency change to water of hydration as seen in a different study for adsorption of polyions by the light guiding attenuation measurement.\textsuperscript{79} There was a 10% loss in the adsorbed polyion film upon rinsing the film with DI water in between adsorption steps.

Although, polyelectrolyte adsorption in layer by layer form is widely used for different applications, there are not enough studies about the fundamentals of layer by layer deposition. Considering that higher values of mass deposited from the QCM as compared to corresponding data obtained from other optical techniques such as ellipsometry and optical waveguide lightmode spectroscopy (OWLS) is attributed mainly to water of hydration in these films,\textsuperscript{52} most of the adsorption studies done using the QCM fail to explain the high values of mass deposited even after attributing 50-60 %, estimated from optical measurements, of that mass as mass of water of hydration. Also, the effect of
changes in viscosity and density on frequency changes has not been taken into account in most of the studies, which can lead to significant error, as discussed above. Other than this, most of the studies do not report how reproducible are their experiments which could be quite important, considering the sensitivity of this technique.

### 2.5 Silver nanop prism synthesis

Metal nanoparticles have various applications in sensors, plasmonic devices and surface-enhanced Raman spectroscopy (SERS). Formation of anisotropic nanoparticles provides a convenient tool to control the optical response mainly through the variation of the aspect ratio. The intensity and the wavelength of the surface plasmon depend on the shape and size of the nanoparticles. Numerical simulations using the discrete dipole approximation (DDA) method were done on nanoparticles of different shapes and sizes to study the local electric enhancement near the particle surface. For silver nanoparticles triangular in shape with an edge length of 60 nm and thickness of 12 nm, the enhancement for the local electric field which was at the edges of the particles was found to be 3500 times the applied electric field. When the DDA simulations were performed on silver nanospheres, an electric-field enhancement of only 25 was observed, much less compared to the value at the edges of triangular nanoparticles, indicating the importance of edges in these nanostructures where the maximum enhancement in the surface plasmon is found. It was also found that there was a red shift in the surface plasmon wavelength when the edge length of the silver nanoprisms was increased, whereas there was a blue shift when the silver nanoprisms were snipped.

There are two main techniques that can be used to incorporate silver nanoparticles triangular in shape on a substrate to increase the SHG efficiency. The first involves using nanosphere lithography and the second one involves synthesizing silver nanoprisms using a photochemical reaction and incorporating those on substrates by means of physisorption. The nanosphere lithography technique involves depositing a monolayer of polystyrene nanospheres onto the substrate and allow the spheres to self-assemble in a closed pack monolayer. Silver is then deposited by electron beam evaporation onto the substrate through the interstices of the spheres in the monolayer and
the spheres are then removed by ultrasonication in dichloromethane. This leads to the formation of silver nanoparticles triangular in shape on a glass substrate with a surface plasmon in the range of 900-1000 nm. Silver nanoprisms with a thickness of 50 nm were fabricated with this technique on top of a PAH/PCBS film and an increase in SHG efficiency by a factor of 1600 was seen. However, this approach did not lead to significant enhancement of the SHG intensity when PAH/PB films were used, presumably because the latex removal step involving the use of an organic solvent damaged the PAH/PB films. This along with the fact that an E-beam deposition step is required led to the alternative approach of physisorbing pre-formed silver nanoprisms onto organic NLO films, a step that does not require an organic solvent step.

Silver nanoprisms can be synthesized by using a photochemical reaction which involves synthesizing silver seeds which are silver nanospheres < 5 nm in diameter and then exposing the silver seeds suspension to light at a controlled wavelength and temperature to synthesize silver nanoprisms. Silver seeds have been synthesized in previous work by reducing solutions of silver nitrate with sodium borohydride in the presence of sodium citrate. To stabilize the silver seeds, the seeds were either capped with bis(p-sulfonatophenyl)phenylphosphine dihydrate dipotassium salt (BSPP) or with poly(vinylpyrrolidone) (PVP). The silver seeds showed a peak absorbance at a wavelength of ~397 nm. Upon exposure to light at a particular wavelength, the absorbance peak at 397 nm decreased over time and a new absorbance peak at higher wavelength started to form. It was found that the surface plasmon wavelength scales with the edge length of the silver nanoprisms. The edge length can be increased by increasing the wavelength of the light to which silver seeds were exposed. In one study, the surface plasmon wavelength increased from approximately 500 nm to 750 nm by using wavelengths of 470 nm and 633 nm respectively. In another study, low intensity light emitting diodes (LED) were used to prepare silver nanoprisms from a silver seed solution. The effect of temperature on the formation of silver nanoprisms was also studied and it was found that increasing the temperature from 25°C to 37°C reduced the reaction time from 159 hrs to 69 hrs when green LEDs were used and from 185 hrs to 96 hrs when red LEDs were used. The mechanism of silver nanoprisms formation has been
studied by transmission electron microscopy and three distinctive stages were noticed. The first stage was the induction stage where silver seeds aggregated to form nanoclusters in the presence of light. This is followed by the growth of nanocrystal structure which consumes the nanocrystals and silver seeds to form silver nanoprisms at which point the reaction terminates.

In a typical experiment to synthesize silver seeds, 2 mL of 5 mM freshly prepared silver nitrate solution (AgNO₃) and 1 mL of 30 mM freshly prepared trisodium citrate were mixed with 95 mL of nanopure water in a 250 mL flask. The flask was immersed in ice bath and the solution was stirred for 30 minutes. An aqueous sodium borohydride (NaBH₄) (1 mL of 50 mM) freshly prepared, was quickly injected into the vigorously stirred, ice-cold solution. The clear solution immediately turned yellow. The reaction was allowed to proceed for 15 minutes and during this time 3-5 drops of NaBH₄ solution was added every 2 minutes to the solution to ensure complete reduction of Ag⁺ ions in the solution. After that 1 mL of 5 mM freshly made bis(p-sulphonatophenyl)phenylphosphine dihydrate potassium (BSPP) solution and 0.5 mL of NaBH₄ solution was added to the reaction mixture in a dropwise fashion over a period of 5 minutes. The resulting solution was stirred overnight in dark. TEM analysis of the seeds synthesized showed an average diameter of 4.8±1.1 nm. The silver seeds produced by this method had a peak absorbance at a wavelength of 397 nm.

![Figure 2.5-1 Structure of BSPP.](image)

BSPP is used as a secondary stabilizing agent to stabilize silver seeds since trisodium citrate alone is not an efficient stabilizing agent for silver colloids. The
structure of BSPP is shown in the Figure 2.5-1. BSPP gradually degrades in air, which is accompanied by a solution color change from clear to yellow. Ag colloids synthesized with citrate (no BSPP) with broad size distributions of particles can be converted to nanoprisms but only after removing particles bigger than 15 nm by centrifugation at 18000 rpm for 30 minutes.
2.6 References:


Chapter 3 Polar Orientation of a Pendant Anionic Chromophore in Thick Layer-by-Layer Self-Assembled Polymeric Films

3.1 Abstract
Multilayer films with up to 600 bilayers and 740 nm thickness were fabricated using the alternating deposition of poly(allylamine hydrochloride) (PAH) and poly{1-[p-(3’-carboxy-4’-hydroxyphenylazo)benzenesulfonamido]-1,2-ethanediyl} (PCBS) on glass substrates. Linear relationships for absorbance, thickness, and the square root of the second harmonic intensity vs. the number of bilayers demonstrate that the films have long range polar order and optical homogeneity. The deposition conditions (i.e., pH of the solutions, solvent quality, deposition and rinsing times) are critical variables in fabricating layer-by-layer thick films that exhibit long range polar orientation of chromophores. The ability to fabricate non-centrosymmetric films on the order of a micron thick with bulk second order nonlinear optical responses is crucial because it enables the development of nonlinear optical waveguide devices such as electro-optic modulators.

3.2 Keywords
layer-by-layer films, polyelectrolyte multilayers, ionic self-assembled multilayers, polyelectrolytes, nonlinear optics, second harmonic generation

3.3 Introduction
The alternate adsorption of polycations and polyanions on a charged surface leads to the formation of Ionic Self-Assembled Multilayer (ISAM) films, also commonly referred to as layer-by-layer (LbL) films. When a polyelectrolyte adsorbs onto an oppositely charged surface, charge reversal on the surface typically occurs; this facilitates the adsorption of the next layer of oppositely charged polymer. In principle, films with an arbitrary number of bilayers can be fabricated in this fashion. This method, developed by Decher et al.,\textsuperscript{1} has many potential applications in fields such as integrated molecular optics, electronic devices, and biosensors.\textsuperscript{2} Films made in this way can exhibit second
order nonlinear optical (NLO) effects if they satisfy the criterion that one of the constituents contains a chromophore that can be oriented in a polar manner. Films exhibiting second order NLO effects have applications in electro-optic (EO) modulators which convert electrical signal to optical signal and thus play an important role in today’s communication network.

For non-centrosymmetric organic films, the second order nonlinear susceptibility, \( \chi^{(2)} \) is directly proportional to the chromophore density and hyperpolarizability as given by the equation:

\[
\chi^{(2)} = NF\beta\left\langle \cos^3 \bar{\psi} \right\rangle
\]

in which \( N \) is the chromophore density, \( F \) is the local field factor, \( \beta \) is the hyperpolarizability and \( \bar{\psi} \) is the orientation angle of the chromophores with respect to the surface normal. Rational design thus involves choosing a chromophore with a suitably high \( \beta \) and incorporating it into a film with high density \( N \), and low tilt angle \( \bar{\psi} \).

There are several requirements for a practical, organic, electro-optic modulator film, including: (1) the absorbance of the chromophores should be minimal in the wavelength range in which it operates, (2) film \( \chi^{(2)} \) should exhibit no significant loss upon heating needed for device integration; typically a long term thermal stability for operating temperatures as high as 125°C and short term stability for temperatures approaching 200°C, (3) the film thickness needs to be \( \geq 1 \ \mu\text{m} \) in order to sustain waveguiding at wavelengths typically used in optical fibers for telecommunications, (4) polar ordering of the chromophores should be maintained over this film thickness, and (5) films should be compositionally and hence optically homogeneous to minimize losses due to scattering. In this chapter, we work with films that satisfy criteria (1-2) and focus on requirements (3-5) with films of thicknesses up to 740 nm. This is a substantial increase over the 120 nm thickness for the previously reported thickest films that exhibited proper scaling of thickness and nonlinear optical response and indicates the suitability of ISAM films for electro-optic waveguide devices.
Approaches for fabricating organic films for EO modulator applications include guest/host poled polymeric materials which have been shown to exhibit high $\chi^{(2)}$. In the guest/host poled polymer method, the chromophores are heated above the glass transition temperature and an electric field is applied; this leads to chromophore orientation. The chromophores are frozen in this position when the temperature of the system is rapidly brought down to room temperature. While the eventual randomization of the orientation back to the isotropic state has proven a challenging problem, advances continue to be made through use of higher $T_g$ hosts, covalent attachment of the chromophore to the polymer, cross-linked polymers, and dendrimeric structures. Using supramolecular self-assembled molecular glasses, an electro-optic coefficient as high as 327 pm/V was achieved, ~10 times higher than LiNbO$_3$, and showed 83% temporal alignment stability for three months at room temperature. Noncentrosymmetric Langmuir Blodgett (L-B) films with $\chi^{(2)}$ values as large as 760x10$^{-9}$ esu have been fabricated, ~4 times larger than that of LiNbO$_3$. However, L-B films tend to possess poor mechanical and thermal stabilities owing to the relatively weak van der Waals interactions between layers. Alternatively, several variations have been developed for growth of polar, self-assembled multilayers using siloxane chemistry. A recent procedure can deposit one monolayer in 40 min with $\chi^{(2)} = 430 \times 10^{-9}$ esu. A related approach involving sol-gel chemistry resulted in ternary films consisting of alternating layers of ZrO$_2$, carboxyl-functionalized azobenzene dyes, and poly(diallyldimethylammonium chloride) which led to $\chi_{zzz}^{(2)}$ values of 222-899 x $10^{-9}$ esu. The processing time for a ternary layer deposition cycle was approximately 25 minutes and film thicknesses up to 140 nm were reported.

For materials exhibiting NLO effects, polar ordering of the chromophores can be studied using second harmonic generation (SHG) measurements. The second harmonic intensity should increase quadratically with the film thickness if polar order is maintained and the film thickness is much less than the coherence length (typically on the order of 10 μm.). For layer-by-layer films formed via electrostatic and hydrogen bonding effects, polar ordering depends on several factors including the chemistry and architecture of the component polymers. In one study, complexation between a cationic cyclodextrin derivative and a polyanion with an azobenzene side group led to quadratic growth of
SHG for films up to 30 bilayers thick but not beyond that. 18 Non-quadratic growth of SHG was found for films consisting of up to 10 bilayers made with a cationic polionene containing an azobenzene side group and poly(vinyl sulfate). 19 Similar results were reported for films consisting of up to 6 bilayers made with a quaternary polyamine and the anionic azobenzene-containing polymer that is the focus of the present work. 20 Another study showed a linear increase in absorbance up to at least 80 bilayers; however, the SHG failed to show quadratic scaling above 50 bilayers. 21 The effect of polycation type – branched poly(ethyleneimine) and linear poly(diallyldimethylammonium chloride) – on the orientation of the azo group in polycation/PCBS LbL films was studied using absorbance measurements although NLO effects were not probed. 22 A lyotropic, cationic polionene and strong polyanions were used to make highly ordered films consisting of up to 50 bilayers, but SHG was not studied. 23 In most of these studies where film thickness was measured, it was found that the film thickness and chromophore content – the latter characterized by absorbance measurements – scaled linearly with the bilayer number. While this linear scaling is not required for chromophore ordering that gives rise to significant values of $\chi^{(2)}$, linear scaling is necessary to yield films with a uniform value of $\chi^{(2)}$ throughout the film which would be desirable for an optical waveguide in an electro-optic modulator. Thus, one of the issues that we explore in this present work is the set of processing conditions that give rise to linear growth in film thickness and chromophore concentration, as well as quadratic scaling of the SHG intensity with the film thickness.

Prior to the present work, the only studies involving layer by layer film deposition that showed long range polar ordering at thicknesses greater than 100 nm were those by Kang et al. 17 and by Heflin et al.; the latter involved films made by the ISAM process using a polyanion with an azobenzene side group and PAH. 6 A very interesting feature of these ISAM films is their excellent thermal and temporal stability, an important factor for EO modulator applications and one that has been a significant limitation for commercialization of organic EO modulator materials. In the previous work by Heflin et al., ISAM films made with PAH (1) and an azobenzene-containing polyanion, PS-119, exhibited complete recovery in $\chi^{(2)}$ after the films were heated at 150° C for 15 hours and
then cooled to room temperature. These films have shown no measurable loss in $\chi^{(2)}$ upon storage under atmospheric conditions at room temperature for 10 years. Although the temporal and thermal stability measurements were not performed on the films fabricated in this study using PAH/PCBS, the similarity between PCBS and PS-119 suggests that the films fabricated using PCBS may show similar levels of thermal and temporal stability. However, this is yet to be verified and is a subject of a future study. Finally, films fabricated using a hybrid covalent/ionic self-assembled technique have also exhibited excellent thermal stability at temperatures as high as 150°C for 24 hrs and temporal stability for over 14 months under ambient conditions. The sample maintained 90% of the SHG signal upon heating for 24 hrs at 150°C and completely recovered after cooling to room temperature; the change at elevated temperature was believed to be due to trans-cis isomerization of the azobenzene chromophore.

The main focus of the present work is a study of the processing conditions – deposition and rinsing times and solution pH values which affect the degree of ionization of the polyelectrolytes – necessary to fabricate organic ISAM films with the requisite long range polar ordering at thicknesses approaching the 1 μm limit and with the necessary optical homogeneity.

### 3.4 Experimental

#### 3.4.1 Materials

Poly(allylamine hydrochloride) (PAH, Figure 3.4-1 (a)) was used as the polycation ($M_w$ ca. 70 kDa; Aldrich). Poly{1-[p-(3’-carboxy-4’-hydroxyphenylazo)benzenesulfonamido]-1,2-ethandiy1} (PCBS, Figure 3.4-1 (b)); Aldrich; was used as the polyanionic chromophore. Deionized (DI) water (Barnstead ROpureST; model # D6311) with a resistivity of over 17 MΩ.cm was used. PAH was chosen as a polycation because it has shown good film quality and scaling of the SHG intensity, in contrast to other polycations, in our prior work on ISAM NLO films. PCBS has an azobenzene pendant group that has a sufficiently high hyperpolarizability, $\beta$, to give a substantial SHG signal. Microscope slides (Fisher Scientific) frosted on the end of one side were used as substrates. Ammonium hydroxide (28-30%, Aldrich), hydrogen
chloride (35.5-38%, EM Science) and hydrogen peroxide (31.8%, Fisher) were used for cleaning the glass substrate using the procedure described below.

![Figure 3.4-1. Structures of (a) Poly(allylamine hydrochloride) (PAH) and, (b) Poly{1-[p-(3'-carboxy-4'-hydroxyphenylazo)benzenesulfonamido]-1,2-ethandiyl} (PCBS).]

### 3.4.2 Fabrication of Slides

To obtain films with good compositional and optical homogeneity, the substrates were cleaned carefully using the RCA cleaning procedure. The slides were immersed in a solution of 6:2:1 H₂O, H₂O₂ and NH₄OH at 70°C for 20 minutes, rinsed carefully with DI water, immersed in a fresh solution of 6:2:1 H₂O, H₂O₂, HCl at 70°C for 20 minutes, rinsed again with DI water and baked at 130°C for at least an hour.

A first set of the films was made using a StratoSequence™ Mark VI robotic deposition system (nanoStrata Inc.). It consists of 8 beakers on a rotating platform that is raised and lowered by nitrogen gas pressure controlled by a computer. The polyelectrolytes (PAH and PCBS) and the rinse water were placed in 150 ml beakers. Four slides were held in a fixture that can either be stationary or can be made to rotate when immersed in the beakers. To minimize convection and diffusion transport effects, the slide fixture was always rotated at 60 rpm. An effective Reynolds number of 320 was estimated using the width of the slide as the characteristic length. There were two
separate dipping cycles used: (1) slides were dipped in a polyelectrolyte solution for 2 minutes followed by three rinsing steps using DI water, each lasting 45 seconds and (2) slides were dipped in a polyelectrolyte solution for 45 seconds followed by one rinsing step using DI water lasting 45 seconds. In both dipping cycles, the rinse water was replaced after every rinsing cycle whereas the polyelectrolyte solution was replaced after every 6 hours to avoid dilution.

Another set of the films was fabricated using a Richard-Allen Scientific DS/50 automated slide stainer. The slide stainer was equipped with 20 polyphenylene sulfide (PPS) Ryton static deposition chambers, one rinse bath (also constructed of PPS) and a drying chamber. An aquarium powerhead pump was added to the active-rinse bath to increase fluid circulation and thus rinsing efficiencies. No convection was used in the deposition baths. The films were deposited onto glass microscope slides (Fisher Scientific) prepared as noted above. For all films made with the DS/50 slide stainer, the polymer deposition and water rinse times were 2 minutes.

For all experiments, the concentrations of the PAH and PCBS solutions were 10 mM on a repeat unit basis. The repeat unit molecular weight of PAH is 93.56 g/mol and of PCBS is 369.3 g/mol; the concentration (in mg/ml) of PAH was 0.936 mg/ml and for PCBS was 3.693 mg/ml. The pHs of the polymer solutions were adjusted using 1.0 M or 0.1 M solutions of sodium hydroxide and hydrogen chloride. The pH of the solutions drifted no more than ± 0.1 pH units during the course of the experiment.

3.4.3 Film Characterization

Absorbance measurements were done using a Perkin Elmer Lambda 25 UV/vis system. The films exhibited an absorbance maximum, $\lambda_{\text{max}}$, at 360 nm. At 360 nm, the absorbance values of the thicker films surpassed the maximum absorbance value of 6.63 that the instrument can measure and therefore the measurements were taken at 450 nm wavelength. Film thicknesses were measured using a variable angle spectroscopic ellipsometer (J. A. Woolam ellipsometer VB-200 with WVASE32 software version 3.361). The ellipsometric analysis was done in the vicinity of the Brewster angle because ellipsometry measurements are most sensitive to film characteristics in the vicinity of the
Brewster angle \(^{27,28}\) An initial scan was done for wavelengths from 300 to 800 nm at 50 nm intervals and this wavelength range was then repeated over angles from 50-70° at 4° intervals to find the Brewster angle, which for the PAH/PCBS system was found to be 62°. Following the determination of the Brewster angle, the sample was scanned at wavelengths from 300 to 800 nm at 10 nm intervals in the vicinity (±2°) of the Brewster angle in 1° increments. The sample was scanned at three different positions to check for the film homogeneity. The experimental data collected this way were then fitted with one Lorentz oscillator; the wavelength of the absorbance peak was fixed at the value of 360 nm as measured by UV-Vis spectroscopy. Atomic force microscopic (AFM) pictures were taken using a Veeco Dimension 3100 Nanoman AFM. A representative area of 20 \(\mu\text{m} \times 20 \mu\text{m}\) was selected on each slide fabricated at different deposition conditions to study the morphology of these films.

SHG measurements were used to calculate the second order susceptibility, \(\chi^{(2)}\). A linearly polarized Nd:YAG fundamental beam with the wavelength of 1064 nm, a pulse width of 10 ns, and a pulse energy of \(~1\text{ mJ}\) was used. The second harmonic intensity was measured as a function of the incident angle. The incident angle/intensity data were used to calculate the \(\chi^{(2)}\) parameter. Figure 3.4-2 shows a representative plot of angle versus intensity for the PAH/PCBS films.
The effective second order susceptibility $\chi^{(2)}_{\text{eff}}$ was calculated using:

$$\chi^{(2)}_{\text{eff}} = \chi^{(2)}_{\text{ref}} \left( \frac{l_{\text{ref}}}{l_{\text{s.bilayer}}} \right) \left( \frac{m}{\sqrt{I^{2\omega}_{\text{ref}}}} \right)$$

in which $\chi^{(2)}_{\text{ref}}$ is the second order susceptibility of the reference material, $1.5 \times 10^{-9}$ esu, $l_{\text{ref}}$ is the thickness of the reference material, 75.3 nm, $m$ is the slope of square root of SHG intensity vs. number of bilayers, $I^{2\omega}_{\text{ref}}$ is the intensity of the reference material and $l_{\text{s.bilayer}}$ is the thickness per bilayer obtained from ellipsometric measurements.

The reference used was a 68 bilayer PS-119/PAH ISAM film that has had a constant value of thickness and second order susceptibility over the past ten years.\textsuperscript{6}
For a p-polarized light at a given incident angle $\theta$, $\chi^{(2)}_{\text{eff}}$ is related to the $\chi^{(2)}$ tensor components $\chi^{(2)}_{zzz}$ and $\chi^{(2)}_{zxx}$ by,

$$\chi^{(2)}_{\text{eff}} = 3\chi^{(2)}_{zxx} \sin \theta \cos^2 \theta + \chi^{(2)}_{zzz} \sin^3 \theta$$

(3)

The tilt angle was determined by comparing the SHG intensity generated for incident s- and p- polarizations of the light. The maximum harmonic intensity generated from p-polarized light is represented by $I_{2\omega}^{p\rightarrow p}$ and the maximum harmonic intensity generated from s-polarized light is represented by $I_{2\omega}^{s\rightarrow p}$. $I_{2\omega}^{p\rightarrow p}$ and $I_{2\omega}^{s\rightarrow p}$ are related to the ratio of $\chi^{(2)}_{\text{eff}}$ tensor components $\chi^{(2)}_{zzz}$ and $\chi^{(2)}_{zxx}$ by

$$\frac{\chi^{(2)}_{zzz}}{\chi^{(2)}_{zxx}} = \sqrt{\frac{I_{2\omega}^{p\rightarrow p}}{I_{2\omega}^{s\rightarrow p}}} \csc^2 \theta - 3\cot^2 \theta$$

(4)

The tilt angle is related to the ratio of tensor components by the equation,

$$2 \cot^2 \psi = \frac{\chi^{(2)}_{zzz}}{\chi^{(2)}_{zxx}}$$

(5)

Using Equations (2) - (5), the tilt angle and $\chi^{(2)}_{zzz}$ component of the $\chi^{(2)}_{\text{eff}}$ tensor were calculated. All film measurements were made after drying the films in air under ambient conditions. SHG, tilt angle, and absorbance measurements were taken by Cemil Durak in Prof. Heflin’s lab.

3.5 Results and Discussion

A series of different bilayer number films was fabricated by depositing PAH and PCBS under three different conditions. The first deposition condition was: PAH 10 mM, pH = 9.0; PCBS 10 mM, pH 8.0 with 2 minutes deposition time for both PAH and PCBS, and a total rinse time of 2 minutes 15 seconds. This is abbreviated as (PAH-9/PCBS-8)2min/2min-15sec: the number after the polymer gives the pH at which it was deposited and subscripts define the polymer deposition time followed by the rinsing time. This was chosen to probe the effect of ionization of PAH on film properties because changing the pH changes the degree of ionization of PAH. The second deposition condition was: PAH and PCBS both 10 mM, pH = 7.0 with deposition time of 2 minutes and rinsing time of 2
minutes 15 second for both polymers, written in short form as (PAH-7/PCBS-7)_{2min/2min-15sec}. The third deposition condition was: PAH and PCBS both 10 mM, pH = 7.0 with deposition time of 45 seconds and rinsing time of 45 second for both polymers, written in short form as (PAH-7/PCBS-7)_{45sec/45sec}. The last two conditions were chosen to probe the effect of deposition and rinsing time on ISAM film properties. These conditions are summarized in Table 3.5-1:

### Table 3.5-1: Different deposition conditions for LbL experiments

<table>
<thead>
<tr>
<th>Deposition Condition</th>
<th>PAH Solution pH</th>
<th>PCBS Solution pH</th>
<th>Deposition time (min:sec)</th>
<th>Rinse Time (min:sec)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1. (PAH-9/PCBS-8)_{2min/2min-15sec}</td>
<td>9.0</td>
<td>8.0</td>
<td>2:00</td>
<td>2:15</td>
</tr>
<tr>
<td>2. (PAH-7/PCBS-7)_{2min/2min-15sec}</td>
<td>7.0</td>
<td>7.0</td>
<td>2:00</td>
<td>2:15</td>
</tr>
<tr>
<td>3. (PAH-7/PCBS-7)_{45sec/45sec}</td>
<td>7.0</td>
<td>7.0</td>
<td>0:45</td>
<td>0:45</td>
</tr>
</tbody>
</table>

The deposition conditions 1 and 2 were used to compare the effect of pH-induced ionization of PAH while deposition and rinsing times were maintained constant. Deposition conditions 2 and 3 were used to study the effect of deposition and rinsing time on properties of films made at the same pH conditions.

### 3.5.1 Effect of deposition and rinsing times

The effects of deposition and rinsing times were studied for the conditions (PAH-7/PCBS-7)_{2min/2min-15sec} and (PAH-7/PCBS-7)_{45sec/45sec}; the concentration and pH were kept the same. For (PAH-7/PCBS-7)_{2min/2min-15sec} and (PAH-9/PCBS-8)_{2min/2min-15sec}, 500 bilayers were deposited on each side of the slide, whereas for the condition (PAH-7/PCBS-7)_{45sec/45sec}, 200 bilayers were deposited on each side of the slide.

As shown in Figure 3.5-1, absorbance measurements for the deposition condition (PAH-7/PCBS-7)_{45sec/45sec} taken at 360 nm show a linear increase up to 50 bilayers; however, when more bilayers are deposited, a nonlinear increase in absorbance is observed, indicating a nonlinear growth in these films. This could be because of
insufficient rinsing times to remove all non-electrostatically adsorbed polyelectrolyte and carry over of contaminants from rinsing baths to the next polyelectrolyte solution; this can lead to higher adsorption of next layer and over subsequent bilayers would result in an exponential growth. The inset shows the thickness vs. number of bilayers as measured by ellipsometry. Above 50 bilayers, thickness data could not be obtained because of low film quality which is noted in Table 3.5-2 in terms of high standard deviations observed at higher bilayer number. The standard deviations for the deposition conditions (PAH-7/PCBS-7)2min/2min-15sec and (PAH-9/PCBS-8)2min/2min-15sec in Table 3.5-2 are discussed later in the chapter.

Film morphology as embodied by the bilayer thickness and the mode of growth – linear versus exponential change in thickness with increasing bilayer number – should also play a role in long-range polar ordering of NLO chromophores. This has not been studied in detail in previous work, but some related, recent studies are relevant here. Nonlinear growth of thickness and absorbance with increasing bilayer number was found for ISAM films comprised of polyelectrolytes with low charge densities, ~ 10 mole % ionic functionality. 29 In a related study, reducing the solvent quality by using water/ethanol mixtures and by adding NaCl resulted in progressively thicker films and exponential growth in thickness and mass loading with increasing bilayer number. 30
Figure 3.5-1. Absorbance at 360 nm vs. number of bilayers on a single side for (PAH-7/PCBS-7)45sec/45sec. The concentrations of PAH and PCBS were 10 mM. The inset shows the thickness of these films up to 50 bilayers on a single side.

Table 3.5-2: Percent standard deviation of $\sqrt{\text{SHG}}$ to characterize optical homogeneity of films at different deposition conditions.

<table>
<thead>
<tr>
<th>Deposition Condition</th>
<th>Bilayer number</th>
<th>$\sigma_{\sqrt{\text{SHG}}} (%)$</th>
</tr>
</thead>
<tbody>
<tr>
<td>(PAH-7/PCBS-7)45sec/45sec</td>
<td>150</td>
<td>14.1</td>
</tr>
<tr>
<td></td>
<td>200</td>
<td>43.4</td>
</tr>
<tr>
<td>(PAH-7/PCBS-7)2min/2min-15sec</td>
<td>200</td>
<td>6.1</td>
</tr>
<tr>
<td></td>
<td>400</td>
<td>9.3</td>
</tr>
<tr>
<td></td>
<td>500</td>
<td>6.2</td>
</tr>
<tr>
<td>(PAH-9/PCBS-8)2min/2min-15sec</td>
<td>200</td>
<td>5.2</td>
</tr>
<tr>
<td></td>
<td>400</td>
<td>17.5</td>
</tr>
<tr>
<td></td>
<td>500</td>
<td>27.3</td>
</tr>
</tbody>
</table>
3.5.2 Effect of pH

The effect of the polymer solution pH on film properties was studied for the conditions (PAH-9/PCBS-8)\(_{2\text{min}/2\text{min-15sec}}\) and (PAH-7/PCBS-7)\(_{2\text{min}/2\text{min-15sec}}\): the concentration of the polyelectrolytes and the deposition and rinsing times were kept constant. The effect of pH on the structure of multilayer ISAM films has been extensively studied. 31-33 PAH has a pK\(_a\) of 8.7 34 and thus depositing it at pH > pK\(_a\) results in relatively thick layers with loops and tails because of the reduced charge repulsion on the polymer, which would, in turn, lead to increased adsorption of PCBS. In a Chapter 4, the effect of pH on bilayer thickness and film composition for hydrated films comprised of PAH and PCBS has been studied using a combination of a quartz crystal microbalance with dissipation monitoring (QCM-D), ellipsometry, and absorbance measurements.35

Film quality was assessed with measurements of absorbance, thickness, AFM, and SHG. The films fabricated at the condition (PAH-7/PCBS-7)\(_{2\text{min}/2\text{min-15sec}}\) exhibited excellent optical homogeneity up to 500 bilayers, the maximum number deposited, whereas films fabricated using the deposition condition (PAH-9/PCBS-8)\(_{2\text{min}/2\text{min-15sec}}\) showed good optical homogeneity up to 300 bilayers. Figure 3.5-2 shows the absorbance vs. bilayer number up to 500 bilayers (each side) for the two series fabricated using different deposition conditions. Although the peak of the absorbance spectrum is at 360 nm, the absorbance values were taken at 450 nm for the deposition conditions: (PAH-9/PCBS-8)\(_{2\text{min}/2\text{min-15sec}}\) and (PAH-7/PCBS-7)\(_{2\text{min}/2\text{min-15sec}}\), because at 360 nm the absorbance value surpassed the maximum limit of the spectrophotometer. The absorbance per bilayer at 450 nm for (PAH-7/PCBS-7)\(_{2\text{min}/2\text{min-15sec}}\) was 9.0 (± 2%) x 10\(^{-4}\) and for (PAH-9/PCBS-8)\(_{2\text{min}/2\text{min-15sec}}\) was 2.9 (± 5%) x 10\(^{-3}\) up to 500 bilayers for both conditions.
Thickness data for the deposition conditions: \((\text{PAH-9/PCBS-8})_{2\text{min}/2\text{min}-15\text{sec}}\) and \((\text{PAH-7/PCBS-7})_{2\text{min}/2\text{min}-15\text{sec}}\) are shown in Figure 3.5-3. The ellipsometric measurements show that the thickness of PAH/PCBS films increases linearly with the number of bilayers for deposition condition \((\text{PAH-7/PCBS-7})_{2\text{min}/2\text{min}-15\text{sec}}\), whereas the thickness increases roughly linearly up to 250 bilayers for the deposition condition \((\text{PAH-9/PCBS-8})_{2\text{min}/2\text{min}-15\text{sec}}\). The thickness per bilayer for \((\text{PAH-7/PCBS-7})_{2\text{min}/2\text{min}-15\text{sec}}\) was \(1.17\ (\pm 0.01)\) nm while the thickness per bilayer for \((\text{PAH-9/PCBS-8})_{2\text{min}/2\text{min}-15\text{sec}}\) was \(2.75\ (\pm 0.09)\) nm up to 250 bilayers. This more than 2-fold increase in bilayer thickness when the PAH was deposited at pH 9 was due to the reduced charge density of the chains which leads to thicker monolayers. These, in turn, provide for more adsorption sites for PCBS chains when deposited at pH 8, leading to thicker bilayers. This is consistent with the observation of Barrett et al. \(^{31}\) in which they deposited PAH and PCBS at different pH conditions and observed that the bilayer thickness increased by approximately six-fold.
and the optical absorbance increased by a factor of 20 as the pH of the deposition solutions varied from 3 to 10. Molecular control over the formation of ISAM films can thus be achieved by manipulating the pH of the weak polyelectrolyte.\textsuperscript{31, 32} Using PAH and poly(acrylic acid) (PAA), bilayers with thicknesses ranging from less than 1 nm to 12 nm have been prepared at different pH conditions.\textsuperscript{36} For the films made with the (PAH-9/PCBS-8)\textsubscript{2min/2min-15sec} deposition conditions for bilayer number > 250, growth in film thickness changed to a sub-linear manner while the plot of absorbance versus bilayer number in Figure 3.5-2 did not. This implies that the PCBS content of the films in this region was higher than for films with bilayer number < 250 since the higher PCBS content would compensate for the thinner bilayers. This loss of linearity correlated with the appearance of optical inhomogeneities for bilayer number > 250 and the loss of long range polar ordering as shown in Figure 3.5-3. These optical defects are scattering centers which most likely arose from compositional heterogeneities that began to propagate during the LbL process at the higher bilayer numbers, although the precise reason for this defect propagation is not known. This is consistent with the AFM images of the ISAM films taken at 200 and 400 bilayers for both (PAH-7/PCBS-7)\textsubscript{2min/2min-15sec} and (PAH-9/PCBS-8)\textsubscript{2min/2min-15sec} deposition conditions as shown in Figure 3.5-4. Films fabricated using the deposition condition (PAH-7/PCBS-7)\textsubscript{2min/2min-15sec} exhibited lower values of the root mean square (RMS) surface roughness of approximately 8 and 15 nm for 200 and 400 bilayers, respectively, as compared to the films fabricated at (PAH-9/PCBS-8)\textsubscript{2min/2min-15sec} which had RMS surface roughness values of approximately 18 and 21 nm for 200 and 400 bilayers, respectively.
Figure 3.5-3. Thickness vs. number of bilayers for (PAH-7/PCBS-7)_{2min/2min-15sec} [open squares] and (PAH-9/PCBS-8)_{2min/2min-15sec} [filled squares]. The thickness obtained per bilayer was 1.17 ± 0.01 nm for the first deposition condition and 2.75 ± 0.09 nm for the second deposition condition up to 250 bilayers. The concentrations of PAH and PCBS were 10 mM for all deposition conditions.
To calculate the second order susceptibility, $\chi^{(2)}$, of the films, SHG measurements were taken. The square root of SHG is plotted vs. the number of bilayers in Figure 3.5-5. For the deposition condition (PAH-9/PCBS-8)$_{2\text{min}/2\text{min}-15\text{sec}}$, a roughly linear relationship between square root of SHG and number of bilayers was observed for the first 200 bilayers implying that the polar orientation of the chromophores was maintained for the first 200 bilayers. The departure from linearity in Figure 3.5-5 is likely related to the apparent decrease in the thickness per bilayer observed at 250 bilayers and higher.
Importantly, the square root of SHG vs. number of bilayers for deposition condition (PAH-7/PCBS-7)_{2\text{min}/2\text{min-15sec}} showed a linear relationship at least up to 500 bilayers; this means that the non-centrosymmetric polar ordering of the chromophores was maintained throughout the deposition process for this condition.

![Graph showing the relationship between square root of SHG intensity and number of bilayers.](image)

Figure 3.5-5. Square root of second harmonic generation intensity vs. the number of bilayers for (PAH-7/PCBS-7)_{2\text{min}/2\text{min-15sec}} [open squares] and (PAH-9/PCBS-8)_{2\text{min}/2\text{min-15sec}} [filled squares].

The film homogeneity was studied by taking three different measurements at different spots on the same sample. The standard deviation of the square root of SHG measurements for deposition conditions (PAH-7/PCBS-7)_{2\text{min}/2\text{min-15sec}} and (PAH-9/PCBS-8)_{2\text{min}/2\text{min-15sec}} are shown in Table 3.5-2 above for 200, 400 and 500 bilayers. For condition (PAH-9/PCBS-8)_{2\text{min}/2\text{min-15sec}}, the standard deviation is comparatively higher for bilayer numbers 400 and 500 than for 200 bilayers and compared to deposition condition (PAH-7/PCBS-7)_{2\text{min}/2\text{min-15sec}} up to 500 bilayers. This higher standard deviation corresponds well with the visual appearance of these films which shows significant inhomogeneity.
Using Equations (2) - (5), $\chi^{(2)}_{zzz}$ and tilt angle were calculated and the results are summarized in Table 3.5-3.

**Table 3.5-3: Thickness, Absorbance per bilayer, tilt angle and $\chi^{(2)}_{zzz}$ of the films fabricated at two different deposition conditions.**

<table>
<thead>
<tr>
<th>Deposition Condition</th>
<th>Thickness per bilayer (nm)</th>
<th>Absorbance/bilayer ($\times 10^{-3}$) at 450 nm</th>
<th>$\langle \theta \rangle$ (degrees)</th>
<th>$\chi^{(2)}_{zzz}$ (10⁻⁹ esu)</th>
</tr>
</thead>
<tbody>
<tr>
<td>(PAH-7/PCBS-7)²min/2min-15sec</td>
<td>1.17 (± 0.01)</td>
<td>0.9*</td>
<td>37.3 (± 2.2)*</td>
<td>1.20 (± 0.10)*</td>
</tr>
<tr>
<td>(PAH-9/PCBS-8)²min/2min-15sec</td>
<td>2.75 (± 0.09) (up to 250 bilayers)**</td>
<td>2.9**</td>
<td>32.5 (± 2.0)**</td>
<td>2.24 (± 0.16) (up to 200 bilayers)**</td>
</tr>
</tbody>
</table>

* For 7/7 pH conditions, the thickness/BL, absorbance/BL, tilt angle and SHG results were based on data up to 500 bilayers
**For 9/8 pH conditions, the data were reported for bilayer numbers as specified or up to 500 bilayers

Although the thickness per bilayer for deposition condition (PAH-9/PCBS-8)²min/2min-15sec is more than two times higher than that for (PAH-7/PCBS-7)²min/2min-15sec, which according to equation (2) and (3) should lead to a lower value of $\chi^{(2)}_{eff}$ and hence a lower value of $\chi^{(2)}_{zzz}$, the slope of square root of SHG vs. number of bilayers is almost three times higher for the elevated pH conditions than for the neutral pH conditions. This results in a higher value of $\chi^{(2)}_{zzz}$ for films deposited at higher pH than for the films deposited at neutral pH. The absorbance per bilayer for films deposited at higher pH conditions is almost three times higher than those deposited at neutral pH; this may imply a much higher concentration of chromophores at higher pH conditions. However, since absorbance of these films depends not only on the concentration of the chromophores but also on the local chemical environment and the orientation of the chromophores, quantitative conclusions cannot be drawn about the chromophore concentration in these films. Since the effect of processing conditions on film properties is a central point of this work, additional films were made with an automated slide stainer that employed somewhat different fabrication conditions. These are discussed next.
3.5.3 Films made using an automated slide stainer – done by Cemil Durak in Prof Heflin’s lab

In another set of experiments, layer-by-layer films were fabricated using an automated slide stainer. PAH and PCBS films up to 600 bilayers were deposited on glass slides. The polyelectrolyte solutions used were at 10 mM concentration and at pH 7, conditions known from the previous work with the StratoSequence™ Mark VI robotic deposition system to result in homogeneous films with long range polar order. The deposition and rinsing times were 2 minutes and this condition is written in abbreviated form as (PAH-7/PCBS-7)_{2\text{min}/2\text{min}}. An absorbance per bilayer of 0.0012 at 450 nm was obtained using the spectrophotometer and a film thickness of 1.25 (± 0.01) nm per bilayer was estimated using the ellipsometer. These compare with an absorbance per bilayer of 0.0009 and a bilayer thickness of 1.17 nm for the films made with the StratoSequence instrument although the rinsing time for the latter films was 2 minutes, 15 seconds. No convection was used in the deposition baths in contrast to the use of convection in the dipper used to fabricate films in the previous section. The absorbance and thickness data as a function of the number of bilayers are shown in Figure 3.5-6.

![Figure 3.5-6. Absorbance (squares) at 450 nm and thickness (diamonds) vs. the number of bilayers for (PAH-7/PCBS-7)_{2\text{min}/2\text{min}} for series made with an automated slide stainer.](image-url)
As shown in Figure 3.5-7, the square root of SHG increased linearly with increasing number of bilayers indicating that the polar orientation of the films was maintained up to 600 bilayers and 740 nm. Using the procedure described above, the tilt angle for these films was $38.0^\circ \pm 2.4^\circ$ and the value of $\chi^{(2)}_{zzz}$ was $1.25 \pm 0.005 \times 10^{-9}$ esu which is in excellent agreement with the values obtained in the previous section for the deposition condition $(PAH-7/PCBS-7)_{2min/2min-15sec}$ using the StratoSequence instrument reported in Table 3.5-3.

![Figure 3.5-7. Square root of SHG intensity vs. the number of bilayers for $(PAH-7/PCBS-7)_{2min/2min}$ for series made with an automated slide stainer.](image)

### 3.6 Conclusions

Films containing an oriented, NLO chromophore were fabricated on glass slides using the ionic self-assembled multilayer (ISAM) process. The polymeric dye poly{1-[p-(3’-carboxy-4’-hydroxyphenylazo)benzenesulfonamido]-1,2-ethandiy} (PCBS) was deposited along with poly(allylamine hydrochloride) (PAH) while varying pH and deposition and rinsing times. It was observed that different deposition conditions strongly
affected the optical properties of the ISAM films such as absorbance, thickness, and second order susceptibility $\chi^{(2)}.$

At deposition and rinsing times of 2 minutes, two series of ISAM films were fabricated at different pH conditions – one at pH 7 for both polyelectrolytes and the other at pH 8 for PCBS and pH 9 for PAH. Higher values of absorbance per bilayer and thickness per bilayer were observed for ISAM films when PAH was deposited at pH 9 due to its reduced charge density which favors deposition with more loops and tails which would, in turn, lead to increased adsorption of PCBS. At the elevated pH condition 9/8, the thickness per bilayer was found to be 2.7 nm as compared to 1.2 nm at the pH condition 7/7. Considering that the deposition and rinsing times were the same, this implies that at higher pH the ISAM film formation process results in more rapid growth of the film to a given thickness. However, ISAM films made at higher pH did not show a linear growth in absorbance or thickness after 300 bilayers and exhibited visual inhomogeneity. By contrast, the films made at neutral pH exhibited linearity in absorbance, thickness, and square root of the SHG intensity as a function of the number of bilayers up to 500 bilayers. Furthermore, a second set of films made with a different automated deposition system at neutral pH also showed linearity of thickness and quadratic scaling of SHG intensity up to a thickness of 740 nm.

These results demonstrate a window in processing conditions in which a trade-off between thickness per bilayer and optical homogeneity can be achieved by adjusting the pH of the polyelectrolyte solutions. The demonstration that ISAM films can be fabricated to thicknesses on the order of 1 μm with a linear increase in thickness and uniform orientation of the chromophores establishes the possibility of fabricating electro-optic waveguide devices with excellent thermal and temporal stability.
3.7 Appendix A for Chapter 3

3.7.1 Ellipsometry Procedure

Film thickness measurements were made using a variable angle spectroscopic ellipsometer (VASE) (J.A. Woolam ellipsometer VB-200 with WVASE32 software version 3.361). Ellipsometry is based on the changes in the polarization of light when it reflects from a surface. Linearly polarized light reflects off the sample and becomes elliptically polarized. This change in the state of polarization can be defined by two quantities, namely $\Delta$ (delta) and $\psi$ (psi). The phase difference between the linearly polarized light and the elliptically polarized light is given by $\Delta$ whereas $\psi$ gives the change in amplitude between the two. The ellipsometric analysis was done in the vicinity of the Brewster angle because ellipsometry measurements are most sensitive to film characteristics at the Brewster angle. An initial scan was done for wavelengths from 300 to 800 nm at 50 nm intervals and this wavelength range was then repeated over angles from 50 deg to 70 deg at 4° intervals to find the Brewster angle. From a graph of $\Delta$ vs. $\lambda$, the Brewster angle was determined as the point at which $\Delta$ quickly passed from 180° through 90° to 0°. The Brewster angle for PAH/PCBS slide series was found to be 62°. Following the determination of the Brewster angle, the sample was scanned at wavelengths from 300 to 800 nm at 10 nm intervals in the vicinity ($\pm2°$) of the Brewster angle in 1° increments. The sample was scanned at three different positions to check for the film homogeneity. The experimental data collected this way were then fitted with a model that is described below in detail.

3.7.1.1 Modeling

The model consists of two layers - one for the glass substrate and the other for the thin film. The model for the glass substrate consists of the refractive index and the extinction coefficient ($n$ and $k$ respectively) values as a function of wavelength and is plotted in Figure 3.7-1 below.
Figure 3.7-1. $n$ and $k$ values versus wavelength for a typical glass substrate used in the film deposition experiments. These values were used to model the experimental data for the ISAM films.

The Lorentz oscillator model represents the thin film and is given by the following equation:\(^2\)

\[
\varepsilon(E) = \varepsilon_i(\infty) + \sum_k \frac{A_k}{E_k^2 - E^2 - iB_k E}
\]

\[
(\text{A1})
\]

in which $\varepsilon_i(\infty)$ represents the value of the real part of the dielectric function at very large photon energy, $A_k$ is the amplitude of the $k^{\text{th}}$ oscillator (eV\(^2\)), $E$ is the photon energy (eV), $E_k$ is the center energy of the $k^{\text{th}}$ oscillator (eV), and $B_k$ is the $k^{\text{th}}$ peak’s width (eV). $E_k$ is given by equation (A2). From $\varepsilon$, values of $n$ and $k$ can be calculated as shown in equations (A3) and (A4).

\[
E_k = h \nu_k = \frac{1.24(eV \cdot \mu m)}{\lambda_k (\mu m)}
\]

\[
(\text{A2})
\]

\[
n = \sqrt{\frac{\varepsilon_1 + \sqrt{\varepsilon_1^2 + \varepsilon_2^2}}{2}}
\]

\[
(\text{A3})
\]

\[
k = \sqrt{-\varepsilon_1 + \sqrt{\varepsilon_1^2 + \varepsilon_2^2}}
\]

\[
(\text{A4})
\]
where $v_k$ and $\lambda_k$ are the frequency and the wavelength of the $k^{th}$ absorbance peak, respectively. A typical value of $\lambda_k$ (as measured by UV-Vis spectroscopy) for PAH/PCBS slide series is 360 nm.

Because only one absorbance peak was observed while scanning the slide for absorbance over a range of wavelength, only one Lorentz oscillator model was used and its oscillating center was fixed at $\lambda_k (= \lambda_1)$. Using the above value for $\lambda_1$, the parameter $E_1$ can be calculated from equation (A2). The value for the parameter $E_1$ for the PAH/PCBS films was calculated to be 3.444 eV.

An initial guess was provided for the other parameters $\varepsilon_{\infty}$, $A_1$ and $B_1$ to estimate the film thickness. Depending on the initial guess, the results might vary. However, there are various ways to determine if the obtained results are optimal. One of the constraints in fitting the parameters is that $k$ should reach a maximum at $\lambda_1$. The goodness of fit was assessed with the values of the mean sum of the errors (MSE). In general, a better fit is obtained with lower values of the MSE. The optical parameters obtained after modeling are shown in the Figure 3.7-2 for the films made using PCBS and PAH.
Figure 3.7-2. Optical parameters for a film consisting of 500 bilayers of PAH/PCBS obtained using VASE. The deposition conditions were: $C_{PAH} = 10$ mM repeat unit (RU), $C_{PCBS} = 10$ mM RU, $pH_{PAH} = 7.0$, $pH_{PCBS} = 7.0$. The dipping times were 2 minutes in both PAH and PCBS solutions. The rinsing time was 135 seconds equally distributed in three baths (45 sec x 3). The maximum value of the dispersion coefficient occurs at the wavelength $\sim 360$ nm. A similar peak is observed at this wavelength by UV-Vis spectroscopy.
3.8 References


Chapter 4 A study of film structure and adsorption kinetics of polyelectrolyte multilayer films: effect of pH and polymer concentration

4.1 Abstract

The alternate adsorption of the polycation poly(allylamine hydrochloride) (PAH) and the sodium salt of the polymeric dye poly{1-[p-(3’-carboxy-4’-hydroxyphenylazo)-benzenesulfonamido]-1,2-ethandiyl} (PCBS) on quartz crystals coated with silica was studied to understand the structural properties and adsorption kinetics of these films using a combination of a quartz crystal microbalance with dissipation monitoring (QCM-D), absorbance, and ellipsometry measurements. In-situ deposition of the polycation PAH on QCM crystals was monitored, followed by rinsing with water and then deposition of the polyanion PCBS. The effects of polymer concentration and pH on film structure, composition and adsorption kinetics were probed. The polymers were adsorbed at neutral pH conditions and at elevated pH conditions where PAH was essentially uncharged to obtain much thicker films. The change in the resonant frequency, $\Delta f$, of the QCM-D showed a linear decrease with the number of bilayers, a finding consistent with absorbance and ellipsometric thickness measurements which showed linear growth of film thickness. By using the $\Delta f$ ratios of PCBS to PAH, the molar ratios of repeat units of PCBS to PAH in the bilayer films as determined by QCM-D were approximately 1:1 at polyelectrolyte concentrations 5-10 mM repeat unit, indicating complete dissociation of the ionic groups. The frequency and dissipation data from the QCM-D experiments were analyzed with the Voigt model to estimate the thickness of the hydrated films which were then compared with thicknesses of dry films measured by ellipsometry. This led to estimates of the water content of the films to be approximately 45 weight %. In addition to the QCM-D, some films were also characterized by a QCM which measures only the first harmonic without dissipation monitoring. For the deposition conditions studied, the deposited mass values measured by the QCM’s first harmonic were similar to the results.
obtained using higher harmonics from the QCM-D, indicating that the self-assembled polyelectrolyte films were rigid.

**4.2 Keywords**

Quartz Crystal Microbalance (QCM, QCM-D), Ionic Self-Assembled Films (ISAM), polymer multilayers, layer-by-layer.

**4.3 Introduction**

Organic materials are of great interest as active components in electronic devices due to the ease with which their properties can be tuned at the molecular level and their ease of fabrication. Thin films of organic materials are particularly interesting for applications in light-emitting diodes, photovoltaics, electrochromic devices, electro-optic modulators, integrated molecular optics, biosensors, and fuel cells. \(^1\text{–}^4\) One of the methods for fabrication of organic thin films involves the alternate adsorption of polycations and polyanions on a charged surface which leads to the formation of ionic self-assembled multilayer (ISAM) films, also commonly referred to as layer-by-layer (LbL) films. \(^5\text{, }^6\) When a polyelectrolyte adsorbs onto an oppositely charged surface, charge reversal on the surface typically occurs; this facilitates the adsorption of the next layer of oppositely charged polymer. In principle, films with an arbitrary number of bilayers can be fabricated in this fashion. Rational applications of this technique require an understanding of the internal architecture of these films, such as composition, structure and mechanical properties \(^7\) and an understanding of how solution parameters such as concentration and pH affects the internal structure of these films. \(^8\text{–}^{11}\)

Our work involves the study of ISAM films at the molecular level to understand the composition of these films which exhibit nonlinear optical (NLO) effects due to inclusion of an NLO chromophore that can be oriented in a polar manner. \(^12\text{–}^{18}\) Films exhibiting NLO effects have applications in electro-optic (EO) modulators which convert electrical signals to optical signals and thus play an important role in communication networks. In organic films, the second order nonlinear susceptibility of an NLO film, \(\chi^{(2)}\) is given by. \(^19\)
\[ \chi^{(2)} = NF\beta \langle \cos^3 \psi \rangle \]  

in which \( N \) is the chromophore density, \( F \) is the local field factor which is a function of the refractive index, \( \beta \) is the hyperpolarizability, and \( \psi \) is the orientation angle of the chromophores. Rational design of NLO films thus involves choosing a chromophore with a suitably high \( \beta \) and incorporating it into a film with high density \( N \) and low tilt angle \( \psi \). In this paper, we probe how processing conditions for film formation affect \( N \) and the bilayer thickness.

There are many studies of ISAM films and their structural properties, but relatively few of films that exhibit significant second order NLO properties.\(^{18,20}\) A study of structural and mechanical properties of NLO-active polyelectrolyte multilayer films was done by Mermut et al.;\(^7\) however, NLO properties were not studied. Other studies to understand the structural properties of ISAM films have employed techniques such as surface plasmon resonance (SPR),\(^{21,22}\) reflectometry,\(^{23}\) in-situ atomic force microscopy,\(^{24}\) streaming potential measurements,\(^{25}\) X-ray photoelectron spectroscopy (XPS),\(^{21}\) ellipsometry and absorbance measurements,\(^8\) quartz crystal microbalance (QCM),\(^{18,21,26-32}\) and QCM-D.\(^{22,33-38}\)

The QCM, which measures the change in the fundamental resonant frequency of a piezoelectric crystal due to deposition, has been widely used in biosensors,\(^{27,28,30,32}\) to study the adsorption of proteins,\(^{39,40}\) to study adsorption of inorganic materials such as nanoparticles,\(^{11,29}\) for measuring thin film growth in deposition and sputtering processes,\(^{41}\) to measure changes in viscosity,\(^{42}\) and to study polymer adsorption\(^{31,37}\) and ISAM formation.\(^{21,22,26-30,32,35,36,43}\) The more recent technique known as QCM-D can measure up to 7 harmonics and their corresponding dissipations, which can provide additional information about the viscoelastic properties of attached films.\(^{33,34,44,45}\)

ISAM film formation has been studied with a QCM, including the polycation:polyanion molar ratio in films as a function of pH,\(^{43}\) the effect of varying polycation structure and concentration in combination with poly(sodium 4-
styrenesulfonate) (PSS),\textsuperscript{26} and the effect of solvent quality on film morphology and the kinetics of film growth.\textsuperscript{46} ISAM formation involving the azobenzene-containing polyanion (PAZO, also known as PCBS, the polyanion used in the present study) has been studied using a QCM as well. \textit{In-situ} adsorption measurements of films composed of poly(dimethyldiallylammonium chloride) (PDDA) and PCBS revealed that the PCBS:PDDA mass ratio was \textasciitilde1:2 corresponding to a PCBS:PDDA molar ratio of 1:4.\textsuperscript{18} While the frequency shift showed a linear growth with the number of bilayers, second harmonic generation (SHG) measurements did not show a quadratic increase with the number of bilayers, indicating that the polar orientation of the chromophores was not maintained as the number of bilayers increased. ISAM formation involving PCBS was also studied using PDDA and poly(ethyleneimine) in which QCM studies of dried films revealed that PCBS adsorbed onto PEI as aggregates, whereas it did not aggregate when adsorbing onto PDDA. However, NLO properties of the films were not studied.\textsuperscript{32}

The present study demonstrates a methodology that combines \textit{in-situ} QCM-D measurements of hydrated films with absorbance and ellipsometry measurements to probe the effect of polymer concentration and pH on the polyanion:polycation ratio, the water content, and the structure of ISAM films. The conditions of polymer concentration and pH were chosen to complement a companion study of the NLO properties of PCBS/PAH ISAM films.\textsuperscript{20} In that study, we found that films deposited at pH 7 where the PAH was highly charged were optically homogeneous and exhibited long range polar ordering of the azobenzene chromophore in PCBS for films consisting of more than 600 bilayers. When the PAH was deposited at pH 9 where it was partly charged, the bilayer thickness was greater than for the pH 7 case, but long range polar ordering disappeared after 200 bilayers. The reason why PAH results in polar orientation of the PCBS chromophore, while PDDA does not in films with bilayer numbers >10-20, is still an open question, leading to a need for a more detailed study of the formation of ISAM films containing PCBS; particularly, we sought to delineate those conditions that lead to homogeneous film formation at high bilayer numbers. In the present study for selected deposition conditions, we compare analyses of films using both QCM-D and QCM and also study the kinetics of multilayer formation.
4.4 Experimental

4.4.1 Materials

Poly(allylamine hydrochloride) (PAH, Figure 4.4-1 a) was used as the polycation (M_w ca. 70 kDa; Aldrich). Poly{1-[p-(3’-carboxy-4’-hydroxyphenylazo)benzenesulfonamido]-1,2-ethandiyl} (Aldrich, PCBS, Figure 4.4-1 b) was used as the polyanionic chromophore. PCBS has an azobenzene side group that has a sufficiently high hyperpolarizability, β, to give a measurable SHG signal. Deionized (DI) water (Barnstead ROpureST; model # D6311) with a resistivity >17 MΩ.cm was used. The ionic strength of the polymer solutions was adjusted using sodium chloride (Fisher Scientific). The pHs of the polymer solutions were adjusted using 1.0 M or 0.1 M solutions of sodium hydroxide and hydrogen chloride.

![Figure 4.4-1](a) Repeat unit structure of PAH; (b) repeat unit structure of PCBS

4.4.2 Characterization

Absorbance and Ellipsometry: Absorbance measurements were done using a Perkin Elmer Lambda 25 UV/Vis system. The films exhibited an absorbance maximum, λ_max, at 360 nm, due to absorption by PCBS. Film thicknesses were measured using a variable angle spectroscopic ellipsometer (J.A. Woolam ellipsometer VB-200 with WVASE32 software version 3.361). Both absorbance and ellipsometry measurements were done on films fabricated on a glass substrate, the details of which can be found in a
companion study.\textsuperscript{20} Details of the ellipsometry procedure are found in the appendix section 4.7.1 later in this chapter.

\textit{Quartz Crystal Microbalance:} Two different quartz crystal microbalances were used in this study – a QCM-D E4 system (Q-Sense Inc.) and a QCM (Maxtek Inc.). The Maxtek QCM measures changes in the first harmonic frequency and the change in resistance, whereas the QCM-D measures seven different harmonics from the 1\textsuperscript{st} to the 13\textsuperscript{th} and their corresponding dissipation factors. Both the QCM and QCM-D instruments had a fundamental resonance frequency of 5 MHz. In all experiments, SiO\textsubscript{2}-coated quartz crystals were used and cleaned with a plasma etcher device (SPI Supplies, Plasma Prep II\textsuperscript{TM}) in the presence of oxygen. All measurements were made with the crystals in flow cells where the crystals were in contact with a liquid phase on only one side. For the QCM-D, the temperature was maintained at 25 ($\pm$0.02)$^\circ$C and, for the QCM, the temperature was maintained at 25 ($\pm$0.1)$^\circ$C. In all experiments, the ionic strength was kept constant at 1.7 mM, the effective ionic strength of a salt-free PCBS solution at 10 mM based on the electrostatic wormlike chain theory.\textsuperscript{47} This corresponds to an effective Debye length of 7 nm. For all experiments, 10 alternate layers of PAH and PCBS were adsorbed on the SiO\textsubscript{2}-coated quartz crystals. All QCM-D measurements were done in triplicate except for the experiments at 5 mM repeat unit concentration which were done in duplicate. All QCM measurements were done in triplicate except for the experiment at 5 mM repeat unit concentration which was done once. The experimental set-up used for the QCM is shown in the supplementary information.

The QCM is an effective tool to understand the process of film formation that gives insight into the compositional properties at the molecular level. It is an ultra-sensitive mass sensor, consisting of a piezoelectric quartz crystal sandwiched between a pair of electrodes. When an AC voltage is applied across the electrodes, the quartz crystal oscillates at its resonant frequency. If a rigid layer is evenly deposited on one or both sides of the electrodes, the resonant frequency will decrease proportionally to the mass of the absorbed layer according to the Sauerbrey equation.\textsuperscript{48}
\[ \Delta f_m = -2 \times f_0^2 \times \Delta \frac{m}{A \times \sqrt{\rho_q \mu_q}} \]  

(2)

in which \( \Delta f_m \) = measured frequency shift, \( f_0 \) = fundamental frequency of the crystal, \( \Delta m \) = mass change per unit area, \( A \) = piezo-electrically active area, \( \rho_q \) = density of quartz (2.648 g/cm\(^3\)), and \( \mu_q \) = shear modulus of quartz (2.947 \times 10^{-11} \text{ dyne/cm}^2).

Equation (2) is not valid if the deposited mass is: a) not rigidly deposited on the electrode surface, b) slips on the surface, or c) is not evenly deposited on the surface of the electrodes. As described by Kanazawa et al.,\(^{49}\) the resonant frequency of the QCM crystal also depends on the viscosity and density of the gas or liquid which is in contact with the crystal. The change in the resonant frequency of the QCM crystal due to density and viscosity effects is given by:

\[ \Delta f_{\text{aqueous}} = -\left[ \frac{n f_0^{3/2}}{(\pi \mu_q \rho_q)^{1/2}} \right] (\rho_L \eta_L)^{1/2} \]  

(3)

in which

- \( n \) = number of crystal faces in contact with the liquid
- \( \rho_L \) = density of the bulk liquid
- \( \eta_L \) = viscosity of the bulk liquid

In addition to the changes in frequency, QCM-D can also measure the dissipation which is inversely proportional to the decay time, \( \tau \), and given by:

\[ D = \frac{1}{\pi f \tau} \]  

(4)

in which \( f \) is the crystal oscillation frequency. For a soft film, the decay time is small due to increased energy loss, leading to higher value of the dissipation, whereas for a rigid film, the dissipation time is large leading to smaller values of dissipation. Thus, the change in dissipation (\( \Delta D \)) can be used to obtain information about the mechanical properties of the films.
4.5 Results and Discussion

The alternate adsorption of PAH and PCBS on quartz crystals coated with silica was studied to understand the composition and structural properties of the ISAM films using in combination with absorbance and ellipsometry measurements. Four different deposition conditions were used, as summarized in Table 4.5-1. In the first deposition condition, the concentrations of both PAH and PCBS were 1 mM based on repeat unit and pH = 7.0. This is abbreviated as (PAH-1/PCBS-1)7/7; the number after the polymer designation gives the concentration and the first and second numbers in the subscript give the pHs of PAH and PCBS, respectively. The other three deposition conditions were: (PAH-5/PCBS-5)7/7, (PAH-10/PCBS-10)7/7, (PAH-10/PCBS-10)9/8. The first three deposition conditions (1, 2 and 3 from Table 4.5-1) were chosen to probe the effect of concentration of the polyelectrolytes. The 3rd and 4th deposition conditions were used to study the effect of the solution pH which affects the ionization of polyelectrolytes which, in turn, affects the adsorbed polymer chain conformation. When the polymer is highly charged, chains tend to adsorb in flat, train-like conformations whereas, when the polymer is relatively uncharged, chains adsorb with thick and loop-like conformations due to decreased repulsion between the chains.8, 9, 50, 51 Because the pKₐ of PAH is 8.7,52 it was expected that the PAH layers would be thicker in deposition condition 4 compared to conditions 1, 2, and 3.

Table 4.5-1. Deposition conditions studied using QCM-D, absorbance and ellipsometry measurements.

<table>
<thead>
<tr>
<th>Deposition Condition</th>
<th>PAH Repeat Unit Conc. (mM)</th>
<th>PCBS Repeat Unit Conc. (mM)</th>
<th>pH_PAH</th>
<th>pH_PCBS</th>
</tr>
</thead>
<tbody>
<tr>
<td>1. (PAH-1/PCBS-1)7/7</td>
<td>1.0</td>
<td>1.0</td>
<td>7</td>
<td>7</td>
</tr>
<tr>
<td>2. (PAH-5/PCBS-5)7/7</td>
<td>5.0</td>
<td>5.0</td>
<td>7</td>
<td>7</td>
</tr>
<tr>
<td>3. (PAH-10/PCBS-10)7/7</td>
<td>10.0</td>
<td>10.0</td>
<td>7</td>
<td>7</td>
</tr>
<tr>
<td>4. (PAH-10/PCBS-10)9/8</td>
<td>10.0</td>
<td>10.0</td>
<td>9</td>
<td>8</td>
</tr>
</tbody>
</table>
The QCM-D results for 10 alternate adsorption cycles of PAH and PCBS on silica coated quartz crystal for the condition (PAH-10/PCBS-10)$_{7/7}$ are shown in Figure 4.5-1. Except for the first harmonic and, in very few cases, the third harmonic, which had high noise levels, the higher harmonics overlapped each other and led to the same final results for film properties (see appendix section 4.7.3 later in this chapter). Thus, all results shown here involve normalized changes in the frequency for the $7^{th}$ harmonic versus time and the corresponding changes in dissipation. The normalization was done by dividing the change in frequency by its harmonic number. In Figure 4.5-1, a baseline was first obtained with DI water and then PAH was injected as shown by the arrow marked “1”. Upon introducing PAH, a drop in frequency was seen which reached a plateau in approximately 60 seconds, indicating complete adsorption. After PAH adsorption was complete, DI water was injected as shown by the arrow marked “2” to rinse the loosely bound polyelectrolyte from the surface; this leads to an increase in frequency. The change in frequency could be due to adsorption or to the effect of bulk properties of the fluid. However, comparing the baseline when the silica coated quartz crystal was in contact with DI water before and after an adsorption step eliminated the effect due to bulk properties of the solution and thus the changes in frequency reflected only the mass uptake by the QCM-D. The adsorption and rinsing steps were repeated for PCBS as shown by arrows marked “3” and “4” respectively. This entire process was repeated for 10 bilayers of PAH and PCBS. The frequency shifted linearly with the number of bilayers, indicating a homogeneous growth of these films. However, linear growth in dissipation was observed only after deposition of 3 bilayers; the slope of the dissipation curve was much less up to 3 bilayers as compared to the slope thereafter. This is possibly due to the effect of the underlying rigid silica layer. A similar interfacial effect due to the underlying gold surface was observed by Caruso et. al.; a linear growth in the change in frequency only after 2 bilayers of PAH/PSS adsorption was observed.
Figure 4.5-1. QCM-D results showing changes in the 7th harmonic frequency and dissipation of 10 adsorption cycles of PAH and PCBS for the deposition condition (PAH-10/PCBS-10)7/7 at an effective ionic strength $I_{eff} = 1.7$ mM and at 25°C. The flow rate was maintained at 0.3 ml/min throughout the experiment. Arrow “1” marks the injection of PAH followed by rinsing with DI water shown by the arrow marked “2”. The PCBS deposition and rinsing steps are shown by arrows marked “3” and “4” respectively. Arrow “5” indicates the beginning of the 4th bilayer.

Figure 4.5-2 shows the enlarged section of the second adsorption step of PAH and PCBS for the results shown in Figure 4.5-1. Timelines “a” and “c” indicate the time for almost complete adsorption (>90% complete adsorption) of PAH and PCBS which is on the order of one minute. The frequency shift for PCBS adsorption, indicated by “d” is much higher as compared to PAH adsorption, indicated by “b”, showing that a higher mass of PCBS is adsorbed for every bilayer of PAH and PCBS. A quantitative estimation of molar ratio of PCBS to PAH adsorbed in the films at different polymer concentrations and pH is shown in a later section. The change in $\Delta D$ when the film is in contact with the polyelectrolyte solutions – either PAH or PCBS - is larger than when the same films are in contact with DI water. This could be due to the viscosity and density of the polyelectrolyte solutions 49 with which the crystal is in contact as well as due to the
presence of loosely bound chains that are ultimately rinsed off with DI water, making the films rigid which in turn leads to a decreased dissipation value. Observing the trends in $\Delta f$ and $\Delta D$ when switching from one solution to another can help to understand whether the adsorption kinetics are affected by the viscosity and density of the liquid phase. For example, for the PCBS curve in Figure 4.5-2, there is a negligible change in $\Delta f$ just before rinsing with DI water compared to after rinsing, whereas there is a noticeable change in $\Delta D$, $\sim 1.5 \times 10^{-6}$. In view of the effect of liquid phase viscosity and density on $\Delta f$ as described by equation (3), we conclude that viscosity and density effects are relatively insignificant for these deposition conditions. Thus, the observed change in $\Delta D$ is most likely due to loosely bound PCBS chains that are rinsed away.

![Figure 4.5-2](image_url)

Figure 4.5-2. An enlarged section from Figure 4.5-1 for the second bilayer of PAH and PCBS. The PAH and PCBS adsorption and rinsing steps are shown by arrows. “a” and “c” denote the times for PAH and PCBS to reach complete adsorption, respectively. “b” and “d” denote the shift in frequency for the PAH and PCBS adsorption steps, respectively. The data shown are normalized from the 7th harmonic.
The kinetics of polyelectrolyte deposition shown in Figure 4.5-2 are summarized in Table 4.5-2 in terms of the time required for 95% complete adsorption for PAH and PCBS. The deposition kinetics were fitted to a single exponential function from which the decay time $\tau_d$ was estimated. The time required for 95% completion of deposition is then $3\tau_d$. The Reynolds Number, Re, ranged between 0.96 – 1.61 based on the hydraulic diameter of the flow cell as the characteristic length which, in this case, was 1.2 mm. In all cases, deposition of both PCBS and PAH as well as the DI water rinsing step appeared to be 95% complete within about 60 seconds, which is relevant for ISAM film formation, particularly for films involving a large number of bilayers. By comparison, an earlier study of deposition kinetics of PCBS and PDDA, done with a QCM under static conditions and comparable polymer concentrations and pH conditions as in the present study, showed deposition was 95% complete within 5-6 minutes. The more rapid deposition kinetics observed here are due to the effects of convection. It is intriguing to note the marked decrease in both the PCBS and PAH adsorption times for the deposition condition (PAH-10/PCBS-10)\textsubscript{9/8} compared to the (PAH-10/PCBS-10)\textsubscript{7/7} condition. This could be due to the increased pH, especially for the PAH step, as well as to the increased flow rate. In a related study of multilayer growth of PAH/PCBS films, Mermut and Barrett found that the kinetics of bilayer thickness growth under static conditions - measured \textit{ex-situ} using ellipsometry - accelerated greatly at pH 9 where the charge density of PAH was reduced. For PAH/PCBS concentrations of 10 mM, their films showed no increase in thickness per bilayer after a deposition time of 60 seconds which is consistent with our observation of the kinetics. A more detailed study of adsorption kinetics is currently underway to probe the separate effects of deposition pH, flow rate, and polymer concentration.
Table 4.5-2. Kinetics of polymer adsorption showing the time required to reach 95% complete adsorption as a function of flow rate and Reynolds number at different deposition conditions. The standard deviations are reported.

<table>
<thead>
<tr>
<th>Condition</th>
<th>Flow Rate (ml/min)</th>
<th>Reynolds number, Re</th>
<th>Time required for 95% complete adsorption, sec</th>
</tr>
</thead>
<tbody>
<tr>
<td>1. (PAH-1/PCBS-1)\text{7/7}</td>
<td>0.40</td>
<td>1.28</td>
<td>39 ± 1</td>
</tr>
<tr>
<td>2. (PAH-5/PCBS-5)\text{7/7}</td>
<td>0.30</td>
<td>0.96</td>
<td>62 ± 4</td>
</tr>
<tr>
<td>3. (PAH-10/PCBS-10)\text{7/7}</td>
<td>0.30</td>
<td>0.96</td>
<td>64 ± 4</td>
</tr>
<tr>
<td>4. (PAH-10/PCBS-10)\text{9/8}</td>
<td>0.50</td>
<td>1.61</td>
<td>29 ± 3</td>
</tr>
</tbody>
</table>

4.5.1 Effect of Concentration and pH on Film Composition

The frequency change $\Delta f$ versus number of bilayers for the various deposition conditions listed in Table 4.5-1 are shown in Figure 4.5-3. A linear change in $\Delta f$ with number of bilayers was observed for all deposition conditions. To avoid the effect of the rigid SiO$_2$ layer on film properties, the slopes of $\Delta f$ versus the number of bilayers were calculated after three bilayers were deposited (Table 4.5-3). The films for the condition (PAH-10/PCBS-10)$\text{7/7}$ showed a linear increase in absorbance and thickness up to 600 bilayers in a previous study.$^{20}$
Table 4.5-3. Change in frequency ($\Delta f$) per bilayer for PAH and PCBS and change in frequency for individual layers of PAH and PCBS averaged over bilayer #s 4-10. The standard deviations are reported.

<table>
<thead>
<tr>
<th>Deposition Condition</th>
<th>$-\Delta f$ per bilayer</th>
<th>$-\Delta f_{\text{PAH}}$ per bilayer</th>
<th>$-\Delta f_{\text{PCBS}}$ per bilayer</th>
</tr>
</thead>
<tbody>
<tr>
<td>1. (PAH-1/PCBS-1)$_{7/7}$</td>
<td>9.6 (± 0.2)</td>
<td>1.1 (± 0.3)</td>
<td>8.2 (± 0.6)</td>
</tr>
<tr>
<td>2. (PAH-5/PCBS-5)$_{7/7}$</td>
<td>13.7 (± 0.2)</td>
<td>2.6 (± 0.4)</td>
<td>10.5 (± 0.7)</td>
</tr>
<tr>
<td>3. (PAH-10/PCBS-10)$_{7/7}$</td>
<td>14.1 (± 0.4)</td>
<td>2.7 (± 0.4)</td>
<td>11.4 (± 0.8)</td>
</tr>
<tr>
<td>4. (PAH-10/PCBS-10)$_{9/8}$</td>
<td>33.9 (± 0.7)</td>
<td>9.6 (± 0.8)</td>
<td>24.1 (± 1.6)</td>
</tr>
</tbody>
</table>

The effect of polymer concentration on frequency change is illustrated in Figure 4.5-4 in which the 1st harmonic data from QCM and the 7th harmonic normalized with the overtone number from the QCM-D are shown. The experimental data from QCM-D and QCM are in good agreement. To our knowledge, this is the first time such a direct
A comparison has been made between a QCM and QCM-D for polyelectrolyte LbL films. The frequency change (-Δf) per bilayer increased with the concentration from 1 mM to 5 mM of PAH and PCBS, whereas there was little change when the concentration of polyelectrolytes increased from 5 to 10 mM. This suggests a saturation limit for polymer adsorption rather like an adsorption isotherm plateau.

The repeat unit molar ratio $M_{PCBS}/M_{PAH}$ in a film can be estimated from the $Δf$ data for the individual PAH and PCBS deposition steps from the QCM-D experiments by:

$$
\frac{M_{PCBS}}{M_{PAH}} = \frac{Δf_{PCBS} \cdot MW_{PCBS}}{Δf_{PAH} \cdot MW_{PAH}}
$$

in which $MW_{PCBS}$ and $MW_{PAH}$ are the repeat unit molecular weights of PCBS and PAH, respectively. In Equation (5), the frequency changes for PAH and PCBS were estimated using the frequency shifts marked by “b” and “d”, respectively, in Figure 4.5-2. To calculate $M_{PCBS}/M_{PAH}$, it was assumed that the PAH and PCBS monolayers have the same water content, i.e., the same hydration level. Since both PAH and PCBS have one ionic group in their repeat units, the molar ratio in which they adsorb can give a quantitative measurement of percent dissociation of these films upon adsorption of one polyelectrolyte on the other.
Values of the molar ratio $M_{PCBS}/M_{PAH}$ are plotted against the repeat unit concentration in Figure 4.5-5. $M_{PCBS}/M_{PAH}$ is close to 1 at 5 and 10 mM polymer concentrations at pH 7 where prior work has shown that these polyelectrolytes are almost fully ionized. A similar result was observed by Lvov et al. for the alternate adsorption of poly(styrene sulfonate) (PSS) and poly(ethyleneimine) (PEI), which using a QCM, were found to adsorb at a 1:1 molar ratio. The value $M_{PCBS}/M_{PAH} \sim 2$ calculated at 1 mM concentration was unexpectedly high and may be due to the relatively high standard deviation in the measurement of $\Delta f_{PAH}$, since the adsorbed amount was so small. For the condition (PAH-10/PCBS-10)$_9$$_8$, $M_{PCBS}/M_{PAH} \sim 0.63$, which is likely due to the deposition of PAH in thick, loop-like layers since the $pK_a$ of PAH is 8.7, which leads to reduced charge repulsion on the polymer chain. The increased adsorption of PAH leads, in turn, to an increased adsorption of PCBS, shown later in Table 4.5-4. However, the relative amount of increased PCBS adsorption is small compared to PAH since PCBS is adsorbed
at pH 8.0 which is far above its pKa (~ 3.3) and hence the PCBS chains are highly charged and tend to absorb in flat train-like conformations. This is evident from Table 4.5-3 which shows an increase in PAH adsorption of almost 3.2 times from neutral pH conditions as compared to a two-fold increase for PCBS.

Figure 4.5-5. Repeat unit molar ratio of PCBS to PAH from equation (5) as a function of polymer concentration while varying pH at constant ionic strength $I_{eff} = 1.7$ mM and 25°C. Filled squares refer to pH of 7/7 at three different concentrations and the open triangle refers to the pH condition of 9/8. “x” in the legend refers to the repeat unit concentration of both polymers.

Previous studies of ISAM film fabrication have shown that film thickness does not always increase linearly with bilayer number. In some cases, nonlinear film growth, particularly exponential growth, has been observed. Nonlinear film growth has been attributed to poor solvent quality, to insufficient rinsing times, and to the diffusion of polyelectrolytes out of the ISAM film. The effect of the degree of charge (DC) of the polymer on formation of polyelectrolyte multilayers has been previously reported; it was found that a minimum DC is a required for formation of stable polymer multilayer films. In studies by Steitz et al. and by Voigt et al., the DC of a random copolymer of
cationic DADMAC monomers and neutral NMVA monomers, poly(diallyl-dimethyl-
ammoniumchloridestat-N-methyl-N-vinylacetamide) was varied while forming multilayers with the sodium salt of poly(styrene sulfonate) (PSS). It was found that a minimum DC of 68% was needed for the formation of stable multilayer films. It was proposed that the 68% threshold was related to a threshold of charge reversal necessary for formation of a multilayer system. In our work, the molar ratio $M_{PCBS}/M_{PAH} \sim 1$ for the deposition condition (PAH-10/PCBS-10)$_{7/7}$ where both PAH and PCBS are fully charged. We believe this is the reason for the formation of stable, optically homogeneous multilayers observed for up to at least 600 bilayers in our earlier study.$^{20}$ By contrast, a molar ratio $M_{PCBS}/M_{PAH} \sim 0.63$ for the deposition condition (PAH-10/PCBS-10)$_{9/8}$, where the DC for PAH is less than 1 may explain the observed lack of stable film formation for more than 200 bilayers due to a possible charge imbalance. Thus, it seems that a molar ratio of close to 1 or complete dissociation of ionic groups may be one of the requirements for linear growth of ISAM films, especially at high bilayer numbers.

The data obtained from QCM-D experiments in the wet state were compared with absorbance measured for the dry films. The absorbance measurements at 360 nm track the deposition of PCBS as a function of concentration since PAH does not absorb at this wavelength. The frequency shift for PCBS, $\Delta f_{PCBS}$, was compared to the absorbance measurements at 360 nm at different deposition concentrations (Figure 4.5-6). Both frequency shift and absorbance data were normalized with respect to the absorbance and $\Delta f_{PCBS}$ at 10 mM to compare results from these different experiments. The absorbance of these films depends not only on the concentration of the PCBS chromophores, but also on the local chemical environment and the orientation of the chromophores. However, for this comparison, it was assumed that the extinction coefficient of these films was not a function of deposition concentration at deposition pH values of 7/7, i.e., the deposition conditions 1-3 in Table 4.5-1. The fact that the QCM-D data track the absorbance results so well supports the validity of the QCM-D analysis. The comparison of absorbance for deposition condition 4, i.e., (PAH-10/PCBS-10)$_{9/8}$, was not made, since the extinction coefficient could vary significantly from neutral pH conditions to elevated pH conditions.
Figure 4.5-6. Comparison of total PCBS in ISAM films obtained from QCM-D compared to the absorbance data obtained from equivalent films deposited on glass slides at PAH/PCBS pH values of 7/7. The absorbance data were measured at 360 nm in the dry state whereas $\Delta f_{PCBS}$ was measured for the hydrated films (Table 4.5-3).

4.5.2 Voigt Model Analysis of Films

The thicknesses of the wet films were calculated by fitting the frequency and dissipation data with the Voigt model which is based on a spring and dashpot connected in parallel.\(^{33, 34, 57}\) This model is one of several that can be used to estimate the thickness and mechanical properties, such as the viscosity and shear modulus of the adsorbed films (see appendix section 4.7.4 later in this chapter). By utilizing data for changes in frequency as well as changes in dissipation, the Voigt model can be used when the Sauerbrey equation, Eq. 2, is not valid. To calculate the hydrated film thickness $t_h$ from the Voigt model (see equations 19 and 20 in appendix section 4.7.4 later in this chapter), it is necessary to specify a value for the density of the hydrated polymer film, $\rho_h$. Since there was no independent measurement of $\rho_h$, a value of $\rho_h$ was initially assumed and
then the hydrated film thickness $t_h$ was calculated. The hydrated film density was then recalculated from the equation:

$$\rho_h = \frac{\rho_d t_d + \rho_w (t_h - t_d)}{t_h}$$  \hspace{1cm} (6)

in which it was assumed that the hydrated film was a combination of a dry film with thickness $t_d$ (measured by ellipsometry) and a layer of coupled water with thickness $(t_h - t_d)$ and $\rho_d$ is the density of a dry polyion film ($1200 \pm 100$ kg/m$^3$ \cite{21, 43}), and $\rho_w$ is the density of water. The value of $\rho_h$ calculated from equation (6) was then used in the Voigt model to recalculate $t_h$ in an iterative fashion until successive values of $\rho_h$ agreed to within $\pm 1\%$. Using this approach, $\rho_h$ was found to be $1100$ kg/m$^3$ and this was the value used to calculate the hydrated film thicknesses shown in Figure 4.5-7 and Table 4.5-4.

![Normalization thicknesses obtained from QCM-D and ellipsometry measurements for PAH and PCBS deposited at different repeat unit concentrations and at PAH/PCBS pH values of 7/7, a constant ionic strength $I_{eff} = 1.7$ mM, and at 25°C. The inset shows the absolute values of thickness per bilayer obtained from the two techniques.](image)

From both QCM-D and ellipsometry, film thicknesses increased with the PAH and PCBS concentrations from 1 to 5 mM, but did not change much upon increasing the concentration to 10 mM. The QCM-D analysis led to thicknesses about 2X greater than
those from the dry films that were measured by ellipsometry (inset in Figure 4.5-7). The water content in these films is listed in Table 4.5-4 and was estimated by:

\[
\% \text{ Water Content} = 100 \times \left( \frac{\rho_d f_h - \rho_d f_d}{\rho_d f_h} \right) \quad (7)
\]

The water content was estimated to vary between 41-46% which is comparable to ~50% water content for ISAM films comprised of PAH and PSS estimated by Ramsden et al. using a polar optical waveguide as the deposition substrate.\(^{58}\) As an additional check on these calculations, the water content was calculated using the Sauerbrey equation in which the Δf per bilayer was converted to the mass deposited per unit area for wet films (\(m_w\)). The mass per unit area for dry films (\(m_d\)) was calculated by multiplying the thickness of dry films, which was determined using ellipsometry with the assumed density of the dry films (1200 ± 100 kg/m\(^3\)). The % water content was calculated by using the equation: % water content = \([(m_w - m_d)/ m_w]\)*100. The values obtained by this procedure and the procedure described above were found to agree to within 2-5% (see appendix section 4.7.6 later in this chapter). Thus, in all cases in the present study, the water content calculated from the Voigt model agreed well with that calculated from the Sauerbrey equation.

General criteria showing when the Sauerbrey equation can be used and when a more general viscoelasticity model is needed were derived by White and Schrag by considering a viscoelastic film (phase 1) with thickness \(t_h\), viscosity \(\eta_1\) and density \(\rho_1\) on a quartz crystal surface in contact with a liquid (phase 2) with viscosity \(\eta_2\) and density \(\rho_2\).\(^{59}\) The Sauerbrey equation and a more generalized viscoelastic model were shown to diverge when \(\beta_1 t_h > 0.28\) and when \(\beta_1/\beta_2 > 0.2\) in which \(\beta_i\) is defined as:

\[
\beta_i = \sqrt{\frac{\omega \rho_i \cos \left( \frac{\pi}{4} - \frac{\phi}{2} \right)}{\eta_i}} \quad (8)
\]

and \(\phi\) is the relative phase angle of the medium. For purely a viscous medium, \(\phi = \pi/2\), whereas \(\phi = 0\) for a purely elastic medium. These criteria were found to explain the
swelling behavior of films of ammonium poly(4-styrenesulfonate) studied with a QCM-D.\textsuperscript{35}

In the present study, exact values for the viscosity of the films could not be calculated using the Voigt model, because the fitted values of the viscosity and shear modulus had unacceptably high standard deviations. The net increase in dissipation after adsorption of one bilayer of PAH and PCBS was small, indicating that the films were relatively rigid. For example, for the deposition condition (PAH-10/PCBS-10)\textsuperscript{9/8}, we observed a maximum dissipation increase $\Delta D = 0.2 \times 10^{-6}$ for every 10 Hz change in frequency and found that the Sauerbrey equation and the Voigt model gave similar results. For these films with $t_h = 52$ nm and $\rho_h = 1100$ kg/m$^3$, we calculated a range of values for $\beta_{1/t_h}$ using Eq. 8 with limiting values of the film viscosity since exact values were not known. Values of $\beta_{1/t_h}$ were calculated to be 0.003 and 0.22 assuming that the films behaved like purely elastic materials ($\eta \approx 10$ Pa s; $\phi = 0$) and purely viscous materials ($\eta = 10^{-3}$ Pa s; $\phi = \pi/2$), respectively. Both limiting cases satisfied the criterion $\beta_{1/t_h} < 0.28$ where the Sauerbrey equation and the Voigt model would converge. For the second criterion involving the ratio $\beta_{1}/\beta_{2}$, values were calculated to be 0.01 (purely elastic) and 0.75 (purely viscous). The ratio for the purely viscous case does not satisfy the criterion of $< 0.2$ for the Sauerbrey equation to apply because the assumed film viscosity in this limit was taken to be that of water. Since these films are actually semidilute, ionically crosslinked polymer gels, the actual film viscosity is certainly several-fold greater than that of water.

The criteria of White and Schrag also are consistent with a QCM-D study of collagen films adsorbed on polystyrene in which $\Delta D = 1.7 \times 10^{-6}$ for every 10 Hz change in frequency was observed and the Sauerbrey equation was found not to apply.\textsuperscript{60} Using values of film viscosity, shear modulus, and thickness from the Voigt model with an assumed range of film densities, values of $\beta_{1/t_h}$ were 0.38 and 0.61 while values of $\beta_{1}/\beta_{2}$ were 0.41 and 0.38 for thicknesses of 170 nm and 130 nm, respectively. In another study of ISAM films consisting of PAH and a polyanionic mixture of poly(L-glutamic acid) (PGA) and PSS, the Sauerbrey equation was found to accurately describe the film
thickness for $\Delta D \sim 0.014 \times 10^{-6}$ for every 10 Hz change in frequency.\(^{38}\) This corresponds well to the supposition that, although there is a positive shift in the dissipation which theoretically should invalidate the Sauerbrey equation, the Sauerbrey equation can still be valid experimentally for low changes in dissipation.

The change in frequency for PCBS, $\Delta f_{\text{PCBS}}$ and PAH, $\Delta f_{\text{PAH}}$ as shown in Table 4.5-3 can be converted to $\%\text{PCBS}$ in these films which, together with the density of films in dry state, can be used to estimate the number density of PCBS chromophores, $N$ (see eq 1) using:

$$N = \frac{\%\text{PCBS} \times \rho \times N_{\text{av}}}{100 \times MW_{\text{PCBS}}} \quad (9)$$

where $N_{\text{av}}$ is Avogadro’s number.

Table 4.5-4 shows the calculated values of $N$ which are in the range of 1.4-1.7 x $10^{21}$ cm$^{-3}$. By comparison, for poled polymer films, an alternative approach for making second order nonlinear optical films, values of $N$ have been reported ranging from 2.2 to 9.8 x 10$^{20}$ cm$^{-3}$.\(^{61,62}\)

<table>
<thead>
<tr>
<th>Deposition Condition</th>
<th>PCBS (mg/m$^2$)</th>
<th>Thickness per bilayer (nm) QCM-D</th>
<th>Thickness per bilayer (nm) Ellipsometry</th>
<th>Water Content* (%)</th>
<th>$N$, #PCBS chromophores (cm$^{-3}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1. (PAH-1/PCBS-1)$_{7/7}$ 0.81</td>
<td>1.55 (± 0.02)</td>
<td>0.77 (± 0.04)</td>
<td>45.8</td>
<td>1.7 x 10$^{21}$</td>
<td></td>
</tr>
<tr>
<td>2. (PAH-5/PCBS-5)$_{7/7}$</td>
<td>1.15</td>
<td>2.20 (± 0.02)</td>
<td>1.20 (± 0.04)</td>
<td>40.5</td>
<td>1.6 x 10$^{21}$</td>
</tr>
<tr>
<td>3. (PAH-10/PCBS-10)$_{7/7}$</td>
<td>1.14</td>
<td>2.20 (± 0.01)</td>
<td>1.16 (± 0.01)</td>
<td>42.5</td>
<td>1.6 x 10$^{21}$</td>
</tr>
<tr>
<td>4. (PAH-10/PCBS-10)$_{9/8}$</td>
<td>2.21</td>
<td>5.16 (± 0.04)</td>
<td>2.75 (± 0.09)</td>
<td>41.8</td>
<td>1.4 x 10$^{21}$</td>
</tr>
</tbody>
</table>

* The water content was calculated using equation 7.
Using the Voigt model and the procedure described above, the hydrated film thickness per bilayer for deposition condition #4 (PAH-10/PCBS-10)\textsubscript{9/8} was calculated to be 5.16 nm, a value 2.3 times higher than that observed for the neutral pH condition (deposition condition #3). By comparison, the dry film thickness obtained from ellipsometry for deposition condition #4 was 2.4 times higher than that for condition #3. The observed increase in the bilayer film thickness with the PCBS concentration for highly charged PAH (Figure 4.5-7 for deposition condition #s 1-3) is also consistent with Voigt et al.\textsuperscript{56} who found that, for the degree of charge DC > 75%, the thickness of stable multilayer films increased with polymer concentration.

### 4.6 Conclusions

The alternate adsorption of the polycation poly(allylamine hydrochloride) (PAH) and the polymeric dye poly\{1-[p-(3’-carboxy-4’-hydroxyphenylazo)benzenesulfonamido]-1,2-ethandiyl\} (PCBS) on quartz crystals coated with silica was studied to understand the film structure and adsorption kinetics using a combination of quartz crystal microbalance with dissipation monitoring (QCM-D), QCM, absorbance, and ellipsometry measurements. The effects of polymer concentration and pH on the structural properties of these films were studied. For adsorption from pH 7, there was a significant increase in the mass adsorbed when the polymer concentration was increased from 1 to 5 mM. However, the mass adsorbed remained essentially the same when the concentration was increased from 5 to 10 mM, akin to the saturation of an adsorption isotherm. At PAH and PCBS concentrations of 5-10 mM, the polymers adsorbed in a molar ratio of 1, implying a complete dissociation of ionic groups. The absorbance measurements, which track the amount of PCBS in these films, were found to be in good agreement with the QCM-D results for the PCBS deposition step. In a second set of experiments, the pH of the polymer solutions was increased to study the charge effects on the adsorption behavior of the polymers. Higher values of pH resulted in increased mass adsorbed for PAH due to reduced charge density on the polymer chains, which favored the deposition of the polymer in loops and tails. A higher mass of PAH adsorbed, in turn, led to an increased adsorption of PCBS. The molar ratio of PCBS to PAH at pH of 8 and 9, respectively, was found to be 0.63. By comparing
these results with recent nonlinear optical work by our group, it is believed that the molar ratios in which the polymers adsorb might play a role in the polar ordering of chromophores in films. The normalized thicknesses obtained by the QCM-D results for the hydrated films were found to be in good agreement with thicknesses for the corresponding dry films obtained from ellipsometry. By comparing the thickness obtained by the QCM experiments with the thickness obtained by ellipsometry, the water content in these films was found to be in the range of 41-46% by weight.

The combination of QCM-D results with ellipsometry and absorbance data indicates that QCM-D can be reliably used to study the structural and compositional properties of thin polymer films. A more detailed study on the adsorption kinetics of polyelectrolytes using QCM-D is the subject of a future paper.

4.7 Appendix A for Chapter 4

4.7.1 Ellipsometry Procedure

Film thickness measurements were made using a variable angle spectroscopic ellipsometer (VASE) (J.A. Woolam ellipsometer VB-200 with WVASE32 software version 3.361). Ellipsometry is based on the changes in the polarization of light when it reflects from a surface. Linearly polarized light reflects off the sample and becomes elliptically polarized. This change in the state of polarization can be defined by two quantities, namely Δ (delta) and ψ (psi). The phase difference between the linearly polarized light and the elliptically polarized light is given by Δ whereas ψ gives the change in amplitude between the two. The ellipsometric analysis was done in the vicinity of the Brewster angle because ellipsometry measurements are most sensitive to film characteristics at the Brewster angle. An initial scan was done for wavelengths from 300 to 800 nm at 50 nm intervals and this wavelength range was then repeated over angles from 50 deg to 70 deg at 4° intervals to find the Brewster angle. From a graph of Δ vs. λ, the Brewster angle was determined as the point at which Δ quickly passed from 180° through 90° to 0°. The Brewster angle for PAH/PCBS slide series was found to be 62°. Following the determination of the Brewster angle, the sample was scanned at wavelengths from 300 to 800 nm at 10 nm intervals in the vicinity (±2°) of the Brewster
angle in $1^\circ$ increments. The sample was scanned at three different positions to check for the film homogeneity. The experimental data collected this way were then fitted with a model that is described below in detail.

### 4.7.1.1 Modeling

The model consists of two layers - one for the glass substrate and the other for the thin film. The model for the glass substrate consists of the refractive index and the extinction coefficient ($n$ and $k$ respectively) values as a function of wavelength and is plotted in Figure 4.7-1 below.

![Figure 4.7-1. n and k values versus wavelength for a typical glass substrate used in the film deposition experiments. These values were used to model the experimental data for the ISAM films.](image)

The Lorentz oscillator model represents the thin film and is given by the following equation\textsuperscript{64}

$$\varepsilon(E) = \varepsilon_i(\infty) + \sum_k \frac{A_k}{E_k^2 - E^2 - iB_kE}$$

in which $\varepsilon_i(\infty)$ represents the value of the real part of the dielectric function at very large photon energy, $A_k$ is the amplitude of the $k^{th}$ oscillator (eV$^2$), $E$ is the photon energy (eV), $E_k$ is the center energy of the $k^{th}$ oscillator (eV), and $B_k$ is the $k^{th}$ peak’s width.
(eV). $E_k$ is given by equation (11). From $\varepsilon$, values of $n$ and $k$ can be calculated as shown in equation #12 and equation #13.

$$E_k = h\nu_k = \frac{1.24(eV \cdot \mu m)}{\lambda_k (\mu m)}$$  \hspace{1cm} (11)$$

$$n = \sqrt{\frac{\varepsilon_1 + \sqrt{\varepsilon_1^2 + \varepsilon_2^2}}{2}}$$  \hspace{1cm} (12)$$

$$k = \sqrt{-\varepsilon_1 + \sqrt{\varepsilon_1^2 + \varepsilon_2^2}}$$  \hspace{1cm} (13)$$

in which $\nu_k$ and $\lambda_k$ are the frequency and the wavelength of the $k^{th}$ absorbance peak, respectively. A typical value of $\lambda_k$ (as measured by UV-Vis spectroscopy) for PAH/PCBS slide series is 360 nm.

Because only one absorbance peak was observed while scanning the slide for absorbance over a range of wavelengths, only one Lorentz oscillator model was used and its oscillating center was fixed at $\lambda_k (= \lambda_1)$. Using the above value for $\lambda_1$, the parameter $E_1$ can be calculated from equation #11. The value for the parameter $E_1$ for the PAH/PCBS films was calculated to be 3.444 eV.

An initial guess was provided for the other parameters $\varepsilon_\infty$, $A_1$ and $B_1$ to estimate the film thickness. Depending on the initial guess provided, the results might vary. However, there are various ways to determine if the obtained results were optimal. One of the constraints in fitting the parameters is that $k$ should reach a maximum at $\lambda_1$. The goodness of fit was assessed with the values of the mean sum of the errors (MSE). In general, a better fit is obtained with lower values of the MSE. The optical parameters obtained after modeling are shown in the Figure 4.7-2 for the films made using PCBS and PAH.

When making the films, PAH and PCBS solutions were used with a concentration of 10 mM based on their repeat units and at pH 7. The glass slides were dipped in PAH and PCBS solutions for 2 minutes. The rinsing time after each dipping cycle was 135 sec.
Figure 4.7-2. Optical parameters for a film consisting of 500 bilayers of PAH/PCBS obtained using VASE. The deposition conditions were: $C_{PAH} = 10$ mM repeat unit (RU), $C_{PCBS} = 10$ mM RU, $pH_{PAH} = 7.0$, $pH_{PCBS} = 7.0$. The dipping times were 2 minutes in both PAH and PCBS solutions. The rinsing time was 135 seconds equally distributed in three baths (45 sec x 3). The maximum value of the dispersion coefficient occurs at the wavelength $\sim 360$ nm. A similar peak is observed at this wavelength by UV-Vis spectroscopy.
4.7.2 Design of flow loop for QCM experiments

Figure 4.7-3. The experimental set-up for experiments done using Maxtek’s QCM. A peristaltic pump is used to control the flow rates at which the solutions are passed. Pulse dampeners are used to virtually eliminate pulsations caused by peristaltic pump. The solutions are then passed through a system of two 4-way valves and the tubes are connected such that there is always a constant flow of solutions. One of the outlets through the system of valves goes to the QCM flow cell. The QCM crystal is placed inside the QCM flow cell and only one surface comes in contact with the solution. The change in frequency as a function of time is monitored though a computer connected to the QCM electronics via a serial port.

The flow loop system used with the QCM is shown in Figure 4.7-3. The experimental set up consisted of: a peristaltic pump, three pulse dampeners, two 4-way valves, the QCM flow cell and electronics. The peristaltic pump was used to provide a continuous flow over a range of 0.6 ml/min to 10 ml/min and was connected to multiple pump heads through which three different fluids were passed. Each of the tube lines then went through a pulse dampener (Cole Parmer) which mostly eliminated the pulsation caused by the peristaltic pump. Uttenthaler et al. used pulse dampeners to decrease the pulsation caused by a peristaltic pump. The pulse dampeners were very useful for our
experimental set up because of the sensitivity of the QCM to even very small pressure pulses. The tube then went to a system of two 4-way valves arranged so that the pumping through all three lines was continuous throughout the duration of the experiment. This was done to keep the pressure the same in all the lines at all times. One of the output lines through the valve system went into the QCM flow cell and the other two lines went to waste or were recycled as needed. The QCM flow cell has a volume of 0.1 ml. It took almost 2 hours for the Maxtek QCM to warm up and give a stable baseline. For the experiments done with the crystal in contact with liquid, the crystal was first allowed to stabilize in air and a reading in air was recorded to see the noise and drift levels in air and then the liquid was introduced.

4.7.3 Higher harmonics from the QCM-D data.

![Graph](image.png)

Figure 4.7-4. Change in frequency per bilayer for QCM-D at different harmonics for deposition conditions at three different polymer concentrations and for PAH and PCBS pH = 7.
4.7.4 Voigt Model

The Voigt model \(^{33, 34, 57}\) which is based on a spring and dashpot connected in parallel can be used to estimate the thickness and mechanical properties such as the viscosity and shear modulus of the adsorbed films. In the Voigt model, the complex shear modulus of the film is given by:

\[
\mu^* = \mu_f + i2\pi \eta_f
\]  

(14)

where \(\mu_f\) is the elastic shear modulus and \(\eta_f\) is the shear viscosity of the film. The characteristic relaxation time \(\tau = \eta_f / \mu_f\) (see eq 4 in paper). The film is assumed to lie in contact between the QCM electrode and a semi-infinite Newtonian liquid under no-slip conditions and is represented with a uniform thickness \(\delta_f\) and a density \(\rho_f\), referred to as the effective hydrodynamic thickness and density, respectively. In this case, the changes in the resonant frequency \(\Delta f\) and the dissipation factor \(\Delta D\) are:

\[
\Delta f = \frac{\text{Im}(\beta)}{2\pi h_q \rho_q} \quad \text{and} \quad \Delta D = -\frac{\text{Re}(\beta)}{\pi h_q \rho_q}
\]  

(15)

where \(h_q\) and \(\rho_q\) are the thickness and specific density of quartz plate and,

\[
\beta = \xi_1 \frac{2\pi \eta_f - i\mu_f}{2\pi} \left(1 - \alpha \exp(2\xi_1 \delta_f)\right) \quad 1 + \alpha \exp(2\xi_1 \delta_f)
\]  

(16)

\[
\alpha = \frac{\xi_1}{\xi_2} \frac{2\pi \eta_f - i\mu_f}{2\pi \eta_f} + 1
\]  

(17)

\[
\xi_1 = \sqrt{-\frac{(2\pi f)^2 \rho_f}{\mu_f + i2\pi \eta_f}}, \quad \xi_2 = \sqrt{i \frac{2\pi f \rho_f}{\eta_1}}
\]  

(18)

in which \(\rho_f\) is the density of the bulk liquid, \(\eta_f\) and \(\eta_1\) are the viscosity of the layer and the bulk liquid, respectively, and \(\mu_f\) is the elastic modulus of the film. For an aqueous environment, \(\rho_1\) and \(\eta_1\) are approximately 1.0 kg m\(^{-3}\) and 1.0 Ns m\(^{-2}\), respectively. In air, the viscosity remains essentially the same, but the density is a factor of about 1 x10\(^3\) lower.
For thin films, the above equations for $\Delta f$ and $\Delta D$ can be expressed in simpler forms by a Taylor’s series expansion: \cite{33}

$$
\Delta f \approx -\frac{1}{2\pi \rho \sigma q h_q} h_f \rho_f \omega \left( 1 + \frac{2h_f^2 \chi}{3\delta^2 (1 + \chi^2)} \right) \tag{19}
$$

$$
\Delta D \approx \frac{2h_f^3 \rho_f \omega}{3\pi \rho \sigma q h_q} \frac{1}{\delta^2 (1 + \chi^2)} \tag{20}
$$

in which $\chi = \frac{\mu_f}{\eta_f \omega}$ and $\delta = \sqrt{\frac{2\eta_f}{\rho_f \omega}}$.

Equations (19) and (20) are the main equations that describe the Voigt model for thin films.

We used the Voigt model to estimate the thicknesses of the adsorbed PAH and PCBS bilayers. To do these calculations, three parameters need to be specified: the film density (ultimately calculated to be 1100 kg/m$^3$) and the density and viscosity of the solvent, in the present case taken to be that of water at 25$^\circ$C, 1000 kg/m$^3$ and 0.001 Pa s, respectively.
4.7.5 A comparison of the thickness fit by Voigt model and Sauerbrey equation

Figure 4.7-5. A comparison of thickness obtained by the Voigt model and Sauerbrey equation for different deposition conditions. For deposition condition: (PAH-10/PCBS-10)$_{9/8}$, the data points are marked by an arrow; whereas, for deposition conditions (PAH-1/PCBS-1)$_{7/7}$, (PAH-5/PCBS-5)$_{7/7}$, (PAH-10/PCBS-10)$_{7/7}$ the data points are not marked by an arrow.
### Table 4.7-1. Comparison of %water content obtained using Sauerbrey equation and Voigt model.

<table>
<thead>
<tr>
<th>Conc.</th>
<th>-(Δf) per bilayer</th>
<th>Mass per unit area, ( m_w ) (mg/m²) – wet*</th>
<th>Ellipsometry thickness (nm)</th>
<th>Mass per unit area, ( m_d ) (mg/m²) – dry**</th>
<th>%water*** - (Compare with Table 4.5-4 in the chapter)</th>
<th>%deviation from water content calculated using Voigt model – see paper</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>9.27</td>
<td>1.64</td>
<td>0.77</td>
<td>0.92</td>
<td>43.68</td>
<td>4.6</td>
</tr>
<tr>
<td>5</td>
<td>13.27</td>
<td>2.35</td>
<td>1.2</td>
<td>1.42</td>
<td>38.69</td>
<td>4.4</td>
</tr>
<tr>
<td>10</td>
<td>13.51</td>
<td>2.39</td>
<td>1.16</td>
<td>1.39</td>
<td>41.78</td>
<td>1.7</td>
</tr>
</tbody>
</table>

* Calculated using Sauerbrey equation  
** Calculated by assuming a density of 1200 kg/m³ for dry films²¹, ⁴³  
*** Calculated using equation \( \frac{m_w - m_d}{m_w} \)
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5.1 Abstract

The adsorption of the polyelectrolytes poly(allylamine hydrochloride) (PAH) and poly{1-[p-(3’-carboxy-4’-hydroxyphenylazo)benzenesulfonamido]-1,2-ethandiyl} (PCBS) on SiO₂ substrates was studied experimentally using a quartz crystal microbalance with dissipation (QCM-D). PAH and PCBS were alternately deposited on to the SiO₂ substrate to build up layer-by-layer (LbL) films. The effect of convection on the mass transfer coefficient, \( k_t \), was studied and the results were compared with theoretical values of \( k_t \). A variation of the LbL process, referred to as hybrid LbL deposition, which involves attaching PAH electrostatically and Procion Brown (PB) dye covalently to the underlying PAH layer, was also studied using the QCM-D. Film composition and structure were studied for the PAH/PB films. A rate constant for covalent coupling of the PB on the underlying PAH layer was also calculated.

5.2 Keywords

Layer-by-layer, kinetics of polymer adsorption, kinetics of polyelectrolyte adsorption, rate constant calculation, quartz crystal microbalance (QCM, QCM-D).

5.3 Introduction

This chapter is the second of two which study the formation of layer-by-layer (LbL)¹, ² organic thin films using QCM-D. The first chapter #4³ discussed briefly the kinetics of film formation and studied in detail the film composition and structure of LbL films fabricated using poly(allylamine hydrochloride) (PAH) and poly{1-[p-(3’-carboxy-4’-hydroxyphenylazo)benzenesulfonamido]-1,2-ethandiyl} (PCBS) on SiO₂ substrates. This chapter studies in detail the kinetics of the formation of PAH/PCBS LbL films and PAH/Procion Brown (PB) hybrid LbL films as well as the structure and composition of
the PAH/PB films. These films exhibit nonlinear optical (NLO) properties due to the presence of PCBS in PAH/PCBS films and PB in PAH/PB films, both of which are polarizable and lack a center of symmetry when deposited under certain conditions of concentration, pH, and ionic strength.\textsuperscript{4,6} During the formation of these films, the polyelectrolyte deposition is driven by transport from the bulk solution to the surface and by electrostatic interactions. Depositing a charged polymer on an oppositely charged substrate leads to charge reversal which stops further adsorption of the polyelectrolyte. This charge reversal facilitates the deposition of the next oppositely charged polyelectrolyte film, thereby building the LbL film. By comparison the hybrid LbL approach involves alternately depositing PAH by means of electrostatic interactions and depositing the PB dye by means of covalent bonding,\textsuperscript{6} the covalent bond leads to better orientation of the films leading to enhanced second-order susceptibility, \( \chi^{(2)} \) as shown in Equation 1:\textsuperscript{7}

\[
\chi^{(2)} = N F \beta \langle \cos^3 \varphi \rangle
\]

in which \( N \) is the chromophore density, \( F \) is the local field factor which is a function of the refractive index, \( \beta \) is the hyperpolarizability, and \( \varphi \) is the orientation angle of the chromophores. Rational design of NLO films thus involves choosing a chromophore with a suitably high \( \beta \) and incorporating it into a film with high density \( N \) and low tilt angle \( \varphi \).

One of the key requirements for fabricating a practical EO modulator is that the film thickness should be of the order of 1 \( \mu \)m since signals in optical fiber systems are often transmitted at a wavelength of 1064 nm. Given that the thickness per bilayer of LbL films is approximately of the order of 1 nm, fabricating a 1 \( \mu \)m thick film would involve depositing 1000 bilayers. At current deposition conditions of 10 minutes per bilayer,\textsuperscript{5} this would involve a time of the order of days to fabricate the LbL film for a practical EO modulator. Thus, it is important to develop a fundamental understanding of the kinetics of film formation. A detailed study of kinetics will be useful in predicting how parameters such as polymer concentration, pH, salt concentration, effect of convection and temperature can be controlled to minimize the fabrication time.
Generally, the adsorption of polymers on a substrate consists of two steps: the first is the mass transfer from bulk to the surface and second is the attachment step at the surface. In some cases, a third step which involves rearrangement of polymer on a surface is also reported. To study the adsorption of polymers on substrates, well defined hydrodynamics is important. One case of well defined hydrodynamics of particular interest is stagnation point flow geometry which consists of a jet of polymer solution aimed towards a flat substrate creating a stagnation point at the intersection of the jet and the substrate. The stagnation point flow geometry was first studied in detail by Dabros and Van de Ven \(^8\) and has been used extensively to study the adsorption of polymers on various substrates using reflectometry.\(^9\)-\(^12\) In one such study, the adsorption of uncharged poly (ethylene oxide) (PEO) onto a silica substrate was monitored.\(^9\) The mass transfer coefficient was calculated experimentally as well as theoretically. The effect of varying the flow rate and polymer concentration was studied and good agreement between experimental and theoretical values was found. It was found that the rate of deposition was greatest when the surface was bare which provided more binding sites for the polymer. As the adsorption progressed, the surface available for polymer adsorption decreased which led to a decrease in the rate of polymer adsorption and eventually reached zero thereby stopping further polymer adsorption. The decrease in the rate of adsorption was observed at 75% or more surface saturation. Up to that surface coverage, a linear increase in surface coverage with time was seen and the rate limiting step was the mass transfer from the bulk to the substrate. In a related paper,\(^13\) Dijt et al. studied the adsorption of PEO onto a glass substrate using streaming potential measurements in a capillary flow. Mass transfer coefficients were calculated theoretically and comparable results were obtained experimentally.

The adsorption of charged polymers is not only affected by the mass transfer of polymers to the surface but it has been shown that the electrostatic interactions (attractive or repulsive) play an important role in the adsorption of polyelectrolytes. Some studies have suggested that the rate of polyelectrolyte adsorption is greater than that predicted by a simple mass transfer when a charged polymer is adsorbed onto an oppositely charged surface.\(^14\) Also, the effect of pH and ionic strength has been found to affect the rate of
polyelectrolyte adsorption on a substrate. Stable polyelectrolyte multilayers are formed when highly charged polyelectrolytes are used for LbL deposition.\textsuperscript{12} The adsorption of a cationic polyelectrolyte, polyvinylamine on a charged cellulose substrate was investigated by Geffroy et al.\textsuperscript{11} by using reflectometry in a stagnation point flow.\textsuperscript{9} They studied the adsorption as a function of polyelectrolyte pH and salt concentration and found that the electrostatic interactions were the main forces that controlled the adsorption kinetics. Although the effect of pH and salt concentration on the adsorption kinetics were studied in detail, the effect of convection was not studied. The kinetics and dissolution of LbL polyelectrolyte films fabricated using poly(dimethylaminoethyl methacrylate) (PAMA) and anionic polyelectrolyte poly(acrylic acid) (PAA) on silica substrate was studied using reflectometry.\textsuperscript{15} It was found that the LbL films dissolved in the presence of high salt concentration or in the presence of low salt concentration and low concentration of polyelectrolyte. The mass transfer coefficients were not calculated.

This is the first study which uses a quartz crystal microbalance with dissipation (QCM-D) technique to measure the mass transfer coefficient of polyelectrolyte adsorption on a silica substrate. This work studies the adsorption kinetics of LbL films on SiO\textsubscript{2} surface and deposition of hybrid LbL films on gold surface using the QCM-D technique. A flow cell set-up was used to study of the effect of convection on the kinetics of film formation. A theoretical mass transfer model based on the Graetz theory was developed to calculate the mass transfer coefficient of for PCBS which was compared with the experimental mass transfer coefficient.

\textbf{5.4 Experimental}

\textbf{5.4.1 Materials}

Poly(allylamine hydrochloride) (PAH, Figure 5.4-1 (a)) was used as the polycation (M\textsubscript{w} ca. 70 kDa; Aldrich). Poly\{1-[p-(3'-carboxy-4'-hydroxyphenylazo)-benzenesulfonamido]-1,2-ethandiyl\} (PCBS, Figure 5.4-1 (b)); was used as the polyanionic chromophore (Aldrich). The repeat unit molecular weight of PAH was 93.56 g/mol and of PCBS was 369.3 g/mol. PCBS has an azobenzene side group that has a sufficiently high hyperpolarizability, $\beta$, to give a measurable SHG signal. Procion Brown
dye (PB) (M<sub>w</sub> 767 g/mol, MX-GRN Reactive Brown 23, Figure 5.4-1 (c); Pro Chemical and Dye, Somerset, MA) was used as the chromophore in the deposition experiment. Figure 5.4-1 (d) shows the reaction between the PAH and PB. Deionized (DI) water (Barnstead ROpureST; model # D6311) with a resistivity of over 17 MΩ cm was used. The ionic strength of the polymer solutions was adjusted using sodium chloride (NaCl, Fisher Scientific). The pHs of the polymer solutions were adjusted using 1.0 M or 0.1 M solutions of sodium hydroxide and hydrogen chloride.

![Chemical structures](image-url)
5.4.2 Dye Purification

Commercially available Procion dyes are not pure materials and contain salts, anti-caking agents, and buffering agents. Solid-phase extraction (SPE) with octadecylsilyl functionalized silica (RediSep Reverse Phase C-18, 35-60 μm particle size) was used to desalt Procion Brown MX-GRN prior to film fabrication. The dye was dissolved in aqueous 50 mM ammonium acetate at 20 mg/mL and filtered with a 0.45 μm filter to remove particulates. The SPE columns were washed with 7 volumes of HPLC grade methanol (Burdick & Jackson), equilibrated with 3 volumes of aqueous 50 mM ammonium acetate, and then 200 ml of the filtered dye solutions were applied to the columns. The columns were washed with 2 volumes of 50 mM ammonium acetate. The dye was then eluted with HPLC-grade methanol. The methanol was removed by drying it in a stream of nitrogen.
5.4.3 Characterization

Dynamic Light Scattering (DLS) was used to calculate the diffusion coefficient of the polyelectrolytes PAH and PCBS. DLS was performed using a Malvern Nano-ZS instrument. The diffusion coefficient was calculated using the Stokes-Einstein’s equation 2:

\[ D = \frac{kT}{6\pi\eta R_H} \]

where \( k \) is Boltzmann’s constant, \( T \) is the temperature, \( \eta \) is the viscosity of the solution, and \( R_H \) is the hydrodynamic radius of the polymer. All measurements were done at 25°C.

A Quartz Crystal Microbalance with Dissipation (QCM-D) system (Q-sense Inc, E-4 system) was used to study film deposition. The QCM-D measures seven different harmonics from the 1st to the 13th and their corresponding dissipation factor. The QCM-D has a fundamental resonance frequency of 5 MHz. For PAH/PCBS films, SiO2-coated quartz crystals were used while for PAH/PB films, gold-coated crystals were used. The SiO2 and gold-coated crystals were cleaned with a plasma etcher device (SPI Supplies, Plasma Prep II™) in the presence of oxygen. They were cleaned for 30 minutes at the pressure between 400-600 millitorr and at a current setting of 70 mA. All measurements were made with the crystals in flow cells where the crystals were in contact with a liquid phase only on one side. The temperature was maintained at 25 (±0.5)°C at all times. All QCM-D measurements were done in triplicate.

QCM is an effective tool for studying the process of film formation and it gives insights into compositional properties of these films at the molecular level. It is an ultra-sensitive mass sensor, consisting of a piezoelectric quartz crystal sandwiched between a pair of electrodes. When the electrodes are connected to an oscillator and an AC voltage is applied over the electrodes, the quartz crystal starts to oscillate at its resonant frequency due to the piezoelectric effect if the correct frequency of AC voltage is chosen. If a rigid layer is evenly deposited on one or both sides of the electrodes, the resonant frequency will decrease proportionally to the mass of the absorbed layer according to the Sauerbrey equation 17:
\[ \Delta f_m = -\frac{2 \times f_0^2 \times \Delta m}{A \times \sqrt{\rho_q \mu_q}} \]  \tag{3}

in which \( \Delta f_m \) = measured frequency shift, \( f_0 \) = fundamental frequency of the crystal, \( \Delta m \) = mass change per unit area, \( A \) = piezo-electrically active area, \( \rho_q \) = density of quartz (2.648 g/cm\(^3\)), and \( \mu_q \) = shear modulus of quartz (2.947 x 10\(^{-11}\) dyne/cm\(^2\)).

Equation 3 is not valid if the deposited mass is: a) not rigidly deposited on the electrode surface, b) slips on the surface, or c) is not evenly deposited on the surface of the electrodes. For these reasons, QCM was for many years used primarily as a gas-phase mass detector. In the early 1980’s, it was realized that a quartz crystal can be excited to a stable oscillation when it is completely immersed in a liquid. As described by Kanazawa et al., the resonant frequency of the QCM crystal also depends on the viscosity and density of the gas or liquid which is in contact with the crystal. The change in the resonant frequency of the QCM crystal due to density and viscosity effects is given by equation 4:

\[ \Delta f_{\text{aqueous}} = -\left[ \frac{n f_0^{3/2}}{\left(\pi \mu_q \rho_q \right)^{1/2}} \right] \left( \rho_L \eta_L \right)^{1/2} \]  \tag{4}

in which,

\( n \) = number of faces of the QCM in contact with the liquid
\( \rho_L \) = density of the bulk liquid
\( \eta_L \) = viscosity of the bulk liquid

In addition to the changes in frequency, QCM-D can also measure changes in dissipation which is inversely proportional to the decay time, \( \tau \), and given by equation 5;

\[ D = \frac{1}{\pi f \tau} \]  \tag{5}

in which \( f \) is the oscillating frequency of QCM. For a soft film, the decay time is small due to increased energy loss, leading to higher values of the dissipation. For a rigid film, the dissipation time is large, leading to smaller values of dissipation. Thus, the change in
dissipation (ΔD) can be used to obtain information about the mechanical properties of the films.

### 5.4.4 Mass Transfer Coefficient Model

From prior studies, the radial amplitude distribution of an AT-cut quartz resonator with a fundamental frequency of 5 MHz was studied by electroplating copper while measuring frequency change.\(^{20}\) It was found that the change in frequency, \(Δf\) was maximum at the center of the crystal and decreased with increasing radius away from the center in a Gaussian distribution. This study was done only on the first harmonic of the crystal. Another study which was not published and was done on QCM-D crystals on 1\(^{st}\), 3\(^{rd}\), 5\(^{th}\) and 7\(^{th}\) harmonic also show that there is a radial distribution of \(Δf\).

(communication from Q-sense) Their results showed that for a 14 mm diameter QCM-D crystal, the 1\(^{st}\) harmonic’s amplitude distribution covered the entire crystal from one edge to the other. With the center of the crystal at the origin, one edge would be at “-7 mm” and the other edge would be at “+7 mm”. Interestingly, for the 7\(^{th}\) harmonic the amplitude distribution was from -3 mm to 3 mm. This is the region which we refer to as the active sensor region. (See Section 5.7 for a detailed derivation) We make use of this “active sensor region” as shown in Figure 5.4-2 to model the velocity profile fluid flow across the crystal surface over this region. The velocity profile over this region which was derived using the lubrication approximation is given by equation 6

\[
\nu_x = \frac{3Q}{8HR(x)} \left[ 1 - \left( \frac{y}{H} \right)^2 \right] 
\]

(6)

in which \(Q\) is the volumetric flow rate, \(H\) is the half-height of the flow cell, \(y\) is the coordinate axis, and \(R(x) = \sqrt{(R^2 - x^2)}\), \(R\) is the radius of the QCM-D crystal and \(x\) is the distance away from the surface in the x-direction. Note that this approximation is valid in the center of the flow cell, where wall edge effects are negligible. For the 7\(^{th}\) harmonic, \(x\) varies from -3 mm to 3 mm where \(x\) denotes the coordinates for the active sensor region.

Using the velocity profile equation #6, the mass transfer coefficient, \(k_t\) was estimated based on the Graetz theory\(^{21}\) and is given by equation
\[ k_t = 1.553 \left( \frac{D}{H} \right)^{2/3} \text{Re}^{1/3} \left( \frac{\nu}{x} \right)^{1/3} \]  

(7)

in which \( D \) is the diffusion coefficient, \( \text{Re} \) is the Reynolds number (See Equation (10)), and \( \nu \) is the kinematic viscosity of the solution. A value of \( k_t \) averaged over the sensing region was calculated by integrating equation #7 over the entire active sensor region (see Figure 5.4-2) with \( x \) varying from -3 mm to 3 mm. The expression for the average \( k_t \) is given by equation:

\[ k_{t, \text{avg}} = 1.5 \times 1.553 \left( \frac{D}{H} \right)^{2/3} \text{Re}^{1/3} \left( \frac{\nu}{x_s} \right)^{1/3} \]  

(8)

where \( x_s = 3 \) mm.

---

**5.5 Results and Discussion**

Organic films were fabricated using the LbL process (PAH/PCBS films) and the hybrid LbL process (PAH/PB). First the kinetics of formation of PAH/PCBS LbL films are discussed and in the next section the structure, composition and the kinetics of film formation of PAH/PB hybrid LbL films are discussed.
5.5.1 Kinetics of formation of PAH/PCBS LbL films

The deposition kinetics of the PAH/PCBS LbL films was studied at a repeat unit concentration of 0.01 mM for both polyelectrolytes at pH 7. The flow rate was varied from 0.1 ml/min to 1.5 ml/min to study the effect of convection. At pH 7, both PAH and PCBS are highly charged and leads to adsorption in flat conformation.\textsuperscript{22, 23} Also, it was found in Chapter 3 that at pH 7, the PAH/PCBS films showed long range polar orientation of PCBS chromophore.\textsuperscript{5} De-ionized (DI) water was used to rinse in between the deposition steps. A repeat unit concentration of 0.01 mM was chosen for both PAH and PCBS to slow down the kinetics since the initial rate of adsorption is directly proportional to the bulk concentration. By slowing down the kinetics, it was possible to obtain a linear increase in the change in frequency versus time for a period of times greater than the residence times at different flow rates. The residence time in the flow cell is given by:

\[ t = \frac{V}{Q} \]  \hspace{1cm} (9)

in which \( t \) is the residence time in minutes, \( V \) is the volume in ml of the active sensor region of the flow cell, and \( Q \) is the volumetric flow rate in ml/min.

Table 5.5-1 shows the Reynolds number and the residence times at different flow rates. The Reynolds Number, Re was based on the hydraulic diameter of the flow cell as the characteristic length which, in this case, was 1.2 mm and is given by:

\[ \text{Re} = \frac{uL\rho}{\mu} \]  \hspace{1cm} (10)

in which \( u \) is the flow velocity calculated by using the equation \( u = \frac{Q}{A} \), where \( A \) is the cross-sectional area at the center of the flow cell, \( L \) is the characteristic length calculated using the equation \( L = \frac{2\times h \times 2R}{h+2R} \) where, \( h (=0.64 \text{ mm}) \) is the height of the flow cell, \( \rho \) is the fluid density, and \( \mu \) is the shear viscosity of the fluid.
Table 5.5-1. Reynolds number and residence times in the QCM-D flow cell at different flow rates.

<table>
<thead>
<tr>
<th>Flow Rate (ml/min)</th>
<th>Reynolds number, Re</th>
<th>Residence time, $t_{res}$ (sec)*</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.1</td>
<td>0.32</td>
<td>22.1</td>
</tr>
<tr>
<td>0.3</td>
<td>0.96</td>
<td>7.4</td>
</tr>
<tr>
<td>0.7</td>
<td>2.25</td>
<td>3.2</td>
</tr>
<tr>
<td>1.5</td>
<td>4.82</td>
<td>1.5</td>
</tr>
</tbody>
</table>

*The residence time was calculated by dividing the active volume of the flow cell with the flow rate. The active volume of the flow cell was calculated based on the active sensor region.

Figure 5.5-1 shows the 7th harmonic QCM-D results for the 5th bilayer for the PAH/PCBS deposition done at 0.7 ml/min. After rinsing the 4th bilayer with DI water, PAH was introduced as shown by the arrow marked “PAH” in the figure. During the adsorption of PAH, a decrease in frequency with time was observed which leveled off after some time. After the PAH adsorption step was complete, PCBS was introduced which is shown by the arrow marked “PCBS” in the figure. Again, a decrease in frequency with time was observed which leveled off after some time after which DI water was introduced to rinse of excess polymer from the surface. The time it takes to complete almost 90% of the adsorption of PAH and PCBS is marked by “a” and “c”, respectively. The change in frequency is marked with “b” and “d” for the PAH and PCBS deposition steps respectively.
Figure 5.5-1. 7th harmonic QCM-D results for deposition steps for 5th bilayer of PAH and PCBS at a repeat unit concentration of 0.01 mM, pH 7, and $I_{\text{eff}} = 1.7$ mM for both PAH and PCBS at a flow rate of 0.7 ml/min. A flow rate of 0.7 ml/min was used for rinsing step with DI water.

The change in frequency was converted to fractional coverage by using:

$$\theta = \frac{\Delta f}{(\Delta f)_{\text{max}}}$$  \hspace{1cm} (11)$$

in which $\Delta f$ is the change in frequency and $(\Delta f)_{\text{max}}$ is the maximum frequency change upon complete adsorption of the polyelectrolyte. Figure 5.5-2 shows a plot of fractional coverage, $\theta$ versus time for PCBS adsorption step at a flow rate of 0.7 ml/min. A linear slope in $\theta$ versus time was observed at least up to 50 seconds which is much greater than the residence time (3.2 seconds) in the flow cell at the flow rate of 0.7 ml/min (Table 5.5-1). The time up to which the slope in $\Delta f$ remained linear with time, $t_{\text{linear}}$ varied from 41 sec to 145 sec for a flow rate of 1.5 ml/min to 0.1 ml/min respectively. Compared to $t_{\text{linear}}$, the residence times, $t_{\text{res}}$, in the flow cell varied from 1.5 sec to 22.1 sec for flow rates of 1.5 ml/min to 0.1 ml/min, respectively (see Table 5.5-2). A linear increase in $\theta$ with $t$ was observed for almost 70-80% saturation of the surface indicating that the mass transfer rate was the rate limiting step up to at least 70-80% of surface saturation.
compared with a linear increase in amount of mass adsorbed, $\Gamma$ with time, $t$ for up to at least 75% saturation while studying the adsorption of PEO on silica substrates using the reflectrometry technique.\textsuperscript{9}

![Graph showing coverage versus time with a linear fit line and slope](image)

**Figure 5.5-2. $\theta$ versus $t$ for 6\textsuperscript{th} layer of PCBS adsorption step at a flow rate of 0.7 ml/min. The repeat unit concentration of PCBS was 0.01 mM and the pH was 7.**

### 5.5.2 Measurement of Experimental Mass Transfer Coefficient

The adsorption of a polyelectrolyte is a two-step process which involves the transport of polyelectrolyte from bulk to the solution and the attachment of the polyelectrolyte at the surface.\textsuperscript{9, 11, 13, 14} When the polyelectrolyte is adsorbed onto an oppositely charged surface, the adsorption step is transport limited at low surface coverage and as the polyelectrolyte adsorbs on the surface, the charge reversal takes place which results in a resistance to the incoming polyelectrolyte. In general for the transport limited regime,

$$\left. \frac{d\theta}{dt} \right|_{t \to 0} = \frac{k_c c_b}{\Gamma_{\text{max}}} \tag{12}$$
in which \( \theta \) is the fractional surface coverage (see equation 11), \( k_t \) is the mass transfer coefficient, \( c_b \) is the bulk concentration, and \( \Gamma_{\text{max}} \) is the maximum amount of mass adsorbed on the surface.

In equation 12, the parameters – \( (d\theta/dt)t \rightarrow 0 \), \( c_b \) and \( \Gamma_{\text{max}} \) are known or measurable and therefore after rearranging equation (9), \( k_t \) can be calculated experimentally. The mass transfer coefficient, \( k_t \) was estimated for PCBS at a bulk concentration of 0.01 mM. \( \Gamma_{\text{max}} \) was calculated by using the QCM-D data for \( \Delta f_{\text{PCBS}} \) which was converted to mass per unit area using the Sauerbrey equation and was calculated to be 1.42 mg/m\(^2\) for the hydrated PCBS films. The Sauerbrey equation was used here since it was found to be valid for PAH/PCBS LbL films fabricated in an earlier study discussed in Chapter 4.\(^3\) The slope \( (d\theta/dt)t \rightarrow 0 \) was calculated for different flow rates from 0.1 ml/min to 1.5 ml/min. The mass transfer coefficient of PAH was not calculated experimentally since the \( \Delta f_{\text{PAH}} \) was very low (~1.3 Hz) and led to high standard deviations due to the noise (± 0.3 Hz) while estimating \( (d\theta/dt)t \rightarrow 0 \).

The theoretical mass transfer coefficient (see equation 8) was derived using the Graetz theory\(^{21}\) which was adapted for the QCM-D flow cell geometry (See Section 5.7 for detailed derivation). The diffusion coefficients for PAH and PCBS were measured using DLS. Diffusion coefficients for PAH, \( D_{\text{PAH}} \) and PCBS, \( D_{\text{PCBS}} \) were measured as a function of repeat unit concentration are shown in Figure 5.5-3 and Figure 5.5-4 respectively. The repeat unit concentrations of both PAH and PCBS were varied from 0.01 to 10 mM at a pH 7 and at a constant ionic strength, \( I_{\text{eff}} \) of 1.7 mM at all concentrations. The Debye length at that ionic strength was 7 nm for both PAH and PCBS. Volume average sizes of the polymer chains were estimated using the DLS and Stokes-Einstein’s (see equation 2) was used to calculate the diffusion coefficients of these polymers. Both PAH and PCBS show an increase in diffusion coefficients with polymer concentration. At pH 7, both polymers, PAH and PCBS, are charged and so repulsive electrostatic interaction between segments on neighboring chains have a range on the order of the Debye length which was 7 nm at an ionic strength of 1.7 mM for all concentrations studied. As the concentration of the charged polymer is increased,
repulsive interactions between the polymer chains enhance the diffusion coefficient, an effect seen with polyelectrolytes such as DNA\textsuperscript{24} and also with charged monodisperse silica spheres\textsuperscript{25, 26} at low ionic strengths. To avoid this, the DLS measurements should be taken at low concentrations of polymer solutions and at high ionic strength to minimize the effect of electrostatic interactions among polymer chains. In this study, the DLS experiments were performed at a constant ionic strength of 1.7 mM since that was the ionic strength at which the adsorption kinetics of the polymers was studied using QCM-D.

![Graph](image)

**Figure 5.5-3.** Diffusion coefficient of PAH as a function of repeat unit concentration done at pH 7. A constant I\textsubscript{eff} = 1.7 mM NaCl was maintained at all polyelectrolyte concentrations.
Figure 5.5-4. Diffusion coefficient of PCBS as a function of repeat unit concentration done at pH 7. A constant $I_{\text{eff}} = 1.7$ mM NaCl was maintained at all polyelectrolyte concentrations.

Figure 5.5-5 shows a plot of the experimental and theoretical mass transfer coefficient values as a function of $Re^{\frac{1}{3}}$. The experimental values are higher than those obtained using the theory. This is most likely because the theory does not incorporate the effect of electrostatic interactions which increases the rate of mass transfer from bulk to the surface.\(^{14}\) From equation 8, a linear increase in the mass transfer coefficient is obvious for the theoretical values. It is interesting to see a linear increase in the experimental mass transfer coefficient values. The deviation in the slope of theory compared from that of experimental values in Figure 5.5-5 may suggest how to incorporate the electrostatic interactions in the theoretical model to accurately predict the mass transfer of polyelectrolytes on surfaces in the mass transfer limited regime. Figure 5.5-6 shows the initial rate of adsorption, $(d\Gamma/dt)_{t \rightarrow 0}$ as a function of $Re$ for the PCBS deposition step at a repeat unit concentration of 0.01 mM or 3.7 mg/l. Values of $(d\Gamma/dt)_{t \rightarrow 0}$ were found to vary from 0.0088 mg/m\(^2\).sec for $Re = 0.32$ to 0.031 mg/m\(^2\).sec for $Re = 4.8$ (see Table 5.5-2). This is compared with $(d\Gamma/dt)_{t \rightarrow 0}$ varying approximately between 0.002 at Re of 6 to 0.01 at Re of 200 for adsorption of PEO in silica substrate.\(^{9}\)
Figure 5.5-5. Comparison of experimental and theoretical mass transfer coefficients for physisorption of PCBS as a function of $Re^{(1/3)}$. The repeat unit concentration of PCBS was 0.01 mM at pH 7. The $I_{eff} = 1.7$ mM NaCl. The experiment was conducted at 25°C.

Figure 5.5-6. Initial rate of adsorption as a function of Reynolds number for PCBS adsorption step at a repeat unit concentration of 0.01 mM, pH 7 and $I_{eff} = 1.7$ mM.
The effect of electrostatic interactions on the rate of polymer deposition was not studied since there is a need to improve the electrostatic model to study the polyelectrolyte adsorption. The overall equation describing the kinetics of deposition can be written as:

\[
\frac{d\Gamma}{dt} = R_{total} \frac{d\theta}{dt} = c_b - c_s
\]

in which \(\Gamma_m\) is the maximum surface coverage in mg/m\(^2\), \(\theta\) is fraction of surface covered, \(c_b\) is the bulk concentration, \(c_s\) is the subsurface concentration, and \(R_{total}\) is the total resistance which includes the resistance due to transport in the solution, \(R_t\) and the electrostatic resistance, \(R_e(\theta)\) and is given by the expression,

\[
R_{total} = R_t + R_e(\theta)
\]  
(14)

The expression for energy barrier is given by:

\[
R_e(\theta) = \frac{u(\Gamma)}{D} \left(\frac{e^{\frac{kT}{\kappa z}}}{\kappa^{-1}}\right)
\]

in which \(D\) is the diffusion coefficient of the charged chromophore, \(u(\Gamma;z)\) is the potential energy felt by an adsorbing molecule which is at a distance \(z\) from where it first touches the surface, and \(\kappa^{-1}\) is the debye length. The resistance barrier given by equation 15 can be easily calculated.

In the expression given by equation 15, the value of electrostatic resistance, \(R_e(\theta)\), is \(\sim 0\) when there is a net attraction between the polyelectrolyte and the substrate since \(u(\Gamma)\) is negative. Substituting this in equation 14, we see that the expression for \(R_{total}\) is reduced to the resistance provided only by the transport in the solution, \(R_t\). The value of \(R_{total}\) is not affected by the value of \(R_e(\theta)\) until sufficient surface coverage has been achieved and the substrate charge is reversed so that there is repulsion between the substrate and the incoming polyelectrolyte. Thus a modification of the current electrostatic model is required to incorporate the effect of attractive electrostatic forces on the adsorption rate.
Table 5.5-2. Initial rate of adsorption, theoretical and experimental mass transfer coefficient as a function of flow rate and Reynolds number. $t_{res}$ and $t_{linear}$ are also mentioned. The repeat unit concentration of PCBS was 0.01 mM at pH 7. The $I_{eff} = 1.7$ mM NaCl. The experiment was conducted at 25°C.

<table>
<thead>
<tr>
<th>Flow Rate (ml/min)</th>
<th>Reynolds Number, Re</th>
<th>$t_{res}$, sec</th>
<th>$t_{linear}$, sec</th>
<th>$\Gamma/\mathbf{dt}$, mg m$^{-2}$ sec$^{-1}$</th>
<th>Theoretical mass transfer coefficient, $k_t$,avg (m/sec)*</th>
<th>Experimental mass transfer coefficient, $k_t$, Exp(m/sec)**</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.1</td>
<td>0.32</td>
<td>22.1</td>
<td>145</td>
<td>0.008</td>
<td>$1.96 \times 10^{-6}$</td>
<td>$2.38 (\pm 0.19) \times 10^{-6}$</td>
</tr>
<tr>
<td>0.3</td>
<td>0.96</td>
<td>7.4</td>
<td>65</td>
<td>0.017</td>
<td>$2.80 \times 10^{-6}$</td>
<td>$4.60 (\pm 0.37) \times 10^{-6}$</td>
</tr>
<tr>
<td>0.7</td>
<td>2.25</td>
<td>3.2</td>
<td>55</td>
<td>0.022</td>
<td>$3.76 \times 10^{-6}$</td>
<td>$6.14 (\pm 0.47) \times 10^{-6}$</td>
</tr>
<tr>
<td>1.5</td>
<td>4.82</td>
<td>1.5</td>
<td>41</td>
<td>0.031</td>
<td>$4.80 \times 10^{-6}$</td>
<td>$8.44 (\pm 1.18) \times 10^{-6}$</td>
</tr>
</tbody>
</table>

*calculated from equation #8  
**calculated from equation #12.

5.5.3 Film Structure and Composition and Kinetics of hybrid PAH/PB LbL Films

The film structure and composition as well as kinetics of film formation were studied for hybrid LbL PAH/PB films using the QCM-D technique. Up to 15 bilayers of PAH/PB were deposited on a gold-coated quartz crystal. Bilayers 1 and 2 were deposited at a flow rate of 0.5 ml/min, 3-8 were deposited at a flow rate of 1 ml/min, 9 and 10 at a flow rate of 0.7 ml/min, 11-13 at a flow rate of 0.5 ml/min, and 14 and 15 at a flow rate of 1.5 ml/min. Figure 5.5-7 shows the PAH/PB deposition step for bilayer #10. The deposition conditions were: PAH: 10 mM repeat unit concentration, pH 7; PB: 5 mg/ml, pH 10.5. In Figure 5.5-7, after the 9th bilayer was deposited and rinsed with DI water, the baseline was allowed to stabilize. PAH was injected as indicated by the arrow “PAH” followed by rinsing with DI water and then PB was injected followed by rinsing with DI water to complete the formation of 10th bilayer. The corresponding curve for dissipation is also shown. No significant change in frequency was observed upon rinsing the PAH film with DI water; however the dissipation decreased significantly indicating that the films became rigid. This was due to the removal of loosely bound PAH on the surface. Upon rinsing after the PB deposition step, both the frequency as well as dissipation changed significantly. This could be either due to removal of adsorbed mass from the surface or due to the changes in viscosity and density. Interestingly, upon rinsing after the PB adsorption step with DI water, the frequency first increased and then started to
decrease at a very slow rate. This decrease in frequency is most likely due to the uptake of water from the system since the PB films are hydrophobic at pH 10.5 when they are formed and by introducing DI water at pH 7 in the system, the films becomes hydrophilic and can uptake water from the system. There was no significant change in dissipation when the PB films uptake water suggesting that the films did not become softer upon water uptake. In the figure, “f” and “h” denote the change in overall frequency upon complete adsorption of the PAH and PB respectively. “e” and “g” denotes the time it takes for greater than 90% complete coverage of PAH and PB respectively.

![Graph showing change in frequency and dissipation](image)

**Figure 5.5-7.** PAH/PB deposition step at a flow rate of 0.7 ml/min. The concentration of PAH was 10 mM at pH 7. The concentration of PB was 5 mg/ml at pH 10.5

Figure 5.5-8 shows the change in frequency as a function of bilayer number at a flow rate of 0.7 ml/min. It is interesting to note that these films behave quite differently from the PAH and PCBS adsorption case studied in Chapter 4 which showed a linear change in frequency with number of bilayers. In this case, initially the frequency changed linearly with # bilayers up to 6 bilayers of PAH and PB and then the slope changed after 6 bilayers were deposited, although a linear increase in frequency with #bilayers was observed. For the PAH and PCBS deposition step, a linear change in
frequency was observed after 3 bilayers were deposited which was due to interfacial effects. In the present case, the change in slope after 6 bilayers were deposited was also most likely due to interfacial effects since the thickness per bilayer in the dry state of PAH/PB films was much less at 0.27 nm per bilayer compared to 1.17 nm for PAH/PCBS films. Thus interfacial effects might be expected to show up at larger bilayer numbers for PAH/PB films. The slope up to 6 bilayers was $7.62 \pm 0.36$ Hz/bilayer and the slope after 6 layers was $18.55 \pm 1.79$ Hz/bilayer. The slopes were averaged over three different experiments on three different crystals.

![Graph showing change in frequency versus bilayer number for PAH and PB adsorption steps.](image)

**Figure 5.5-8. Change in frequency versus bilayer number for PAH and PB adsorption steps.** Bilayers 1 and 2 were deposited at a flow rate of 0.5 ml/min, 3-8 were deposited at a flow rate of 1 ml/min, 9 and 10 at a flow rate of 0.7 ml/min, 11-13 at a flow rate of 0.5 ml/min, and 14 and 15 at a flow rate of 1.5 ml/min

The change in frequency and dissipation were used to calculate the thickness per bilayer of PAH/PB films in wet state using the Voigt model. To calculate the thickness of the hydrated films, $t_h$, using the Voigt model, a density value of these films in hydrated state needs to be specified. The density of these films, $\rho_h$, was calculated using the iterative procedure described in Chapter 3 (Appendix A) and was found to be
1012 kg/m$^3$. Following the determination of $\rho_h$, the thickness of hydrated films, $t_h$ was calculated using the Voigt model which was found to be 3.67 nm per bilayer for more than 7 bilayers. (See Appendix) and these values were used to calculate the water content of the hydrated PAH/PB films by using the equation #16,

$$\% \text{ Water Content} = 100 \times \left( \frac{\rho_h t_h - \rho_d t_d}{\rho_h t_h} \right) \quad (16)$$

in which density of dry films, $\rho_d$, was assumed to be 1200 (± 100) kg/m$^3$ and the thickness of the dry PAH/PB films, $t_d$, was taken from a previous study as 0.27 nm per bilayer for the films fabricated under similar deposition condition. The water content of these films was found to be 91%. This was much higher compared to the %water content in the polymer/polymer ISAM films which was between 40-45%.3

The validity of the Sauerbrey equation was checked by comparing the thicknesses obtained using the Sauerbrey equation and the Voigt model. The Sauerbrey equation gave significantly different results for thickness of these films as compared to the Voigt model as shown in Figure 5.5-9. Further testing of the validity of Sauerbrey equation was done by using the model derived by White and Schrag by considering a viscoelastic film (phase 1) with thickness $t_h$, viscosity $\eta_1$ and density $\rho_1$ on a quartz crystal surface in contact with a liquid (phase 2) with viscosity $\eta_2$ and density $\rho_2$. The Sauerbrey equation and a more generalized viscoelastic model were shown to diverge when $\beta_1 t_h > 0.28$ and when $\beta_1/\beta_2 > 0.2$ where $\beta_i$ is defined as:

$$\beta_i = \sqrt{\frac{\alpha \rho_i}{\eta_i} \cos \left[ \frac{\pi}{4} - \frac{\phi}{2} \right]} \quad (17)$$

in which $\phi$ is the relative phase angle of the medium. For purely a viscous medium, $\phi = \pi/2$, whereas $\phi = 0$ for a purely elastic medium. These criteria were found to explain the swelling behavior of films of ammonium poly(4-styrenesulfonic acid) studied with a QCM-D.34

To calculate the $\beta$ parameter for the films, the value of the viscosity of these films which was calculated using the Voigt model to be 7.3 (±0.4) $\times 10^{-3}$ kg/ms for a 15 bilayer
PAH/PB film of 44.1 nm thickness. The viscosity of these films is approximately 8 times higher than that of water at 25°C. Compared to this a value of 13 (± 0.3) x 10^3 kg/ms was obtained using QCM-D for 116 nm swollen Poly(4-ammonium styrenesulfonic acid) films deposited using spin coating. The shear modulus of these films was calculated using the Voigt model to be 2.42 (± 0.4) x 10^5 Pa. This value is compared with 1.8 (± 1.0) x 10^6 Pa obtained using atomic force microscopy (AFM) for films fabricated using PAH/PCBS at a pH of 7 for both the polyions. For the calculations, φ was assumed to be π/2. Using these values, the parameter β_1t_h was found to be 0.04 and β_1/β_2 was found to be 0.35. So, although these films satisfy the criteria of β_1t_h, these films did not satisfy the second criteria, thereby leading to the divergence of Sauerbrey equation from the Voigt model.

![Figure 5.5-9. Comparison of thickness obtained from Sauerbrey and Voigt model at a wet film density, ρ_d = 1012 kg/m^3.](image)

The Δf ratio of PB to PAH, Δf_{PB}/Δf_{PAH} in these films was found to be 1.44 ± 0.2 and this ratio was converted to the molar ratio of PB to PAH, M_{PB}/M_{PAH} by using the equation:
\[
\frac{M_{PB}}{M_{PAH}} = \frac{\Delta f_{PB}}{\Delta f_{PAH}} \frac{MW_{PB}}{MW_{PAH}}
\]  

(18)

in which \(MW_{PB}\) is the molecular weight of PB and \(MW_{PAH}\) is the and repeat unit molecular weight of PAH. From equation #18, the \(M_{PB}/M_{PAH}\) was found to be 0.17. The low molar ratio, \(M_{PB}/M_{PAH}\), is consistent with the presence of unreacted amine groups left over in the bilayer films.\(^{36}\) The ratio of change in frequency for PB to PAH (\(\Delta f_{PB}/\Delta f_{PAH}\)) can be converted to \(\%PB\) in these films which, together with density of films in dry state, can be used to estimate the number density of PB chromophores, \(N\) (see equation 1) using:

\[
N = \frac{\%PB \times \rho_d \times N_{av}}{100 \times MW_{PB}}
\]

(19)

in which \(N_{av}\) is Avogadro’s number. Base on equation 13, the value of \(N\) was calculated to be 5.5 (± 0.6) \(\times 10^{20}\) cm\(^{-3}\). By comparison, the value of \(N\) for LbL polyelectrolyte films consisting of PAH and poly{1-[p-(3’-carboxy-4’-hydroxyphenylazo)benzenesulfonamido]-1,2-ethanediyl} (PCBS) varied from 1.4 – 1.7 \(\times 10^{21}\) cm\(^{-3}\). For poled polymer films, an alternative approach for making second order nonlinear optical films, values of \(N\) have been reported ranging from 2.2 to 9.8 \(\times 10^{20}\) cm\(^{-3}\).\(^3\)\(^{37,38}\)

The PAH/PB films had highest \(\chi^{(2)}_{zzz}\) values when the PB was deposited at 0.5 M NaCl.\(^6\) However, this condition was not studied using the QCM-D due to the irreversible damage caused to the gold-coated quartz crystal at pH 10.5 and 0.5 M salt concentration. Figure 5.5-10 shows the results of the control experiments done on a gold-coated quartz crystal. A baseline was obtained using DI water and then a 0.01 N Na\(_2\)CO\(_3\) buffer solution which has a pH of 10.5 was introduced into the system. A change in frequency and dissipation was observed which is most likely due to viscosity effects. After ~ 10 minutes, DI water was introduced and the baseline returned to its original value with no net change in the frequency or dissipation. This was done two times as shown in the figure. However, when a solution containing the buffer at pH 10.5 and 0.5 M NaCl (Aldrich, 99.999%) salt was introduced into the system, a much higher change in frequency and dissipation was seen and the frequency never reached a stable baseline. This effect was seen with both silica-coated and gold-coated quartz crystals. Upon rinsing
with DI water after ~ 10 minutes, a net change in the frequency was seen when compared with the original baseline. Although the exact reason for this permanent shift in the baseline is not known, it is certain that the combination of high pH of 10.5 and at 0.5 M NaCl concentration causes irreversible damage to the gold-coated quartz crystals. Instead of NaCl, sodium nitrate (NaNO₃) (Aldrich, 99%) was also used with similar results leading to an irreversible change in the gold-coated quartz crystals.

Figure 5.5-10. Control experiment with the QCM-D on gold-coated crystals using DI water, Na₂CO₃, and 0.5 M NaCl.
During the formation of PAH/PB films, PB was attached to the underlying PAH film by means of a covalent bond. The adsorption of PB on the underlying PAH could be either transport limited or rate limited. To calculate the true rate constant for the reaction step, the adsorption step should be rate limited and not transport limited.\(^{39}\) To achieve this, the flow rate of the PB was varied from 0.5 ml/min to 1.5 ml/min. Figure 5.5-11 shows the fractional coverage, \(\theta\) (see equation 11) of PB deposition step versus time at different flow rates. No increase in adsorption rate was observed upon increasing the flow rate which implied that the adsorption step was rate limited for all the flow rates studied. The adsorption step can be defined by assuming that the binding of PB to the underlying PAH by means of a first order reaction

\[
\Gamma_{\text{max}} \frac{d\theta}{dt} = k_d c_p (1 - \theta)
\]  

\[\text{(20)}\]
in which $k_a$ is the reaction rate constant. The equation can be integrated and rearranged to calculate the reaction constant, $k_a$.

$$k_a = -\frac{\Gamma_{\text{max}} \ln(1 - \theta)}{c_b t}$$

Using equation 21, the rate constant for the PB deposition step was calculated by using the $\theta$ from 0.1 to 0.8 and the corresponding time, $t$. These ranges of $\theta$ and $t$ were chosen to avoid the initial adsorption period ($t=0$) and the plateau region ($\theta = 1$) where equation 21 becomes infinite. The rate constant was calculated to be $3.31 (\pm 0.2) \times 10^{-8}$ m/s averaged over three different PB deposition steps at a flow rate of 1.5 ml/min. Based on this rate constant, the average time for 95% completion of PB adsorption was calculated to be ~45 sec.

### 5.6 Conclusions

The kinetics of formation of layer-by-layer (LbL) polycation poly(allylamine hydrochloride) (PAH) and the polymeric dye poly{1-[p-(3’-carboxy-4’-hydroxyphenylazo)benzenesulfonamido]-1,2-ethandiyl} (PCBS) on quartz crystals coated with silica was studied using a quartz crystal microbalance with dissipation monitoring (QCM-D). A flow cell was used to vary the flow rate over the SiO$_2$ substrate on which the films were deposited. The effect of convection was studied on the initial rate of adsorption of the polyelectrolytes on the substrate. Experimental and theoretical values of mass transfer coefficient, $k_t$, were calculated at different Reynolds numbers. The experimental values were found to give a higher estimate of the mass transfer coefficient than the theoretical values possibly due to the electrostatic effects which increase the initial rate of adsorption due to attractive forces between oppositely charged polyelectrolyte and the substrate.

The film structure and composition of hybrid LbL PAH/Procion Brown (PB) films was also studied on quartz crystal coated with gold using QCM-D. The wet thickness per bilayer, $t_w$, of PAH/PB films in hydrated state was calculated and compared with the dry thickness per bilayer, $t_d$, to obtain the water content in these films. The water content in these films was found to be ~ 90% and the chromophores number density was 5.5 (± 0.6)
x 10^{20} \text{cm}^{-3}. Viscoelastic properties of the PAH/PB films was also calculated and the viscosity of these films was found to be approximately 7.3 (±0.4) x 10^{-3} \text{kg/ms}.

The rate constant, $k_a$, for the attachment of PB to the underlying PAH by means of covalent bond was calculated. To estimate the true reaction constant, the flow rate of the PB solution over the gold coated crystal was varied so that the binding of PB to the underlying PAH was not transport limited. The value of $k_a$ was calculated to be 3.31 (± 0.2) x 10^{-8} \text{m/s}. The time required for 95% completion of PB deposition step was ~45 seconds.

5.7 Appendix A for Chapter 5

5.7.1 Modeling

Figure 5.7-1 shows the top view of the flow cell and Figure 5.7-2 shows the side view of the flow cell. The active region or the sensor region is shown by the smaller inner circle. The height of the flow cell is given by $2H$. As shown in Figure 5.7-2, the fluid enters the flow cell from the inlet and flows over the quartz crystal coated with silica or gold and then leaves the flow cell from the outlet. Inside the flow cell, the fluid has a parabolic velocity profile as shown in the Figure.

Figure 5.7-1. Top view of the QCM flow cell. It has an inlet to let the fluid inside the flow cell and an outlet.
For the 7th harmonic, the sensor region is the middle circular region of radius $x_s = 0.3$ mm. The 7th harmonic frequency change in a QCM-D is affected only by the changes occurring on the sensor region.

### 5.7.2 Velocity profile inside the flow cell

To obtain the equation for mass transfer coefficient, first the expression for velocity profile in the flow cell was derived. The velocity profile for a fully developed flow obtained by solving the two dimensional Navier-Stokes equation by finite Fourier transform method in a rectangular cross section given by the equation 21

$$\Theta = \frac{v_x}{U} = \frac{3}{2}(1 - Y^2)$$

(A1)

in which the non-dimensional parameters are defined by the equations

$$Y \equiv \frac{y}{H}, \quad Z \equiv \frac{z}{H}, \quad \text{and} \quad \Theta \equiv \frac{v_x}{U}$$

(A2)

And U is the mean flow velocity for a flow in a parallel channel with a spacing $2H$ and is given by
\[ U = -\frac{H^2}{3\mu} \frac{dP}{dx} \]  

Substituting equation (A3) in equation (A2) and writing the equation in the dimensional form,

\[ v_x = -\left(\frac{H^2}{2\mu}\right) \frac{dP}{dx} \left(1 - \left(\frac{y}{H}\right)^2\right) \]  

(A4)

The volumetric flow rate is given by the equation,

\[ Q = \int \int_A v_x \, dy \, dz \]  

(A5)

where the limits of \( y \) are from \(-H\) to \(H\) and the limits of \( z \) are from \(-R(x)\) to \(R(x)\).

where, \( R(x) = \sqrt{R^2 - x^2} \)

Integrating Equation (A5) to solve for \( Q \),

\[ Q = -\frac{4H^3 R(x)}{3\mu} \frac{dP}{dx} \]  

(A6)

or,

\[ \frac{dP}{dx} = -\frac{3\mu Q}{4H^3 R(x)} \]  

(A7)

which leads to,

\[ v_x = \frac{3Q}{8HR(x)} \left[1 - \left(\frac{y}{H}\right)^2\right] \]  

(A8)

Equation (A8) gives the expression for the velocity profile in the flow cell.

5.7.3 Mass transfer model

The velocity function derived above can be used to derive the expression for mass transfer coefficient. Since, \( c = c(x, y) \), we can write,

\[ v_x \frac{dc}{dx} = D \frac{d^2c}{dy^2} \]  

(A9)

The following boundary conditions apply

\[ c(x = x_s, y) = c_b \]  

(A10)
\[ \frac{\partial c}{\partial y} \bigg|_{y=0} = 0 \]  
\[ c(x, y = -H) = c_s \]  

Using the dimensionless variables,
\[ \eta = \frac{y}{H}, \quad \zeta = \frac{x}{H P e}, \quad \Theta = \frac{c - c_b}{c_s - c_b}, \quad P e = \frac{U H}{D} \]
in which \( U \) is the mean velocity obtained by substituting equation (A7) in equation (A3),
\[ U = \frac{Q}{4 R(x) H} \]  

Scaling the equation, we get,
\[ \frac{3}{2} (1 - \eta^2) \frac{d\Theta}{d\zeta} = \frac{d^2\Theta}{d\eta^2} \]  

The boundary conditions for the above differential equation are,
\[ \Theta(\zeta, \eta) = 0 \]
\[ \frac{\partial \Theta}{\partial \eta} (\zeta, 0) = 0 \]
\[ \Theta(\zeta, -1) = 1 \]

Using the following substitution, \( \chi = 1 - \eta \). We get,
\[ \frac{3}{2} (2 \chi - \chi^2) \frac{d\Theta}{d\zeta} = - \frac{d^2\Theta}{d\chi^2} \]  

An order-of-magnitude analysis will be done to find the dominant terms in equation (A15) and to infer how the penetration depth grows with distance along the wall of the flow cell. We are concerned with the axial positions such that \( \tilde{\delta} \ll 1 \), where \( \tilde{\delta} \) is the penetration depth divided by the height of the flow cell. At these axial positions the solutions remains at bulk concentration, except near the wall. Thus, \( \Theta \) varies from zero at the inlet (bulk concentration) to one (the subsurface concentration) as \( \chi \) varies by the amount \( \tilde{\delta} \). Comparable variations in \( \Theta \) occurs over the axial distance \( \zeta \). It follows that for the region near the wall where there is a concentration gradient,
\[ (2 \chi - \chi^2) \frac{\partial \Theta}{\partial \zeta} \sim \left( \tilde{\delta} \right) \left( \frac{1}{\zeta} \right) \]  

159
\[ \frac{\partial^2 \Theta}{\partial \zeta^2} - \frac{1}{\delta^2} \]  
(A17)

Considering that \( \chi^2 \ll \chi \), we can rewrite equation (A15) as,

\[ (3\chi) \frac{d \Theta}{d \zeta} = -\frac{d^2 \Theta}{d \chi^2} \]  
(A18)

The boundary conditions for \( \Theta(\zeta, \chi) \) are,

\[ \Theta(\zeta, \chi) = 0 \]
\[ \Theta(\zeta, 0) = 1 \]
\[ \Theta(\zeta, \infty) = 0 \]

Making the following substitution,

\[ s \equiv \frac{\chi}{g(\zeta)} \]  
(A19)

Rewriting equation (A9)

\[ \frac{d^2 \Theta}{ds^2} + 3s^2 (g^2 g') \frac{d \Theta}{ds} = 0 \]  
(A20)

For \( s \) to be only independent variable, the term \( (g^2 g') \) must be a constant. For convenience, the constant is chosen as 1.

\[ (g^2 g') = 1 \quad \text{or} \quad \frac{1}{3} (g^3) = 1 \]  
(A21)

\[ g = \left( \frac{3x}{HPe} \right)^{1/3} \]  
(A22)

Rewriting equation (A20),

\[ \frac{d^2 \Theta}{ds^2} + 3s^2 \frac{d \Theta}{ds} = 0 \]  
(A23)

The solution of the above equation is given as,

\[ \frac{d \Theta}{ds} = ae^{-s^3} \]  
(A24)

in which \( a \) is a constant

\[ Sh = \frac{k, L}{D} \]

in which \( L = H \) is the characteristic length.
\[ Sh = \frac{k_t H}{D} = \frac{6}{\Gamma(1/3)g(\zeta)} \]  \quad (A25)

where \( \Gamma(1/3) = 2.67894 \)

Solving the above equation for mass transfer coefficient, \( k_t \)

\[ k_t = \frac{6D}{H\Gamma(1/3)g(\zeta)} \]  \quad (A26)

Substituting for \( g(\zeta) \) in above equation,

\[ k_t = \frac{1.553D}{H} \left( \frac{HPe}{x} \right)^{1/3} \]  \quad (A27)

As a function of Reynolds number, the above equation can be written as,

\[ k_t = 1.553 \left( \frac{D}{H} \right)^{2/3} \text{Re}^{1/3} \left( \frac{\nu}{x} \right)^{1/3} \]  \quad (A28)

Equation (A28) gives the expression for mass transfer coefficient in a QCM flow cell. The mass transfer coefficient is calculated by integrating over the entire surface area of the active sensor region.
5.8 References


6.1 Abstract

A novel flow cell was used to fabricate layer-by-layer (LbL) polyelectrolyte films. Polyelectrolyte solutions and de-ionized water were passed alternately through the flow cell to build up LbL films. A set of computer controlled solenoid valve was used to control the flow of polyelectrolytes and DI water through the flow cell. This device has the potential of minimizing the fabrication time which is an important factor in fabricating 1μm thick LbL films which corresponds to approximately 1000 bilayers, an important parameter in fabricating a practical electro-optic (EO) modulator. The properties of the films fabricated by using custom build device were comparable to those obtained using the conventional dipping device.

6.2 Introduction

Layer-by-layer (LbL) films are formed by alternately adsorbing polymer on a substrate by means of electrostatic interactions, hydrogen bonding, and hydrophobic interactions or covalent bonding or by combination of these. This technique provides for easy molecular and structural control by manipulating the solution properties of the polyelectrolyte solutions such as concentration, pH, and ionic strength. Due to this, these films have many potential applications in biosensors, biomaterials, electronic devices, and molecular optics. The most common fabrication approach is the dipping procedure which involves manually dipping the substrate alternately in solution of polyelectrolytes with a rinsing step in between. In addition to manually spending hours to deposit multilayers, reproducing the results have been a major drawback of this procedure. Another approach to deposit layer-by-layer films is to use an automated deposition system in which a robotic arm to which the substrate is attached dips alternately into baths filled with polyelectrolyte solutions and deionized (DI) water. Automation of this technique made it easier to rapidly fabricate films with high bilayer
numbers and excellent reproducibility. However, these devices use large amounts of deionized (DI) water and are expensive.

Among the automated deposition techniques, there are various ways to deposit and form LbL multilayer films on a substrate which are discussed. Instead of dipping the substrate alternately in polymer solutions and DI water, another technique employs alternately spraying the polymer solutions and DI water on a substrate. Films consisting of poly(diallyldimethylammonium) (PDAD) and poly(styrenesulfonate) (PSS) were fabricated using both dipping and spraying procedure. Although similar bilayer thickness was observed for both procedures at 10 s deposition but at 5 minute deposition time using dipping, the film thickness was considerably different from that fabricated at 10 seconds spraying time. Another technique also involves spraying the polymer solutions and DI water on a substrate; however, in this case the substrate was spun. It was found that the each bilayer formed using the spin-coating self-assembly process consisted of densely packed monomolecular film. In another study, a modified ink-jet printer was used to deposit a pattern of PAH on 3 bilayers of PAH/poly(acrylic acid) (PAA) deposited on a substrate. A commercially available color ink-jet printer was used and the original ink cartridge was replaced by Tygon® tubing containing the PAH solution. In another study, a quartz crystal microbalance (QCM) was used to determine the time it takes for 90% complete adsorption of SiO₂ nanoparticles and a polycation poly(diallyldimethyl-ammonium chloride) (PDDA). A 100-fold reduction in time was achieved by using the optimal deposition time of the nanoparticles and the polycation. Since none of the studies discussed above applied their work towards the nonlinear optical materials, it still remains an open question whether or not these techniques can be used to form NLO materials which require unprecedented homogeneity.

This present work is particularly relevant for fabricating a film for use in a practical electro-optic (EO) modulator application where the film fabrication should be reasonably rapid and use minimal amount of materials. The thickness of one bilayer of polycation and polyanion that is deposited on a glass substrate is approximately 1 nm and for a practical EO modulator device operating in a waveguide mode, a film of the order
of 1 μm thick or approximately 1000 bilayers is needed. At present, it takes about 10 minutes to deposit each bilayer which means that it would take approximately 1 week of continuous processing to make a 1 micron thick film requiring 900 L of DI water.

This study concerns the fabrication of a custom made device which is completely automated and can be used to alternately deposit LbL films on a substrate. The thick film device consists of a flow cell with an approximate volume of 350 μl and which can hold a standard 1” x 3” microscope slide. The flow cell design is related to that used in the quartz crystal microbalance with dissipation (QCM-D) devices. The polyelectrolyte solutions and the DI water are passed alternately through the flow cell; their flow is controlled by a set of four three-way solenoid valves which are operated by a programmable controller. The properties of the films fabricated with this device were compared with those fabricated by the conventional dipping device.

6.3 Experimental

6.3.1 Materials Used

Poly(allylamine hydrochloride), referred to as PAH, was used as a polycation (Mw ca. 70,000; Aldrich, item number 283223-25G, Figure 6.3-1 1 (a)). Poly{1-[4-(3-carboxy-4-hydroxyphenylazo)-benzenesulfonamido]-1,2ethanediyl} (PCBS, sometimes referred to as ‘PAZO’; Aldrich; item number 346411-25G, Figure 6.3-1 (b)) was used as the polyanionic chromophore in the deposition experiment. The repeat unit molecular weight of PAH was 93.56 g/mol and of PCBS was 369.3 g/mol. Deionized (DI) water (Barnstead) was used with a resistivity of over 17 MΩ.cm. The pH of the polymer solutions was adjusted to 7.0 using standard solutions of NH₄OH and HCl before starting the experiment. Premium microscope glass slides (Fisher Scientific) frosted on one end were used. To clean the slides, they were rinsed with ethanol (Fisher Scientific) and then rinsed with DI water. They were cleaned using oxygen plasma etcher for 30 minutes at the vacuum pressure between 400-600 mTorr and at the current setting of 70 mA. Medical grade ultra elastic natural latex rubber (97% natural rubber, McMaster Carr, P/Ns 85995K11, 85995K12, 85995K13, 85995K14, 85995K15, 85995K16), 0.006 inch – 0.014 inch in thickness was used as the gasket material. High impact strength
polycarbonate (McMaster Carr, P/N 8574K32), ¼ and ½ inches in thickness was used to fabricate the flow cell. Pulse dampeners (Cole Parmer) were used to de-aerate the polyelectrolyte solutions and DI water. The program to control the solenoid valves was written by Riley Chan, Department of Chemical Engineering using the basic stamp II editor (ver 2.4, Parallax Inc.) (see section 6.6 for program). This program was made user friendly where the parameters such as, the deposition time, rinsing time and the #bilayers can be modified in the program given in the “USER’S PARAMETER ENTRY” column. After modification, the updated program is fed in the processing unit of the microprocessor by pressing the “run” button on the basic stamp II editor.

![Figure 6.3-1. Structure of (a) PAH and (b) PCBS](image)

6.3.2 Fabrication of custom built device

The custom-built device consists of a rectangular flow cell which can accommodate one standard 1” x 3” glass slide with a thickness of 1 mm, a set of four three-way solenoid valves (Cole-Parmer: Part No. EW-98302-42), and the electronics to control the valves. The flow cell used is shown in the Figure 6.3-1 6.3-2 (a). The experimental set-up is shown in Figure 6.3-2 (b). It consists of two slabs made from polycarbonate. In one slab, a groove was cut so that the glass slide could fit in that groove. The groove was 1 mm in depth to accommodate a standard microscope glass
slide so that the top part of the slab was even with the top part of the slide. The top part of the flow cell was then put on top of this and the separation between the glass slide and the top part was provided by using the latex rubber gaskets which were cut into desired shape. The thickness and hence the volume of the flow cell can be changed by changing the thickness of the gasket. A gasket thickness of 0.01” (≈ 254 μm) gave the optimal results. The effective thickness of the gasket would be less than 0.01” due to compression. However, the exact thickness could not be determined. Use of thinner gasket resulted in channeling of fluid inside the flow cell leading to inhomogeneous formation of the LbL films. The gasket was tightened carefully with a screwdriver to prevent breaking of the glass slide and to prevent leakage of the fluid through the flow cell.
6.3.3 Fabrication of LBL films

To fabricate the LBL films, first the polycation (PAH) was passed through the flow cell. After polycation is adsorbed on the initially negatively charged glass slide, the excess polycation was rinsed off with DI water. After this, the polyanion (PCBS) was passed through the flow cell and again the excess polyanion was removed with DI water. Three-way solenoid valves were used to recycle the polymer solutions and the DI water when they were not being passed through the flow cell. The solenoid valves were controlled through electronics which can easily be programmed to change the number of bilayers and deposition and rinsing times.

The first generation of the flow system consisted of three tubes for polycation, polyanion and DI water. These three tubes merged together to form a single tube through which one of the three solutions passed through the flow cell at any given time. At the point where the three tubes merged in to a single tube that fed into the flow cell, the polycation and polyanion came in direct contact with each other. This was not a problem for fabricating films with low bilayer numbers. However, when high bilayer numbers
were fabricated using the above set-up, the polycation and polyanion mixed together at the intersection of three tubes to form aggregates leading to blockage of the tube. To avoid this blockage in the tube in the second generation design shown in Figure 6.3-2 (b), an additional three-way solenoid valve with DI water was used so that each of the polymer solutions came in direct contact with DI water first and never come in direct contact with other polymer solution. This was done by changing the valve arrangement as shown in Figure 6.3-2 (b). Pulse dampeners were used to reduce or completely eliminate the flow of air bubbles through the tube. De-aeration of solutions was not practical since these solutions were to be left in contact with air for very long periods of time.

The Reynolds number, Re inside the flow cell is calculated by Equation 1:

$$Re = \frac{\rho v H}{\mu}$$

in which $\rho$ is the density of the fluid, $v$ is the flow velocity which is calculated by dividing the flow rate with the cross-section area of the flow cell, $H$ is the characteristic length of the flow cell which is the height of the flow cell, and $\mu$ is the viscosity of the fluid.

For all experiments, the concentrations of the PAH and PCBS solutions were 10 mM on a repeat unit basis, the same concentration used in Chapter 3.² The pHs of the polymer solutions was adjusted using 1.0 M or 0.1 M solutions of sodium hydroxide and hydrogen chloride. The pH of the solutions drifted no more than ± 0.1 pH units during the course of the experiment.

6.3.4 Film Characterization

Absorbance measurements (done by Cemil Durak, Department of Physics) were done using a Perkin Elmer Lambda 25 UV/vis system. The films exhibited an absorbance maximum, $\lambda_{max}$, at 360 nm. Film thicknesses were measured using a variable angle spectroscopic ellipsometer (J. A. Woolam ellipsometer VB-200 with WVASE32 software version 3.361). The ellipsometric analysis was done in the vicinity of the Brewster angle because ellipsometry measurements are most sensitive to film characteristics in the
vicinity of the Brewster angle\textsuperscript{15, 16} An initial scan was done for wavelengths from 300 to 800 nm at 50 nm intervals and this wavelength range was then repeated over angles from 50-70\textdegree at 4\textdegree intervals to find the Brewster angle which, for the PAH/PCBS system was found to be 62\textdegree. Following the determination of the Brewster angle, the sample was scanned at wavelengths from 300 to 800 nm at 10 nm intervals in the vicinity (±2\textdegree) of the Brewster angle in 1\textdegree increments. The sample was scanned at three different positions to check for the film homogeneity. The experimental data collected this way were then fitted with one Lorentz oscillator where the wavelength of the absorbance peak was fixed at the value of 360 nm as measured by UV-Vis spectroscopy. Refer to the appendix in Chapter 3 for details of the analysis of PAH/PCBS LbL films.

SHG measurements (done by Cemil Durak, Department of Physics) were used to calculate the second order susceptibility, $\chi^{(2)}$. A linearly polarized Nd:YAG fundamental beam with the wavelength of 1064 nm, a pulse width of 10 ns, and a pulse energy of ~1 mJ was used. The second harmonic intensity was measured as a function of the incident angle. The incident angle/intensity data were used to calculate the $\chi^{(2)}$ parameter.

The effective second order susceptibility $\chi_{\text{eff}}^{(2)}$ was calculated using:

$$\chi_{\text{eff}}^{(2)} = \chi_{\text{ref}}^{(2)} \left( \frac{l_{\text{ref}}}{l_{\text{s, bilayer}}} \right) \left( \frac{m}{\sqrt{I_{\text{ref}}^{2\omega}}} \right)$$  \hspace{1cm} (2)

in which $\chi_{\text{ref}}^{(2)}$ is the second order susceptibility of the reference material, $1.5 \times 10^{-9}$ esu, $l_{\text{ref}}$ is the thickness of the reference material, 75.3 nm, $m$ is the slope of square root of SHG intensity vs. number of bilayers, $I_{\text{ref}}^{2\omega}$ is the intensity of the reference material and $l_{\text{s, bilayer}}$ is the thickness per bilayer obtained from ellipsometric measurements.$^2$

The reference used was a 68 bilayer PS-119/PAH LBL film that has had a constant value of thickness and second order susceptibility over the past ten years.$^{17}$
For a p-polarized light at a given incident angle \( \theta \), \( \chi_{\text{eff}}^{(2)} \) is related to the \( \chi^{(2)} \) tensor components \( \chi_{zzz}^{(2)} \) and \( \chi_{zxx}^{(2)} \) by,

\[
\chi_{\text{eff}}^{(2)} = 3 \chi_{zxx}^{(2)} \sin \theta \cos^2 \theta + \chi_{zzz}^{(2)} \sin^3 \theta
\]  

(3)

The tilt angle was determined by comparing the SHG intensity generated for incident s- and p- polarizations of the light. The maximum harmonic intensity generated from p-polarized light is represented by \( I_{2\omega}^{p-p} \) and the maximum harmonic intensity generated from s-polarized light is represented by \( I_{2\omega}^{s-p} \). \( I_{2\omega}^{p-p} \) and \( I_{2\omega}^{s-p} \) are related to the ratio of \( \chi_{\text{eff}}^{(2)} \) tensor components \( \chi_{zzz}^{(2)} \) and \( \chi_{zxx}^{(2)} \) by

\[
\frac{\chi_{zzz}^{(2)}}{\chi_{zxx}^{(2)}} = \sqrt{\frac{I_{2\omega}^{p-p}}{I_{2\omega}^{s-p}}} \csc \theta - 3 \cot^2 \theta
\]  

(4)

The tilt angle is related to the ratio of tensor components by the equation,

\[
2 \cot^2 \psi = \frac{\chi_{zzz}^{(2)}}{\chi_{zxx}^{(2)}}
\]  

(5)

Using Equations (2) - (5), the tilt angle and \( \chi_{zzz}^{(2)} \) component of the \( \chi_{\text{eff}}^{(2)} \) tensor were calculated. All film measurements were made after drying the films in air under ambient conditions.

6.4 Results and Discussion

Four series of slides were fabricated by varying the deposition times and the flow rates of the polyelectrolyte solution and the DI water. In the first series, the deposition time was 2 minutes at a flow rate of 5 ml/min. This deposition condition is abbreviated as: \( (\text{PAH/PCBS})_{2/5} \), where the “2” in the subscript refers to the deposition time in minutes and “5” refers to the flow rate in ml/min. For all the cases the polyelectrolyte concentration of 10 mM at pH 7 was used for both PAH and PCBS. At these conditions, both the PAH and PCBS are highly charged and led to formation of LbL films in flat train-like conformation. These deposition conditions were found to give long range polar ordering of chromophores at least up to 600 bilayers details of which can be found in Chapter 3. The rinsing times for all the deposition condition was 2 minutes. The
deposition conditions are summarized in Table 6.4-1. The deposition times and flow rates were chosen based on a previous kinetics study done using a quartz crystal microbalance with dissipation (QCM-D) in which it was found that the at a Reynolds number of 0.96, the PAH and PCBS adsorption was 95% complete in approximately 60 seconds at 10 mM concentration and at pH 7. For the thick film device, the flow rates of 3 mL/min and 5 mL/min led to Reynolds numbers of 2.6 and 4.3, respectively. Comparing these with the QCM-D results shown in Chapter 4, where at Re of 0.96, the deposition of both PAH and PCBS was >95% complete within 60 sec, the deposition of PAH and PCBS in the thick film device was expected to be completed in <60 sec since the Re was 2-4 times higher than that used in the QCM-D experiments. The effect of convection or Reynolds number on the deposition rate was studied in Chapter 5 for the deposition of PCBS. It was found that the deposition rate increased with the increasing flow rate.

Table 6.4-1. Deposition conditions for the experiments. The repeat unit concentration of both PAH and PCBS was 10 mM and the pH was 7.

<table>
<thead>
<tr>
<th>Deposition Condition</th>
<th>Deposition Time (min)</th>
<th>Flow Rate (mL/min)</th>
<th>Residence time, ( t_{\text{res}} ) sec</th>
<th>Reynolds Number, Re</th>
</tr>
</thead>
<tbody>
<tr>
<td>1. (PAH/PCBS)( _{2/5} )</td>
<td>2</td>
<td>5</td>
<td>4.1</td>
<td>4.3</td>
</tr>
<tr>
<td>2. (PAH/PCBS)( _{2/3} )</td>
<td>2</td>
<td>3</td>
<td>6.7</td>
<td>2.6</td>
</tr>
<tr>
<td>3. (PAH/PCBS)( _{1/5} )</td>
<td>1</td>
<td>5</td>
<td>4.1</td>
<td>4.3</td>
</tr>
<tr>
<td>4. (PAH/PCBS)( _{1/3} )</td>
<td>1</td>
<td>3</td>
<td>6.7</td>
<td>2.6</td>
</tr>
</tbody>
</table>

The absorbance and thickness measurements of the four deposition conditions mentioned in Table 6.4-1 are shown in Figure 6.4-1 and Figure 6.4-2 respectively. For all the conditions, a linear growth in absorbance and thickness was seen.
Figure 6.4-1. Absorbance vs. number of bilayers of slides fabricated at different deposition conditions summarized in Table 6.4-1.

Figure 6.4-2. Thickness vs. number of bilayers of slides fabricated at different deposition conditions summarized in Table 6.4-1.
The results for SHG measurements are shown in Figure 6.4-3. A linear increase in square root of SHG vs. #bilayers was observed for all deposition conditions indicating that the polar ordering of the chromophores was maintained over high bilayer numbers. The absorbance, thickness and SHG data is used to calculate the $\chi^{(2)}_{zzz}$ parameter and essentially identical values of $\chi^{(2)}_{zzz}$ were obtained for the four different deposition conditions as shown in Table 6.4-2, indicating that a flow rate of 3 ml/min and a deposition time of 1 min is sufficient to fabricate these films. This means that the films with reduced deposition time and flow rate gave similar results to the films fabricated at higher deposition times and flow rates. This translates into reduced time requirement and reduced usage of polymer solutions over time. These results agree well with the QCM-D results which showed that at similar polymer concentration and pH, the adsorption was essentially complete in approximately 60 seconds at a Reynolds number of 0.96. The values of $\chi^{(2)}_{zzz}$ obtained for all the deposition conditions are in excellent agreement with the $\chi^{(2)}_{zzz}$ values obtained using the conventional NanoStrata dipping device which was $1.2 \times 10^{-9}$ esu as shown in Chapter 3. The values of thickness and absorbance per bilayer, 1.42 nm and 0.0054 respectively, obtained using custom built deposition device also agree well with those obtained using a conventional dipping device, 1.17 nm and 0.0064 respectively. 2

![Graphs showing square root of SHG vs. number of bilayers for different conditions.](image)

**Figure 6.4-3.** Square root of SHG vs. number of bilayers of slides fabricated at different deposition conditions summarized in Table 6.4-1.
Table 6.4-2. Summary of results at different deposition conditions summarized in Table 6.4-1. The standard deviations (± 1σ) are reported.

<table>
<thead>
<tr>
<th>Deposition Condition</th>
<th>Absorbance per bilayer (x 10^3)</th>
<th>Thickness per bilayer (nm)</th>
<th>Tilt Angle ψ (deg)</th>
<th>Tilt Angle χ(2)zzz (x 10^9) esu</th>
</tr>
</thead>
<tbody>
<tr>
<td>1. (PAH/PCBS)2/5</td>
<td>7.6 (± 1.1)</td>
<td>1.46 (± 0.2)</td>
<td>37.8</td>
<td>1.19 (± 0.1)</td>
</tr>
<tr>
<td>2. (PAH/PCBS)2/3</td>
<td>6.6 (± 0.2)</td>
<td>1.37 (± 0.3)</td>
<td>35.4</td>
<td>1.18 (± 0.2)</td>
</tr>
<tr>
<td>3. (PAH/PCBS)1/5</td>
<td>5.0 (± 0.3)</td>
<td>1.33 (± 0.1)</td>
<td>36.2</td>
<td>1.27 (± 0.1)</td>
</tr>
<tr>
<td>4. (PAH/PCBS)1/3</td>
<td>5.4 (± 2.5)</td>
<td>1.41 (± 0.1)</td>
<td>36.3</td>
<td>1.21 (± 0.1)</td>
</tr>
</tbody>
</table>

Table 6.4-3 shows a comparison of the amount of material used with the conventional dipping device\(^2\) and the custom built deposition device. In the conventional dipping device, the polymer solutions were replaced every 6 hrs and the DI water was replaced during each dipping cycle which is equivalent to using 150 ml of polymer solutions and 36 L of DI water for every 40 bilayers. In contrast, 120 ml of polymer solutions and 0.5 L of dipping solutions were used to fabricate 40 bilayers using the custom built thick film device.

<table>
<thead>
<tr>
<th>Usage of materials</th>
<th>Conventional dipping machine(^2)</th>
<th>Custom built deposition device at a flow rate of 3 ml/min and 1 min dep time</th>
<th>Decrease in material usage</th>
</tr>
</thead>
<tbody>
<tr>
<td>Polymer solutions used for making 40 bilayers</td>
<td>150 ml</td>
<td>120 ml</td>
<td>20 %</td>
</tr>
<tr>
<td>De-Ionized water used to make 40 bilayers</td>
<td>36 L</td>
<td>0.5 L</td>
<td>98 %</td>
</tr>
</tbody>
</table>

### 6.5 Conclusions

A custom built deposition device was fabricated to deposit multilayers on a standard 1” x 3” microscope slides. It uses a flow cell module through which the
polyelectrolyte solutions and DI water were passed alternately. A set of four three-way solenoid valves were used to allow one of the solutions to pass through the flow cell at any given time. The polyelectrolyte solutions and DI water were recycled to minimize the solution usage. The properties of the films obtained using the custom build device were comparable to those obtained using an automated dipping device operated at the same concentrations and pH conditions. Film properties made with the two techniques agreed well. The custom-built deposition device uses a fraction of DI water compared to the conventional dipping device and can be useful in scaling-up the LbL process.

6.6 Program to control solenoid valve

====================================================================
' 
' File .... DAVIS Quad_VALVE-control.BS2
' version .... 0.2
' Purpose .... VALVEs Controller
' Author .... riley chan       (Copyright 2006, All Rights Reserved)
' Started .... riley, MAY 2006
' Updated .... Akhilesh Garg
' modified .... See Modification History Below
'
' {$STAMP BS2}
' {$PBASIC 2.5}
',

====================================================================

====================================================================

' Modification History
====================================================================

' May 03’06 - Introduced two new variables NO_OF_BILAYERS and Counters
to take into account the number of bilayers - AG
' If-Then statement added before the do loop to take account of the
' above step. - AG

' May 04’06 - Did some major revisions such as changing the order in
' which valves are opened and closed - AG.

' May 09’2006 - Found that one of the valves does not work - changed the
' order in which valves are operated. Also, logic is added where the user
' can specify the exact number of bilayers to be put on glass slides.
' Everything works fine - AG

' July 10, 2006 - Program changed to accomodate the new plumbing
' arrangement To reduce aggregation of PAH and PCBS in the tubes - AG.

' July 19, 2006 - Program made more user friendly and this shows a summary
' of the experiment in form of a report at the end of experiment - AG.

' Nov 29, 2006 - User can specify time in seconds instead of minutes. Also
' program changed so that the total rinsing time specified by the user is
' divided into two equal time which refer to the time the DI water flows
' through the two rinsing tubes - AG.

====================================================================
' -----<USER'S PARAMETERS ENTRY>-------------------------------------------
SECONDS_PAH_DEP = 120                      ' PAH Deposition time in seconds
TOTAL_RINSE_TIME_PAH = 120                ' PAH Rinsing time in seconds
SECONDS_PCBS_DEP = 120                     ' PCBS Deposition time in seconds
TOTAL_RINSE_TIME_PCBS = 120               ' PCBS Rinsing time in seconds
NO_OF_BILAYERS = 40                       ' Specify the number of bilayers here
' -----</USER'S PARAMETERS ENTRY>------------------------------------------

' -----<NOTES>-------------------------------------------------------------
' program written for Davis.
' PAUSE = about 1 millisecond, 1 to 65535 counts
' -----</NOTES>------------------------------------------------------------

' -----<Program Description>-----------------------------------------------
' Program to control FOUR (4) SOLENOID VALVES to switch ON and OFF as defined
' by a Time_Base, "MINUTE", as defined above. The four VALVEs are switched in
' sequence.
' A switch is used to START and STOP the control sequence.
' Restart is effected by the RESET switch.
' PAUSE 1000 command is used establish a 1 SECOND time basis. The SECOND interval is
' also used to drive a HeartBeat LED display, connected to PIN 11.
' At the end of the count rates, the OUTPUT pin(s) associated with a VALVE is TOGGLED.
' A switch, connected to PIN 9, is used to START/STOP the sequence using the
' BUTTON command.
' -----</Program Description>----------------------------------------------

' -----<APPENDs>-----------------------------------------------------------
'
' -----</APPENDs>----------------------------------------------------------

' -----<Block Diagram>-----------------------------------------------------
'
' +Vin (12V)_________________________  
' |                                  |
' |                                  |
' |                                  |
' BasicSTAMP II                   |
' |                                  |
' | HeartbeatPIN11--LED driver |
' |                                  |
' | Pins 1 1 1 1 | |
' | 5 4 3 2 | Driver Transistor |
' | | and Drive Module | to OUTPUT 1|
' | | |
' | | Driver Transistor |
' | | and Drive Module | to OUTPUT 2|
' | | |
' | | Driver Transistor |
' | | and Drive Module | to OUTPUT 3|
' | |

---<Block Diagram>--------------------------------------------------------

---<BS2 PIN assignment>-----------------------------------------------------

DIRL = %0000000000011111        ' "0" means input, "1" means output

' pin 0
' pin 1
' pin 2
' pin 3
' pin 4
' pin 5
' pin 6
' pin 7
' pin 8 --- (not defined)
' pin 9 --- OFF/ON Switch
' pin 10 --- RESET Latch (if used with OFF/ON Switch)
' pin 11 --- HeartBeat driver
' pin 12 --- Valve 1 POLYMER
' pin 13 --- Valve 2 DI WATER
' pin 14 --- Valve 3 DYE
' pin 15 --- NOT WORKING

---<Variables>-------------------------------------------------------------

btnCHK                                   VAR Byte          ' workspace for BUTTON check, active LOW
period                      VAR Byte          ' counter variable to count seconds elapsed
NO_OF_BILAYERS              VAR Byte          ' Number of Bilayers Values 0 to 65535
Counter                      VAR Byte          ' Counter to count number of bilayers done
SECONDS_PAH_DEP              VAR Byte          ' PAH Deposition time in minutes
SECONDS_PAH_RINSING          VAR Byte          ' PAH Rinsing time in minutes
SECONDS_PCBS_DEP             VAR Byte          ' PCBS Deposition time in minutes
SECONDS_PCBS_RINSING         VAR Byte          ' PCBS Rinsing time in minutes
RINSE_PAH_TIME               VAR Byte          ' Rinsing Water through PAH line
RINSE_PCBS_TIME              VAR Byte          ' Rinsing Water through PCBS line
RINSE_BOTH_TIME              VAR Byte          ' Rinsing Water through both lines
TOTAL_RINSE_TIME_PAH         VAR Byte          ' Total Rinse time for PAH
TOTAL_RINSE_TIME_PCBS        VAR Byte          ' Total Rinse time for PCBS

---<Variables>-------------------------------------------------------------

---<Program Code>---------------------------------------------------------

Start:

---<START switch>---------------------------------------------------------

waitLoop:
  BUTTON 9, 0, 255, 250, btnCHK, 0, noPress  ' goto noPress if PIN9 is LOW

DEBUG CLS

---<Initialization>-------------------------------------------------------

Initialize:
  btnCHK = 0
  LOW 12                                  ' reset VALVES to close
  LOW 13
LOW 14
LOW 15
Counter = 1

' -----</Initialization>---------------------------------------------------

' -----</START switch>-----------------------------------------------------

' -----<LOOPing>-----------------------------------------------------------
DO

Main:

' -----<Program START>-----------------------------------------------------
DEBUG CLS ' clear display SerialPort
DEBUG CRSRXY, 5 , 1 , "This program will put ", DEC NO_OF_BILAYERS, " number of bilayers"
DEBUG CRSRXY, 5 , 2 ,
"================================================================="
DEBUG CRSRXY, 5 , 3 , "Bilayer Number = ", DEC Counter ' Display the number of bilayers
DEBUG CRSRXY, 5 , 4 , "Started" ' display Start at SerialPort

' -----<VALVEs Control>----------------------------------------------------
'

' -----<PIN-12 Control>-----POLYMER----------------------------------------
HIGH 12
LOW 14
LOW 13
LOW 15
DEBUG CRSRXY, 5 , 6 , CLREOL, "PAH Deposition - Dep time: ", DEC SECONDS_PAH_DEP, " sec"
FOR period = 1 TO SECONDS_PAH_DEP ' number of minutes
DEBUG CRSRXY, 20 , 7 , "Time Elapsed: ", CLREOL, DEC period, " sec"
GOSUB SECONDS_TIME_base
NEXT

' -----<PIN-13 Control>-----DI WATER---------------------------------------
LOW 12
HIGH 13
LOW 14
LOW 15
RINSE_PAH_TIME = 30
DEBUG CRSRXY, 5 , 6 , CLREOL, "DI WATER - PAH line: ", DEC RINSE_PAH_TIME, " sec"
FOR period = 1 TO RINSE_PAH_TIME ' number of minutes
DEBUG CRSRXY, 20 , 7 , "Time Elapsed: ", CLREOL, DEC period, " sec"
GOSUB SECONDS_TIME_base
NEXT

' -----<PIN-13 and PIN-15 Control>-----DI WATER through PAH and PCBS-------
HIGH 15
LOW 14
HIGH 13
LOW 12
RINSE_BOTH_TIME = TOTAL_RINSE_TIME_PAH - RINSE_PAH_TIME
DEBUG CRSRXY, 5 , 6 , CLREOL, "DI WATER - both lines: ", DEC RINSE_BOTH_TIME, " sec"
FOR period = 1 TO RINSE_BOTH_TIME ' number of minutes
DEBUG CRSRXY, 20 , 7 , "Time Elapsed: ", CLREOL, DEC period, " sec"
GOSUB SECONDS_TIME_base
NEXT

' -----<PIN-14 Control>-----DYE--------------------------------------------
LOW 12
LOW 13
HIGH 14
LOW 15
DEBUG CRSRXY, 5, 6, CLREOL, "PCBS Deposition Step - Dep time (in sec): ", DEC SECONDS_PCBS_DEP, " sec"
FOR period = 1 TO SECONDS_PCBS_DEP ' number of minutes
DEBUG CRSRXY, 20, 7, "Time Elapsed: ", CLREOL, DEC period, " sec"
GOSUB SECONDS_TIME_base
NEXT

'------<PIN-15 Control>-----DI WATER---------------------------------------
LOW 12
LOW 13
LOW 14
HIGH 15
RINSE_PCBS_TIME = 30
DEBUG CRSRXY, 5, 6, CLREOL, "DI WATER - PCBS line: ", DEC RINSE_PCBS_TIME, " sec"
FOR period = 1 TO RINSE_PCBS_TIME ' number of minutes
DEBUG CRSRXY, 20, 7, "Time Elapsed: ", CLREOL, DEC period, " sec"
GOSUB SECONDS_TIME_base
NEXT

'------<PIN-13 and PIN-15 Control>----------DI WATER through PAH and PCBS--------------
LOW 12
HIGH 13
LOW 14
HIGH 15
RINSE_BOTH_TIME = TOTAL_RINSE_TIME_PCBS - RINSE_PCBS_TIME
DEBUG CRSRXY, 5, 6, CLREOL, "DI WATER - both lines: ", DEC RINSE_BOTH_TIME, " sec"
FOR period = 1 TO RINSE_BOTH_TIME ' number of minutes
DEBUG CRSRXY, 20, 7, "Time Elapsed: ", CLREOL, DEC period, " sec"
GOSUB SECONDS_TIME_base
NEXT

Counter = Counter + 1 ' Go to next bilayer
IF Counter > NO_OF_BILAYERS THEN GOTO Display

'------<VALVE Control>-----------------------------------------------------
LOOP

'------<LOOPing>----------------------------------------------------------
'------<Program START>---------------------------------------------------

'------<Establish Time BASE in Seconds>-----------------------------------
SECONDS_Time_base:
    PAUSE 1000 ' establish seconds basis (1000mS)
    TOGGLE 11 ' HeartBeat LED driver
'------<TERMINATE switch>------------------------------------------------
    BUTTON 9, 0, 255, 250, btnCHK, 0, cont ' goto forcedTerminate if PIN9 is LOW
    GOTO forcedTerminate
'------<TERMINATE switch>------------------------------------------------
cont:
    RETURN

'------</Establish Time BASE in Seconds>-----------------------------------

'------<Forced terminate>--------------------------------------------------
forcedTerminate:

    LOW 12
    LOW 13
    LOW 14
    LOW 15

    DEBUG CLS
    DEBUG " ", CRSRXY, 5, 5, "--- This program was forced terminated---"
    GOTO noPress

END

' -----</forced terminate>--------------------------------------------------

' -----<display at the end of the experiment>------------------------------

display:

    LOW 12
    LOW 13
    LOW 14
    LOW 15

    DEBUG CLS
    DEBUG " ", CR, "Stopped: DI Water TURNED OFF."                    ' reset VALVES to close
    DEBUG CRSRXY, 2, 6, "====================================================================="
    DEBUG CRSRXY, 2, 7, "Experiment Finished: Summary"
    DEBUG CRSRXY, 2, 8, "====================================================================="
    DEBUG CRSRXY, 2, 9, "Total numbers of bilayers: ", DEC NO_OF_BILAYERS
    DEBUG CRSRXY, 2, 10, "Deposition time for PAH: ", DEC SECONDS_PAH_DEP, " sec"
    DEBUG CRSRXY, 2, 11, "Rinsing time for PAH: ", DEC TOTAL_RINSE_TIME_PAH, " sec"
    DEBUG CRSRXY, 2, 12, "Deposition time for PCBS: ", DEC SECONDS_PCBS_DEP, " sec"
    DEBUG CRSRXY, 2, 13, "Rinsing time for PCBS: ", DEC TOTAL_RINSE_TIME_PCBS, " sec"

    GOTO noPress

END

' -----</display at the end of the experiment>-------------------------------

' -----<switch WAIT>-------------------------------------------------------

noPress:

    DEBUG CRSRXY, 5, 15, "Press switch to continue..."
    GOTO waitLoop

END

' -----</switch WAIT>-------------------------------------------------------
6.7 References


Chapter 7 Effect of pH on the Optical Properties of Hybrid Covalent/Electrostatically Fabricated Layer-by-Layer Films

7.1 Abstract

Multilayer thin films were fabricated using sequential adsorption of Poly(allylamine hydrochloride) (PAH) and a reactive dye Procion brown (PB), on a glass substrate to study the nonlinear optical (NLO) properties of these films. PB is a rodlike molecule with a reactive trichlorozine group on one end and three charged groups, with two located on the other end. Formation of these films is a two-step process which involves alternating electrostatic deposition of PAH and covalent attachment of the PB. Covalent attachment leads to a better chromophore orientation which, in turn, leads to an increase in the second-order susceptibility, $\chi^{(2)}$, a measure of NLO properties. We study the effect of systematically varying the pH of both PAH and PB solutions on the film properties. In one part of this work, PAH was deposited at pH 7 onto an underlying substrate that was negatively charged. When the PB is deposited at pH 10.5, where the underlying PAH is largely uncharged, the attachment step is mostly covalent leading to the highest orientation of the chromophores. When the PB is deposited at pH 8.5, where the underlying PAH is partially charged, the attachment step was due to a combination of both electrostatic and covalent interactions leading to decreased orientation of the chromophores. The “reverse pH” conditions were also studied in which PB was deposited electrostatically at pH 7 and the pH of PAH was varied systematically from pH 10.5 where the PAH was uncharged and adsorbed in form of tails and loops to pH (8.5) where the PAH was charged and adsorbed in a flat train-like conformation. It was found that the best deposition condition was obtained when the pH of PAH was 7 and 10.5 for PB.

7.2 Keywords

Hybrid layer-by-layer films, Covalent bonding, Procion Brown, nonlinear films, electro-optic modulators.
7.3 Introduction

The alternate adsorption of cationic and anionic polyelectrolyte to the formation of ionic self-assembled multilayer (ISAM) films due to electrostatic interactions.\(^1\) Films made via this technique have many potential applications in fields such as integrated molecular optics, electronics, and biosensors.\(^2-5\) These films are of interest due to their application in electro-optic modulators which are devices that convert electrical signals to optical signals and are used in telecommunications. Materials exhibiting nonlinear optical (NLO) properties are a key to the development of electro-optic modulators. These films can exhibit a significant NLO response if one of the constituents is polarizable and can be oriented. Interestingly, polar orientation in these films has been achieved in layer-by-layer (LbL) polymeric films which are ionically self-assembled on a substrate.\(^6\) However, the second-order nonlinear susceptibility, \(\chi^{(2)}\) of those films were approximately two orders of magnitude lower than that of lithium niobate (LiNbO\(_3\)) which is a state-of-the-art inorganic material used in EO modulators. To better orient the chromophores in these films, a modification of the above technique which involves depositing one of the constituents electrostatically and then attaching the other constituent covalently to the underlying polymer or dye film was used to fabricate organic hybrid covalent/ionic self-assembled films, referred in this paper as “hybrid LbL” films.\(^7-9\) The second-order nonlinear susceptibility, \(\chi^{(2)}\) of an organic NLO material is given by\(^10\)

\[
\chi^{(2)} = NF\beta \langle \cos^3 \psi \rangle
\]

in which \(N\) is the chromophore density, \(F\) is the local field factor, \(\beta\) is the hyperpolarizability and \(\psi\) is the orientation angle of the chromophores. Thus, to maximize \(\chi^{(2)}\), a chromophore with a suitably high \(\beta\) should be incorporated into a film with high density \(N\), and low tilt angle \(\psi\).

For weak polyelectrolytes, the pH of the solution affects the ionization of the adsorbed polyelectrolyte which affects the properties of the LbL films.\(^5, 8, 11-14\) The effect of varying pH on hybrid LbL films made using PAH and procion red dye (PR) was studied by Van Cott et al.\(^8\) When the pH of PAH was held constant at 4.5, and the pH of
PR was increased from 7.0 and 10.5, the absorbance per bilayer and $\chi^{(2)}$ increased which was due to the combined increase in chromophore density and increased covalent-coupling efficiency which increased the molecular ordering of the PR molecules. At pH 7.0, PR was found to be incorporated in the films by a combination of electrostatic, hydrogen bonding and covalent coupling. At pH 10.5, covalent reaction between PAH and PR was favored and therefore, a high degree of ordering was observed which led to an increase in $\chi^{(2)}$.

The properties of hybrid LbL films are also affected by the ionic strength of the solution. Heflin et al. studied the effect of the ionic strength of PB solutions on the properties of hybrid LbL films at a fixed pH of 10.5. PB has a higher polarizability, $\beta$, than PR and this resulted in films with $\chi^{(2)}_{eff}$ values three times higher. The $\chi^{(2)}_{zzz}$ values of the hybrid LbL films peaked at 0.5 M NaCl salt concentration in the PB solution. Increasing the ionic strength led to a decrease in the Debye length so that the charged chromophores packed more closely, leading to an increase in $\chi^{(2)}_{zzz}$. Although the effect of ionic strength on the properties of the hybrid LbL films was studied in detail, the effect of pH was not studied. In addition to affecting the conformation of the adsorbed polyelectrolyte layer which could affect chromophore deposition and orientation, the pH of the PB solution affects the rate of hydrolysis of PB in solution which makes the PB moieties unreactive in the solution and affects its pot life.

This work probes the effect of pH of PAH and PB solutions on the properties of the ISAM films including thickness, absorbance, and the chromophore orientation. In the first set of experiments, the pH of PAH was kept constant at 7 and the pH of PB was systematically increased from 8.5 to 10.5. In the second set of conditions, pH of PB was kept constant at 7.0 and pH of PAH was varied from 8.5 to 10.5. Film growth was characterized by absorbance measurements, SHG measurements, tilt angle measurements, and ellipsometry measurements.
7.4 Experimental

7.4.1 Materials

Poly(allylamine hydrochloride) referred to as PAH was used as a polycation (Mw ca. 70,000, repeat unit Mw = 93.56 g/mol; Aldrich, item number 283223-25G, Figure 7.4-1 (a)). Procion Brown dye (PB) (MX-GRN Reactive Brown 23, Mw = 767 g/mol, Figure 7.4-1 (b); Pro Chemical and Dye, Somerset, MA) was used as the chromophore in the deposition experiment. Microscope slides frosted on one side (Fisher Scientific) were cleaned using the oxygen plasma etcher device (SPI Supplies, Plasma Prep II™) in the presence of oxygen. They were cleaned for 30 minutes at the pressure between 400-600 millitorr and at a current setting of 70 mA. Deionized water (Barnstead) was used with a resistivity of over 17 MΩ·cm. The pHs of the polymer solution and the dye solution were adjusted using standard solutions of NaOH and HCl before starting the experiment.
Figure 7.4-1. (a) Structure of PAH and (b) structure of PB (c) reaction between PAH and PB

Figure 7.4-2. Reaction between PB and PAH for the reverse pH conditions.
7.4.2 Dye Purification

Commercially available Procion dyes are not pure materials and contain salts, anti-caking agents, and buffering agents. The dye purification was done using a Combiflash retrieve flash chromatography system. Solid-phase extraction (SPE) with octadecylsilyl functionalized silica (RediSep Reverse Phase C-18, 35-60 μm particle size) was used to desalt Procion Brown MX-GRN prior to film fabrication. The dye was dissolved in aqueous 50 mM ammonium acetate at 20 mg/mL and filtered with a 11 μm filter to remove particulates. The SPE columns were washed with 7 volumes of HPLC grade methanol (Burdick & Jackson), equilibrated with 3 volumes of aqueous 50mM ammonium acetate, and then 200 ml of the filtered dye solutions were applied to the columns. The columns were washed with 2 volumes of 50 mM ammonium acetate. The dye was then eluted with HPLC-grade methanol. The methanol was removed by drying it in a gentle stream of nitrogen overnight.

7.4.3 Fabrication of Slides

The slides were made using a StratoSequence™ Mark VI robotic deposition system details of which can be found in a previous paper. The rinse water was replaced after every use whereas the PAH and PB solution was replaced after every 6 hours to avoid dilution and excessive hydrolysis of PB solution. The slides were dipped in the PAH and PB for 2 minutes each and the rinsing was done for 45 sec in each beaker. Thus, the slides were rinsed for a total of 135 seconds between each polyelectrolyte dipping step. The concentration of PAH was 10 mM (or 0.93 mg/ml) on a repeat unit basis and the concentration of PB was 1 mg/ml for all pH conditions.

7.4.4 Film Characterization

The PAH/PB hybrid LbL films were characterized for absorbance, thickness and second harmonic generation (SHG) measurements. Absorbance measurements of dried films were done using a Perkin Elmer Lambda 25 UV/vis system. The films exhibited an absorbance maximum, λ_max, at 460 nm. Film thicknesses were measured using a variable angle spectroscopic ellipsometer (J. A. Woolam ellipsometer VB-200 with WVASE32 software version 3.361). Details of ellipsometry procedure can be found in the appendix.
The details of the SHG measurements to calculate the second order susceptibility, $\chi^{(2)}_{zzz}$ and tilt angle $\psi$, can be found in a previous study.\textsuperscript{6, 7} The SHG intensity, $I_{2\omega}$, is proportional to the $\chi^{(2)}_{\text{eff}}$ of these films as given by the relation:

$$I_{2\omega} \propto l \chi^{(2)}_{\text{eff}}$$ \hspace{1cm} (2)

in which $l$ is the bilayer thickness.

For a p-polarized light at a given incident angle $\theta$, $\chi^{(2)}_{\text{eff}}$ is related to the $\chi^{(2)}$ tensor components $\chi^{(2)}_{zzz}$ and $\chi^{(2)}_{zxx}$ by,

$$\chi^{(2)}_{\text{eff}} = 3 \chi^{(2)}_{zxx} \sin \theta \cos^2 \theta + \chi^{(2)}_{zzz} \sin^3 \theta$$ \hspace{1cm} (3)

The tilt angle was determined by comparing the SHG intensity generated for incident s- and p- polarizations of the light. The maximum harmonic intensity generated from p-polarized light is represented by $I_{2\omega}^{pp} \rightarrow \omega^2$ and the maximum harmonic intensity generated from s-polarized light is represented by $I_{2\omega}^{ps} \rightarrow \omega^2$. $I_{2\omega}^{pp}$ and $I_{2\omega}^{ps}$ are related to the ratio of $\chi^{(2)}_{\text{eff}}$ tensor components $\chi^{(2)}_{zxx}$ and $\chi^{(2)}_{zzz}$ by

$$\frac{\chi^{(2)}_{zxx}}{\chi^{(2)}_{zzz}} = \sqrt{\frac{I_{2\omega}^{pp}}{I_{2\omega}^{ps}}} \csc^2 \theta - 3 \cot^2 \theta$$ \hspace{1cm} (4)

The tilt angle is related to the ratio of tensor components by the equation,

$$2 \cot^2 \psi = \frac{\chi^{(2)}_{zxx}}{\chi^{(2)}_{zzz}}$$ \hspace{1cm} (5)

Using Equations (2) - (5), the tilt angle and $\chi^{(2)}_{zzz}$ component of the $\chi^{(2)}_{\text{eff}}$ tensor were calculated.

### 7.5 Results and Discussion

To study the effect of solution pH on hybrid LbL film formation, two sets of conditions were studied. In the first set of conditions the pH of PAH was maintained constant at 7.0 and the pH of PB was varied as 8.5, 9.0, 9.5 and 10.5 (Table 7.5-1). In this case, PAH should adsorb with largely flat conformation and the PB would attach by a combination of electrostatic and covalent interactions, depending upon the pH of PB solution. Since PAH is highly charged below the pK$_a$ of PAH (8.7\textsuperscript{15}), the deposition of
PB above the pKₐ value of PAH, where the PAH is partially uncharged, leads to adsorption of PB to the underlying PAH mainly by means of covalent attachment leading to high $\chi^{(2)}$ values, as shown in Figure 7.4-1(c). However, the chlorotriazine end groups of the dye molecules are susceptible to hydrolysis and the rate of hydrolysis increase with the pH of the dye solution.⁹ Thus the variation of pH of PB solution was studied in part to find the optimal pH conditions at which these films can be fabricated to maximize the “pot life” of the PB dye, a significant issue for the practical fabrication of these films for devices. In the second set of conditions the pH of PB was maintained constant at 7.0 and the pH of PAH was varied as 8.5, 9.0, 9.5 and 10.5. This was done to study the “reverse pH” conditions where PB is deposited electrostatically and PAH is deposited by means of covalent bonding between the amines and the PB, as shown in Figure 7.4-2.

Table 7.5-1. Deposition conditions used for the experiments. For all deposition conditions, the deposition time was 2 minutes and the rinsing time was 2 minutes 15 sec for both PAH and PB and the repeat unit concentration of PAH used was 10 mM and for PB was 1 mg/ml, 0.5 M NaCl.

<table>
<thead>
<tr>
<th>Deposition Condition</th>
<th>pHₚₐ</th>
<th>pHₚₜ</th>
</tr>
</thead>
<tbody>
<tr>
<td>(PAH-7/PB-8.5)</td>
<td>8.5</td>
<td></td>
</tr>
<tr>
<td>(PAH-7/PB-9.0)</td>
<td>9.0</td>
<td></td>
</tr>
<tr>
<td>(PAH-7/PB-9.5)</td>
<td>9.5</td>
<td></td>
</tr>
<tr>
<td>(PAH-7/PB-10.5)</td>
<td>10.5</td>
<td></td>
</tr>
<tr>
<td>(PAH-8.5/PB-7)</td>
<td>8.5</td>
<td></td>
</tr>
<tr>
<td>(PAH-9.0/PB-7)</td>
<td>9.0</td>
<td></td>
</tr>
<tr>
<td>(PAH-9.5/PB-7)</td>
<td>9.5</td>
<td></td>
</tr>
<tr>
<td>(PAH-10.5/PB-7)</td>
<td>10.5</td>
<td></td>
</tr>
<tr>
<td>(PAH-9.0/PB-10.5)</td>
<td>9.0</td>
<td>10.5</td>
</tr>
</tbody>
</table>
7.5.1 Effect of variation of pH of PB

In the set 1 experiments (refer to Table 7.5-1), the pH of PAH was maintained constant at 7.0 and the pH of PB was systematically varied from 8.5 - 10.5. The absorbance and the thickness data for the set 1 deposition conditions are shown in Figure 7.5-1 for films made with 40 bilayers of PAH/PB deposited on each side of the glass slide. The absorbance vs. bilayer number for all pH values of the PB solutions showed a linear increase (see Figure 7.7-5 in the appendix) indicating that layer-by-layer growth of these films was observed at all deposition conditions of set 1. Films of PAH/PB had a peak absorbance in the vicinity of 460 nm. It is interesting to note that absorbance per bilayer did not vary significantly with pH of the PB solution indicating that the adsorbed amount depended mainly on the ionic strength of the solution which affects the Debye length and hence the overall dye packing density. The thickness per bilayer and hence the $\chi^{(2)}$ values were measured only for the condition (PAH-7/PB-10.5) since other conditions did not give measurable values of thickness due to very low thicknesses of these films.

![Graph showing absorbance and thickness data for hybrid LbL films fabricated at the set 1 deposition conditions: PAH pH = 7.0 and PB 0.5 M NaCl, pH = as mentioned. The absorbance for each series was taken at 460 nm. Typical error bars are smaller than the size of the data points.](image-url)
Slides made at PB pH values of 10.5, 9.5, 9.0, and 8.5 showed a linear increase in √SHG with the number of bilayers as shown in Figure 7.5-2 which implied that chromophore orientation for these slides was maintained. The slope of the square root of SHG vs. number of bilayers increased with the pH of the PB solution. This was because that, at higher pH of PB, most of the deposition of PB on the underlying PAH layer occurred mainly due to covalent attachment between the amine groups of PAH and PB chromophore which led to better chromophore orientation. As the pH of the PB solution decreased, the underlying PAH became partially charged and so PB deposition occurred due to a combination of electrostatic as well as covalent attachment which led to a decrease in the slope. The slope of √SHG vs. number of bilayers is approximately a factor of 3 lower for PB at pH 9.5 as compared to PB at pH 10.5.

![Figure 7.5-2. √SHG per bilayer of hybrid LbL films fabricated with PAH and PB as a function of pH of PB at the set 1 deposition conditions: PAH pH 7.0 and PB 0.5 M NaCl, pH as specified. Typical error bars are smaller than the size of the data points.](image-url)
The results are summarized in Table 7.5-2. The $\chi_{zzz}^{(2)}$ value obtained in this study at pH 10.5 $\sim$ 54 x $10^{-9}$ esu is comparable to the value of $\chi_{zzz}^{(2)}$ obtained during earlier studies\(^7\) which was 50 x $10^{-9}$ esu for similar pH and ionic strength conditions. However, the concentration of PB used in this study was 1 mg/ml compared to 5 mg/ml in the previous study. Decreasing the concentration resulted in a decrease in the thickness per bilayer from 0.57 nm to 0.23 nm per bilayer and also in the absorbance per bilayer from 2.9 x $10^{-3}$ to 1.7 x $10^{-3}$. The tilt angle value in this study was calculated to be 43° compared to 38° in the previous study. From equation (2), $\chi^{(2)}$ is inversely proportional to the thickness per bilayer of these films and from equation (1), $\chi^{(2)}$ is directly proportional to the chromophore density which is proportional to the absorbance. So while the reduced thickness per bilayer would potentially increase the $\chi^{(2)}$ of these films, the lower values of absorbance at 1 mg/ml would decrease the value of $\chi^{(2)}$ and due to a combination of both of these, a value of $\chi^{(2)}$ at 1 mg/ml similar to the value of $\chi^{(2)}$ at 5 mg/ml was obtained. No significant variation in the tilt angles was observed for the various deposition conditions studied in this set of experiments.

<table>
<thead>
<tr>
<th>Deposition Condition</th>
<th>pH(_{PAH})</th>
<th>pH(_{PB})</th>
<th>Abs/ Bilayer (x10(^{-3}))</th>
<th>Thickness/BL (nm)</th>
<th>Tilt Angle (\Psi)</th>
<th>$\chi_{zzz}^{(2)}$ 10(^9) esu</th>
</tr>
</thead>
<tbody>
<tr>
<td>(PAH-7/PB-8.5)</td>
<td>8.5</td>
<td>1.8 (± 0.04)</td>
<td>N/A*</td>
<td>36.3 (± 3.1)</td>
<td>N/A</td>
<td></td>
</tr>
<tr>
<td>(PAH-7/PB-9.0)</td>
<td>9.0</td>
<td>1.9 (± 0.09)</td>
<td>N/A*</td>
<td>40.4 (± 1.2)</td>
<td>N/A</td>
<td></td>
</tr>
<tr>
<td>(PAH-7/PB-9.5)</td>
<td>9.5</td>
<td>2.0 (± 0.03)</td>
<td>N/A*</td>
<td>43.4 (± 1.8)</td>
<td>N/A</td>
<td></td>
</tr>
<tr>
<td>(PAH-7/PB-10.5)</td>
<td>10.5</td>
<td>1.7 (± 0.02)</td>
<td>0.23 (± 0.04)</td>
<td>43.2 (± 0.5)</td>
<td>54.35 (± 0.1)</td>
<td></td>
</tr>
</tbody>
</table>

* Too thin to measure

7.5.2 Effect of variation of pH of PAH

In set 2 experiments (see Table 7.5-1), the pH of PB was kept constant at 7.0 and the pH of PAH was varied systematically from 8.5 – 10.5. At pH 7.0, PB was adsorbed
electrostatically to the underlying PAH layer. In turn, the pH of PAH controls whether the PAH is adsorbed due to electrostatic interactions or covalent bonding or by a combination of both. The $pK_a$ of PAH is 8.7;\textsuperscript{15} thus at pH 8.5, the PAH is approximately 50% charged and the degree of ionization of PAH decreases with an increasing pH of the PAH solution reaching less than 35% at pH 10.5.\textsuperscript{16} The absorbance and thickness measurements of the films fabricated at pH of PB 7.0 and at varying pHs of PAH are shown in Figure 7.5-3. Results for the deposition condition (PAH-10.5/PB-7) are not shown since the films fabricated were inhomogeneous (see Figure 7.7-4 in the appendix). For the deposition condition (PAH-9.5/PB-7), a thickness per bilayer of 4.6 nm was measured which is 20X higher than the thickness per bilayer of 0.23 nm for the deposition condition (PAH-7/PB-10.5). At the higher pH of PAH which led to lower degrees of ionization, PAH adsorbs more as tails and loops due to reduced inter-repulsion between polymer chains leading to thicker film formation.\textsuperscript{6,11,17} The thicknesses per bilayer of 4.5 and 3.1 nm were measured for the deposition conditions (PAH-9.0/PB-7) and (PAH-8.5/PB-7), respectively. Except for the deposition condition (PAH-10.5/PB-7) at which the ellipsometry measurements were not done due to inhomogeneity of the films, the thickness and absorbance increased linearly with the number of bilayers for all deposition conditions in this set of experiments. The absorbance per bilayer of these slides also increased with an increase in the pH of PAH. A higher amount of PAH is adsorbed when the pH is increased which, in turn, leads to a higher amount of PB deposited on the underlying PAH layer. The absorbance at the deposition condition (PAH-9.5/PB-7) is almost a factor of 3X higher than the films fabricated at the deposition condition (PAH-7/PB-10.5).
The variation of $\sqrt{\text{SHG}}$ with the number of bilayers is shown in Figure 7.5-4 for set 2 experimental conditions and the results are summarized in Table 7.5-3. A linear increase in $\sqrt{\text{SHG}}$ with the number of bilayers was observed only for the deposition condition (PAH-9.5/PB-7) whereas, for the other two deposition conditions, (PAH-9/PB-7) and (PAH-8.5/PB-7), no linear growth in $\sqrt{\text{SHG}}$ with number of bilayers was observed. At the deposition condition (PAH-9.5/PB-7), a net chromophore orientation was maintained since PAH attached to the underlying PB through covalent as well as electrostatic and hydrogen bonding coupling. However, at the lower pH of PAH, PAH has a greater degree of ionization and so electrostatic interactions play a greater role than the covalent bonding which led to higher disorientation of the PB. It is interesting to note that the highest tilt angle value was observed for the deposition condition (PAH-8.5/PB-7) which is expected since at pH 7 for PB, the underlying PAH is highly charged and the
adsorption of PB occurs due to a combination of electrostatic as well as covalent bonding, resulting in higher disorientation or higher values of tilt angle.

![Graph showing square root of SHG intensity per bilayer of hybrid LbL films as a function of pH of PAH at set 2 deposition conditions: PAH pH as specified and PB 0.5 M NaCl, pH = 7.0. Typical error bars are smaller than the size of the data points.]

**Figure 7.5-4.** $\sqrt{\text{SHG}}$ per bilayer of hybrid LbL films fabricated with PAH and PB as a function of pH of PAH at the set 2 deposition conditions: PAH pH as specified and PB 0.5 M NaCl, pH = 7.0. Typical error bars are smaller than the size of the data points.

**Table 7.5-3.** Summary of results for set 2 deposition conditions: PAH: pH = as specified. PB: 0.5 M NaCl, pH 7.

<table>
<thead>
<tr>
<th>Deposition Condition</th>
<th>pH$_{PAH}$</th>
<th>pH$_{PB}$</th>
<th>Abs/ Bilayer (x10$^{-3}$)</th>
<th>Thickness/BL (nm)</th>
<th>Tilt Angle, $\Psi$</th>
<th>$\chi^{(2)}_{zzz}$ 10$^6$ esu*</th>
</tr>
</thead>
<tbody>
<tr>
<td>(PAH-8.5/PB-7)</td>
<td>8.5</td>
<td>3.5 (± 0.2)</td>
<td>3.1 (± 0.2)</td>
<td>43.5 (± 7.2)</td>
<td>N/A*</td>
<td></td>
</tr>
<tr>
<td>(PAH-9.0/PB-7)</td>
<td>9.0</td>
<td>4.6 (± 0.2)</td>
<td>4.5 (± 0.5)</td>
<td>40.8 (± 4.9)</td>
<td>N/A*</td>
<td></td>
</tr>
<tr>
<td>(PAH-9.5/PB-7)</td>
<td>9.5</td>
<td>6.4 (± 0.3)</td>
<td>4.6 (± 0.4)</td>
<td>37.1 (± 2.5)</td>
<td>2.8</td>
<td></td>
</tr>
<tr>
<td>(PAH-10.5/PB-7)</td>
<td>10.5</td>
<td>N/A</td>
<td>N/A</td>
<td>N/A</td>
<td>N/A*</td>
<td></td>
</tr>
</tbody>
</table>

* $\chi^{(2)}_{zzz}$ was not measured for these deposition conditions since a linear increase in square root of SHG vs. #bilayers was not observed.
7.5.3 pH 9/10.5 deposition condition

In addition to the pH conditions described above, one additional pH condition was studied. In this pH condition, the pH of PAH was 9.0 and the pH of PB was 10.5. The pKₐ of PAH is 8.7 \(^{16}\) and so at pH 9, PAH should be partially charged and deposit in thick layers with tails and loops. A thicker PAH layer would, in turn, provide more reaction sites for the PB to attach to. The PB was deposited at pH 10.5 since at that pH the PB chromophores are optimally oriented from the set 1 deposition conditions. A schematic of the hybrid LbL formation at pH 7 of PAH vs. pH 9 of PAH is shown in Figure 7.5-5. The concentration of PAH was 10 mM on repeat unit basis and the concentration of PB was 1 mg/ml in 0.5 M NaCl solution.

(a) ![PAH and PB adsorption on a substrate at pH 7/10.5 of PAH/PB](image)
(b) ![PAH and PB adsorption on a substrate at pH 9/10.5 of PAH/PB](image)

Figure 7.5-5. PAH and PB adsorption on a substrate (a) at pH 7/10.5 of PAH/PB (b) at pH 9/10.5 of PAH/PB.

Thickness and absorbance vs. # bilayers data are shown in Figure 7.5-6. Both thickness and bilayer show a linear increase with the number of bilayers up to 30 bilayers and then the absorbance and thickness increases exponentially. The reason for this deviation from a linear increase in thickness and absorbance with # bilayers is not clear. The square root of SHG with #bilayers, shown in Figure 7.5-7, does not show a linear growth implying that the polar orientation was not maintained. A thickness per bilayer for of 1.6 nm was obtained as compared to 0.23 nm for (PAH-7/PB-10.5) in set 1 and 4.6 nm for (PAH-9.5/PB-7) in set 2. An absorbance per bilayer of 0.009 was obtained compared to 0.0017 for (PAH-7/PB-10.5) in set 1 and 0.0064 for (PAH-9.5/PB-7) in set 2.
Figure 7.5-6. Thickness and absorbance vs. # bilayers for the set 3 deposition condition: PAH pH 9; PB pH 10.5, 0.5 M NaCl. Typical error bars are smaller than the size of the data points.
The effect of pH on the structure and optical properties of layer-by-layer films fabricated using the polycation PAH and the NLO active chromophore PB was studied. The properties of the films such as absorbance, thickness, and second harmonic generation intensity were found to depend strongly on the pH of the PAH and PB solutions. A good NLO film should be an optically homogeneous film to maintain similar characteristics at different spots on the film. In general, the thickness, absorbance, and square root of SHG intensity should grow linearly with the number of bilayers.

For the films where the pH of PAH was kept constant at 7.0 and the pH of PB was varied systematically from 8.5 to 10.5, a linear increase in square root of SHG was observed for all the deposition conditions studied. However, the slope of the square root of SHG with number of bilayers decreased with the pH of the PB solution, indicating that
high pH of PB is important to achieve the high order of polar orientation of PB chromophores.

In experiments, where the pH of PB was kept constant at 8.5 and the pH of PAH was varied systematically from 8.5 to 10.5, a linear increase in square root of SHG was observed only for the condition where pH of PAH was kept at 9.5. There was a significant difference in the SHG behavior for the films fabricated at pH of PAH 9.5 and 9.0 indicating the sensitivity of these films to the pH of the solution. At pH 9.5, where PAH was mostly uncharged, a thickness per bilayer of 4.6 nm was obtained. From set 1 and set 2 experiments, it is clear that covalent bond attachment is necessary for these PAH/PB films to show quadratic scaling of SHG intensity with number of bilayer. In experiments where the PAH was deposited at pH 9 and the pH of PB was kept constant at 10.5, no quadratic scaling of SHG with number of bilayers was observed since the underlying PAH film was adsorbed in form of tails and loops.

### 7.7 Appendix A for Chapter 7

#### 7.7.1 Ellipsometry Procedure

Film thickness measurements were made using a variable angle spectroscopic ellipsometer (VASE) (J.A. Woolam ellipsometer VB-200 with WVASE32 software version 3.361). Ellipsometry is based on the changes in the polarization of light when it reflects from a surface. Linearly polarized light reflects off the sample and becomes elliptically polarized. This change in the state of polarization can be defined by two quantities, namely $\Delta$ (delta) and $\psi$ (psi).\(^1\) The phase difference between the linearly polarized light and the elliptically polarized light is given by $\Delta$ whereas $\psi$ gives the change in amplitude between the two. The ellipsometric analysis was done in the vicinity of the Brewster angle because ellipsometry measurements are most sensitive to film characteristics at the Brewster angle.\(^2\) An initial scan was done for wavelengths from 300 to 800 nm at 50 nm intervals and this wavelength range was then repeated over angles from 50 deg to 70 deg at 4° intervals to find the Brewster angle. From a graph of $\Delta$ vs. $\lambda$, Brewster angle was determines as the point at which $\Delta$ quickly passed from 180° through 90° to 0°\(^2\). The Brewster angle for PAH/PB ISAM films was found to be between 56 to
Following the determination of the Brewster angle, the sample was scanned at wavelengths from 300 to 800 nm at 10 nm intervals in the range of the Brewster angle in $1^\circ$ increments. The sample was scanned at three different positions to check for the film homogeneity. The experimental data collected this way were then fitted with a model that is described below in detail.

### 7.7.1.1 Modeling

The model consists of two layers - one for the glass substrate and the other for the thin film. The model for the glass substrate consists of the refractive index and the extinction coefficient ($n$ and $k$ respectively) values as a function of wavelength and is plotted in Figure 7.7-1 below.

![Figure 7.7-1](image)

**Figure 7.7-1.** $n$ and $k$ values versus wavelength for a typical glass substrate used in the film deposition experiments. These values were used to model the experimental data for the ISAM films.

The Lorentz oscillator model represents the thin film and is given by the following equation:

$$
\varepsilon(E) = \varepsilon_1(\infty) + \sum_k \frac{A_k}{E_k^2 - E^2 - iB_kE} 
$$

in which $\varepsilon_1(\infty)$ represents the value of the real part of the dielectric function at very large photon energy, $A_k$ is the amplitude of the $k^{th}$ oscillator (eV$^2$), $E$ is the photon energy (eV), $E_k$ is the center energy of the $k^{th}$ oscillator (eV), and $B_k$ is the $k^{th}$ peak’s width.
(eV). \( E_k \) is given by equation (A2). From \( \varepsilon \), values of \( n \) and \( k \) can be calculated as shown in equations (A3) and (A4).

\[
E_k = h \nu_k = \frac{1.24(eV \cdot \mu m)}{\lambda_k(\mu m)} \tag{A2}
\]

\[
n = \sqrt{\varepsilon_1 + \sqrt{\varepsilon_1^2 + \varepsilon_2^2}} \tag{A3}
\]

\[
k = \frac{-\varepsilon_1 + \sqrt{\varepsilon_1^2 + \varepsilon_2^2}}{2} \tag{A4}
\]

in which \( \nu_k \) and \( \lambda_k \) are the frequency and the wavelength of the \( k^{th} \) absorbance peak, respectively. A typical value of \( \lambda_k \) (as measured by UV-Vis spectroscopy) for PAH/PB slide series is 460 nm.

Because only one absorbance peak was observed while scanning the slide for absorbance over a range of wavelength, only one Lorentz oscillator model was used and its oscillating center was fixed at \( \lambda_1 \). Using the above value for \( \lambda_1 \), the parameter \( E_1 \) can be calculated from equation (A2). The value for the parameter \( E_1 \) for the PAH/PB films was calculated to be 2.6956 eV.

An initial guess was provided for the other parameters \( \varepsilon_\infty, A_1 \) and \( B_1 \) to estimate the film thickness. Depending on the initial guess provided, the results might vary. However, there are various ways to determine if the obtained results were optimal. One of the constraints in fitting the parameters is that \( k \) should reach a maximum at \( \lambda_1 \). The goodness of fit was assessed with the values of the mean sum of the errors (MSE). In general, a better fit is obtained with lower values of the MSE. The optical parameters obtained after modeling are shown in the Figure 7.7-2 for the films made using PCBS and PAH.
Figure 7.7-2. Optical parameters for a film consisting of 40 bilayers of PAH/PB obtained using VASE. The deposition conditions were: $C_{PAH} = 10\ \text{mM repeat unit (RU)}$, $C_{PB} = 1\ \text{mg/ml}$, $pH_{PAH} = 7.0$, $pH_{PB} = 10.5$ and $C_{NaCl} = 0.5\text{M}$. The dipping times were 2 minutes in both PAH and PB solutions. The rinsing time was 135 seconds equally distributed in three baths (45 sec x 3). The maximum value of the dispersion coefficient occurs at the wavelength $\sim 460\ \text{nm}$. A similar peak is observed at this wavelength by UV-Vis spectroscopy.
Figure 7.7-3. Picture of slide series made using PAH and PB when the pH of PAH was kept constant at 7.0. The concentration of PAH used was 10 mM for all the cases. The pH of PB was (a) 10.5, (b) 9.5, (c) 9.0 and (d) 8.5. The concentration of PB used was 1 mg/ml with 0.5 M NaCl concentration for all the cases. Each slide was coated with 40 layers of PAH and 40 layers of PB on each side of the slide.

Figure 7.7-4. Picture of the 40 bilayers of LbL hybrid films fabricated using PAH and PB when the pH of PB was kept constant at 7.0. The concentration of PB used was 1 mg/ml with 0.5 M NaCl concentration for all the cases. The pH of PAH was (a) 10.5, (b) 9.5, (c) 9.0 and (d) 8.5. The concentration of PAH used was 10 mM (repeat unit) for all the cases. Note the inhomogeneity in the films made at higher pH values of PAH.
Figure 7.7-5. Absorbance for deposition condition at pH of PAH 7 and varying pH of PB. The concentration of PAH was 10 mM on repeat unit basis at pH 7. The concentration of PB was 1 mg/ml at $I_{eff} = 0.5$ M NaCl. The pH of PB is mentioned in the legend. Typical error bars are smaller than the size of the data points.

Figure 7.7-6. Thickness vs. #bilayers for pH of PB 7.0. The concentration of PAH was 10 mM on repeat unit basis. The pH of PAH is mentioned in the legend. The concentration of PB was 1 mg/ml at $I_{eff} = 0.5$ M NaCl and pH 10.5. Typical error bars are smaller than the size of the data points.
Figure 7.7-7. Absorbance vs. #bilayers for pH of PB 7.0. The concentration of PAH was 10 mM on repeat unit basis. The pH of PAH is mentioned in the legend. The concentration of PB was 1 mg/ml at $I_{eff} = 0.5$ M NaCl and pH 10.5. Typical error bars are smaller than the size of the data points.
7.8 References


Chapter 8 Enhancement of Second Harmonic Generation Intensity by incorporating Silver Nanoprisms in Layer-by-Layer Films

8.1 Abstract

Silver nanoprisms were synthesized using a photochemical process and were physisorbed on nonlinear optical (NLO) films to study the enhancement in the second harmonic generation (SHG) intensity. The NLO films were fabricated by using a layer-by-layer (LbL) approach which involves alternately depositing a positively and negatively charged polymer. NLO films were fabricated using cationic polymer poly(allylamine hydrochloride) (PAH) and the anionic polymer poly{1-[p-(3’-carboxy-4’-hydroxyphenylazo)-benzenesulfonamido]-1,2-ethandiyl} (PCBS). A variation of the above technique was used to deposit PAH electrostatically and deposit the reactive chromophore procion brown (PB) covalently to increase the SHG intensity. The effect of physisorbing silver nanoprisms was studied on both LbL films - PAH/PCBS and PAH/PB. An enhancement in SHG intensity was observed for both films.

8.2 Keywords

Silver nanoprisms, surface plasmon, nonlinear optical materials, second harmonic generation (SHG).

8.3 Introduction

Second-order nonlinear optical (NLO) materials exhibit second harmonic generation (SHG) and have various applications in electro-optic (EO) modulators, optical switches, second harmonic imaging microscopy (SHIM), and as components in high power green lasers.\(^1\) Currently used NLO inorganic materials such as lithium niobate (LiNbO\(_3\)) are limited by fabrication costs. By contrast, NLO organic materials are easy to fabricate but are limited by their SHG intensity. Incorporating silver and gold nanoparticles into organic NLO films can increase the SHG intensity by using surface plasmon effects.\(^2\) Surface plasmons are electromagnetic waves that propagate along the
surface of a conductor, usually silver or gold. These waves are trapped on the surface because of their interaction with the free electrons of the conductor. In this interaction, the free electrons respond collectively by oscillating in resonance with the light wave. One interesting consequence of the interaction between the surface charges and the electromagnetic waves is that, in contrast to the surface plasmon which propagates along the surface, the field perpendicular to the surface decays exponentially with distance away from the surface. This type of decaying field is known as evanescent field and is a consequence of the bound, non-radiative nature of surface plasmons which prevents energy from propagating away from the surface. This phenomenon has been used extensively in surface enhanced Raman spectroscopy (SERS).³

The surface plasmon can enhance the second order NLO properties of an organic NLO film by providing a very high localized electric field. In SERS experiments, the electronic state of the organic molecules undergo coupling with the surface plasmon of the metal nanoparticles resulting in an amplification of the Raman signal.⁴ When polarizable chromophores arranged in a non-centrosymmetric fashion that exhibits NLO effects were coupled with the surface plasmons from silver nanoparticles, an enhancement in NLO effects was seen.⁵ Due to the evanescent nature of the surface plasmons, the NLO enhancement was observed only up to an order of few nm (~1-10).

The intensity and the wavelength of the surface plasmon depend on the shape and size of the nanoparticles. Numerical simulations using the discrete dipole approximation (DDA) method were done on nanoparticles of different shapes and sizes to study the local electric enhancement near the particle surface.⁶-⁸ For silver nanoparticles triangular in shape with an edge length of 60 nm and thickness of 12 nm, the enhancement for the local electric field at the edges of the particles was found to be 3500 times the applied electric field. When the DDA simulations were performed on silver nanospheres, an electric-field enhancement of only 25 was observed, much less compared to the value at the edges of triangular nanoparticles, indicating the importance of edges in these nanostructures. It was also found that there was a red shift in the surface plasmon
wavelength when the edge length of the silver nanoprisms was increased, whereas, there was a blue shift when the silver nanoprisms were snipped.

There are two main techniques that can be used to incorporate silver nanoparticles triangular in shape on a substrate to increase the SHG efficiency. The first involves using nanosphere lithography and the second one involves synthesizing silver nanoprisms and incorporating those on substrates by means of physisorption. Nanosphere lithography involves depositing a monolayer of polystyrene nanospheres onto the substrate which allows the spheres to self-assemble in a closed packed monolayer. Silver is then deposited by electron beam evaporation onto the substrate through the interstices of the spheres in the monolayer and the spheres are then removed by ultrasonication in dichloromethane. This leads to the formation of silver nanoparticles triangular in shape on a glass substrate with a surface plasmon in the range of 900-1000 nm. Silver nanoprisms with a thickness of 50 nm were fabricated with this technique on top of a PAH/PCBS film and an increase in SHG efficiency by a factor of 1600 was seen. However, this approach did not lead to significant enhancement of the SHG intensity when PAH/PB films was used, presumably because the latex removal step involving the use of an organic solvent damaged the PAH/PB films. This along with the fact that an E-beam deposition step is required led to the alternative approach of physisorbing pre-formed silver nanoprisms onto organic NLO films, a step that would not require an organic solvent step that can damage the LbL films.

Silver nanoprisms can be synthesized by using a photochemical reaction which involves synthesizing silver seeds which are silver nanospheres < 5 nm in diameter and then exposing the silver seed suspension to light at a controlled wavelength and temperature to synthesize silver nanoprisms. Silver seeds have been synthesized in previous work by reducing solutions of silver nitrate with sodium borohydride in the presence of sodium citrate. To stabilize the silver seeds, the seeds were either capped with bis(p-sulfonatophenyl)phenylphosphine dihydrate dipotassium salt (BSPP) or with poly(vinylpyrrolidone) (PVP). The silver seeds showed a peak absorbance at a wavelength of ~397 nm. Upon exposure to light at a particular wavelength, the
absorbance peak at 397 nm decreased over time and a new absorbance peak at higher wavelength formed. Addition of disodium tartrate to the initial reaction solution to prepare silver seeds resulted in formation of silver tetrahedral nanocrystals instead of silver nanoprisms when exposed to light. It was found that the surface plasmon wavelength scales with the edge length of the silver nanoprisms. The edge length can be increased by increasing the wavelength of the light to which silver seeds were exposed. In one study, the surface plasmon wavelength increased from approximately 500 nm to 750 nm by using wavelengths of 470 nm and 633 nm respectively. In another study, low intensity light emitting diodes (LED) were used to prepare silver nanoprisms from a silver seed solution. The effect of temperature on the formation of silver nanoprisms was also studied and it was found that increasing the temperature from 25°C to 37°C reduced the reaction time from 159 hrs to 69 hrs when green LEDs were used and from 185 hrs to 96 hrs when red LEDs were used. The temperature increase did not affect either the final shape or size of the particles. The mechanism of silver nanoprism formation has been studied by transmission electron microscopy and three distinctive stages were noticed. The first stage was the induction stage; silver seeds aggregate to form nanoclusters in the presence of light. This is followed by the growth of nanocrystal structure which consumes the nanocrystals and silver seeds to form silver nanoprisms at which point the reaction terminates.

In the present study, silver nanoprisms were synthesized and physisorbed on PAH terminated PAH/PCBS LbL films and PAH/PB hybrid LbL films. The adsorption of silver nanoprisms on these films was characterized by scanning electron microscopy. Second harmonic generation (SHG) measurements of bare PAH/PCBS LbL films and hybrid PAH/PB LbL films were compared with those coated with silver nanoprisms.

8.4 Experimental

8.4.1 Materials Used

Silver nitrate (AgNO₃) (Sigma Aldrich), trisodium citrate (Sigma Aldrich), Sodium borohydride (NaBH₄) (Sigma Aldrich), and bis(p-sulfonatophenyl)phenylphosphine dihydrate dipotassium salt (BSPP) (Strem Chemicals)
were used to synthesize silver nanoprisms. A xenon lamp (300W, Newport) with a band-gap filter (550 ± 20 nm, Andover Corporation) was used as a light source to carry out the photochemical reaction. Nanopure water in which the deionized (DI) water (Barnstead ROpureST; model # D6311) with a resistivity of over 17 MΩ cm was passed through two 20 nm filters (Fisher Scientific) connected in series. Poly(allylamine hydrochloride) (PAH, Figure 8.4-1 (a)) was used as the polycation (M_w ca. 70 kDa; Aldrich). Poly\{1-[p-(3’-carboxy-4’-hydroxyphenylazo)-benzenesulfonamido]-1,2-ethanediyl\} (PCBS, Figure 8.4-1 (b)); Aldrich; was used as the polyanionic chromophore. The repeat unit molecular weight of PAH was 93.56 g/mol and of PCBS was 369.3 g/mol. Procion Brown dye (PB) (M_w 767 g/mol, MX-GRN Reactive Brown 23, Figure 8.4-1 (c); Pro Chemical and Dye, Somerset, MA) was used as the chromophore in the deposition experiment. Figure 8.4-1 (d) shows the reaction between the PAH and PB. PAH was chosen as a polycation because it has shown good film quality and scaling of the SHG intensity, in contrast to other polycations, in our prior work on ISAM NLO films. PCBS has an azobenzene pendant group that has a sufficiently high hyperpolarizability, β, to give a substantial SHG signal. Microscope slides (Fisher Scientific) frosted on the end of one side were used as substrates. An oxygen plasma etcher was used to clean the substrate. The ionic strength of the polymer/dye solutions was adjusted using sodium chloride (NaCl, Fisher Scientific). The pHS of the polymer/dye solutions were adjusted using 1.0 M or 0.1 M solutions of sodium hydroxide and hydrogen chloride.
8.4.2 Dye Purification

Commercially available Procion dyes are not pure materials and contain salts, anti-caking agents, and buffering agents. Solid-phase extraction (SPE) with
octadecylsilyl functionalized silica (RediSep Reverse Phase C-18, 35-60 μm particle size) was used to desalt Procion Brown MX-GRN prior to film fabrication. The dye was dissolved in aqueous 50 mM ammonium acetate at 20 mg/mL and filtered with a 0.45 μm filter to remove particulates. The SPE columns were washed with 7 volumes of HPLC grade methanol (Burdick & Jackson), equilibrated with 3 volumes of aqueous 50 mM ammonium acetate, and then 200 ml of the filtered dye solutions were applied to the columns. The columns were washed with 2 volumes of 50 mM ammonium acetate. The dye was then eluted with HPLC-grade methanol. The methanol was removed by drying in a stream of nitrogen.

### 8.4.3 Synthesis

Silver nanoprisms were synthesized using a photochemical reaction by illuminating silver seeds under different illumination conditions.\(^7,\ 10,\ 12\) This is a two-step process; synthesizing silver seed solution which are <10 nm silver spherical particles and then exposing them to light at a particular wavelength to obtain the desired nanoprisms. The synthesis of the correct silver seed solution is very critical to the growth of silver nanoprisms and this is described in detail below.

#### 8.4.3.1 Synthesis of Silver Seeds

Silver nanoprisms were synthesized by reducing silver nitrate solution (AgNO\(_3\)) with sodium borohydride (NaBH\(_4\)) in the presence of trisodium citrate. The procedure was provided by Can Xue from C. Mirkin’s group at Northwestern University (Department of Chemistry). The synthesis of silver seeds was carried out in the dark and a red light was used during the synthesis process to carry out the reaction. All solutions were prepared in 20 ml disposable glass vials which were cleaned using concentrated 3:1 HCl HNO\(_3\) also known as aqua-regia to remove any impurities. The vials were rinsed thoroughly with DI water. Once the vials were cleaned, all vials except for the one used to make NaBH\(_4\) solution, are wrapped in aluminum foil to prevent any light from entering the vial. For the reaction and for preparing the solution, nanopure water was used. First, a 20 mM AgNO\(_3\) solution and 30 mM trisodium citrate solutions were prepared. 0.5 ml of AgNO\(_3\) and 1 ml of trisodium citrate solution was added to 95 ml of nanopure DI water.
in a 200 ml flask. The solution was stirred vigorously under a gentle stream of nitrogen for 5 minutes to remove oxygen. Then ice was put around the flask. A vial with 10 ml nanopure DI water was kept in the ice to prepare the NaBH₄. After 20 minutes, 50 mM NaBH₄ solution was prepared by adding NaBH₄ to the ice cold water in the vial. The solution was stirred for 5 minutes and then 1 ml of NaBH₄ solution was rapidly injected in the reaction solution. After this, 5 drops of NaBH₄ solution was added to the reaction mixture every 2 minutes for 15 minutes to ensure complete reduction of the silver nitrate solution. After 15 minutes, 1 ml of BSPP and 1 ml of NaBH₄ was added to the reaction mixture in a drop-wise fashion. The resulting reaction mixture was stirred for 5 hours in ice cold bath in a gentle stream of nitrogen and then it was stored overnight in dark at 4°C. The resulting silver seed solution was characterized using an ocean optics USB4000 UV-vis spectroscope (Figure 8.4-2 (a)) and transmission electron microscopy (TEM) which is shown in Figure 8.4-2 (b). The TEM sample was prepared on a copper grid with a carbon mesh (SPI Supplies) by drop-casting silver nanoprism solution on the grid.

![Figure 8.4-2. (a) Absorbance of the silver seeds; (b) TEM image of the silver seed solution.](image)

**8.4.3.2 Synthesis of Silver Nanoprisms Using the Xenon Light Source**

After the silver seed synthesis was complete, they were exposed to 550 nm ± 20 nm light using a band-gap filter. This light source was designed and provided by Prof. H. Robinson in the Physics Department. The set-up is shown in Figure 8.4-3. The silver seed solution was placed in a 60 ml vial which was wrapped with aluminum foil. The vial was then inserted in the holder and the xenon lamp was turned on. The temperature of the
reaction chamber was maintained at 37°C. Due to the photochemical reaction which takes place upon exposure to the light, the absorbance of the solution changed when it was exposed to light. Absorbance measurements were taken after every 7-8 hours and the reaction was stopped when no measurable change in absorbance was observed. It took approximately 24 hrs for the reaction to be completed. The resulting silver nanoprisms solution was centrifuged twice using a Fisher Scientific accuSpin Micro centrifuge at 10000 rpm for 30 minutes to remove organics and smaller particles. The silver nanoparticles were redispersed in DI water by low power sonication (Fisher Scientific) in DI water for 5 minutes. In the study done by Xue et al., synthesizing the silver nanoprisms at a wavelength of 550 nm and at a pH 9.5, which was the original pH of silver seed solution, resulted in a bimodal distribution of edge lengths resulting in two absorbance peaks at 616 and 1032 nm. The pH of the silver seed solution was found to affect the charge on the particles, thereby affecting the inter-particle forces between the seeds. When the silver nanoprisms were synthesized at a pH of 11.2, a unimodal distribution of silver nanoprisms was obtained with the absorbance peak at 616 nm due to an increased charge repulsion which inhibited the growth of nanoprisms with larger edge length. However, when the synthesis was done at pH 7.4, the peak at 616 nm decreased and the peak at 1032 nm increased, but there was still a bimodal distribution of silver nanoprisms. The zeta potential of silver nanoprisms was found to be ~ -35 mV at pH 9.6 and ~ -33 mV at pH 7.4. At pH 7.4, we found that the silver nanoprisms solution was not stable and led to aggregation of the silver seed solution. Instead, pH 8.7 silver seed solution was used. Figure 8.4-4 shows the absorbance measurements of the silver nanoprisms synthesized at pH 9.6 and at pH 8.7. Figure 8.4-5 shows the TEM image of the final silver nanoprisms obtained at the two pH conditions. In both cases, silver nanoprisms were present with edge lengths 110 nm and 180 nm. However, at pH 8.7 condition, the concentration of 180 nm edge length nanoprisms was higher than those at pH 9.6.
Figure 8.4-3. Experimental set-up showing the incubator along with the optics and the 60-ml vial holder to synthesize silver nanoprisms.

Figure 8.4-4. Absorbance spectra of silver nanoprisms exposed to light at a wavelength of 550 ± 20 nm at pH 9.6 and pH 8.7 and at a temperature of 37°C.
8.4.4 Fabrication of Slides

A first set of the films were fabricated using a StratoSequence™ Mark VI robotic deposition system (nanoStrata Inc.). It consists of 8 beakers on a rotating platform that was raised and lowered by nitrogen gas pressure controlled by a computer. The polyelectrolytes/dye (PAH and PCBS/PB) and the rinse water were placed in 150 ml beakers. Four slides were held in a fixture that can either be stationary or can be made to rotate when immersed in the beakers. To minimize convection and diffusion transport effects, the slide fixture was always rotated at 60 rpm. An effective Reynolds number of 320 was estimated using the width of the slide as the characteristic length. The slides were dipped in a polyelectrolyte/dye solution for 2 minutes followed by three rinsing steps using DI water, each lasting 45 seconds. During the dipping cycles, the rinse water was replaced after every rinsing cycle whereas the polyelectrolyte/dye solution was replaced after every 6 hours to avoid dilution.

For the PAH/PCBS LbL film deposition, the concentrations of the PAH and PCBS solutions were both 10 mM on a repeat unit basis. A pH of 7 for both PAH/PCBS was used. For the PAH/PB hybrid LbL films, the concentration of PAH was 10 mM on a repeat unit basis and 1 mg/ml for PB. The pH of PAH was 7 and the pH of PB was 10.5. The ionic strength of PB solution was 0.5 M NaCl since PAH/PB films fabricated at that ionic strength were shown to give the highest value of second order susceptibility, $\chi^{(2)}_{zzz}$. The pHs of the polymer/dye solutions were adjusted using 1.0 M or 0.1 M solutions of sodium hydroxide and hydrogen chloride.
8.4.5 Silver Nanoparticles and LbL Film Characterization

Transmission electron microscope (TEM) images of silver nanoseeds and silver nanoprisms were taken using a Philips EM 420 instrument. Scanning electron microscope (SEM) images of LbL films coated with silver nanoprisms were taken using a LEO (Zeiss) 1550 field-emission SEM. Absorbance measurements on silver nanoparticle solutions and LBL films coated with silver nanoprisms were done using an Ocean Optics USB4000 UV-vis spectroscope which has a wavelength range of ~200-900 nm and/or a Varian Cary 5000UV-vis-nIR which has a range from 175-3300 nm. SHG measurements were used to study the enhancement of the SHG signal generated from the LbL films with physisorbed silver nanoprisms as compared to the SHG signal generated from LbL films without any silver nanoprisms. A linearly polarized Nd:YAG fundamental beam with the wavelength of 1064 nm, a pulse width of 10 ns, and a pulse energy of ~40 μJ/1 mJ was used. The second harmonic intensity was measured as a function of the incident angle by Kai Chen in Prof. Robinson’s group. All film measurements were made after drying the films in air under ambient conditions.

8.5 Results and Discussion

Different bilayer numbers (1 to 40) of PAH/PCBS LbL films and PAH/PB hybrid LbL films were fabricated on glass substrate by alternately depositing the polymer and polymer/dye solution. The LbL films were terminated with a PAH layer to make these films positively charged so as to facilitate the adsorption of silver nanoprisms which are negatively charged. Silver nanoprisms were synthesized at a pH of 8.7 to obtain a surface plasmon at a wavelength greater than 900 nm. Approximately 100 μl of silver nanoprisms solution was dropped on one side of the PAH terminated PAH/PCBS and PAH/PB LbL films. To give sufficient time for the silver nanoparticles to adsorb on the LbL films, the solution was left on the slides for approximately 30 minutes without letting it dry and then rinsed off with DI water. Figure 8.5-1 shows the image of the PAH/PCBS and PAH/PB LbL films coated with silver nanoprisms.
Figure 8.5-1. Images of PAH/PCBS and hybrid PAH/PB LbL films coated with silver nanoprisms. The yellow colored films are made with PAH/PCBS. The silver nanoprisms shown in the figure were deposited on 1 and 25 bilayers of PAH/PCBS and PAH/PB LbL films.

Figure 8.5-2 and Figure 8.5-3 shows the SEM image of silver nanoprisms adsorbed on 1 bilayer PAH/PB hybrid LbL films and 25 bilayers PAH/PCBS LbL films respectively. The images give an idea of the surface coverage of the LbL films with silver nanoprisms, although the exact surface coverage was not calculated due to the background noise. The presence of nanoprisms with wide distribution of size range can be seen in both SEM images. Some aggregation of silver nanoprisms during the adsorption process can also be seen. In addition to that, both the images show a presence of background noise which can be due to the small particles or due to the presence of LbL films on which these silver nanoprisms were adsorbed. Since silver nanoprisms were centrifuged twice before doing the adsorption experiments, the background noise is most likely due to the presence of LbL films. This is further proved by taking SEM images of bare LbL films (without any nanoparticles) as shown in Figure 8.5-4 which looks very similar to the background of SEM images of LbL films coated with silver nanoprisms.
Figure 8.5-2. SEM image of silver nanoprisms coated on 1 bilayer of PAH/PB film terminated with PAH.
Figure 8.5-3. SEM image of silver nanoprisms coated on 25 bilayers of PAH/PCBS film terminated with PAH.
The absorbance spectra taken using Varian Cary 5000UV-vis-nIR spectrometer of 1 bilayer of PAH/PCBS LbL films is shown in Figure 8.5-5. One bilayer of a PAH/PCBS LbL film was chosen as the reference slide to obtain the absorbance spectra of only the silver nanoparticles adsorbed on the slide. PAH/PCBS LbL films and PAH/PB hybrid LbL films showed similar absorbance spectra. The absorbance spectra show that the films with the silver nanoparticles had two surface plasmon peaks – one at ~650 nm and another at ~950 nm. This correlates well with the absorbance spectra of the silver nanoparticles synthesized at pH 8.7 in solution shown in Figure 8.4-4. The two peaks in the absorbance spectra are due to the bimodal distribution of the edge length of the silver nanoparticles. The smaller peak at ~670 nm corresponds to 110 nm edge length silver nanoparticles, whereas the larger peak at ~960 nm corresponds to 180 nm edge length silver nanoparticles. In the study done by Xue et al., synthesizing the silver nanoparticles at a wavelength of 550 nm and pH 9.5, resulted in a bimodal distribution of edge lengths resulting in two absorbance peaks at 616 and 1032 nm. The pH of the silver seed solution was found to affect the charge on the particles, thereby affecting the inter-particle forces between the seeds. When the silver nanoparticles were synthesized at a pH of 11.2, a unimodal distribution of silver nanoparticles was obtained with the absorbance peak at 616 nm. However, when the synthesis was done at pH 7.4, the peak at 616 nm
decreased and the peak at 1032 nm increased but there was still a bimodal distribution of silver nanoprisms. We found that at pH 7.4, the silver nanoprisms solution was not stable and led to aggregation of silver seed solution.

Figure 8.5-5. Absorbance spectra of 1 bilayer PAH/PCBS LbL film coated with silver nanoprisms synthesized at pH 8.7. The inset shows the absorbance spectra of 40 bilayers of PAH/PCBS LbL films and PAH/PB hybrid LbL films without nanoprisms.

To study the effect of silver nanoprisms on the second harmonic generation (SHG) measurements, the SHG measurements were done on the PAH/PCBS LbL films and PAH/PB hybrid LbL films coated with silver nanoprisms and compared with SHG intensity of these LbL films without any silver nanoprisms. Figure 8.5-6 and Figure 8.5-7 shows the SHG measurements done on PAH/PCBS LbL films and PAH/PB hybrid LbL films respectively. SHG measurements for films with and without silver nanoprisms are shown in the figures. For PAH/PCBS LbL films, higher SHG values were obtained up to at least 40 bilayers whereas, for the PAH/PB hybrid LbL films, a higher value of SHG was observed only up to 5 bilayers. The SHG intensity of films coated with silver nanoprisms did not change much with number of bilayers, whereas both PAH/PCBS LbL films and PAH/PB hybrid LbL films not coated with silver nanoprisms showed a quadratic increase in SHG with the number of bilayers.
Figure 8.5-6. SHG measurements for PAH/PCBS LbL films with and without silver nanoprisms. The silver nanoprisms were synthesized at a pH 8.7, 550 ± 20 nm, and 37°C. The horizontal line is drawn to guide the eye.

Figure 8.5-7. SHG measurements for PAH/PB hybrid LbL films with and without silver nanoprisms. The silver nanoprisms were synthesized at a pH 8.7, 550 ± 20 nm, and 37°C. The horizontal line is drawn to guide the eye.
Figure 8.5-8 shows the SHG enhancement versus number of bilayers for both PAH/PCBS LbL films and PAH/PB hybrid LbL films. SHG enhancement is the ratio of the SHG intensity from films with silver nanoprisms to the same film without silver nanoprisms. SHG enhancement of ~ 50 for PAH/PCBS and ~ 300 for PAH/PB was observed for 1 bilayer films. In comparison, an enhancement in SHG intensity in PAH/PCBS films by a factor of 1600 was observed when the silver nanoprisms were deposited using the nanosphere lithography. The lower SHG enhancement in this study was due to the polydispersity in the shape and size of the silver nanoparticles. The SHG enhancement decreased with the number of bilayers for both PAH/PCBS and PAH/PB films since the bulk SHG intensity of both these films increased at higher bilayer number. It is interesting to note that for PAH/PCBS films, SHG enhancement were observed for at least up to 40 bilayers. By comparison PAH/PB films, SHG enhancement was observed for up to 5 bilayers. The decrease in enhancement is due to the fact that the surface plasmons have a decay length which is of the order of few (1-5 nm) nm. From Figure 8.5-6 and Figure 8.5-7, no increase in SHG was observed for the LbL films coated with silver nanoprisms upon increasing the bilayer numbers from 1 to 2. Thus, it is fair to assume that the decay length of the surface plasmon in this case is of the order of thickness of 1 bilayer which is ~ 1 nm. In comparison, a decay length of 3-4 nm was obtained for silver nanoprisms coated using the nanosphere lithography. It is relevant to mention here that the thickness of synthesized silver nanoprisms used for this study was ~ 10 nm compared to 50 nm for the silver nanoparticles deposited using nanosphere lithography.
Figure 8.5-8. SHG enhancement for PAH/PCBS LbL films and PAH/PB hybrid LbL films. Horizontal line is drawn to guide the eye at SHG enhancement of “1” where the SHG from films is equal to SHG from films with silver nanoprisms. The silver nanoprisms were synthesized at a pH 8.7, 550 ± 20 nm, and 37°C.

8.6 Conclusions

Silver nanoprisms were synthesized by a photochemical reaction which involves exposing silver seeds to light at a wavelength of 550 ± 20 nm. The silver seeds were synthesized by reducing silver nitrate with sodium borohydrate in the presence of trisodium citrate. They were incorporated in PAH terminated PAH/PCBS LbL and PAH/PB hybrid LbL films by using electrostatic interactions. The PAH/PCBS and PAH/PB films have been shown to exhibit nonlinear optical properties. Second harmonic generation (SHG) measurements from LbL films coated with silver nanoprisms were compared with those without silver nanoprisms. An enhancement in SHG by a factor of ~50 for PAH/PCBS and ~300 for PAH/PB was observed for 1 bilayer films upon addition of silver nanoprisms to the film. The enhancement factor decrease with increasing number of bilayers reaching 5 for 40 BL PAH/PCBS films and 1 for 7 BL PAH/PB films. The magnitude of enhancement is not sufficient to make a thin transmissive EO
modulator. Further work involves improving the synthesis step to make more uniform nanoprisms with unimodal size distribution with the surface plasmon in the wavelength of ~1000 nm. Since the decay length of the surface plasmons is of the order of 1-5 nm, multiple layers of silver nanoprisms should be adsorbed after every 1 – 2 bilayers of LbL films to maximize the SHG enhancement.
8.7 References


Chapter 9 Conclusions and Future Work

9.1 Conclusions

There were several objectives of this thesis that focus on the ultimate goal of fabricating practical electro-optic (EO) modulators. These objectives are listed below:

4. Study the formation of thick ISAM films needed for practical electro-optic modulators using:
   (a) conventional dipping techniques
   (b) a custom-built deposition device with potential for minimizing fabrication time

5. Understand the parameters affecting the formation of ISAM films at the molecular level. This includes studies of:
   (a) the structure and composition of polymer-polymer ISAM films
   (b) the structure and composition of LbL films comprised of a hybrid polyelectrolyte-reactive dye system
   (c) kinetics of film formation including a mass transfer model to understand deposition kinetics

6. Exploring the effects of surface plasmon to enhance the electro-optic coefficient of NLO material by incorporating silver nanoparticles in the ISAM films.

In view of these objectives, the main conclusions of this work are listed below.

In Chapter 3, which addresses objective #1(a), a conventional dipping device was used to fabricate thick LbL films containing an oriented, NLO chromophore on a glass slides using the ionic self-assembled multilayer (ISAM) process. The polymeric dye poly{1-[p-(3’-carboxy-4’-hydroxyphenylazo)benzenesulfonamido]-1,2-ethanediyl} (PCBS) and the polycation poly(allylamine hydrochloride) (PAH) was deposited alternately on a glass substrate while varying pH and deposition and rinsing times. It was observed that different deposition conditions affected the optical properties of the ISAM films such as absorbance, thickness, and second order susceptibility $\chi^{(2)}$. Although, the elevated pH condition, pH 9/8 for PCBS and PAH respectively, resulted in thicker film formation due to the adsorption of polyelectrolytes in form of tails and loop, it did not
show linear growth in absorbance, thickness and square root of SHG intensity above 200-300 bilayers. However, when the polyelectrolytes were deposited at neutral pH conditions when both PAH and PCBS were strongly charged, the adsorption took place in flat, train like structures. A linear increase in absorbance, thickness and square root of SHG intensity was seen up to at least 600 bilayers. This work showed that it was possible to obtain polar orientation of chromophores in LbL films with thicknesses approaching 1 μm. However, the long duration of time (~ 4 days for 600 bilayers) and the amount of material used to fabricate these films calls for the need to optimize the deposition time to optimize the deposition conditions. It appears to be necessary that the polyelectrolytes should be highly soluble in the solution from which they are deposited to allow for their deposition as single chains and not as aggregates which can lead to defect in the LbL films.

In Chapter 4, using a quartz crystal microbalance with dissipation (QCM-D), it was found that at pH 7/7 of PAH/PCBS and at a repeat unit concentration of 10 mM for both PAH and PCBS, the polymer adsorption was 95% complete in ~ 60 seconds. Based on these results, in Chapter 6, which addresses objective #1(b), a custom built deposition device was used to fabricate 100 bilayers of PAH/PCBS LbL films on a glass substrate at a pH of 7/7. Various deposition and rinsing time as well as the flow rates were used to optimize the usage of polymer solutions and DI water. Compared to conventional dipping device, a 20% decrease in polymer solution was seen and a 98% decrease in DI water usage was seen. Using the results from the QCM-D experiments, the deposition time of 1 minute was used for PAH/PCBS adsorption instead of 2 minutes used in the conventional dipping device. This led to a reduction in time required to fabricate per bilayer from ~ 9 minutes for conventional dipping device to 6 minutes for the custom built deposition device.

Chapter 4 addresses objective #2(a). In this study, a combination of quartz crystal microbalance with dissipation (QCM-D), ellipsometry and absorbance measurements were used to study the structure and composition of PAH/PCBS LbL ISAM films deposited on silica. It was found that at neutral pH conditions, the
PAH/PCBS deposited at a molar ratio of 1:1 whereas at elevated pH conditions 9/8, the molar ratio of PCBS to PAH at pH of 8 and 9, respectively, was 0.63. By comparing these results with findings from chapter 3 where PAH/PCBS films showed homogeneous film growth up to at least 600 bilayers, it was concluded that the adsorption of PAH/PCBS in molar ration of 1:1 is an important factor in achieving homogenous film growth over high bilayer numbers. Combining QCM-D results which give the thickness of these films in wet state with the ellipsometry results which give the thickness of these films in dry state, %water content in these films was calculated to vary between 41-45%. The number density of chromophores, N in varied in the range of 1.4-1.7 x 10^{21} cm^{-3}. It was also found that time it took for 95% complete adsorption of PAH and PCBS was of the order of 1 minute. This is the first ever measurement of composition of the NLO ISAM films and of their water content. To understand the kinetics of film formation in greater detail, further studies were done and are described in Chapter 5.

Chapter 5 addresses objectives #2(b) and #2(c). The kinetics of PAH/PCBS LbL film formation was studied by using a model to calculate the mass transfer coefficient in a QCM-D flow cell. The rate of deposition for PCBS was found to increase by increasing the rate of convection. The experimental values of mass transfer coefficient were found to be higher than those obtained using theory. This was because the attractive electrostatic forces led to an increase in initial mass transfer rate from the bulk to the surface. The structure and composition as well as kinetics of film formation of PAH/Procion Brown (PB) hybrid LbL films can also be found in Chapter 5. By comparing the thicknesses obtained from QCM-D and ellipsometry, a %water content in these films was calculated to be 91% and the chromophores number density, N was 1.4 x 10^{20} cm^{-3}. The highly non-stoichiometric charge ratio and high water content are consistent with the presence of large number of unreacted amine groups left over in the bilayer films. The rate constant for covalent attachment of PB to underlying PAH was calculated to be 3.31 (± 0.2) x 10^{-8} m/s. These are the first ever measurements of the composition of the hybrid LbL films and of their water contents.
Chapter 7 addresses objective #2(b); the effect of varying pH on the properties such as thickness, absorbance and SHG on the PAH/PB hybrid LbL films was studied. It was found that at pH 10.5 of PB solution, the PB attachment step to the underlying PAH, which was deposited at pH 7, was covalent. However, when the pH of the PB was decreased below 10.5, the attachment to the underlying PAH was due to combination of both electrostatics and covalent attachment which led to a decrease in SHG intensity in these films. The covalent attachment of PAH to PB was found necessary for these films maximize the SHG intensity of these films. The covalent attachment of the PB to the underlying PAH film leads to a preferred orientation of the PB chromophores in these films, thereby maximizing the SHG intensity of these films. When the PB attached to the underlying PAH by means of electrostatic adsorption, the PB chromophores are randomly oriented in the film, leading to a decrease in the SHG intensity of these films.

Chapter 8 addresses objective #3. In this work, silver nanoprisms were synthesized using a photochemical reaction and physisorbed on organic NLO films. The enhancement in SHG intensity of these films was studied. An SHG enhancement of ~300 for PAH/PB LbL films and ~50 for PAH/PB LbL films was observed.

9.2 Future Work

One of the key areas that need to be explored to fabricate a practical electro-optic modulator is to improve the SHG intensity of these LbL films. This can be done by synthesizing novel chromophores with high hyperpolarizability. These chromophores can be incorporated into the LbL films by means of covalent attachment to achieve maximum orientation. Another way to increase the SHG intensity is to use the surface plasmon effects of metallic nanoparticles. This are was explored in the current research and gives the promise of enhancing the SHG intensity of LbL films. However, there is a need to improve the synthesis of silver nanoprisms to obtain monodisperse silver nanoprisms. The high power laser used to characterize the NLO films was found to decrease the stability of the silver nanoprisms adsorbed on the organic NLO film. One of the ways to overcome that problem is to coat these nanoprisms with very thin layer of Al₂O₃ to increase the stability of silver nanoprisms against the laser. A 1 nm thick Al₂O₃ film
deposited on top of silver nanoprisms by E-beam was found to increase the stability of silver nanoprisms by a factor of 10 against the laser intensity.\textsuperscript{1} Since the surface plasmons are evanescent waves that have a decay length which is of the order of 1 nm for the synthesized silver nanoprisms. Thus to achieve high SHG enhancement, multiple layers of silver nanoprisms should be adsorbed after every 1 – 2 bilayers of LbL films. This will require silver nanoprisms with much narrower size distribution so that the LbL film formation is not disrupted.

To rapidly fabricate the hybrid LbL films, the adsorption of PB chromophores should be studied using a quartz crystal microbalance (QCM-D) at elevated temperature. Since the PB attachment step follows a first-order reaction kinetics, an elevated temperature should increase the rate constant for the PB attachment step. The results obtained form the QCM-D can then be used to fabricate these film rapidly using thick film device discussed in Chapter 6. Electrochemical deposition of PB to the underlying PAH film can also be tried. This can possibly help to increase the mass transfer rate from the bulk solution to the surface; however, in the reaction limited regime this step may not lead to significant increase in the deposition rate.

The kinetics of deposition of polyelectrolytes and reactive dye was discussed in Chapter 6 by using a mass transfer model. The effect of electrostatic interactions on the rate of polymer deposition was not studied since there is a need to improve the electrostatic model to study the polyelectrolyte adsorption. The overall equation describing the kinetics of deposition can be written as\textsuperscript{2}

\[
R_{total} \frac{d\Gamma}{dt} = R_{total} \Gamma_m \frac{d\theta}{dt} = c_b - c_s
\]

in which \( \Gamma_m \) is the maximum surface coverage in mg/m\(^2\), \( \theta \) is fraction of surface covered, \( c_b \) is the bulk concentration, \( c_s \) is the subsurface concentration, and \( R_{total} \) is the total resistance which includes the resistance due to transport in the solution, \( R_t \) and the electrostatic resistance, \( R_e(\theta) \) and is given by the expression,

\[
R_{total} = R_t + R_e(\theta)
\]
The expression for energy barrier is given by

$$R^e(\theta) = \frac{e^{\frac{u(\Gamma)}{kT}} K^{-1}}{D}$$

(3)

in which $D$ is the diffusion coefficient of the charged chromophore, $u(\Gamma;z)$ is the potential energy felt by an adsorbing molecule which is at a distance $z$ from where it first touches the surface, and $K^{-1}$ is the debye length. The resistance barrier given by equation 3 can be easily calculated.

In the expression given by equation 3, the value of electrostatic resistance, $R_e(\theta)$ is $\sim 0$ when there is a net attraction between the polyelectrolyte and the substrate since $u(\Gamma)$ is negative. Substituting this in equation 2, we see that the expression for $R_{total}$ is reduced to the resistance provided only by the transport in the solution, $R_t$. The value of $R_{total}$ is not affected by the value of $R_e(\theta)$ until sufficient surface coverage has been achieved and the substrate charge is reversed so that there is repulsion between the substrate and the incoming polyelectrolyte. Thus a modification of the current electrostatic model is required to incorporate the effect of attractive electrostatic forces on the adsorption rate.

The LbL films have been shown to exhibit unprecedented thermal and temporal stability. In the previous work by Heflin et al., ISAM films made with PAH and an azobenzene-containing polyanion, PS-119, exhibited complete recovery in $\chi^{(2)}$ after the films were heated at $150^\circ$ C for 15 hours and then cooled to room temperature. These films have shown no measurable loss in $\chi^{(2)}$ upon storage under atmospheric conditions at room temperature for 10 years. The thermal stability of films fabricated using PAH/PB was also studied and no measurable loss in SHG was seen upon cooling these films back to room temperature after keeping them at $150^\circ$C for over 20 hrs. Although the films fabricated using PAH/PCBS are expected to show similar level of thermal and temporal stability, this has not been confirmed and is a subject of future study.
9.3 References


