Nonlinear Optical Properties and Structural Characteristics of Ionically Self-Assembled Nanoscale Polymer Films Influenced by Ionic Concentration and Incorporation of Monomer Chromophores

by

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ABSTRACT

Ionically self-assembled monolayer (ISAM) films are typically an assemblage of oppositely charged polymers built layer by layer through coulombic attraction utilizing an environmentally friendly process to form ordered structures that are uniform, molecularly smooth, and physically robust. ISAM films have been shown to be capable of the noncentrosymmetric order requisite for a second-order nonlinear optical response. However, films fabricated with a nonlinear optical (NLO) polymer result in significant cancellation of the chromophore orientations. This cancellation occurs by two mechanisms: competitive orientation due to the ionic bonding of the polymer chromophore with the subsequent polycation layer, and random orientation of the chromophores within the bulk of each polyanion layer. A reduction in film thickness accompanied by an increase in net polar ordering is one possible avenue to obtain the second-order nonlinear optical susceptibility \( \chi^{(2)} \) necessary for electro-optic devices. In this thesis, we will discuss the structural characteristics of ISAM films and explore three novel approaches to obtain the desired characteristics for nonlinear optical response. One approach involves the variation of solution parameters of several different cationic polymers separately from the polyanion solution in order to reduce the competitive chromophore orientation at the layer interfaces and to reduce the thickness of the inactive polycation layer. We have found that the complexity of ISAM films does not allow large \( \chi^{(2)} \) values in polyion-based films, and that the selection of the polymer cation is vital to achieve second harmonic generation (SHG) at all. The
second approach involves the incorporation of dianionic molecules into ISAM films in order to eliminate both competitive chromophore orientation and random chromophore orientation inherent with polymer chromophores. We have also studied the effects of complexing dianionic chromophores with β-cyclodextrin in order to increase solubility and improve chromophore orientation. This approach fails because the outermost monolayer of dianionic chromophore is only tethered to the preceding polycation layer by a single ionic bond for each molecule, so each chromophore can by dissociated during the following immersion into the cation solution. Finally, we have introduced a novel approach of hybrid covalent / ionic self-assembly which overcomes these disadvantages and yields a substantial increase in $\chi^{(2)}$ due to the chromophore being locked in place to the preceding polycation layer by a covalent bond. The films fabricated in this manner yield a $\chi^{(2)}$ that rival any polymer-polymer films despite the very low first-order molecular hyperpolarizability $\beta$ of the incorporated monomer. This suggests that incorporation of high $\beta$ molecules may result in significant improvement of $\chi^{(2)}$, holding high promise for the hybrid covalent / ionic self-assembly technique.
To Julia, and those yet without names
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CHAPTER 1

SECOND-ORDER NONLINEAR OPTICS:
APPLICATIONS AND MATERIALS

This thesis presents an investigation into a novel technique for the fabrication of nanometer scale organic multilayer films for use in nonlinear optical (NLO) applications. Ionically self-assembled monolayer (ISAM) films are an assemblage of oppositely charged polymers built layer by layer through coulombic attraction utilizing an environmentally friendly process to form ordered structures that are uniform, molecularly smooth, and physically robust. The effects of film deposition parameters have previously been studied by this research group through variation of the pH and NaCl concentration of the dipping solutions. The goal of this work is to provide a more complete characterization of the effect of deposition parameters upon the NLO properties of ISAM films, and to introduce a novel hybrid covalent / ionic self-assembly technique utilizing monomer chromophores that shows great promise for incorporation into electro-optic devices. In addition, this study has provided valuable information into the structure of the ISAM films which will be presented as a secondary goal of this thesis.
Optics is the study of the interaction of electromagnetic radiation and matter. Nonlinear optics (NLO) is the study of the phenomena that occur as a consequence of the modification of the optical properties of a material system by the presence of light. The phenomena are nonlinear in the sense that the polarization response is related in a nonlinear manner to the incident electromagnetic field. The second-order nonlinear optical effect known as second harmonic generation (SHG) was first observed in 1961 by excitation of a quartz crystal with light of wavelength $\lambda = 694$ nm from a ruby laser, resulting in the creation of $\lambda = 347$ nm light. Since that discovery, the utilization of SHG and related phenomena from crystals has been of great interest, including the ability to convert the light from a laser to a different wavelength selectable from a continuum of wavelengths via optical parametric oscillation, discovered in 1968. The optical parametric oscillator (OPO), which converts a single photon into two photons such that the sum of their energies equals the energy of the original photon, has afforded scientists the ability to study the interaction of light with matter using coherent, collimated light ranging from ultraviolet to far into the infrared, and is one of many significant discoveries stemming from the advent of the laser.

The electro-optic effect is perhaps the most technologically important application of nonlinear optics being researched today. The electro-optic effect affords the use of a DC electric field to alter the index of refraction of a material, allowing the fabrication of various types of optical modulators and switches for use in fiber optics networks and communication devices as well as in future optical computing components. As with the second-order NLO effect, a suitable material must possess noncentrosymmetry (no inversion center). Devices generally incorporate inorganic crystals, but each switch is very expensive due to the complexity of inorganic crystal waveguide fabrication. The need for a single product to incorporate thousands of switches has focused attention on finding suitable organic thin films that can be fabricated inexpensively and have a suitable operating lifetime.

Many types of film fabrication processes for the development of noncentrosymmetric thin organic films have been utilized including molecular crystals, liquid crystals, Langmuir Blodgett (LB) films, covalently self-assembled films (SAMs) and poled polymer guest-host films.
progress has been made in device fabrication utilizing the latter three methods, incorporating polymers into the structure. Poled polymer films (in which dipoles are aligned through application of an electric field above the polymer glass transition temperature $T_g$) have gained the most attention in the research community, and have recently been successfully utilized in electro-optic modulators$^{5,6}$ and waveguides$^{7,8}$ but exhibit relatively poor thermal and temporal stability. Covalent SAMs have been demonstrated in organic light emitting diodes (OLEDs),$^9$ phase modulators$^{10}$ and waveguides$^{11}$, but suffer from fabrication difficulties that hinder their usability in various devices. Each of these methods has inherent drawbacks which will be discussed in detail later in this chapter.

A technique which has been shown to bypass many of these problems was first introduced by Gero Decher in 1992,$^{12,13}$ and was an innovation of a technique involving colloids presented by Iler in 1966$^{14}$. The ionically self-assembled monolayer (ISAM) technique utilizes coulombic interactions between polyelectrolytes to readily produce robust, noncentrosymmetric thin films that can have significant second-order nonlinear optical susceptibilities without any need for post-fabrication processes. Recently, the influence of pH and ionic strength of the polyanion solution upon film formation and structure as well as second-order nonlinear optical characteristics has been studied.$^{15,16}$ These films have been shown to exhibit excellent thermal and temporal stability along with significant second harmonic generation.$^{17}$ ISAM films have also been successfully utilized in photovoltaic devices,$^{18,19,20,21,22,23,24}$ OLEDs,$^{25,26,27,28}$ electrochromic devices,$^{29,30,31}$ humidity sensors,$^{32}$ and biosensors$^{33}$.

This study involves extending the characterization to the variation of pH of the polycation solution. Improved second-order nonlinear optical response and more detailed modeling of ISAM films for other purposes are of interest. Further, additional techniques involving incorporation of dianionic molecules and cyclodextrin have been studied, leading to a novel technique combining ionic and covalent self-assembly techniques. This hybrid covalent / ionic technique will be the focus of future study.
1.1 A Brief Introduction to Nonlinear Optics

Electromagnetic radiation is described by Maxwell’s equations:
\[
\nabla \cdot \vec{D} = 4\pi \rho \\
\nabla \times \vec{H} - \frac{1}{c} \frac{\partial \vec{D}}{\partial t} = \frac{4\pi}{c} \vec{J} \\
\n\nabla \times \vec{E} + \frac{1}{c} \frac{\partial \vec{B}}{\partial t} = 0 \\
\n\nabla \cdot \vec{B} = 0
\]
Equation 1.1.1

For a non-magnetic material with no free charges and no free currents, the electric displacement field \( \vec{D} \) is the total electric field within the material, and is given by
\[
\vec{D} = \vec{E} + 4\pi \vec{P},
\]
where \( \vec{E} \) is the incident electric field and \( \vec{P} \) is the polarization field generated from electric-field induced dipoles within the medium. For a linear, isotropic material, the polarization field is considered to be linearly related to the incident electric field
\[
\vec{P} = \chi \vec{E},
\]
where the electrical susceptibility \( \chi \) is a second-rank tensor. This first-approximation is commonly employed in most electromagnetic interactions, and is generally sufficient for incident fields with low field strengths in most materials. When a high strength electric field is incident upon an anisotropic material, we must utilize the general expression for polarization. For a monochromatic or nearly monochromatic electric field, the polarization may be expanded in a Taylor series to obtain
\[
\vec{P} = \chi^{(1)} \vec{E} + \chi^{(2)} \vec{E}^2 + \chi^{(3)} \vec{E}^3 + \cdots
\]
Equation 1.1.4.a
\[
P_i = \chi^{(1)}_{ij} E_j + \chi^{(2)}_{ijk} E_j E_k + \chi^{(3)}_{ijkl} E_j E_k E_l + \cdots
\]
Equation 1.1.4.b
where terms are summed over repeated indices that represent the three components of Cartesian coordinates. Equation 1.1.4.b is shown in its standard notation, but may be more comprehensively written as
\[
\vec{P} = \sum_{i=1}^{3} \left[ \sum_{j=1}^{3} \chi^{(1)}_{ij} E_j + \sum_{j,k=1}^{3} \chi^{(2)}_{ijk} E_j E_k + \sum_{j,k,l=1}^{3} \chi^{(3)}_{ijkl} E_j E_k E_l + \cdots \right],
\]
Equation 1.1.4.c
where \( \{1,2,3\} = \{x,y,z\} \) and \( \chi^{(n)}_{ij} \) are components of an \((n+1)^{th}\)-rank tensor. The first coefficient, \( \chi^{(1)} \), is the linear electrical susceptibility for an anisotropic material. The remaining coefficients \( \chi^{(n)} \) are called the \( n^{th} \) order nonlinear susceptibilities. For this thesis, we will discuss only the second-order nonlinear susceptibility for non-magnetic, nonlinear, anisotropic, noncentrosymmetric materials containing no free charges and no free currents. The requirement of noncentrosymmetry will be discussed in Section 1.3.

As an example of a second-order nonlinear optical process, consider the interaction of an optical electric field at frequency \( \omega \) and amplitude \( E_\omega \)

\[
E_\omega(t) = \frac{1}{2} E_\omega (e^{i\omega t} + e^{-i\omega t}),
\]

with a static electric field \( E_0 \) in a medium with a nonzero \( \chi^{(2)} \). The second-order polarization field in this medium is

\[
\vec{P}^{(2)}(t) = \chi^{(2)} \vec{E}^2(t) = \chi^{(2)} [E_\omega \cos (\omega t) + E_0]^2
\]

\[
= \chi^{(2)} \left[ \frac{1}{2} E_\omega e^{i\omega t} + \frac{1}{2} E_\omega e^{-i\omega t} + E_0^2 \right]^2
\]

\[
= \chi^{(2)} \left[ \frac{1}{2} E_\omega^2 (e^{i2\omega t} + e^{-i2\omega t}) + E_0 E_\omega (e^{i\omega t} + e^{-i\omega t}) + \frac{1}{2} E_0^2 + E_\omega^2 \right]^2
\]

The resulting polarization field contains components oscillating at various frequencies. The first term in equations 1.1.6 oscillates at \( 2\omega \) and may radiate light at that frequency. This term depends only on the presence of the optical electric field and not the static field. This effect is referred to as second harmonic generation (SHG), or frequency-doubling. The second term in equations 1.1.6 oscillates at \( \omega \) and causes variation in the refractive index of the medium. This effect is the linear electro-optic effect and will be discussed in the following section. The third term is known as optical rectification, and is a conversion of an oscillating electric field to a static electric field.

These and other phenomena arise from the mixing of electric fields of various frequencies in a nonlinear medium. Because the nature of the polarization field is dependent upon the incident fields, the effects resulting from the nonlinear susceptibilities are given a shorthand notation in accordance with the appropriate susceptibility and the incident and resultant electric field.
frequencies. For the second-order polarization field oscillating at frequency $\omega_3$ induced by two electric fields oscillating at frequencies $\omega_1$ and $\omega_2$, from equation 1.1.4.b we write

$$P_i^{(2)} = \chi_{ijk}^{(2)}(-\omega_3;\omega_1,\omega_2)E_j^{\omega_1}E_k^{\omega_2}. \quad (1.1.7)$$

The negative-sign and semicolon are simply a convention to indicate that $\omega_3$ is the output frequency. The input frequencies can be positive or negative dependent upon their relative phases. For instance, $\chi_{ijk}^{(2)}(0;\omega,\omega)$ represents optical rectification. The frequencies are related such that

$$\omega_3 = (\omega_1 + \omega_2). \quad (1.1.8)$$

Some of the effects characterized by the second-order susceptibility are:

- $\chi_{ijk}^{(2)}(-2\omega;\omega,\omega)$: Second Harmonic Generation (SHG)
- $\chi_{ijk}^{(2)}(-\omega;\omega,0)$: Linear Electro-optic Effect (LEO)
- $\chi_{ijk}^{(2)}(-\omega_1 - \omega_2;\omega_1,\omega_2)$: Sum Frequency Generation (SFG)
- $\chi_{ijk}^{(2)}(-\omega_1 + \omega_2;\omega_1,\omega_2)$: Difference Frequency Generation (DFG).

The nonlinear polarizations act as source terms in the optical wave equation

$$\nabla^2 E - \frac{n^2}{c^2} \frac{\partial^2 E}{\partial t^2} = \frac{4\pi}{c^2} \frac{\partial^2 P}{\partial t^2}. \quad (1.1.9)$$

The polarization fields arising from the nonlinear susceptibilities, due to the acceleration of charges within the medium, generate electromagnetic radiation that is observable and can be utilized in practical applications.

### 1.2 Applications of Second-Order Nonlinear Optical Materials

One of the most widely used applications for nonlinear media is the generation of second harmonic radiation. As illustrated in eq. 1.1.6, radiation at frequency $\omega$ is converted into radiation at frequency $2\omega$ within the nonlinear medium. This process generally occurs through virtual transitions (no photon absorption takes place) where two photons at $\omega$ are simultaneously destroyed while a single photon at $2\omega$ is created in a single quantum mechanical process. This process can result in upwards of 50% conversion of the incident fundamental energy into the
second harmonic, and is used extensively in the laboratory to obtain coherent optical radiation with wavelengths other than the fundamental of the fixed-wavelength laser source. Phase-matching concerns as well as the use of second harmonic generation as a probe technique will be discussed in Chapter 3.

For further investigation into the electro-optic effect, consider the case of a linear medium where \( \bar{P} = \chi^{(1)} \bar{E} \). Utilizing eqs. 1.1.2 and 1.1.3, we write the displacement field as

\[
\bar{D} = \bar{E} + 4\pi\bar{P} = (1 + 4\pi\chi^{(1)})\bar{E}.
\]

Further, we know that the displacement field is related to the electric field by

\[
\bar{D} = \varepsilon\bar{E},
\]

where \( \varepsilon \) is the electrical permittivity of the material. Since the index of refraction \( n \) of a material is

\[
n = \sqrt{\varepsilon},
\]

the index of refraction is related to the electrical susceptibility as

\[
n = \sqrt{1 + 4\pi\chi^{(1)}}.
\]

The refractive index in this case is clearly independent of the applied field, and relies solely upon the material parameters represented by the second-rank susceptibility tensor.

In order to understand why a material with an appreciable \( \chi^{(2)} \) is an electro-optic material, we refer to the second-order polarization field shown in eq. 1.1.6 arising from an optical electric field and static DC field combined in a noncentrosymmetric medium. The amplitude of the total polarization field oscillating at frequency \( \omega \) is

\[
P_{\omega} = \chi^{(1)}E_{\omega} + \chi^{(2)}[2E_{0}E_{\omega}]\).
\]

The magnitude of the displacement field is then given by

\[
D_{\omega} = E_{\omega} + 4\piP_{\omega}
\]
\[
= E_{\omega} + 4\pi\left[\chi^{(1)}E_{\omega} + \chi^{(2)}(2E_{0}E_{\omega})\right]
\]
\[
= \left[1 + 4\pi\chi^{(1)}\right]E_{\omega} + 8\pi\chi^{(2)}E_{0}E_{\omega}
\]
\[
= \left[1 + 4\pi\chi^{(1)} + 8\pi\chi^{(2)}E_{0}\right]E_{\omega} = \left[\varepsilon^{(1)} + 8\pi\chi^{(2)}E_{0}\right]E_{\omega} = \varepsilon E_{\omega}.
\]


Therefore, the refractive index for this material is given by

\[ n'(E_0) = \sqrt{n^2 + 8\pi\chi^{(2)}E_o} \approx n + \left( \frac{4\pi}{n} \right) \chi^{(2)}E_0. \]  

(1.2.7)

The refractive index of a second-order nonlinear optical material is linearly dependent upon the applied DC field and can be controlled by altering the magnitude of the field. This is known as the linear electro-optic effect or Pockel’s effect, and the \( \chi^{(2)} \) determines the extent of this effect in a given material.

One of the simplest and most useful applications of the electro-optic effect is in a Mach-Zehnder interferometer used to modulate wave amplitude. An incident electric wave \( E = E_0 e^{i(kz-\omega t)} \) with intensity \( I_0 \) is split into the two arms of an interferometer that is patterned in a second-order nonlinear optical medium with equal lengths as shown in Figure 1.2.1. The shaded portion of the interferometer represents the portion of one arm that has electrodes above and below the medium. With no voltage across the electrodes, the optical pathlength is the same for both arms and the waves recombine constructively to obtain the initial intensity \( I_0 \). When voltage is applied, the optical pathlength of one arm is changed due to an induced change in index of refraction as described in the following analysis.

The linear electro-optic tensor \( r_{mpq} \) is a third-rank tensor that describes the modification of the index of refraction due to an incident electric field in the following manner. The impermeability tensor \( \eta_{np} \) is the inverse of the permittivity tensor \( \varepsilon_{ij} \) introduced in eq. 1.2.2, and relates the displacement field \( D \) in a medium to the applied electric field \( E \) as

\[ \bar{E} = \eta \bar{D}. \]  

(1.2.8)

The linear electro-optic tensor is related to the impermeability tensor as

\[ \eta_{np} = \eta_{np}^{(0)} + \sum_q r_{npq}E_q + \cdots. \]  

(1.2.9)

For lossless media, the permittivity tensor is real and symmetric, and its inverse must also be real and symmetric, causing \( r_{npq} \) to be symmetric in its first two indices. Therefore, \( r_{npq} \) is commonly represented by a two-dimensional tensor \( r_{mq} \) using the following convention:
The optical indicatrix, or index ellipsoid, for an anisotropic material in the presence of an electric field is given by\textsuperscript{34}

\[
m = \begin{cases}
1 & \text{for } np = 11 \\
2 & \text{for } np = 22 \\
3 & \text{for } np = 33 \\
4 & \text{for } np = 23, 32 \\
5 & \text{for } np = 13, 31 \\
6 & \text{for } np = 12, 21 \\
\end{cases}.
\]  

(1.2.10)

\[
\left(\frac{1}{n^2}\right)_1 x^2 + \left(\frac{1}{n^2}\right)_2 y^2 + \left(\frac{1}{n^2}\right)_3 z^2 + 2 \left(\frac{1}{n^2}\right)_4 yz + 2 \left(\frac{1}{n^2}\right)_5 xz + 2 \left(\frac{1}{n^2}\right)_6 xy = 1,
\]

(1.2.11)

where

\[
\left(\frac{1}{n^2}\right)_m = \eta_m
\]

(1.2.12)

\[\text{Figure 1.2.1:} \text{ Mach Zehnder interferometer as an electro-optic switch and/or amplitude modulator. Electrodes of length } l \text{ are positioned above and below the upper arm of the device. Incident light is polarized along the extraordinary axis of the electro-optic material, whose axis of noncentrosymmetry is normal to the electrodes.}\]
utilizing the convention of eq. 1.2.10. Therefore, the modifications of the index ellipsoid due to the linear electro-optic effect are

\[ \Delta \left( \frac{1}{n^2} \right)_m = \sum_q r_{mq} E_q \ . \]  

(1.2.13)

If the medium in the waveguide of Figure 1.21 is a uniaxial crystal with \( C_{\infty v} \) symmetry with the extraordinary axis normal to the electrodes, for light travelling along the waveguide and polarized along the extraordinary axis, eq. 1.2.13 becomes

\[ \Delta \left( \frac{1}{n^2} \right)_3 = r_{33} E_3 \ , \]  

(1.2.14)

where the index ‘3’ represents the z-axis, which is the extraordinary axis. For a DC field \( E_{0z} \) applied along the z-axis, the modified index ellipsoid may be written as

\[ \frac{x^2}{n_0^2} + \frac{y^2}{n_0^2} + \frac{z^2}{n_e^2} + r_{33} E_{0z} z^2 = 1 \ , \]  

(1.2.15)

where \( n_0 \) and \( n_e \) are the unmodified ordinary and extraordinary indices of refraction. Equation 1.2.15 may be written as

\[ \frac{x^2}{n_0^2} + \frac{y^2}{n_0^2} + \left( \frac{1}{n_e^2} + r_{33} E_{0z} \right) z^2 = 1 \ . \]  

(1.2.16)

The modified index ellipsoid may be alternatively written as

\[ \frac{x^2}{n_0^2} + \frac{x^2}{n_0^2} + \frac{z^2}{n_e^2} = 1 \ . \]  

(1.2.17)

Therefore, the modified extraordinary index of refraction is given by

\[ \frac{1}{n_e'^2} = \frac{1 + n_e^2 r_{33} E_{0z}}{n_e^2} \ , \]  

(1.2.18)

so that

\[ n_e' = \left[ \frac{n_e^2}{1 + n_e^2 r_{33} E_{0z}} \right]^{\frac{1}{2}} = n_e \left[ 1 + n_e^2 r_{33} E_{0z} \right]^{-\frac{1}{2}} \ . \]  

(1.2.19)

In the physically realistic limit \( n_e^2 r_{33} E_{0z} \ll 1 \), the extraordinary refractive index \( n_e \) varies with a DC field \( E_{0z} \) applied along the extraordinary axis as
\[ n'_e(E_{oz}) = n_e - \frac{1}{2} n^3_e r_{33} E_{oz} \]  

(1.2.20)

If the DC field is applied across electrodes of length \( l \), a phase difference \( \Delta \phi \) is introduced as

\[
\Delta \phi = \frac{2\pi l}{\lambda} (\Delta n) \\
= \frac{\pi l}{\lambda} n^3_e r_{33} E_{oz}
\]

(1.2.21)

and the recombined wave has an electric field

\[
E' = E_o \cos \left( \frac{\Delta \phi}{2} \right) e^{i(kx-\omega t)}
\]

(1.2.22)

with intensity

\[
I = I_o \cos^2 \left( \frac{\Delta \phi}{2} \right).
\]

(1.2.23)

The electric field strength between the plates of a capacitor relative to the applied voltage is independent of the material between the plates and is given by

\[
E_o = \frac{V}{d},
\]

(1.2.24)

where \( d \) is the distance between the plates. Therefore, given electrode spacing \( d \) (plates located above and below one waveguide arm) and potential difference \( V \), the voltage required to obtain a phase shift of \( \pi \) for a wave with wavelength \( \lambda \), polarized along the extraordinary axis is

\[
V_{\pi} = \frac{d \lambda}{ln^3_e r_{33}}.
\]

(1.2.25)

The interferometer can act as an on/off switch for \( V = 0, V_{\pi} \) respectively, or as an amplitude modulator for intermediate voltages.
1.3 Second-Order Nonlinear Optical Materials

The primary requirement for a material to generate a second-order nonlinear optical response is noncentrosymmetry of the material structure along the direction of the electric field. Consider a material with an inversion center such that it is centrosymmetric in all directions. If an electric field
\[ E(t) = E_0 \cos \omega t \]  
(1.3.1)
is incident upon such a medium, the resultant second-order polarization field will be
\[ P_2(t) = \chi^{(2)} E^2(t). \]  
(1.3.2)
Due to the inversion symmetry, the following relation must exist:
\[ -P_2(t) = \chi^{(2)} \left[ -E(t) \right]^2 \]
\[ -P_2(t) = \chi^{(2)} E^2(t). \]  
(1.3.3)
This is true only if the polarization field is zero, indicating \( \chi^{(2)} \) is zero for centrosymmetric media. This would also be the case for a polarized optical wave where centrosymmetry exists along the electric field vector. This can be further illustrated by considering the induced dipole moment of a second-order nonlinear molecule in a sinusoidal electric field polarized in the plane of the page as shown in Figure 1.3.1.a. Both linear media (Figure 1.3.1.b) and centrosymmetric nonlinear media (Figure 1.3.1.c) yield a polarization field that includes only odd harmonics. The nonlinear medium of Figure 1.3.1.c yields a response that can only result from a noncentrosymmetric medium.
Figure 1.3.1: Electric field and corresponding polarization fields in various media.

(a) Incident electric field,
(b) Polarization field of ‘a’ in a linear, centrosymmetric medium,
(c) Polarization field of ‘a’ in a nonlinear, centrosymmetric medium,
(d) Polarization field of “a” in a nonlinear, noncentrosymmetric medium.
Noncentrosymmetric NLO media have generally been fabricated using inorganic crystals. Potassium dihydrogen phosphate (KDP), β-barium borate (BBO) and lithium niobate (LNB) are typical examples frequently used in high power applications. These crystals exhibit $\chi^{(2)}$ values on the order of $10^{-9}$ to $10^{-7}$ esu arising from the electron polarizability due to the crystal’s band structure and the asymmetry of the crystal structure. Crystal growth procedures are complicated and time consuming, requiring precise variational control of temperature ranging from 600-1000 °C at pressures ranging from high vacuum to 1700 atm. Growth times can range from 10 days to 8 weeks to produce crystals of dimension 20 mm x 30 mm x 60 mm. Many inorganic crystals exhibit moderate to poor environmental stability with particular weakness to humidity.

1.3.1 Organic Chromophores

As an alternative to inorganic crystals, organic molecules and polymers have been of considerable interest for use in nonlinear optics due to their large optical nonlinearities, as well as ease of processability. The polarization of such a molecule can be expanded as a Taylor series in the same manner as the polarization field in eq. 1.1.4.b. This results in a molecular polarization $p$ with higher-order corrections

$$p_i(\omega) = \mu_i + \alpha_{ij}(-\omega)E_j(\omega) + \beta_{ijk}(-\omega;\omega_1,\omega_2)E_j(\omega_1)E_k(\omega_2) + \gamma_{ijkl}(-\omega;\omega_1,\omega_2,\omega_3)E_j(\omega_1)E_k(\omega_2)E_l(\omega_3) + \ldots$$

where $\mu_i$ is the permanent dipole moment of the material, $\alpha_{ij}$ is the polarizability associated with the linear optical effects, and $\beta_{ijk}$ and $\gamma_{ijkl}$ are the first- and second-order molecular hyperpolarizabilities associated with the second- and third-order nonlinear optical effects, respectively. For a collection of $N$ molecules, the macroscopic second-order nonlinear susceptibility $\chi^{(2)}$ can be expressed as an orientational average over the molecules’ hyperpolarizabilities $\beta_{\mu\nu\rho}$

$$\chi^{(2)}_{jk}(-\omega;\omega_1,\omega_2) = N \sum \langle R_{ij}, R_{jk}, R_{kp} \rangle \beta_{\mu\nu\rho}, f(\omega)f(\omega_1)f(\omega_2)$$

where $R$’s are direction cosines between lab axes $(i,j,k)$ and molecular axes $(\mu,\nu,\rho)$, and $f$’s are local field factors representing corrections to the electric field experienced by each molecule due to the electric fields of its neighbors.
Large molecular hyperpolarizabilities require highly polarizable electrons (to be able to respond to an electric field) and asymmetry on the molecular level. Large polarizability is achieved through conjugation, where $\pi$ electron bonds between unsaturated atoms in organic compounds are delocalized and easily moved over large distances by electric fields. Asymmetry is provided through the use of electron donor and acceptor groups attached at opposite ends of the molecule. These groups provide a permanent dipole moment which causes the resulting induced moment to be asymmetric. Analogous to the first-order dipole moment of two static charges, increased strength of the donor / acceptor groups and increased conjugation length between these groups generally results in larger hyperpolarizabilities as illustrated in Table 1.3.1.4

The first-order hyperpolarizability $\beta$ can be measured by several techniques. Most common is the electric-field induced SHG (EFISH) method. An electric field is used to align the chromophores in solution, producing an asymmetric medium for a second harmonic generation measurement. A comparison with a reference sample, generally quartz, allows a calculation of $\beta$. When the chromophore in question possesses ionic groups, the EFISH method results in a separation of chromophore from solution (literally ‘plating’ the field electrodes). In these cases, the method of Hyper Rayleigh scattering (HRS) is used. HRS measures incoherently scattered SHG from even isotropic solutions. Coherent SHG intensity is proportional to the square of $<\cos^3 \theta>$, with molecular orientation angle $\theta$. If the sample is completely isotropic, this result is zero. Scattered SHG intensity, however, depends only on $<\cos^2 \theta>$, which is nonzero even for random orientation. Analysis of the polarization of scattered second harmonic with respect to the polarization of the incident fundamental allows resolution of $\beta_{zzz}$ and $\beta_{xxx}$ components of the hyperpolarizability.
Table 1.3.1: Hyperpolarizabilities $\beta_0$ and structures of selected organic chromophores. $\beta_0$ indicates the primary component of hyperpolarizability, with all field polarizations aligned with the long axis of molecule.

<table>
<thead>
<tr>
<th>Chromophore</th>
<th>Structure</th>
<th>$\beta_0 (10^{-30} \text{ cm}^2/\text{esu})$</th>
</tr>
</thead>
<tbody>
<tr>
<td>DMNA</td>
<td>![Structure DMNA]</td>
<td>12</td>
</tr>
<tr>
<td>NB-DMAA</td>
<td>![Structure NB-DMAA]</td>
<td>37</td>
</tr>
<tr>
<td>Disperse Red 1</td>
<td>![Structure Disperse Red 1]</td>
<td>47</td>
</tr>
<tr>
<td>DMA-NS</td>
<td>![Structure DMA-NS]</td>
<td>52</td>
</tr>
<tr>
<td>DMA-DCVS</td>
<td>![Structure DMA-DCVS]</td>
<td>133</td>
</tr>
<tr>
<td>DEA-TCVAB</td>
<td>![Structure DEA-TCVAB]</td>
<td>154</td>
</tr>
</tbody>
</table>
1.3.2 Poled Polymers

The most general method of utilizing these molecules for $\chi^{(2)}$ applications is through polymer films fabricated by mechanical techniques such as spin-casting, then breaking the centrosymmetry by aligning the dipoles via an electric-field poling process. This technique was first theoretically derived and demonstrated for fabrication of nonlinear optical materials by Singer and co-workers, and was inspired by a technique used for liquid crystal film displays. Chromophores are doped into an optically inactive polymer and deposited on a substrate. The deposition leaves the chromophores with randomized orientation and therefore with zero $\chi^{(2)}$. In order to make useful $\chi^{(2)}$ materials, these films are heated above their glass-transition temperature, $T_g$, allowing the chromophores some degree of orientational mobility. A strong electric field is applied (typically $\sim 10^5$-$10^6$ V/m) to ‘pole’ the chromophores, aligning them with the electric field. The field is maintained as the film is cooled down below its transition temperature, effectively ‘freezing in’ the chromophore alignment. This process, producing what are known as ‘poled polymers’, yields typical $\chi^{(2)}$ values of $10^{-8}$ to $10^{-7}$ esu. For comparison, $\beta$-barium borate, one of the commonly used $\chi^{(2)}$ crystal materials, has a value of $9.2 \times 10^{-9}$ esu. Unfortunately, the chromophore orientation of poled polymers tends to decay over time due to randomization of chromophore alignment. For example, at room temperature, the second-order susceptibility in some guest-host systems has shown a sharp initial decay (10-50% in the first 24 hours) followed by a slower decay (20% over a year).

This decay rate is increased as temperatures approach the glass transition temperature, at which point decay is nearly instantaneous. This decay has been diminished by covalent attachment of the chromophore to the polymer and through the use of cross-linking polymers. When exposed to UV radiation, bonds are formed between photo-reactive groups present on the polymers, reducing the orientational mobility of the polymer. When poled, crosslinked polymers can show smaller $\chi^{(2)}$ than uncrosslinked polymers, but show reduced decay rates (10% vs. 50% over 500 hours at 25 °C) due to this reduction of orientational mobility.
Further increases in orientational stability have been achieved through the use of polyimides to reduce orientational mobility in poled polymers through densification of the material. As shown in Figure 1.3.2.a, chromophores are doped into polyamic acid (they may also be covalently attached as side-groups) and deposited (spin-cast) onto a substrate. A poling field is applied, orienting the guest chromophores. Simultaneously, the film is heated to above \( T_g \) (>250°C), which causes the polyamic acid to condense to form imide rings (Fig. 1.3.2.c). This imidization restricts the allowed motion of the chromophores and increases the thermal stability of the films. Because the formation of each imide ring produces a water molecule, a final curing step (called densification) is performed at higher temperature (~350°C) to decrease the moisture content of the films. This can result in a decrease in film thickness by 40%, further limiting the reorientational mobility of the guest chromophores. This densification has been shown to be crucial to the increased thermal stability exhibited by these films. It is only after cooling to room temperature after this final curing step that the poling field is removed. This process has resulted in films that exhibit improved thermal stability, and has become the focus of research attention. It is important to note, however, that the necessary processing temperatures are generally above thermal breakdown temperatures of most nonlinear optical chromophores.

More recently, attempts have been made to overcome the thermal stability issue by using high \( T_g \) (~380 °C) donor-embedded polyimides and high \( T_g \) (~400 °C) diamine functionalized chromophores. The latter is an even more complex procedure wherein the chromophore is embedded in the polyimide prior to film casting, as opposed to post casting imidization of the former, resulting in chromophore functionalized polyimides. The chromophore-embedded polyimides exhibited a much improved room temperature temporal stability, showing only a 5% initial drop followed by negligible loss of \( \chi^{(2)} \) after 1200 hours. However, the films exhibited 20% irrecoverable loss of SHG at a temperature \( T \approx 0.65 T_g \approx T_g - 250 \) °C, followed by a rapid total loss of SHG. The chromophore-functionalized polyimides exhibited poor temporal stability, and similar thermal stability. Further, neither method showed any improvement in initial \( \chi^{(2)} \), which has remained largely unimproved for poled polymer films since 1992.
Figure 1.3.2: Post-processing of polyimide films.

(a) Guest/host polyamic acid film.
(b) Poling field is applied, orienting chromophores in one general direction.
(c) Imidization process restricting chromophore mobility.
(d) Excess moisture from imidization is driven out in densification, further restricting chromophore mobility.
1.3.3 Langmuir-Blodgett Deposition

In order to avoid the orientational relaxation (depoling) that occurs in poled polymers, various attempts have been made to fabricate nonlinear films with an intrinsic structural asymmetry. These assembly techniques involve molecules that are aligned by the deposition procedure itself. They generally fall into two categories – Langmuir-Blodgett deposition and covalent self-assembly.

In the simplest form of Langmuir-Blodgett (LB) deposition, introduced in the 1930s, molecules that are hydrophilic at one end and hydrophobic at the opposite end are spread on a water surface. This layer is then compressed until the molecules are close-packed (and therefore aligned). This is the formation of the actual monolayer. In order to transfer this monolayer onto a substrate, a substrate is immersed in the water through the monolayer in a vertical orientation (Figure 1.3.3.a). If the substrate is hydrophobic, the first layer will be formed upon immersion. When the substrate is removed, a second layer is deposited on top of the first. When a monolayer is transferred to the substrate on both immersion and removal, the resulting structure is called ‘Y-Type’. Most LB capable molecules form this type structure. X- and Z-Type structures are formed when monolayers are deposited on insertion or withdrawal only. Both X- and Z-Type structures possess an inherent structural asymmetry, as molecules in adjacent layers are oriented head-to-tail. Z-Type films have been shown to produce nonlinear susceptibilities approximately 10 times that of β-barium borate, a crystal commonly used for second harmonic generation and optical parametric oscillation applications. Though Y-Type structures are inherently structurally symmetric, several tricks may be utilized to obtain films with non-zero $\chi^{(2)}$. For example, molecules can be chosen which exhibit non-zero hyperpolarizability in the plane of the monolayer.

In a slightly more complicated arrangement, a net orientation perpendicular to the substrate is possible by utilizing two different LB films. The substrate is immersed through a non-absorbing, nonlinear inactive molecular monolayer, adsorbing the first layer. The substrate is then moved, while immersed, through a gate and into a second water bath where it is withdrawn through a
monolayer that contains an NLO chromophore. Though a Y-Type structure is formed, the chromophores exist only on the withdrawal monolayer, behaving as a Z-Type structure. Films deposited in this fashion have shown non-linear susceptibilities of $\chi^{(2)} = 16 \times 10^{-7}$ esu, roughly 20 times larger than that of \(\beta\)-barium borate.$^{53}$

Langmuir-Blodgett deposition is complicated by the need to maintain a constant surface pressure of the molecules during insertion and removal. Since that pressure causes the molecules to be close-packed, if pressure is decreased, molecules are allowed to relax their orientation. If pressure is too high, the monolayer can break down with molecules folding on top of each other. Constant pressure is generally maintained by a series of compression and removal rollers in the bath in conjunction with the application of ‘piston oils’, which serve to apply pressure to the LB molecules.$^{54}$ The deposition apparatus and procedure is complicated and sensitive to environmental conditions and contaminants.

Perhaps most significantly, Langmuir-Blodgett films show poor mechanical and thermal stability due to the van Der Waals interactions between layers. The few X- and Z-Type molecules commonly decay to Y-Type structures, destroying the asymmetry.$^{54}$ Increased heat and elapsed time serves to collapse Langmuir-Blodgett layers, randomizing any chromophore orientation. It is worth noting that LB films incorporating polyimides to stabilize structure have been investigated and appear to possess some amount of thermal stability up to 240 °C,$^{52}$ but $\chi^{(2)}$ measurements have not been made on these films.
Figure 1.3.3: Langmuir-Blodgett and covalent self-assembly processes. (a) Deposition of Langmuir-Blodgett molecules (hydrophilic ends represented as arrowheads) on a hydrophobic substrate. Deposition occurs on both substrate insertion and removal (Y-Type). (b) X, Y, and Z type LB films. (c) Covalent self-assembly process of (dialkylamino) stilbazole onto benzyl chloride surface. Step (iii) crosslinks hydroxy groups and serves as activation for deposition of next layer, beginning at step (i).
1.3.4 Covalent Self-Assembly

Covalently self-assembled films, commonly known as self-assembled monolayers (SAMs) or chemisorbed films, introduced by Netzer and Sagiv in 1983, overcome several of the drawbacks of Langmuir-Blodgett films. In this method, hydroxylated substrates are immersed in an amphophilic fluid (solution, melt or vapor) and a thermodynamically stable film is covalently bonded to the surface. This layer may be followed by alternating steps that chemically activate the new surface layer and then deposit further layers (Figure 1.3.3.c). In this process, highly organized multilayer structures may be fabricated. SAM films show exceptional mechanical, chemical and electrical stability, and may be cross-linked to further increase these characteristics. The organization of these structures is particularly conducive to producing $\chi^{(2)}$ materials, and films have been produced with second-order susceptibilities of up to $3.0\times10^{-7}$ esu, over 30 times that of $\beta$-barium borate. Production of covalently self-assembled films is extremely time consuming. Immersion times per layer may range greater than 1 hour to several days. Both adsorption and layer activation steps must, in general, be conducted at elevated temperatures. These factors are aggravated by the necessity of 100% reactance of the surface layer in order to assure proper molecular orientation.

1.3.5 Ionically Self-Assembled Monolayer (ISAM) Technique

A new deposition technique that has been shown to bypass many of the problems of these other methods was first demonstrated by Decher and co-workers in 1991. The technique, referred to here as ionically self-assembled monolayers (ISAM), utilizes the coulombic attraction between oppositely charged polymers to form ultra thin layers of organic polymers in a precisely controlled fashion. The deposition process involves the immersion of a charged substrate into an oppositely charged aqueous polyelectrolyte solution. As the polyelectrolyte forms ionic bonds with the substrate surface, some fraction of the ionic groups extends away from the substrate. These groups cause an effective reversal of the surface charge, which limits further polyelectrolyte adsorption. The substrate is removed from solution at this point, rinsed with deionized water to remove unbonded polymer and immersed in a second aqueous polyelectrolyte
solution of opposite charge to the first. The process is repeated, with polyelectrolyte adsorption again reversing the surface charge. This process can be repeated in the (AB)_n fashion until the desired film thickness is obtained. Since deposition requires only that successive layers have opposite ion charge (anion/cation), it is possible to construct films whose structure is more complicated than the (AB)_n bilayer repeat unit. Films with (ABAC)_n structures, for example, have been fabricated and other structures are also possible. This allows polymer layers with different functionality to be easily incorporated into a single film with precise structural control.

The subject of this thesis is the exploration of ISAM deposition to provide inherently noncentrosymmetric $\chi^{(2)}$ films. In addition to absorbance and film thickness measurements, we will use second harmonic generation to provide information about chromophore orientation within the film. ISAM films have already been shown to be easier to design and fabricate than other self-assembled films, and exhibit better thermal characteristics than poled polymer films. We will present methods which further optimize ISAM film fabrication and characterization for improvement of polymer-polymer bilayers. Finally, in order to fabricate films with increased $\chi^{(2)}$ values, we will present investigation into films incorporating monomer chromophores in place of polymer chromophores in order to improve chromophore orientation and to reduce bilayer thickness.

Evidence of the structural characteristics of ISAM films will be presented in Chapter 2, using both published results from literature, as well as drawing upon our own experience from previous studies and those presented later in this thesis. The ISAM film deposition process will be described, and several established adsorption models will be presented in order to provide insight into the structure of ISAM films. No single model has yet been developed to completely explain the process, but several models considered simultaneously afford an insight into the nature of the adsorption of polyelectrolytes onto ISAM films. Experimental evidence of film morphology will be presented as a literature review, and combined with our own experience from SHG measurements to provide an intuitive picture of the structure of the films. Additionally, short-range structures of the molecules used in our studies will be presented to
offer further insight. Finally, previous studies performed by our group will be presented in order to introduce the motivation of the studies presented in this thesis.

Description of the SHG apparatus and various measurement techniques will be presented in Chapter 3. Arriving at a value of the second-order nonlinear susceptibility is an extensive process which requires several calibration steps. The calibration of a reference standard film to quartz, which has a well established $\chi^{(2)}$ value, will be presented, as well as the methodology for determination of the average chromophore tilt angle within the film. Further, the nuances of SHG measurements for double-sided ISAM films samples will be discussed.

Also included in Chapter 3 will be the study of the effect of variation of pH of the polycation solution, as well as the importance of choice of polycation used in ISAM films. Data reduction techniques and the propagation of error will be discussed. SHG experiments will be used to provide an insight into the structural characteristics of the polymer layers, specifically the difference between the layer interfaces, and the bulk with the chromophore layers. Finally, SHG experiments will show that the choice of polycation is critical to the fabrication of an ISAM film suitable for electro-optic applications.

A novel technique for fabrication of NLO films will be presented in Chapter 4. The insight into the structure of polymer-polymer ISAM films provided by the preceding SHG experiments will be used to introduce a new concept. The incorporation of monomer chromophores into ISAM films will be utilized to overcome the inherent weakness of polymer-polymer films by providing improved dipole orientation and thinner chromophore layers. The incorporation of dianionic chromophores will be explored, and the nuances of measuring single-sided films will be discussed. In order to improve the dianionic films, complexation with $\beta$-cyclodextrin will be studied. The lessons learned from these studies afford the novel concept of incorporation of monomer chromophores between two polycation layers by a hybrid covalent / ionic self-assembly process.


Ionically self assembled monolayer (ISAM) films are a revolutionary class of materials that allow detailed structural and thickness control at the molecular level combined with ease of manufacturing and low-cost. In this chapter, the ISAM film deposition process is described, and several established adsorption models are presented in order to provide insight into the structure of ISAM films. No single model has yet been developed to completely explain the process, but several models considered simultaneously afford an insight into the nature of the adsorption of polyelectrolytes onto ISAM films.
2.1 ISAM Film Deposition Process

The ISAM method simply involves the alternate dipping of a charged substrate into an aqueous solution of a cation followed by dipping into an aqueous solution of an anion. This procedure is carried out at room temperature and ambient conditions without the need for special facilities of any kind, and utilizes readily available environmentally friendly materials, resulting in molecularly smooth, uniform, physically robust films.

The glass microscope slide substrates (Fisher Scientific) were prepared using the RCA cleaning process\textsuperscript{59} which involves a 20 minute bath at 70°C in a 5:1:1 by volume NH\textsubscript{4}OH-H\textsubscript{2}O\textsubscript{2}-H\textsubscript{2}O solution, followed by a 20 minute bath at room temperature in 6:1:1 by weight HCl-H\textsubscript{2}O\textsubscript{2}-H\textsubscript{2}O solution. The slides were rinsed thoroughly in purified H\textsubscript{2}O after each bath and finally dried at 130 °C for 1 hour. When immersed in the initial cationic dipping solution, OH\textsuperscript{-} ions hydrogen bonded to the polar SiO\textsubscript{2} substrate form an anionic layer which affords initiation of the ISAM process. The purified water used in solutions and for rinsing was provided by a Barnstead Nanopure II filtration / deionization system.

The polymer-polymer bilayers were produced using an anionic polymer dye as the NLO-active layer, with an NLO-inactive cationic polymer serving as an “adhesive.” Typically, Poly S-119 (from Sigma) and PCBS (from Aldrich), which have a poly(vinyl amine) backbone with an ionic azo-dye chromophore as shown in Figure 2.1.1 were used as the NLO-active layer, while poly(allylamine hydrochloride) known as PAH (from Sigma) was used for the NLO-inactive layer. PCBS is benzoic acid, 5-[[4-[(ethenylamino)sulfonyl]phenyl]azo]-2-hydroxy-, monosodium salt, homopolymer (9Cl); Poly S-119 is 2-Naphthalenesulfonic acid, 6-hydroxy-5-[[4-[(1-methylethenyl)amino] sulfonyl]phenyl]azo]-, monosodium salt, homopolymer (9Cl); and PAH is 2-Propen-1-amine, hydrochloride, homopolymer (9Cl). The weight average molecular weight for PAH was \textasciitilde 70,000 g/mol, and no molecular weight values for the polyions were provided by the vendors. Solutions of these polymers ranged from approximately 1-10 mM with 0-1 M NaCl content, and pH was varied from 3-10. Variation of pH and NaCl affords control of number of ionized sites along the polymers as well as counterions in solution, allowing precise
Figure 2.1.1: Typical molecules used in ISAM film fabrication. Either PCBS or Poly S-119 anion chromophore is used with PAH cation to form an ISAM film.
control of layer thickness as discussed below. The values of pKa for PCBS, Poly S-119 and PAH are approximately 4.5, 0.5 and 8.7, respectively.

A first-approximation of the ISAM film growth is illustrated in Figure 2.1.2. The arrows represent a small fraction of the anionic chromophore sidegroups of the NLO active polyanion located at the layer interface. Also illustrated is the net chromophore orientation toward the substrate that will be addressed in Section 2.5. The cleaned, charged substrate is immersed in the polycation solution resulting in bonding of the polymer to the surface through coulombic attraction until the surface charge is reversed due to screening by the adsorbed polymer layer. The substrate is removed and rinsed in purified water, then immediately immersed in a polyanion solution. Again the surface charge is reversed, halting film deposition when the available sites are either all occupied by polyions or counterions, or are screened by interposed polymer. This process can be repeated indefinitely resulting in an (AB)_n bilayer structure utilized in this study. Each bilayer ranges in thickness from less than 0.5 nm up to 10 nm as measured by variable angle ellipsometry. The process could be modified to incorporate a wide variety of structures utilizing molecules of varying functionalities resulting in (ABAC)_n, (ABCDAB)_n, etc., with the only requirement being that adjacent layers possess opposite charge.

Physical characterization of ISAM films is of great interest across many areas of study as mentioned in Chapter 1, and has been proven to be quite difficult. Since the structure scale of ISAM films is far less than a wavelength of visible light, and due to the sensitive nature of organic material to X-rays, physical characterization by conventional means is limited. A primary focus of this study, in addition to developing an improved organic $\chi^{(2)}$ film, is to demonstrate the value of second-order nonlinear optical measurements in revealing the structure of ISAM films.
Figure 2.1.2: Illustration of ISAM film deposition modeled as discrete layers. (a) One monolayer of NLO-inactive polycation is adsorbed onto the surface of a negatively charged microscope slide, (b) a layer of the NLO-active anion is adsorbed onto the preceding polycation forming a single bilayer, and (c) the process can be continued for as many layers as desired.
2.2 Polyelectrolyte Adsorption

The adsorption of polyelectrolytes at the solid-solution interface is an area of extensive research, and is a complex and often counterintuitive phenomenon. Many models and theories exist which attempt to more thoroughly explain the phenomenon, but we will only explore the basic principles in order to understand the adsorption process. We consider electrolytic polymer molecules in a solvent, water in our case, and the effect of changing the concentration of counterions in solution. The models presented here exclude effects from parameters such as free volume and polymer composition, and are intended to give the reader an intuitive understanding of the conformation of polymers in ISAM films.

2.2.1 Adsorption of Uncharged Polymers

The conformation of polymer molecules in dilute solution is determined by a thermodynamic balance between the entropy and enthalpy of the polymer chains.\(^6\) As with any reaction, adsorption is spontaneous when the Gibbs free energy change

\[
\Delta G = \Delta H - T\Delta S
\]

is negative. The enthalpy of mixing is determined by the polymer-solvent interaction-energy parameter \(\chi\), the well-known Flory-Huggins parameter introduced by Flory in 1953,\(^61\) and the total number of polymer-solvent contacts as

\[
\chi = Z\left[\frac{\epsilon_{oo} - \frac{1}{2}(\epsilon_{pp} - \epsilon_{oo})}{kT}\right],
\]

where \(\epsilon\) is the interaction energy between polymer segments (\(p\)) and solvent molecules (\(o\)), and \(Z\) is the coordination number. In a good solvent (\(\chi < \chi'\)), the polymer chain will expand to increase the number of polymer-solvent contacts to an extent determined by the entropy of mixing. Likewise a poor solvent (\(\chi > \chi'\)) will cause the polymer to contract. At a solid-solution interface, either adsorption or depletion will occur, and the extent of these effects is a balance between solution parameters and the net enthalpy of adsorption parameter \(\chi_s\) as defined by Silberberg in 1968:\(^62\)

\[
\chi_s = \frac{1}{2}(Z - Z_s)\left[\frac{\epsilon_{oo} - (\epsilon_{pp} - \epsilon_{oo}) + \frac{1}{2}(\epsilon_{oo} + \epsilon_{pp})}{kT}\right],
\]
where \((s)\) denotes the interface surface, sometimes referred to as the subphase. Silberberg qualifies this parameter as a measurement of the mixing of a site in the subphase in contact with the adsorbant, which is assumed to be composed of unattached polymer segments. Adsorption occurs when \(\chi_s\) is greater than the critical value, \(\chi_{sc}\), which is determined only by the configurational entropy of the chain. These parameters affect the conformation of the adsorbed polymer which takes on a configuration often modeled by trains, loops and tails as illustrated in Figure 2.2.1.63 Trains are composed of adjacent polymer segments along the interface, loops are unbound portions of a polymer chain that extend into the bulk between two bonding sites, and tails are bonded to the interface at one end with the free end extending into the bulk. The extent to which adsorption occurs depends upon how interaction energies in eq. 2.2.3 change with increased adsorption.

Important from the argument presented thus far is that given the correct solution and interface parameters, adsorption is a spontaneous process which could be limited only by the supply of polymer segments in solution. Of course, in reality the polymer segments are attached to each other. When a polymer becomes entangled in the adsorption layer, its configurational entropy decreases thus becoming a potential adsorption-limiting factor. We will see from the following section how the process is limited in the case of ionic polymers.

Figure 2.2.1: Illustration of possible polymer conformations at the adsorption interface. Trains are adsorbed at the interface while tails and loops extend into the bulk phase and out from the adsorption interface.
2.2.2 Electric Double-Layer

When considering ionic solutions, one must consider the electric potential between the ions of the outermost bounded polymer layer, ions of the polymer in solution, and free counterions for both. A polyelectrolyte solution contains free ions of same charge, and free counterions of opposite charge. The concentration of each depends upon the pH and salt (NaCl) concentration of the solution. Further, the outermost layer of polyelectrolyte adsorbed onto the ISAM film is believed to contain free counterions which make the film electrically neutral when not in solution. A current topic of controversy is whether positive and negative free ions exist throughout the film, or are completely replaced by subsequent polyelectrolyte adsorption. Importantly, when considering adsorption of polyelectrolytes, one must consider all the ions at the solid-solution interface. This interface is not discrete, but varies in thickness depending largely upon the polymer conformation within the film and in the solution.

In order to understand the contribution of the electrolytes upon the adsorption process, consider the electric double-layer which consists of an inner region known as the Stern layer, which includes adsorbed ions, and a diffuse region in which ions are distributed according to the influence of electrical forces and thermal motion. The inner region modeled by Stern in 1924 considers the solid part of the interface to be impenetrable. When interpenetration into the “solid” phase occurs to a significant extent (greater than a few atoms), there is no longer a finite layer for which the Stern model applies. For this analysis, we will consider the entire interface to be diffuse.

Consider a flat, infinite, uniformly charged surface consisting of point charges which obey the Boltzmann distribution immersed in an electrolyte solution, with all ions having the same charge number in a solvent that influences the double-layer only through its dielectric constant. Let the surface electric potential be $\psi_0$ at a distance $x$ from a positively charged surface. Then,

\[
n_+ = n_0 \exp\left[-\frac{ze\psi}{kT}\right], \\
n_- = n_0 \exp\left[\frac{+ze\psi}{kT}\right],
\]

(2.2.4)
where \( n_o \) is the bulk concentration of each ionic species, \( e \) is the charge of an electron and where \( n_+, n_- \) are the number of positive and negative ions per unit volume at regions of \( \psi \) potential. It is important to point out that \( n_o \) is the concentration of ions of each charge, both attached to the polymer and free ions, so that there are \( n_o \) total negative ions and \( n_o \) total positive ions. Therefore, the net volume charge density \( \rho \) at regions of \( \psi \) potential is

\[
\rho = ze(n_+ - n_-)
\]

\[
= zen_0 \left\{ \exp \left[ -\frac{ze\psi}{kT} \right] - \exp \left[ \frac{+ze\psi}{kT} \right] \right\}.
\]

\[
= -2zen_0 \sinh\left( \frac{ze\psi}{kT} \right).
\]

Poisson’s equation for a flat double-layer is given by

\[
\frac{d^2\psi}{dx^2} = -\frac{\rho}{\varepsilon},
\]

where \( \varepsilon \) is the dielectric constant. Combination of eqs. 2.2.4 and 2.2.5 results in

\[
\frac{d^2\psi}{dx^2} = \frac{2zen_0}{\varepsilon} \sinh\left( \frac{ze\psi}{kT} \right).
\]

The solution of this expression, considering the boundary conditions \( \psi(x = 0) = \psi_0, \) and \( \psi = 0, \)
\[ d\psi/dx = 0 \text{ when } x = \infty, \] can be written in the form

\[
\psi = \frac{2kT}{ze} \ln \left( \frac{1 + \gamma \exp[-\kappa x]}{1 - \gamma \exp[-\kappa x]} \right)
\]

(2.2.8.a)

where

\[
\gamma = \frac{\exp[ze\psi_0/2kT] - 1}{\exp[ze\psi_0/2kT] + 1}
\]

(2.2.8.b)

and

\[
\kappa = \left( \frac{2e^2n_0z^2}{ekT} \right)^{1/2} = \left( \frac{2e^2N_Acz^2}{ekT} \right)^{1/2}
\]

(2.2.8.c)

where \( N_A \) is Avogadro’s number, and \( c \) is the molar concentration of ions of each species counting both free ions and ions attached to polymers. Thus, for a solution of an NLO-active polyanion, the electrolyte molar concentration as a function of measurable quantities is given by
\[ c \cong c_{\text{polyions}} + c_{\text{salt}} + 10^{-(14-pH)} \]  

(2.2.9)

The last term in equation 2.2.9 is the molar concentration of OH\(^-\) ions, the molar concentration of Cl\(^-\) ions is equal to \(c_{\text{salt}}\). Recall that \(c\) represents the molar concentration of electrolytes of one charge species, attached to a polymer or free in solution, and is equivalent for both species. It is customary to count the number of counterions to the surface interface, as is done in eq. 2.2.9. Alternately, the number of cations could be counted by counting \(c_{\text{polyions}}, c_{\text{salt}}\) and \(10^{pH}\) since the number of positive counterions attached to the polyanion in the solid state is given by \(c_{\text{polyions}}\). However, the polycations on the “surface” of the film would also have to be counted, so eq. 2.2.9 represents the simplest and most accurate method. Equation 2.2.9 does not account for possible negative counterions trapped just below the surface of the film, which has been measured to be at most equal to one third of number of polycations on the film surface\(^{67,68}\). The issue of trapped counterions is a center of debate and is still unresolved. This is why eq. 2.2.9 is given as an approximation, and is the more accurate of the two counting methods.

It is customary to refer to \(\kappa^{-l}\), the distance at which \(\psi = (1-1/e)\psi_0\), as the thickness of the diffuse part of the double-layer, or the Debye length. For the case when \(ze\psi_0/2kT \ll 1\), the Debye-Hückel approximation

\[
\exp\left[\frac{ze\psi_0}{2kT}\right] \approx 1 + \frac{ze\psi_0}{2kT}
\]

(2.2.10)

applies, and eq. 2.2.8 becomes

\[
\psi = \psi_0 \exp[-\kappa\chi]
\]

(2.2.11)

which shows that the potential decreases exponentially with distance from the charged surface. It is important to point out that the “diffuse part” of the double-layer represents the portion of a layer wherein the ions intermingle, while the ions of opposite charge are still attracted to the solid surface \(\kappa^{-l}\) distance away, and accounts for most of the layer thickness. Due to the assumptions of this model, it is most applicable for the initial layer, if we consider the ions attached to the polymer to be unhindered by the polymer backbone.
While this model does not consider physical impediment to the motion of the electrolytes, it does give an illustration of the formation of ISAM layers. For instance, for 1 mM aqueous solution of a symmetrical electrolyte at 25 °C where \( z = 1 \) for all electrolytes, eq. 2.2.8.c becomes

\[
\kappa = \left( 0.329 \times 10^{10} \text{ m}^{-1} \sqrt{\frac{\text{dm}^3}{\text{mol}}} \right) \cdot \sqrt{c}. \tag{2.2.12}
\]

A “symmetrical” electrolyte is defined as a symmetrical local distribution of electrolytes about the region being considered such that the ion concentration is the same for both regions. Equation 2.2.12 combined with equation 2.2.9 predicts that 1 mM repeat unit of polyanion solution with pH 7 and \( c_{salt} = 0 \) would result in an adsorbed diffuse layer thickness of 10 nm, while increasing \( c_{salt} \) to 1 mM would reduce the thickness to 3 nm.

Our films fabricated with solutions of similar electrolyte concentration result in film thickness ranging from less than 1 nm up to 10 nm bilayer, where film thickness increases with increased salt concentration. This is opposite of the prediction of the electric double-layer model. This illustrates that this model represents one of many mechanisms governing ISAM film deposition. More detailed modeling of ISAM layers would necessitate considering the effect of polymer loops and tails extending into the dipping solution, as well as the intermingling of the dipping solution polymers into the already adsorbed ISAM film. Important is the effect of electronic screening of adsorbed polymer ions by the polymer ions of opposite charge in the dipping solution.

### 2.2.3 Electrostatic Exclusion Volume

Utilization of this same model in the vicinity of an ionic group helps to explain why increased free ion concentration serves to increase adsorbed layer thickness. This model is also useful in considering the distance between ionic groups on the backbone of a polymer in solution, in addition to the enthalpy of adsorption \( \chi_s \) from eq. 2.2.3. Approximation of the interaction of double-layers around spherical particles introduced by B. Derjaguin is widely used in colloid science.\(^{65}\) Let’s consider the ionic group at the end of the chromophore attached to the
polymer backbone to be a sphere. Utilization of the Poisson-Boltzmann distribution for a spherical interface, the same boundary condition and the Debye-Hückel approximation, eq. 2.2.5 becomes\(^{64}\)

\[
\psi = \psi_0 \frac{a}{r} \exp[-\kappa(r-a)]
\]

(2.2.13)

where \(r\) is the distance away from the center of the sphere, and \(a\) is the radius of the sphere such that \(\psi(r=a) = \psi_0\). This model falls short in that the Debye-Hückel approximation is often not a good one in the treatment of small spheres (colloids for instance), and due to the fact that the ion concentration on the surface of the sphere (\(c=1\)) is not equal to the surrounding counterion concentration.

The electrostatic exclusion volume model is beneficial in illustrating the point that increased counterion concentration decreases the electronic exclusion zone, with radius \(\kappa^{-1}\), resulting in a less restricted polymer conformation and smaller root-mean-square end-to-end distance. With decreased electrostatic exclusion volume due to increased salt concentration, for instance, the polymer obtains more degrees of freedom, thus higher configurational entropy and more negative \(\Delta G\) which results in increased adsorption as well as more loopy polymer conformation. This can result not only in a thicker adsorbed layer due to increased diffusion layer thickness and increased polymer looping and dangling from that layer, but also greater interpenetration into the previously adsorbed layers due to the more loopy polymer conformation of previous layers and increased configurational entropy of the penetrating polymer chains. Therefore, for a polyelectrolyte, the thickness of the adsorbed layer is largely controlled by the two competing effects of electrostatic exclusion. While increased free counterion concentration increases the ability for polymer chains to intermingle and form thicker layers due to an increased electrostatic exclusion zone around the polymer sidechain ionic groups, it also serves to govern the thickness due to a macroscopic electronic screening illustrated by the diffuse double-layer model.
2.3 Experimental Evidence of ISAM Film Morphology

The morphology of ISAM films has been studied extensively over the past decade. Most studies have used the NLO-inactive polyanion poly(styrene sulfonic acid) known as PSS, along with PAH. Several measurement techniques have revealed the tendency for the polymer layers to interpenetrate the preceding layers. In addition, the process of ISAM film formation has been shown to exhibit a self-healing property unique to these films.

ISAM film formation has been shown to be governed by “kinetically hindered equilibrium.” When a polyanion layer, for instance, is completely adsorbed onto a preceding polycation layer, only a third to a half of the positive polycation bonding sites are neutralized by direct contact with negative polyanions. It is believed that a charge overcompensation occurs due to the non-adsorbed loops and tails dangling into the subphase, which is the solid-solution mixed phase where adsorption occurs. Although unbonded to positive polyions, the dangling anions serve to screen the preceding layer from other polyanions, and repel them from the surface. Utilization of atomic force microscopy (AFM) with a charged cantilever afforded the determination of the charge of the outermost layer of an ISAM film immersed NaCl solution. This method revealed a charge reversal on the film surface after each layer adsorption. Further, in-situ fluorescence measurements revealed that the films arrived at a dynamic equilibrium with the surrounding solution. Both of these findings are in agreement with the polyelectrolyte adsorption model presented in Section 2.2.2.

X-ray reflectivity measurements on PSS / PAH films have revealed useful information about the morphology of ISAM films. These measurements have shown that the surface roughness decreases with increased number of bilayers, revealing the self-healing nature of ISAM films. The root-mean-square (rms) roughness of the surface for the first layer reflects the surface roughness of the substrate, but the subsequent layers become increasingly smooth arriving at an equilibrium value of about 4 Å after 5 to 10 bilayers, depending upon the thickness of the bilayers. X-ray reflectivity measurements have also shown that the thickness of each bilayer follows a similar trend, illustrating that the layers are interpenetrated, rather than
discrete.\textsuperscript{68,71,72,73} The first bilayer is typically on the order of 7-15 Å, and subsequent layers become increasingly thick arriving at an equilibrium value ranging from 30-60 Å for these PSS / PAH ISAM films, with PAH typically accounts for roughly 15% of the bilayer thickness. In addition, the layer thickness increases with increased salt concentration of the dipping solutions.\textsuperscript{71,72,74} These experiments were performed prior to the effect of pH upon adsorption becoming well known, so pH was not reported except to say the solutions were “weakly acidic” in order to be below the pKa value of PAH (~8.7). Since the polyelectrolyte adsorption model presented in Section 2.2.2 predicts that increased salt concentration would decrease the bilayer thickness, it is believed that the thickness increase is due to increased interpenetration in accordance with the electrostatic exclusion volume model also presented in Section 2.2.2. To complicate the modeling of ISAM films even further, it is widely believed that the polymers from one layer intertwine with the preceding and subsequent 2 to 6 layers. These results also illustrate that, after the first few bilayers, each subsequent bilayer results in the addition of equivalent amounts of polymer. Although X-ray reflectivity measurements have not been performed on our films, absorption measurements in conjunction with ellipsometry measurements have been used to measure bilayer thickness and relative thickness of the anionic and cationic layers.

Additional morphological and mechanical properties of ISAM films are worthy of mention. Polar organic multilayer films typically exhibit \( C_{\infty v} \) symmetry.\textsuperscript{75,76} This symmetry is an infinite rotational symmetry about the axis normal to the film surface, with a noncentrosymmetry along that axis. This will be illustrated further in Chapter 3, and holds true for our films. Finally, 15° peel tests of pressure sensitive tape from an ISAM film bound to a poly(ethylene terephthalate) (PET) surface in combination with X-ray photoelectron spectroscopy (XPS) illustrated the physical robustness of ISAM films.\textsuperscript{73} Cohesive failure was observed in the PET substrate which XPS revealed on the post-test surface of the tape. A weak boundary layer, consisting of PET oligomers was removed from the PET substrate indicating that the ISAM assembly was at least as strong as the weak boundary layer.
2.4 Beyond the First-Approximation: A More Complete Picture

The thickness per bilayer as measured from the previous studies is actually the total film thickness increase due to the adsorption of an additional bilayer. Due to interpenetration, it follows that each adsorbed layer serves to increase the thickness of a few preceding layers, dependent upon the degree of interpenetration. When considering films with greater than 10 bilayers, it is safe to consider the bilayers discrete when evaluating the contribution of an adsorbed layer, while differentiating the bulk film behavior from the behavior at the film-substrate and film-air interfaces.

Figure 2.4.1 extends the first-approximation illustrated in Figure 2.1.2, giving a second-approximation of the film morphology by illustrating interpenetration without considering true polymer configuration, trapped ions or ionic attractions between the polymers. This figure serves to illustrate several of the well-known and commonly accepted morphological properties of ISAM films as previously discussed. The outermost layer is drawn smooth to illustrate the self-healing effect, and the remaining layers are drawn to illustrate the layer thickness increase of the first few layers as well as interpenetration. Each adsorbed layer exhibits the self-healing effect, but when a subsequent layer is adsorbed the dangling tails from the previous layer, activated by the dipping solution, are able to interpenetrate the adsorbing layer. It is commonly accepted that interpenetration occurs over a small number of layers depending upon layer thicknesses and morphologies as well as solution parameters, and most likely occurs toward the substrate more so than away. ISAM films are an ionically cross-linked network structure with trapped entanglements. In solution, a certain percentage of the ionic bonds at any given time are dynamically dissociating and re-associating, held in position by neighboring bonds and entanglements. This is why interpenetration away from the substrate is limited to dangling tails. Interpenetration toward the substrate is believed to be limited by film density reptation hindrances due to the networked structure. As a result, Figure 2.4.1 illustrates the approximately sinusoidally varying concentrations of ISAM films. While the interfaces are not discrete and interpenetration may occur over several layers, the existence of SHG suggests that the films have fuzzy interfaces that still allow for a net dipole orientation.
Figure 2.4.1: A second-approximation of ISAM film morphology. Interfaces are “fuzzy” rather than discrete resulting in a sinusoidally varying density of each material. The self-healing nature of ISAM films is illustrated, as well as single-layer interpenetration (interpenetration is likely more than one bilayer) and the tendency for the bilayers to increase in thickness over the first few bilayers.
Figure 2.4.2, obtained from ChemDraw Pro, illustrates the tendency of the NLO materials Poly S-119 and PCBS (Figure 2.1.1) to form coil structures across a small number of repeat units, and the tendency for PAH to form relatively straight segments across a small number of repeat units, thus allowing one to imagine a third-approximation of ISAM film morphology. PCBS and Poly S-119 demonstrate similar short-range structures, but only Poly S-119 is shown in the following figures since the biphenyl allows improved 3-D rendering. This diagram helps to illustrate the reason for the thickness difference between polyanion and polycation layers. Three-dimensional modeling of these structures using Chem3D Pro affords a picture of the conformation theses polymers may adopt, and should be treated only as illustrations. PAH, in the absence of external forces, prefers a 2-dimensional winding or wavy conformation that would be in the plane of the paper and could appear as a wave in Figure 2.4.2, with a “wave” radius of curvature of about 20 Å. Under the same conditions, Poly S-119 and PCBS prefer to form roughly a helical configuration with a helix inner radius of about 3 Å with the chromophore ends pointing away from the helix axis forming a helix outer radius of roughly 15 Å. Various views of three-dimensional representations of these are given for 19 repeat units of PAH in Figure 2.4.3, and 9 repeat units of Poly S-119 in Figures 2.4.4 through 2.4.6. These figures are intended to provide further intuitive appreciation of the overall polymer conformation.

These models and vantage points help to demonstrate the complexity of ISAM films. As with modeling light sometimes as a wave and other times as a particle, each ISAM model has a regime in which it accurately predicts behavior of film formation, and in combination, the set of models help to provide a better understanding of the morphology of ISAM films. The models presented here are not based solely upon the experimental evidence shown in this section, but are largely based upon the experience we have gained through nonlinear optical measurements of ISAM films. That experience will encompass the remainder of this thesis.
Figure 2.4.2: Illustration of short-range morphology of a 5 repeat-unit segment of Poly S-119 attached to PAH. Poly S-119 prefers a helical conformation with helix axis into the paper, while PAH prefers a slowly winding conformation in the plane of the paper.
Figure 2.4.3: Nine repeat units of PAH in the absence of external forces, illustrating tendency for short-range wavy conformation. The radius of curvature in (a) is approximately 20 Å. Only carbons and nitrogens are shown.
Figure 2.4.4: Nine repeat units of Poly S-119 at in the absence of external forces, showing short-range helical conformation. The helix axis is along z-axis which is into the paper. The inner circle of carbons is the polymer backbone spiraling into the paper with a helix inner radius of approximately 3 Å and outer radius of approximately 15 Å.
**Figure 2.4.5:** Poly S-119 from Figure 2.4.4 rotated 90° about the y-axis such that the helix axis is now horizontal. The depth of the spiral becomes evident upon careful inspection.
Figure 2.4.6: Poly S-119 from Figure 2.4.4 rotated 90° about the x-axis such that the helix axis is vertical.
2.5 Established Properties of ISAM Films for Nonlinear Optics Applications

In order to be classified as a “good” $\chi^{(2)}$ film, in addition to possessing the required noncentrosymmetry and mechanical properties, the following requirements should be met. Film thickness growth must scale linearly with the number of adsorbed layers, and the intensity of the second harmonic generation (SHG) must scale quadratically with both the incident fundamental light as well as with the number of adsorbed chromophore layers. The first requirement is a necessary element of reproducibility, and the second requirement follows the definition of a second-order NLO phenomenon as illustrated in eq. 1.1.4. The third requirement stems from the relation that intensity, which is the measured quantity, is equal to the square of the electric field strength, which grows linearly with the number of chromophores encountered by the fundamental light. These issues will be addressed in detail in Chapter 3.

ISAM films were first demonstrated to possess these required properties by Heflin and co-workers in 1997, utilizing Poly S-119 in conjunction with PAH. Quadratic growth of SHG as a function of the number of layers was observed up to the maximum of 100 deposited layers with no indication of leveling off. Later, films incorporating Poly S-119 or PCBS along with PAH were shown to be thermally stable for 20 °C beyond the glass transition temperature, which is about 130 °C. Further, experiments conducted up to 250 °C showed that the only loss in SHG was due to chromophore degradation. In addition, these films have been shown to form completely adsorbed layers in less than one minute. Attempts by other groups had failed to produce ISAM films that exhibit these properties, generally exhibiting decay of SHG after 5 bilayers. We believe this is due to the choice of polycation (evidence for this claim will be presented in Section 3.4.3), as well as the method of film fabrication. More recently, Roberts and co-workers have shown quadratic dependence on the number of layers until approximately 30 bilayers, when the SHG begins to decay. The technique incorporated for those films required single layer deposition times of 120 minutes for the best films.

It is interesting to note that “capping” studies performed on our films showed that “capped” films (with PAH as outer layer) consistently exhibit lower SHG than uncapped films (with the
NLO polyanion as the outer layer.\textsuperscript{86} This suggests that the outer chromophores of uncapped films are oriented more towards the substrate than capped films due to the ionic portion of the adsorption process, or that a sufficient amount of unadsorbed tails interpenetrate the capping layer causing a reduction in net orientation.

It is well established that film thickness is proportional to absorbance, so absorbance is commonly used to show film growth due to the ease of measurement. Confirmation of this claim will be given in Chapter 3. We have shown that the bilayer thickness can be controlled by variation of the pH and ionic strength of the immersion solutions.\textsuperscript{87,88} We have also shown that the free ion concentration in solution is the determining factor for film thickness. For example, in a polyanion solution, increased $H^+$ or $Na^+$ ion concentrations (through lowered pH or added NaCl) provide greater electrostatic screening between neighboring charges on the polyanion. This allows increased interpenetration as well as greater curvature of the polymer backbone such that an increased fraction of the polymer segments adsorbs as loops, resulting in a thicker adsorbed layer.

The effect of increased ionic strength is shown in Figure 2.5.1 where the thickness per bilayer is shown as a function of pH and NaCl concentration for Poly S-119 / PAH ISAM films. It is seen that lowered anion pH and increased NaCl concentration dramatically increase the bilayer thickness. Although the SHG produced by these films increases with increased bilayer thickness, it does so much less rapidly. As a result, $\chi^{(2)}$ decreases with decreased pH and increased salt concentration, as shown in Figure 2.5.2. Since increased bilayer thickness corresponds to decreases $\chi^{(2)}$, this indicates that not all of the adsorbed chromophores contribute equally to the SHG, otherwise $\chi^{(2)}$ would remain constant. Rather, $\chi^{(2)}$ is determined primarily from the chromophores at the “fuzzy” monolayer interfaces. Those chromophores within the “bulk” of an individual layer have essentially random orientations, as illustrated in Figure 2.1.2.

Due to the nature of the formation of ISAM films utilizing two polymers, the NLO-active polyelectrolyte must have chromophores oriented in opposite directions in order to provide binding to the preceding and to the subsequent oppositely charged layers. This is schematically illustrated in Figure 2.1.2. The opposing dipole orientations cancel one another and lead to an
overall reduction in the $\chi^{(2)}$ of the film. Thus, polyelectrolyte-based ISAM films suffer from lack of orientation of chromophores within the bulk of a monolayer and partial cancellation of the preferentially oriented chromophores at the lower interface by chromophores at the upper interface. This thesis is devoted to further elucidation of and development of approaches to overcome drawbacks of ISAM films.
Figure 2.5.1: Bilayer thickness as a function of pH and salt concentration of the immersion solutions for Poly S-119 / PAH ISAM films.
Figure 2.5.2: $\chi^{(2)}$ as a function of solution parameters. When compared with Figure 2.5.1, it is evident that $\chi^{(2)}$ decreases with increasing thickness per bilayer.


The primary goal of this work is to develop approaches to increase the second-order susceptibility $\chi^{(2)}$ of ISAM films. $\chi^{(2)}$ is determined by second harmonic generation (SHG) measurements in conjunction with film thickness data. SHG measurements are also utilized to determine the average chromophore orientation within the film. The films considered in this chapter represent an extension of previous work done by this laboratory, and consider the effects of variation of pH of the polycation dipping solution. Variation of the pH controls both the percent ionization of the polyions as well as the free ion concentration in the solution.
3.1 Second Harmonic Generation Measurement Apparatus

The experimental apparatus used for SHG measurements is shown in Figure 3.1.1. The fundamental beam incident upon the sample is provided by a Spectra Physics Quanta-Ray GCR-130 Q-switched Nd:YAG 10 Hz pulsed laser with a 15 ns pulse width. The beam is linearly polarized with a wavelength of 1064 nm (infrared) and a pulse energy of 500 mJ. When a fundamental wavelength other than 1064 nm is desired, an optical parametric oscillator (OPO) is pumped by the third harmonic of the laser which is generated by a pair of inline second harmonic and sum-frequency crystals. This process affords the ability to select a single wavelength from a spectrum ranging from 400 nm to 2500 nm, and was utilized in previous studies in this lab on Poly S-119. It is preferable to utilize the fundamental beam whenever possible as the OPO produces a non-Gaussian and poorly focusing beam which complicates some of the calculations that will be presented later in this chapter. The direction of beam propagation is considered the z-axis by convention, and the Cartesian coordinate system in the vicinity of the sample is shown in the “sample stage” box. This will be the convention used throughout this thesis unless specifically noted otherwise, and optical elements are counted in ascending order along the beam propagation path.

The hypotenuse face of the 45° prism immediately following the laser (i.e.: the first prism) acts as a beam splitter which reflects approximately 4% of the beam (~20 mJ). Conventional beam splitters do not suffice as the reflective coating is quickly destroyed; non-coated beam splitters result in a backside reflection that cannot be completely separated from the front side reflection; and absorbing media that alleviate the backside reflection suffer from thermal cracking within seconds. The glass prism does not produce a reflection in line with the front side reflection, and absorbs negligible energy from the beam. Back reflection into the laser cavity is not a danger as long as the beam is incident on the far half of the hypotenuse face, as drawn. The beam dump gathers the primary transmitted beam, and the weak secondary reflections are gathered by black containment walls. Next, an array of energy reduction filters of various magnitudes is utilized to regulate the maximum energy incident upon the sample, usually about 1.7 mJ, and the second glass prism directs the s-polarized beam to the analysis portion of the
**Figure 3.1.1:** Experimental apparatus for measurement of second harmonic generation (SHG) in thin films. A Q-switched Nd:YAG pulsed laser provides the fundamental beam. A photodiode and a photomultiplier tube collect reference and SHG signal data, respectively. Data are collected and processed by a CAMAC crate interfaced with a PC.
optical setup. A pair of Glan-Taylor polarizers is used to form a three-polarizer intensity selector in conjunction with the incident s-polarized light. The second polarizer determines the polarization of the beam incident upon the sample, and the first polarizer determines the intensity of that beam. The long-pass filter eliminates any SHG produced by preceding elements. In the setup shown, only the Glan-Taylor polarizers might produce SHG, but some experiments require the inclusion of a half-wave plate which produces significant SHG. A fraction of the beam is then diverted via a microscope-slide beam splitter to a large area photodiode (PD) used to measure the reference intensity. The remaining beam is focused onto the sample where the second harmonic is generated. It is well established that the shape of the generated beam matches the shape of the incident beam.\(^\text{89}\) Both beams are recollimated by the collimating lens, and a band-pass filter eliminates the fundamental beam. Finally, a spike filter centered about the second harmonic frequency eliminates all light but the second harmonic, which is then collected by an RCA 8550 large-area photo-multiplier tube (PMT) powered by a Bertran 230-03-R high voltage power supply operating at 1.7 kV.

Data from the photodiode and PMT are sent through a LeCroy 2249W analog to digital converter (ADC) and collected by a KineticSystems 1510-P2C CAMAC minicrate controlled by a KineticSystems 3922-Z1B parallel bus crate controller. Gating of the signal is triggered by the fundamental beam of the Nd:YAG laser and generated by a LeCroy 222 dual gate generator. The signal is passed from the CAMAC to an IBM PC via a 16-bit DMA KineticSystems 2927-Z1A interface. The CAMAC is controlled by an in-house program written in Borland C. Data are analyzed by a combination of Tablecurve 2D v3 (Poly Software International), Origin v5.0 (Microcal), Psi-Plot v4.56 (Jandel Scientific), Mathematica v4.0 (Wolfram Research), and Microsoft Excel 97.

The sample is mounted on a stage consisting of 3 Aerotech stepper-motor linear positioning stages affording 2 \(\mu\)m resolution in all coordinate axes, along with one Aerotech stepper-motor rotation stage affording 1/27° positioning resolution about the \(x\)-axis. A Joerger SMC-R motor controller allows simultaneous control of 2 motors, and is operated by the in-house program via the CAMAC.
Beam energy measurements are taken with an Ophir nova laser power / energy monitor utilizing either a thermopile absorber for high energies (50 mJ to 10 J) or a pyroelectric absorber for low energies (20 µJ to 10 mJ). CAMAC calibration is carried out via a Tektronic TDS 380 digital real-time oscilloscope.

3.2 Experimental Conditions for Second Harmonic Generation

A firm understanding of the relationship between the sample and the incident beam is essential for the analysis presented in this chapter. From the focusing lens forward, the plane of incidence is in the $y$-$z$-plane due to the orientation of the sample, which is perpendicular to the $y$-$z$-plane and rotates about the $x$-axis. Hence, by definition, the light is now p-polarized. It is advantageous to think of polarization as the orientation of the electric-field polarization vector with respect to the film or substrate, rather than with respect to the plane of incidence. This perspective affords a more intuitive picture of the orientation of the polarization with respect to the NLO dipoles within the film, as illustrated in Figure 3.2.1.a for s- and p-polarizations. Accordingly, s-polarization describes the case where the polarization vector is parallel to the $x$-axis and would result in no coupling with chromophore dipoles perpendicular to the substrate for all angles of incidence of the beam with the substrate. Similarly, p-polarization describes the case where the electric field vector has maximum coupling with dipoles perpendicular to the interface where the degree of coupling is dependent upon the incident angle. For non-perpendicular average dipole orientation, which is the case in these films, the ratio of coupling for s-polarized and p-polarized light affords information about the average tilt angle of dipoles within the film. This will be described in detail in Section 3.3.3. Furthermore, the incident angle $\theta$ is given as the angle between the beam and the substrate normal as illustrated in Figure 3.2.1.b. The coupling angle $\alpha$ between the polarization vector and the chromophores differs from $\theta$ due to refraction at the air-film interface and can be calculated using Snell’s law:

$$\alpha = \arcsin \left( \frac{n_{air} \sin \theta}{n_{film}} \right).$$

(3.2.1)
The index of air is approximately 1.0 the index of refraction at $\lambda = 1064$ nm for PCBS / PAH ISAM films is typically ~1.7, as measured by SCI FilmTek2000. An incident angle of 45° thus corresponds to a coupling angle of ~25°, for instance. In addition, it is worthwhile to mention that an interface (e.g. air-film, film-glass) is inherently noncentrosymmetric and accordingly generates some amount of second harmonic.\textsuperscript{91,92}

In order to understand the criteria for choosing a focusing lens, we must first consider the nature of a Gaussian beam at a focus as illustrated in Figure 3.2.2.\textsuperscript{93} The intensity profile at any given value of $z$ is Gaussian, and the thick hyperbolic lines represent the distance away from the $z$-axis where the electric field amplitude is reduced by a factor of $1/e$, and are equidistant from the axis at any given value of $z$ in 3-D space such that a hyperboloid is formed about the $z$-axis. The inscribed circle in any $x$-$y$-plane is known as the “spot” characterized by the “spot radius” $\omega(z)$. The beam “waist” radius $\omega_0$ is the spot radius at $z = 0$, and is related to the spot radius at arbitrary $z$ by

$$\omega^2(z) = \omega_0^2 \left(1 + \frac{z^2}{z_0^2}\right),$$

such that the Rayleigh range $z_0$ is a measure of the beam divergence and is defined as the value of $z$ where

$$\omega(z = z_0) = \sqrt{2} \omega_0.$$

The hyperbolas in Figure 3.2.2 asymptotically approach the paraxial rays, represented by dashed lines, sufficiently far from the focus. Accordingly, paraxial rays may be used to predict the focal point of a lens in a parallel beam, but the nature of the beam within the Gaussian focus is described by the Rayleigh range and beam waist radius which are related by

$$z_0 = \frac{\pi \omega_0^2 n}{\lambda},$$
Figure 3.2.1: Schematic representation of beam propagation in a sample. The perspective is along the length of the sample, looking across the optical table. (a) s-polarized light has no coupling with a chromophore c normal to the substrate, while the degree of coupling with p-polarized light is a function of incident angle $\theta$. (b) Coupling angle $\alpha$ is related to the incident angle by Snell’s law. The pathlength of the beam (at angle $\beta$) through the substrate is governed by the relatively thick glass substrate, and can be determined by Snell’s law and the Pythagorean theorem.
where $\lambda$ is the wavelength and $n$ is the index of refraction of the propagation medium. The waist radius of the focus $\omega_{0,F}$ with respect to the waist radius of an incident beam $\omega_{0,L}$ as a function of the focal length $f$ of the lens is given by

$$\frac{\omega_{0,F}}{\omega_{0,L}} = \frac{f}{z_{0,L}} \sqrt{1 + \left(\frac{f}{z_{0,L}}\right)^2}. \tag{3.2.5}$$

Realizing $z_{0,L} \gg f$ for the laser beam, and utilizing the relationship in eq. 3.2.4, we find

$$\omega_{0,F} \approx \left(\frac{\lambda}{\pi n}\right) \frac{f}{\omega_{0,L}}, \tag{3.2.6}$$

and

$$z_{0,F} \approx \left(\frac{\pi n}{\lambda}\right) \frac{f^2}{\omega_{0,L}^2}. \tag{3.2.7}$$

**Figure 3.2.2:** Focus of a Gaussian beam characterized by the waist radius $\omega_0 = \omega(z=0)$ and the Rayleigh range $z_0$. The hyperbolas mark the distance from the $z$-axis at which the energy drops by a factor of $1/e$, and asymptotically approach the paraxial rays denoted by the dashed lines.
These relationships afford the information necessary to estimate the choice of focal length. SHG is quadratically dependent upon the intensity of the fundamental beam, which increases with decreased beam waist radius. The maximum waist size is dictated by the sensitivity of the PMT. Conversely, the minimum waist size is partially dictated by the damage threshold of the film. In addition, the spot size should be sufficiently large so the SHG is an average over relatively large number of chromophores since the chromophores in an ISAM film are not all parallel to one another. Another consideration for minimum focal length is that the Rayleigh range should be large enough such that the SHG remains constant along a sufficient portion of the \( z \)-axis. This allows for any mounting or substrate variations as well as any \( z \)-translation that may occur due to other translations. The largest factor is rotation about the \( x \)-axis, which brings the front face of the sample closer to the focusing lens and the back face further away from the focusing lens. This results in an optical pathlength (\( OPL \)) given by

\[
OPL = \frac{n_{glass} t_{glass}}{\cos \beta},
\]

where the glass thickness \( t_{glass} = 1 \) mm, and \( \beta \) is given by eq. 3.2.1 with \( n_{film} \) and \( \alpha \) replaced by \( n_{glass} \) and \( \beta \). Since the film is 5-7 orders of magnitude thinner than the substrate, it has negligible effect. Combination of these equations results in:

\[
OPL = n_{glass} t_{glass} \left[ 1 - \frac{\sin^2 \theta}{n_{glass}^2} \right]^{-\frac{1}{2}}.
\]

The index of glass is roughly 1.5, therefore the longest optical pathlength is the limit of \( OPL \) as \( \theta \) approaches 90°, which is 2.0 mm. In practice, most measurements are taken up to 60° which corresponds to \( OPL = 1.8 \) mm. Therefore, a Rayleigh range that corresponds to 2.5 mm of constant SHG intensity along the beam path would leave a comfortable margin of safety.

The beam characteristics of the focus of a \( f = 450 \) mm lens were determined with a \( z \)-scan in the vicinity of the focus and an \( x-y \)-scan at the center of the focus. Utilizing the PCBS / PAH film reference standard at roughly 46° tilt angle, and scanning along the \( z \)-axis, the intensity profile of the beam along the \( z \)-axis was determined, and is shown in Figure 3.2.3. The reference standard is a 5 bilayer, 46 nm thick film fabricated with a 10 mM solution of PCBS at pH 7, and
a 10 mM solution of PAH at pH 10. Since the reference standard has film on both sides, the intensity of the SHG will remain constant only as long as the fundamental beam has similar $x$-$y$-intensity profiles on each side of the substrate. The reason this slide is used as the reference standard will be discussed Section 3.4. It is no accident that the shape in Figure 3.2.3 resembles the hyperbolas in Figure 3.2.2 since the intensity profile of the beam becomes more spread out with increasing distance from the focus as represented by the distance between the hyperbolas for any given value of $z$.

The results shown in Figure 3.2.3 reveal that the SHG remains relatively constant for a 1 mm translation along the beam path in both positive and negative $z$-directions. Therefore, the SHG remains relatively constant for $[2.0 \text{ mm} + OPL(\theta = 46^\circ)] \approx 3.7 \text{ mm}$ along the beam path, and satisfies the condition for minimum lens focal length. Next, an $x$-$y$ intensity scan of the fundamental beam was performed at the beam waist utilizing a 25 $\mu$m pinhole and is shown in Figure 3.2.4. The horizontal and vertical scans are along the $x$- and $y$-axes, respectively. The small shoulder on the far side of the Gaussian surface is an artifact of the pinhole, and rotates position in accordance with rotation of the pinhole. From this scan, the waist radius is estimated to be 30 $\mu$m. As will be shown in the Section 3.4, this spot size is large enough to produce an SHG representative of the average SHG of the chromophores.
Figure 3.2.3: SHG intensity scan of the beam along the z-axis in the vicinity of the focus of a $f = 450$ mm lens, utilizing the double-sided PCBS / PAH reference standard, tilted at 46°. The intensity of the SHG will remain constant as long as the x-y-intensity profile of the fundamental beam is the similar on both sides of the sample. Since the intensity remains constant for ±1.0 mm on either side of the sample, and the beam travels ~1.7 mm within the sample, the “focus length” is ~3.7 mm.
Figure 3.2.4: Intensity scan of the fundamental beam in the $x$-$y$ plane at the middle of the focus of a $f = 450$ mm lens, utilizing a 25 µm pinhole. The small shoulder at rear of the Gaussian surface is an artifact of the pinhole. The beam waist radius is approximately 30 µm.
3.3 SHG Measurement Techniques and Determination of $\chi^{(2)}$

The second-order nonlinear optical susceptibility $\chi^{(2)}$ cannot be easily determined in an absolute manner simply from the relationship between the intensity of the second harmonic generation $I_{2\omega}$ and the incident fundamental pump beam intensity $I_{\omega}$. For a well collimated pump beam incident upon a lossless medium (non-absorbent at both fundamental and second harmonic wavelengths) with a wave vector mismatch, the second harmonic intensity may be expressed as:

$$I_{2\omega} \propto (l_c \chi^{(2)}_{\text{eff}})^2 \sin^2 \left( \frac{\pi l}{2l_c} \right) I_{\omega}^2,$$

(3.3.1)

where $l$ is the physical pathlength over which the beam must traverse (as opposed to the optical pathlength) and is given by

$$l = \frac{t_{\text{film}}}{\cos \alpha} = t_{\text{film}} \left[ 1 - \frac{\sin^2 \theta}{n_{\text{film}}^2} \right]^{1/2},$$

(3.3.2)

and $l_c$ is the coherence length of the material and is given by

$$l_c = \frac{\pi}{\Delta k},$$

(3.3.3)

where $\Delta k$ is the wave vector mismatch within the sample given by

$$\Delta k = 2k_1 - k_2 \propto 2n_i \omega_i - n_2 \omega_2$$

(3.3.4)

for second harmonic generation, where $n_i$ and $k_i$ are the refractive index and wave vector for the $i^{\text{th}}$ harmonic at frequency $\omega_i$. The case where $\Delta k = 0$ is known as phase matching. For second harmonic generation, this would require that $n(\omega_1) = n(2\omega_1)$ which is not typically true due to dispersion.

The difficulty in determination of $\chi^{(2)}$ is imbedded in the proportionality constant of eq. 3.3.1. This constant contains information about many parameters including the beam shape, beam energy, laser modes, intensity profile and waist radius. The experimental considerations are monumental, and performing such a measurement on a regular basis is simply not feasible. A few absolute determinations of the $\chi^{(2)}$ have been made for quartz. Therefore, eq. 3.3.1 affords the ability to determine the relation between the $\chi^{(2)}$ of quartz and that of any material, as long as
the beam properties are the same, or in other words, as long as both experiments are performed in conjunction. As will be discussed later in Section 3.3.1, the quartz measurement is tedious, so we choose a reference standard that is compared to quartz during one experiment. This reference standard becomes the material with known $\chi^{(2)}$ for subsequent experiments on materials, and is valid as long as the subsequent experiment is performed at the same wavelength as the original reference standard experiment.

The final aspect of eq. 3.3.1 that must be explored in order to determine the value of $\chi^{(2)}$ important for electro-optic application is the effective second-order nonlinear optical susceptibility $\chi^{(2)}_{\text{eff}}$. The effective $\chi^{(2)}$ is a sort of sum of all the elements of the $\chi^{(2)}_{ijk}$ tensor that contribute to the SHG. If the frequencies of the optical waves do not fall within the resonant spectrum of the nonlinear medium, Kleinman symmetry can be used to relate components of the nonlinear susceptibility$^{89}$. Under Kleinman symmetry, dispersion effects are considered minimal and the tensor elements of the nonlinear susceptibility are considered to be independent of the frequency. Accordingly, the $\chi^{(2)}$ tensor may be written as a 3x6 matrix, so that the second-order polarization field is described as

$$
\begin{pmatrix}
P_x(2\omega) \\
P_y(2\omega) \\
P_z(2\omega)
\end{pmatrix} =
\begin{bmatrix}
\chi^{(2)}_{11} & \chi^{(2)}_{12} & \chi^{(2)}_{13} & \chi^{(2)}_{14} & \chi^{(2)}_{15} & \chi^{(2)}_{16} \\
\chi^{(2)}_{21} & \chi^{(2)}_{22} & \chi^{(2)}_{23} & \chi^{(2)}_{24} & \chi^{(2)}_{25} & \chi^{(2)}_{26} \\
\chi^{(2)}_{31} & \chi^{(2)}_{32} & \chi^{(2)}_{33} & \chi^{(2)}_{34} & \chi^{(2)}_{35} & \chi^{(2)}_{36}
\end{bmatrix}
\begin{bmatrix}
E_x^2(\omega) \\
E_y^2(\omega) \\
E_z^2(\omega) \\
2E_y(\omega)E_z(\omega) \\
2E_x(\omega)E_z(\omega) \\
2E_x(\omega)E_y(\omega)
\end{bmatrix},
$$

(3.3.5)

using the contracted notation defined in Section 1.2. The $C_{xy}$ crystal structure results in a reduction of the tensor in eq. 3.3.5 to

$$
\begin{pmatrix}
P_x(2\omega) \\
P_y(2\omega) \\
P_z(2\omega)
\end{pmatrix} =
\begin{bmatrix}
0 & 0 & 0 & 0 & \chi^{(2)}_{xx} & 0 \\
0 & 0 & 0 & \chi^{(2)}_{yy} & 0 & 0 \\
\chi^{(2)}_{xx} & \chi^{(2)}_{yy} & \chi^{(2)}_{zz} & 0 & 0 & 0
\end{bmatrix}
\begin{bmatrix}
E_x^2(\omega) \\
E_y^2(\omega) \\
E_z^2(\omega) \\
2E_y(\omega)E_z(\omega) \\
2E_x(\omega)E_z(\omega) \\
2E_x(\omega)E_y(\omega)
\end{bmatrix},
$$

(3.3.6)
Furthermore, Kleinman symmetry allows us to permute input and output fields, so that
\[ \chi_{xx} = \chi_{xy} = \chi_{zx} = \chi_{zy} \quad . \tag{3.3.7} \]

For an arbitrary incident electric field, this results in the polarization field
\[
\bar{P}(2\omega) = \begin{pmatrix}
2E_x E_z \chi_{xzx}^{(2)} \\
2E_y E_z \chi_{zxx}^{(2)} \\
\chi_{xx}^{(2)} (E_x^2 + E_y^2) + \chi_{zz}^{(2)} E_z^2
\end{pmatrix} . \tag{3.3.8}
\]

The convention for the coordinate system for \( \chi_{ijk}^{(2)} \) is relative to the substrate, and is illustrated in Figure 3.3.1.a which is a further look into the film elaborating on Figure 3.2.1. The angle \( \alpha \) is related to the incident angle between the beam and substrate by eq. 3.2.1. As illustrated, the incident electric field for p- and s-polarized beams, respectively, may be written as
\[
\bar{E}^p(\omega) = (E_\omega \cos \alpha, 0, E_\omega \sin \alpha) \quad \text{(3.3.9.a)}
\]
\[
\bar{E}^s(\omega) = (0, E_\omega, 0) \quad \text{(3.3.9.b)}
\]

These incident fields produce the polarization fields
\[
\bar{P}^p(2\omega) = \begin{pmatrix}
2\chi_{xzx}^{(2)} \sin \alpha \cos \alpha \\
0 \\
\chi_{xx}^{(2)} \cos^2 \alpha + \chi_{zz}^{(2)} \sin^2 \alpha
\end{pmatrix} E_\omega^2 \tag{3.3.10}
\]
\[
\bar{P}^s(2\omega) = \begin{pmatrix}
0 \\
0 \\
\chi_{zx}^{(2)}
\end{pmatrix} E_\omega^2 \tag{3.3.11}
\]

To determine the p-polarized intensity, we take
\[
I = (\bar{P} \cdot \hat{p})^2 \quad , \tag{3.3.12}
\]
where
\[
\hat{p} = (\cos \alpha, 0, \sin \alpha) \quad . \tag{3.3.13}
\]

The intensities of p-polarized SHG from p- and s-polarized fundamental beams may then be expressed as
\[
I_{2\omega}^{p\rightarrow p} = (3 \chi_{xzx}^{(2)} \sin \alpha \cos^2 \alpha + \chi_{zzz}^{(2)} \sin^3 \alpha)^2 E_\omega^4 \]
\[
I_{2\omega}^{s\rightarrow p} = (\chi_{zx}^{(2)} \sin \alpha)^2 E_\omega^4 \quad . \tag{3.3.14}
\]
Figure 3.3.1: Geometry and coordinate system for $\chi^{(2)}_{ijk}$ and the polarization calculation. Coupling angle $\alpha$ is related to incident angle $\theta$ as in Figure 3.2.1. (a) p-polarized electric field has $x$ and $z$ components only, and s-polarized electric field is composed of $y$ component only. (b) Chromophore tilt angle with respect to the substrate. The molecular hyperpolarizability is nonzero only along $\xi$ axis. The molecules are oriented with average pitch angle $\psi$ to film $z$-axis and azimuthal angle $\phi$. 
For SHG experiments, only $I_{2\omega}^{p\rightarrow p}$ is typically measured, so the effective $\chi^{(2)}$ is related to the $\chi^{(2)}$ tensor as

$$\chi_{\text{eff}}^{(2), p\rightarrow p} = 3\chi^{(2)}_{zzz} \sin \alpha \cos^2 \alpha + \chi^{(2)}_{zzz} \sin^3 \alpha .$$  \hspace{1cm} (3.3.15)

The final step is to establish the relationship between $\chi^{(2)}_{zzz}$ and $\chi^{(2)}_{zzz}$. This can be done by performing a tilt angle measurement, described later in this chapter, which compares $I_{2\omega}^{p\rightarrow p}$ to $I_{2\omega}^{x\rightarrow p}$ and affords calculation of $\chi^{(2)}_{zzz} / \chi^{(2)}_{zzz}$ for films of a given type, which then can be used to convert $\chi^{(2)}_{zzz}$ to $\chi^{(2)}_{zzz}$. Due to the geometry of a waveguide, the important element of the $\chi^{(2)}$ tensor is $\chi^{(2)}_{zzz}$, so it is the value that will be reported. The purpose of the remainder of this section is to complete the steps necessary for the determination of $\chi^{(2)}_{zzz}$ for the films presented in this thesis.

### 3.3.1 Quartz Measurement and Maker Fringes

The earliest technique of measuring SHG was introduced by P. D. Maker in 1962,\(^95\) and is now known as the Maker fringe technique.\(^96\) Eq. 3.3.1 reveals the nature of Maker fringes, which come about due to wave vector mismatching in the medium. Maxima of these fringes occur when the argument of the sine function is

$$\frac{2l}{l_c} = \frac{2n+1}{2} \pi$$  \hspace{1cm} (3.3.16)

for any integer $n$, which occurs when

$$l = (2n+1)l_c .$$  \hspace{1cm} (3.3.17)

At the maxima, eq. 3.3.1 reveals that the intensity of the second harmonic is given by

$$I_{2\omega} \propto (l_c \chi^{(2)}_{\text{eff}})^2 .$$  \hspace{1cm} (3.3.18)

A $z$-cut quartz wedge with wedge angle $\gamma \sim 1^\circ$ was used to determine $\chi^{(2)}_{\text{eff}}$ of the reference standard. The wedge was placed in the beam path such that the beam was normal to the wedge, and translation along the $y$-axis resulted in increased physical pathlength through the wedge.
The fundamental beam polarization was along the z-axis of the quartz wedge. The change in physical pathlength $\delta l$ due to a translation $\delta y$ is given by the equation

$$\delta l = \delta y \tan \gamma .$$  

(3.3.19)

The result of this measurement is shown in Figure 3.3.2. Sufficient energy of the incoming beam (~1.7 mJ) was required in order to produce a successful measurement on the reference standard to be compared to this quartz measurement. The SHG intensity shown is the result of calculations accounting for the filters that were placed between the sample and the PMT. The fit to the data reveals the negligible resultant offset of $6 \times 10^5$ a.u., as well as the proportionality constant $8.215^2$ and a phase offset given by the fit parameter $b$. The fit equation in Figure 3.3.2 is equation 3.3.1 using an effective coherence length $y_c$ which is related to $l_c$ by equation 3.3.19 with $\delta l$ and $\delta y$ replaced with $l_c$ and $y_c$. Using the well established coherence length for quartz, $l_c = 22.4 \, \mu m$, we find the wedge angle $\gamma = 1.21^\circ$. Importantly, we find that SHG intensity for quartz is $I_{2\omega_{\text{quartz}}} = 7.60 \times 10^7$ a.u. for this experimental setup.
Figure 3.3.2: Y- scan of a quartz wedge used to determine $\chi_{\text{eff}}^{(2)}$ of the reference standard. The second harmonic intensity maxima are $I_{2\omega,\text{quartz}} = 7.60 \times 10^7$ a.u. for this experimental setup.
3.3.2 ISAM Film Measurement and Interference Fringes

In this section, we will explore a technique similar to the maker fringe technique, but first we must consider the nuances of thin film measurements. The coherence length of ISAM films is typically on the order of tens of microns, while the thickness of ISAM films is typically less than 100 nm. For the limit where \( l \ll l_c \), eq. 3.3.1 becomes

\[
I_{2\omega} \propto \frac{\pi}{2} l_L \rho^{(2)}
\]

so that the second harmonic intensity should grow quadratically with film thickness. This is a result that many ISAM films fabricated by other groups have failed to obey, and was first demonstrated by our research group in 1997 by utilizing Poly S-119 in conjunction with PAH.\(^9^7\)

This expression for ISAM films may be divided by eq. 3.3.18 for quartz to obtain the relation

\[
\frac{\chi_L^{(2),\text{std}}}{\chi_L^{(2),\text{quartz}}} = \frac{2l_c,\text{quartz}}{\pi l_L} \sqrt{\frac{I_{2\omega,\text{std}}}{I_{2\omega,\text{quartz}}}},
\]

(3.3.21)

where subscripts \( \text{std}, \text{quartz} \) denote the reference standard film and the quartz wedge. This allows absolute determination of \( \chi^{(2)} \) of a reference ISAM film by comparing its SHG intensity maximum to that of quartz.

Another consideration is the effect of absorption of the second harmonic wavelength upon the measured SHG and reported second-order susceptibility. Absorbance spectra were acquired with a Jasco V-530 UV-Vis spectrophotometer, and analyzed with Jasco Spectra Analysis v1.50. An absorbance spectrum for the highest absorbing double-sided sample presented in this study, which is of the same pH variation as the reference standard, is shown in Figure 3.3.3. This is a 40 bilayer sample composed of PCBS at pH 7 along with PAH at pH 10. This spectrum represents a double-sided sample, so absorbance for one side is one-half at any given wavelength. The film absorbance at 532 nm is 0.070. The spectrophotometer measures absorbance as \( \text{Abs} = -\log \left( \frac{I}{I_0} \right) \), where \( I/I_0 \) is the ratio of transmitted intensity to incident intensity, so that conversion to absorption coefficient is determined from\(^9^9\)

\[
\alpha L = -\ln \left( 10^{-\text{Abs}} \right),
\]

(3.3.22)
Figure 3.3.3: Absorbance spectrum of the most absorbing film in this study, which is a 40 bilayer film composed of PCBS at pH 7 along with PAH at pH 10. This spectrum represents a double-sided sample, so absorbance for one side is one-half at any given wavelength. Absorbance at 532 nm is negligible so that Kleinman conditions exist.
where $\alpha$ is the absorption coefficient, and $L$ is the sample thickness. Therefore $\alpha L = 0.16$ for this film. The SHG conversion efficiency for a medium which is non-absorbing at the fundamental wavelength is given by

$$\frac{I_{2\omega}}{I_{2\omega,0}} = e^{-\alpha L/2} \frac{\sin^2 \left( \frac{\Delta k L}{2} \right) + \sinh^2 \left( -\frac{\alpha L}{4} \right)}{\left( \frac{\Delta k L}{2} \right)^2 + \left( -\frac{\alpha L}{4} \right)^2},$$

(3.3.23)

where $\Delta k$ is the wave-vector mismatch from eq. 3.3.4, $I_{2\omega}$ is the SHG resultant from the absorbance at the second harmonic wavelength, and $I_{2\omega,0}$ is the SHG that would result if the material were non-absorbing at the second harmonic wavelength. Important for determination of the effect of second harmonic absorbance upon SHG conversion is the ratio of $I_{2\omega}/I_{2\omega,0}$ for a given value of $\Delta k$, which is typically on the order of 1 $\mu$m$^{-1}$. For this 369 nm thick film, $\Delta k L/2 < 1$. Utilization of eq. 3.3.23 in this manner reveals that for $0 < \Delta k L/2 < 2$, the SHG conversion efficiency for this film is 94% of the conversion efficiency of this film if it were non-absorbing at the SHG wavelength. Equation 3.3.20 reveals that the effective second-order susceptibility for this film would be reported ~3% lower than its actual value, which is small compared to other sources of error that will be discussed. Since this analysis represents the worst case scenario and results in a conservative estimate, no correction will be applied.

For a sample with film on both sides of the substrate, interference fringes of the SHG intensity as a function of incident angle are created with maxima and minima due to completely constructive and completely destructive interference from the two films. The interference pattern falls within an envelope governed by reflection at the air-film interface, the physical pathlength in the sample, and the coupling between the polarization and the $\chi^{(2)}$ tensor. A typical example is shown in Figure 3.3.4 utilizing the reference standard ISAM film, taken at a different time than the quartz data shown in Figure 3.3.2. The signal increased with increased tilt angle below 60° due to decreased reflective loss of the p-polarized fundamental, increased physical pathlength and increased coupling to the $\chi^{(2)}$ tensor, and the signal decreased afterwards due to increased reflectance for p-polarized light at incident angles larger than Brewster’s angle.
Figure 3.3.4: Typical interference fringe pattern, using the reference standard. The signal increased with increased tilt angle below $60^\circ$ due to decreased reflective loss of the p-polarized light, increased physical pathlength and increased coupling to the $\chi^{(2)}$ tensor, and the signal decreased afterwards due to increased reflectance for p-polarized light at incident angles larger than Brewster’s angle.
Interference fringe maxima occur when the second harmonic from the rear face of the sample is in phase with the second harmonic generated from the front face, travelling through the substrate. The Maker fringes in Figure 3.3.4, for instance, have a periodicity of ~7° in the vicinity of 45° incidence. The relevant length scale for the interference between SHG signal from opposite sides of the glass slide is the physical pathlength $l$ of the beam through the slide, given by eq. 3.3.2 with $\alpha$ and $n_{film}$ replaced by $\beta$ and $n_{glass}$. Using the angles of consecutive maxima or minima, the coherence length ($l_c = \Delta l / 2$) for this periodicity is determined to be 21 $\mu$m, which is typical of glass for a wavelength of 1064 nm.

Since the SHG intensity is the square of the second harmonic electric field, and the electric field components add due to the constructive interference, the maximum SHG measured is $(2E_{2\omega})^2 = 4I_{2\omega,ISAM}$ of one film, so the intensity from one side of the ISAM film is given by

$$I_{2\omega,ISAM} = \frac{1}{4} SHG_{peak@45^\circ},$$

where the peak in the vicinity of 45° incident angle is taken as representative and the $\chi^{(2)}$ tensor elements can be determined from eqs. 3.3.14. Since 45° incident angle is used for tilt angle measurements, which yields $\chi^{(2)}_{zzz}$, an accurate determination of $\chi^{(2)}_{zzz}$ can be made. Typically, the values are averaged over ±1 peak from the peak nearest 45° in order to overcome any anomalies such as shifting of the fringe pattern due to variation in substrate thickness. Figure 3.3.5 shows the SHG data for the reference standard ISAM film taken at the same time as the quartz data in Figure 3.3.2. The data reflect SHG taken at two separate $x$-axis positions. Under identical experimental conditions as the quartz wedge, the reference standard exhibited a second harmonic intensity $I_{2\omega,\text{std}} = 150$ a.u. for peak at $\theta = 46^\circ$.

The final piece information necessary for the determination $\chi^{(2)}_{eff}$ of the reference standard is the thickness of the film. Film thickness measurements were taken with a J. A. Woolum VB-2000 Ellipsometer by M. Guzy of the Chemical Engineering department at Virginia Polytechnic Institute and State University (VPI&SU), who also fabricated the PCBS / PAH films included in
Figure 3.3.5: SHG measurement of the reference standard at two separate x-axis locations taken simultaneously with the quartz measurement shown in Figure 3.3.2.
An interesting and simple technique was utilized to overcome the problem with backside reflections common with transparent substrates. Film thickness measurements were made on the end of the slide that has the sandblasted frosting on one side. The frosting of the microscope slide on the opposite side of the film being measured causes scattering of the light from the ellipsometer, eliminating the backside reflection. Utilizing this technique, the thickness of the film $t_{film}$ for the reference standard was found to be approximately 46 nm. The physical pathlength of the fundamental beam in the sample is given by eq. 3.3.2. Since $\theta = 46^\circ$, $l = 51$ nm. As a convention, $std$ refers to reference standard data taken at the time of calibration to quartz, and $ref$ refers to reference standard data taken along with a given ISAM film. Consequentially, $I_{2\omega,ref} \neq I_{2\omega,std}$ while $\chi^{(2)}_{eff,ref} \equiv \chi^{(2)}_{eff,std}$, and $l_{ref} \equiv l_{std}$.

Finally, eq. 3.3.21 can be utilized to show that $\chi^{(2)}_{eff,ref} = 0.40 \chi^{(2)}_{eff,quartz}$. Furthermore, due to the geometry of the quartz wedge, $\chi^{(2)}_{eff,quartz} = \chi^{(2)}_{zzz,quartz}$ which is a well established value $\chi^{(2)}_{zzz,quartz} = 1.913 \times 10^{-9}$ esu. Therefore, $\chi^{(2)}_{eff,ref} = 7.6 \times 10^{-10}$ esu. The expression for ISAM films given by eq. 3.3.20 may be used to compare any film to the reference standard resulting in the relation

$$\frac{\chi^{(2)}_{eff,ISAM}}{\chi^{(2)}_{eff,ref}} = \frac{l_{ref}}{l_{ISAM}} \sqrt{\frac{I_{2\omega,ISAM}}{I_{2\omega,ref}}}.$$  \hspace{1cm} (3.3.25)

Therefore, for any film compared to this reference standard using 1064 nm fundamental beam

$$\chi^{(2)}_{eff,ISAM} = (3.95 \times 10^{-8} \text{ esu} \cdot \text{nm}) \frac{1}{l_{ISAM}} \sqrt{\frac{I_{2\omega,ISAM}}{I_{2\omega,ref}}}$$ \hspace{1cm} (3.3.26)

where the second harmonic intensities for the ISAM film and reference film are measured simultaneously, and eqs. 3.3.24 and 3.3.2 are applied. Once the relation between $I_{2\omega}^{p\to p}$ and $I_{2\omega}^{s\to p}$ for a film is established via a tilt angle measurement and application of eq. 3.3.14, $\chi^{(2)}_{zzz}$ of that film may be obtained.
3.3.3 Chromophore Tilt Angle Measurements

In addition to allowing determination of $\chi^{(2)}_{zzz}$, the ratio of $I_{zzz}^{p \rightarrow p}$ to $I_{zzz}^{p \rightarrow p}$ affords information about the average tilt angle of the chromophores within the sample with respect to the normal to the substrate as illustrated in Figure 3.3.1.b. The molecular hyperpolarizability is nonzero only along $\xi$ axis, and the molecules are oriented with average pitch angle $\psi$ to film $z$-axis and azimuthal angle $\phi$. As discussed in Chapter 1, the existence of SHG necessitates a net dipole orientation, and the symmetry of the films dictates that direction is along the substrate normal. While it is expected that the chromophores may be distributed in all directions in the bulk of a chromophore layer, the tilt angle describes the average orientation of the distribution. For this measurement, the intensity of the fundamental within the sample must be held constant for all polarizations. Since the incident beam is initially p-polarized with respect to the sample, the pair of Glan-Taylor polarizers can produce only 25% beam intensity for s-polarization. Therefore, the first Glan-Taylor polarizer in Figure 3.1.1 is replaced by a half-wave plate. This affords the ability to rotate the polarization with minimal energy loss. The intensity is determined by the angle between the resultant polarization and the second polarizer.

First, let us complete the derivation of the relationship of $\chi^{(2)}_{zzz}$ to $\chi^{(2)}_{xxx}$ so that the calculation of $\chi^{(2)}_{zzz}$ can be completed. From eq. 3.3.14, we calculate

$$\frac{I_{zzz}^{p \rightarrow p}}{I_{zzz}^{p \rightarrow p}} = \sin^4 \alpha \left( \frac{\chi^{(2)}_{zzz}}{\chi^{(2)}_{xxx}} + 3 \cot^2 \alpha \right)^2$$

so that

$$\frac{\chi^{(2)}_{zzz}}{\chi^{(2)}_{xxx}} = \sqrt{\frac{I_{zzz}^{p \rightarrow p}}{I_{zzz}^{p \rightarrow p}}} \csc^2 \alpha - 3 \cot^2 \alpha .$$

The simple reference technique of splitting off and detecting a small portion of the incident light with a beam splitter does not work for these measurements, since the reflection coefficient $R$ of the reference beam splitter varies with beam polarization. If we bypass the reference beam splitter and hold input energies constant (as measured by a power meter in front of the sample), an oscillating pattern such as that shown in Figure 3.3.6 can be generated as the input
polarization is varied. The SHG intensity data in Figure 3.3.6 are fit to a cosine squared plus offset function, in accordance with Malus’ law, in order to establish the minima and maxima. In addition, the SHG intensity has been corrected to account for reflectance losses at the film-air interface with respect to polarization. Fresnel transmission coefficients at s and p polarizations are

\[
\begin{align*}
\alpha &= \theta - \alpha \\
t_s &= \frac{2 \cos \alpha \sin \theta}{\sin(\alpha + \theta)} \\
t_p &= \frac{2 \sin \alpha \cos \theta}{\sin(\alpha + \theta) \cos(\theta - \alpha)}
\end{align*}
\]

with transmittances

\[
T_{s,p} = \frac{n_{\text{film}} \cos \alpha}{n_{\text{air}} \cos \theta} t_{s,p}^2
\]

At the air-film interface, this yields transmittances of \(T_s = 0.86\) and \(T_p = 0.98\) for incident angle \(\theta = 45^\circ\), for instance. The total transmittance \(T\) of the fundamental for a given polarization angle \(\phi\), where \(\phi = 0\) corresponds to p-polarization, is given by

\[
T = F_s T_s + F_p T_p,
\]

where

\[
F_s = \sin^2 \phi \quad F_p = \cos^2 \phi
\]

Both s- and p-polarized fundamentals produce only p-polarized second harmonic in the \(C_{\infty v}\) structure of the ISAM film. Therefore, there is no difference in second harmonic transmittances at the film-glass or glass-air interfaces with varying fundamental polarization. We can then correct for reflectance losses at the sample by scaling incident intensities as

\[
I_{\omega,\text{actual}} = I_{\omega,\text{measured}} T
\]

where \(I_{\omega,\text{measured}}\) is the fundamental intensity measured from the beam splitter before the sample and was held constant. This result shows that a constant measured fundamental incident intensity does not correspond to a constant actual fundamental intensity in the film. The second
Figure 3.3.6: SHG intensity as a function of fundamental beam polarization. P-polarization corresponds to polarizer angle of $0^\circ$. The data have been corrected for polarization-dependent reflection loss at the air-film interface. Data are fit to a cosine squared function in order to determine extrema.
harmonic intensity must be adjusted accordingly since this measurement requires constant fundamental intensity in the film. Since the second harmonic intensity scales quadratically with the fundamental intensity, and the incident fundamental intensity was held constant, we find

\[ I_{2\omega} = I_{2\omega,\text{measured}} \left( \frac{I_{\omega,\text{actual,average}}}{I_{\omega,\text{actual}}} \right)^2, \quad (3.3.34) \]

where \( I_{\omega,\text{actual,average}} \) is the average \( I_{\omega,\text{actual}} \) over all the polarizer angles. Accordingly, for constant incident angle and fundamental intensity we calculate

\[
\begin{align*}
\frac{I_{\omega \rightarrow p}}{I_{2\omega \rightarrow p}} &= \frac{I_{\omega \rightarrow p}}{I_{2\omega \rightarrow p}} \left( \frac{I_{\omega,\text{measured}}}{I_{\omega,\text{actual}}} \right)^2 \\
&= \left( \frac{I_{\omega,\text{measured}}}{I_{\omega,\text{actual}}} \right)^2 \left( \frac{T_s}{T_p} \right)^2 \\
&= \left( \frac{I_{\omega,\text{measured}}}{I_{\omega,\text{actual}}} \right)^2 \left( \frac{t_s}{t_p} \right)^4 \\
&= \left( \frac{I_{\omega,\text{measured}}}{I_{\omega,\text{actual}}} \right)^2 \left( \cot \alpha \tan \theta \cos(\theta - \alpha) \right)^4 \\
&= \left( \frac{I_{\omega,\text{measured}}}{I_{\omega,\text{actual}}} \right)^2 \left( \cot \alpha \tan \theta \cos(\theta - \alpha) \right)^4 \quad (3.3.35)
\end{align*}
\]

For the case of the data presented in Figure 3.3.6, this adjustment has already been made, and the fit to the curve revealed that \( \frac{I_{\omega \rightarrow p}}{I_{2\omega \rightarrow p}} = 7.76 \). This data were taken at \( \theta = 46^\circ \), or \( \alpha = 25^\circ \), and eq. 3.3.28 reveals \( \chi_{zzz}^{(2)} / \chi_{zxx}^{(2)} = 1.8 \) for the reference standard. Solving eq. 3.3.15 for \( \chi_{zzz}^{(2)} \) as a function of the measured \( p \rightarrow p \) \( \chi_{eff}^{(2)} \) we find

\[
\chi_{zzz}^{(2)} = \frac{\chi_{eff}^{(2)}}{3 \left( \frac{\chi_{zzz}^{(2)}}{\chi_{zxx}^{(2)}} \right)^{-1} \sin \alpha \cos^2 \alpha + \sin^3 \alpha} \quad (3.3.36)
\]

so that for the reference standard \( \chi_{zzz}^{(2)} = 1.5 \chi_{eff}^{(2)} = 1.2 \times 10^{-9} \text{ esu} = 0.61 \chi_{\text{quartz}}^{(2)} \) .

The dependence of the second harmonic intensity on the fundamental polarization also reveals the average chromophore tilt angle away from the substrate normal. Recall from Chapter
1 that the nonlinear susceptibility can be expressed as an orientational average of the molecular hyperpolarizability components

\[ \chi^{(2)}_{ijk}(-\omega;\omega_1,\omega_2) = N \sum \langle R_{ij} R_{jk} R_{kp} \rangle \beta_{\mu
u\rho} f(\omega) f(\omega_1) f(\omega_2). \]  

(1.3.5)

Under the assumption that the chromophores within the film have their dipole moment oriented along one axis only (i.e. a linear, conjugated chromophore), \( \beta \) along that axis will be the only nonzero hyperpolarizability. If the chromophore’s nonzero hyperpolarizability is oriented with the \( \hat{\xi} \) axis in Figure 3.3.1.b, then the orientational average in eq. 1.3.5 can be expressed as

\[ \langle R_{ij} R_{jk} R_{kp} \rangle = \langle \hat{x} \cdot \hat{\xi} \rangle \langle \hat{y} \cdot \hat{\xi} \rangle \langle \hat{z} \cdot \hat{\xi} \rangle, \]  

(3.3.37)

where \( \hat{x}, \hat{y} \) are coordinate axes in the plane of the film, and \( \hat{z} \) is normal to the film. Since it has been shown that net orientation is in the direction of the surface normal, a random distribution within the plane of the film is expected. The azimuthal angle \( \phi \) may be integrated, allowing the nonvanishing susceptibility tensor elements \( \chi^{(2)}_{zz}, \chi^{(2)}_{zx} \) to be written as

\[ \chi^{(2)}_{zz}(-\omega;\omega_1,\omega_2) \propto N \left\langle \cos^2 \psi \right\rangle \beta_{zzz} f(\omega) f(\omega_1) f(\omega_2), \]

\[ \chi^{(2)}_{zx}(-\omega;\omega_1,\omega_2) \propto \frac{1}{2} N \left\langle \cos \psi \sin \psi \right\rangle \beta_{zzz} f(\omega) f(\omega_1) f(\omega_2), \]  

(3.3.38)

where \( \psi \) is the molecular tilt angle from the film normal. If the distribution of this tilt angle is sharply peaked about a particular value \( \overline{\psi} \), the average values of these products may be taken as products of functions of the average value \( \overline{\psi} \), thus allowing the ratio of \( zzz \) and \( zxx \) components of the second-order NLO susceptibility to be written as

\[ \frac{\chi^{(2)}_{zz}}{\chi^{(2)}_{zx}} = 2 \cot^2 \overline{\psi}, \]  

(3.3.39)

which along with eq. 3.3.28 leads to the result

\[ \overline{\psi} = \text{arc cot} \sqrt{\frac{1}{2} \left[ \frac{I_{2\omega}^{\rightarrow p}}{I_{2\omega}^{\rightarrow p}} \csc^2 \alpha - 3 \cot^2 \alpha \right]}. \]  

(3.3.40)

Consequently, the value of \( \overline{\psi} \) for the reference standard is measured to be 47°.
3.3.4 Recipe for Determination of $\chi^{(2)}_{zzz}$ for ISAM Films

Simplicity dictates that a summary for the determination of $\chi^{(2)}_{zzz}$ is warranted before proceeding. For any film that is compared with the PCBS / PAH reference standard characterized in the preceding discussion, the following recipe applies.

From SHG intensity fringes for an ISAM film measured in conjunction with the reference standard, calculate

$$\chi^{(2)}_{\text{eff,ISAM}} = \left(3.95 \times 10^{-8} \text{ esu} \cdot \text{nm}\right) \frac{1}{I_{\text{ISAM}}} \sqrt{\frac{I_{2\omega,\text{ISAM}}}{I_{2\omega,\text{ref}}}},$$  \hspace{1cm} (3.3.26)

where

$$I_{2\omega,\text{ISAM}} = \frac{1}{4} \text{SHG}_\text{peak}@45^\circ$$ \hspace{1cm} (3.3.24)

and

$$I = \frac{t_{\text{film}}}{\cos \alpha} = t_{\text{film}} \left[1 - \frac{\sin^2 \theta}{n_{\text{film}}^2}\right]^{-\frac{1}{2}},$$ \hspace{1cm} (3.3.2)

where $t_{\text{film}}$ is thickness of one side of the film, and $I_{2\omega,\text{ref}}$ is the measurement of the reference standard ISAM film taken along with the ISAM film being studied. Then, from a tilt angle measurement of the ISAM film, or from an established ratio $I_{2\omega}^{p \rightarrow p}/I_{2\omega}^{z \rightarrow p}$ for a film type, calculate

$$\chi^{(2)}_{zzz} = \frac{\chi^{(2)}_{\text{eff}}}{3 \left(\chi^{(2)}_{zzz}/\chi^{(2)}_{xxx}\right)^{-1} \sin \alpha \cos^2 \alpha + \sin^3 \alpha},$$ \hspace{1cm} (3.3.36)

where

$$\frac{\chi^{(2)}_{zzz}}{\chi^{(2)}_{xxx}} = \sqrt{\frac{I_{2\omega}^{p \rightarrow p}}{I_{2\omega}^{z \rightarrow p}}} \csc^2 \alpha - 3 \cot^2 \alpha$$ \hspace{1cm} (3.3.28)

and

$$\alpha = \arcsin \left(\frac{n_{\text{air}} \sin \theta}{n_{\text{film}}}\right).$$ \hspace{1cm} (3.2.1)
3.4 Optimization of the Polycation Layer

Optimization of the solution parameters, prior to this thesis, has involved changing the pH and the salt concentration of the two ionic solutions simultaneously. As discussed in Chapter 2, there is increasing evidence that ISAM layers are quite interpenetrated rather than stratified. When the film is immersed in a dipping solution, the phase at the surface of the film is altered due to the solution parameters, thus the degree of interpenetration is also altered. The pH of the dipping solution also dictates the degree of ionization of the polyelectrolytes as well as the free ion concentration which increases with decreased pH of the anionic solution, and increases with increased pH of the cationic solutions. We refer to the free ion concentration as the concentration of ions of opposite charge to the polyelectrolyte in solution. The free ion concentration of the solutions can also be increased by the addition of NaCl. As we have shown previously, increased free ion concentration leads to a more loopy polymer conformation which leads to greater interpenetration, increased monolayer thickness, and decreased net chromophore orientation.101,102

3.4.1 Data Reduction Technique and Error Analysis

Prior to presentation of the results of the studies contained in this thesis, we shall complete the characterization of the reference standard and discuss the sources and treatment of error propagation. The Jasco V-530 spectrophotometer used for absorbance measurements is calibrated on a regular basis and measurements are considered accurate to ±0.003. Typically, $\chi^2$ measurements are considered to be accurate within ±10%. This error stems from laser beam energy fluctuation, PMT stability and sample variation as well as error propagating from the $\chi^2$ calculation method outlined in Section 3.3. In addition, this normally accepted error is assigned to a measurement technique not yet discussed. This technique is rather straight-forward and involves simply graphing the intensity of the second harmonic versus the intensity of the fundamental, obtaining a quadratic fit factor, and comparing to a similar measurement of the reference standard as outlined in Sections 3.3.1 through 3.3.2. Such a measurement of the reference standard is shown in Figure 3.4.1. The $R^2$ value on the graph is a statistical value which determines the quality of the fit, with $R^2 = 1$ being the highest possible score. The fit
quality \( R^2 = 0.9968 \) illustrates that the film shows quadratic growth of SHG intensity with respect to incident fundamental intensity, fulfilling one of the three requirements for \( \chi^{(2)} \) films mentioned in the beginning of Section 2.5.

For the purposes of studying the effects of solution parameter variation and distinguishing bulk versus interface effects, we utilize the technique outlined in Section 3.3.2. Equation 3.3.24 points out that the maximum signal from a double-sided film is 4 times the maximum signal from a single-sided film. Furthermore, only the fringe maxima need to be determined for a double-sided film, whereas for a single sided film, there is still interference with the SHG from the opposite air-glass interface, but with a varying and non-zero minimum which must be carefully determined. Since the analysis is more complicated for a single-sided film and it is easier to produce double-sided films using the immersion technique, we use the interference fringe technique as our standard method. A typical data set for one sample is shown in Figure 3.4.2 for the reference standard. Interference fringe patterns were measured for three positions along the length of the microscope slide, with 1.0 cm between positions. Each datum is an average of 50 measurements at one angle. The data are offset on the SHG intensity axis for the purpose of distinguishing the three positions where the offset for positions \( \{1, 2, 3\} \) are \( \{0, 400, 800\} \) a.u., respectively. For each fringe pattern, the maximum at 45\(^\circ\) is determined by averaging over the maxima near 45\(^\circ\), and \( \pm 1 \) peak as discussed in Section 3.3.2. Then, the results for all three positions are averaged, and eq. 3.3.24 is applied to determine \( I_{\text{2o,JSAM}} \) for one film (one side of the slide). A data sequence consists of at least 2 such measurements of the reference standard at the beginning and end of the sequence, along with 10 – 20 samples being studied.

It is convenient to compare the square root of the SHG for film measurements taken at different times. The analysis which follows is used partly to account for fundamental beam energy differences between times that data was taken, and should not be confused with the technique for determination of \( \chi^{(2)} \) outlined in Section 3.3. In order to account
Figure 3.4.1: Square root of SHG intensity versus fundamental intensity. The fit shows agreement with one of the three requirements for $\chi^{(2)}$ films listed in Section 2.5.
Figure 3.4.2: SHG interference fringe patterns for three positions along the sample. Data are offset for the purpose of distinguishing the three positions which are 1 cm apart. The SHG intensity offset for positions \{1,2,3\} are \{0, 400, 800\} a.u., respectively.
for possible fundamental beam energy fluctuations and any filters between the sample and the PMT, the following equation is applied:

\[
I'_{2\omega,\text{ISAM}} = \frac{I_{2\omega,\text{ISAM}}}{I_{\text{filter}}} \left( \frac{I_{\omega,\text{ref}}}{I_{\omega,\text{ISAM}}} \right)^2,
\]

where \( I'_{2\omega,\text{ISAM}} \) is the value of SHG used for comparison of data taken at different times. The first term adjusts the SHG intensity to the product of transmittances \( T_{\text{filter}} \) of any filters that may be used. The second term adjusts for any fundamental beam intensity difference between the current data session \( I_{2\omega,\text{ref}} \) and the quartz calibration session \( I_{2\omega,\text{std}} \). Finally, the third term in eq. 3.4.1 adjusts for any fundamental beam intensity fluctuations during the experiment away from the fundamental intensity during the reference standard measurements.

Error analysis was performed using the standard error propagation formula to determine the error \( \sigma_f \) in a function \( f \)

\[
\left( \frac{\sigma_f}{f} \right)^2 = \sum_i \left( \frac{\partial f}{\partial x_i} \right)^2 (\sigma x_i)^2,
\]

where \( \sigma x_i \) is the error of the \( i^{th} \) component \( x_i \) of the function. In addition to the error introduced by the absorption of second harmonic discussed in Section 3.3.2, the two largest sources of error in determination of \( \chi^{(2)} \) come about from the determination of \( I^{p-p}_{2\omega} / I^{x-p}_{2\omega} \) and the determination of film thickness. The SHG absorption error falls within the error bars of the presented data, and the latter two will be considered in the final calculations of nonlinear optical susceptibilities.

The 5-bilayer film of the cation pH 10 variation was chosen as the reference standard for several reasons. Prior to the studies shown here, a complete and more encompassing set of variations was fabricated and tested. From this, we learned the pH boundaries and improved fabrication techniques. Further, the SHG measurement apparatus was vastly improved with the addition of the motorized rotation stage affording more accurate measurements. We could have used a sample from either pH variation presented here, but the pH 10 variation was the first
produced. Importantly, due to the thickness of each layer, the 5-bilayer film was well into the region where absorbance grows linearly with number of bilayers. This matter was discussed in Section 2.3. The final consideration in choice of the reference standard was that the film showed repeatability across the surface. Figure 3.4.3 is a “map” of the surface where interference fringe data are taken for 35 mm along the length of the film, at 0.5 mm intervals. For timeliness, each datum was averaged over 10 counts, which is reflected in the roughness of the “surface.” However, it is obvious that the signal remains constant along the length of the slide. Thus, the final requirement of focus characteristics outlined in Section 3.2 is fulfilled.

It is interesting to look at the behavior shown in Figure 3.4.4, which is the projection of the surface on the SHG-incident angle plane. We expect that there are minor thickness variations in the glass substrate. Interference fringe maxima occur when the second harmonic from the rear face of the sample is in phase with the second harmonic generated from the front face and travelling through the substrate, as discussed in Section 3.3.1. Correspondingly, thickness variations would result in a shift of the peaks due to increased distance between the peaks. Further, we observe the expected behavior, mentioned in Section 3.3.3, that the shifted peaks should remain within the envelope.
Figure 3.4.3: SHG interference fringe surface of data taken for 35 mm along the length of the film, at 0.5 mm intervals. For timeliness, each datum was averaged over 10 counts, which is reflected in the roughness of the “surface.” The signal remained constant along the length of the film.
PCBS / PAH Reference Standard, Consistency Scan

Figure 3.4.4: Projection of interference fringe surface on the SHG-incident angle plane. The incident angle variation of the peaks could be due to slide thickness variation which would cause a shift of the peak locations. Further, the peaks follow the envelope (a negative shift means the peak should lose magnitude).
3.4.2 Variation of the Polycation Solution pH

We chose pH 7 for the polyanion PCBS as it yields a relatively thin monolayer with minimal "bulk" chromophore fraction and minimal interpenetration of the subsequent polycation (PAH) layer. We then varied the pH of PAH without the addition of NaCl. The pKa of PAH is ~8.7. Thus, at pH 7, PAH is nearly fully ionized (protonated); while at pH 10, a large fraction of the amine groups is deprotonated and electrostatic repulsion between neighboring amines is reduced. The molarity per polymer repeat unit was maintained at 0.01 M for both polyions, and each layer was allowed to adsorb for 5 minutes with the exception of the initial layer which was allowed to adsorb for 10 minutes. These “dipping times” are far longer than the established equilibrium time of less than one minute. The chemical structures for PCBS and PAH are shown in Figure 2.1.1.

Absorbance spectra for the cation pH 10 variation, which includes the 5-bilayer reference standard, are shown in Figure 3.4.5. The absorbance peak remains consistently at ~362 nm for all films in this study. The linear increase of the absorbance at 362 nm of one film (one side of the sample) as a function of the number of bilayers, shown in Figure 3.4.6, shows constant chromophore deposition throughout the growth of the film which is also indicative of constant film growth. This fulfills the second requirement for $\chi^{(2)}$ films mentioned in the beginning of Section 2.5. Further, we observed quadratic growth of the SHG with film thickness, as shown in Figure 3.4.7, showing that each successive bilayer has the same degree of chromophore orientation. This is the final requirement for $\chi^{(2)}$ films. The square root of SHG plotted here already accounts for relations in eqs. 3.3.24 and 3.4.1, so the value of $\sqrt{I_{2\omega}}$ for any film can be directly compared to any other film taken along with the reference standard. The film with the greater cation pH exhibited greater SHG, which was as expected. The greater cation pH yields a more loopy polymer conformation which results in a thicker polycation layer and therefore also promotes a thicker polyanion layer. The latter point is illustrated by the larger PCBS absorbance observed in Figure 3.4.6 for the PAH pH 10 films relative to the PAH pH 7 films. The increased amount of PCBS deposited per bilayer leads to the larger SHG signal in the high pH case.
Figure 3.4.5: Absorbance spectra for the cation pH 10 variation, which includes the 5-bilayer reference standard. Films composed 20 and fewer bilayers exhibit negligible absorption in the 532 nm region.
Figure 3.4.6: Absorbance of one film (one side of the sample) as a function of the number of bilayers for the cation pH 10 variation. Linear relation shows constant chromophore deposition throughout the growth of the film which is also indicative of constant film growth.
Figure 3.4.7: $\sqrt{I_{2\omega}}$ as a function of number of bilayers for the cation pH 10 variation. Linear relation shows that each successive bilayer has the same degree of chromophore orientation.
Tilt angle measurements were performed on the entire PAH pH 10 series as well as the 20-bilayer PAH pH 7 film. The tilt angle represents the average chromophore orientation with respect to the substrate normal. The randomly oriented chromophores in the bulk do not contribute to this measurement, and the competitive interface chromophores pointing away from the substrate serve to partially cancel the SHG for all polarizations. Assuming the net orientation in the competitive interface layers are equivalent, then the data represent the average chromophore orientation at the layer interfaces. The latter measurement was performed in order to draw a comparison between the variations, and the results are reported in Table 3.4.1, presented later in this section. Figure 3.4.8 shows the tilt angles for the PAH pH 10 series utilizing eq. 3.3.40. The data in Figure 3.4.8 do not necessarily represent a trend of the chromophore tilt angle within the film since the determination of $I_{2\omega p}^{2p}\rightarrow\omega/|I_{2\omega p}^{2p}|$ is highly sensitive to the s-polarization measurement which has a significant relative error due to weak signal.

The individual measurements are shown in Figure 3.4.9. It is obvious that the data better represent the expected cosine squared behavior with increased signal strength due to increased film thickness. This suggests that the thicker samples better represent the tilt angle. The high percentage error of s-polarization measurements due to inherent low SHG intensity is also illustrated by the distribution of the data about the expected cosine squared trend in the vicinity of s-polarization. In order to further illustrate the sensitivity of variation of s-polarization SHG intensity, Figures 3.4.10 and 3.4.11 show the cosine squared fits normalized to p-polarization and s-polarization, respectively. Normalization to p-polarization illustrates that data are nearly equivalent, considering the distribution of s-polarized SHG measurements about the fits shown in Figure 3.4.9. The 1- through 20-bilayer samples are indistinguishable within error, while the 40-bilayer measurement is only slightly distinguishable. The normalization to s-polarization shown in Figure 3.4.11 serves to represent the difference in ratios of $I_{2\omega p}^{2p}/|I_{2\omega p}^{2p}|$, represented by the $I_{2\omega p}^{2p}$ peaks. Due to these arguments, we report the $zzz$-component of the nonlinear optical susceptibility $\chi^{(2)}_{zzz}$ as a function of the measured tilt angle, and as a function of the weighted average ratio $I_{2\omega p}^{2p}/|I_{2\omega p}^{2p}| = 9.5$, which corresponds to a 37° tilt angle. This tilt angle will be used in the analysis of all PAH pH 10 films.
Figure 3.4.8: Average chromophore orientation at the layer interfaces, with respect to the substrate normal, for the cation pH 10 variation. Due to the sensitivity of the tilt angle to the weak s-polarization SHG, a trend cannot be positively determined.
Figure 3.4.9: Tilt angle measurements for PAH pH 10 series. As the thickness increases, and total signal increases, the data fit increasingly better to the cosine squared expectation. This suggests that when averaging the values, the higher number bilayer films should have a greater weight. The high percentage error in s-polarization ($\pm 90^\circ$) data becomes evident.
Figure 3.4.10: Cosine squared fits to the data used for tilt angle measurements for PAH pH 10 series, normalized to p-polarization. The deviation in the curves for 1 to 20 bilayers can be attributed to the high percentage error of s-polarization SHG intensity measurements illustrated in Figure 3.4.9.
Figure 3.4.11: Cosine squared fits to the data used for tilt angle measurements for PAH pH 10 series, normalized to s-polarization. The large difference in $I_{p ightarrow p}^{2\omega}/I_{s ightarrow p}^{2\omega}$ ratios is illustrated by the peaks. The error in s-polarization measurements can easily account for all of the deviation for the 1- through 20-bilayer samples from the average value for those peaks, and most of the deviation of the 40-bilayer sample from that same value.
Table 3.4.1 shows the measured tilt angles for the PAH pH 10 films, and for the pH 7 20-bilayer film. Also included in the table are the film thickness, absorbance and $\chi^{(2)}$ values for all the films. Error is not included for the $\chi^{(2)}$ due to the uncertainty in the tilt angle discussed earlier in this section. It is interesting to note that, with the exception of the first 5 bilayers of the pH 10 series, the absorbance and film thickness grow at the same rate. A similar trend is observed for the entire PAH pH 7 series where the absorbance and film thickness grow at identical rates. The 20-bilayer film at PAH 10 has a tilt angle of 36.6° and that at PAH pH 7 has a tilt angle of 65.1°. The thicker films formed at pH 10 appear to have a smaller tilt angle away from the surface normal than those at pH 7. This is perhaps not surprising since the length of the azo chromophore side-chain is approximately 1.5 nm. For the 0.2 nm bilayer thickness of the PAH pH 7 series, the chromophore may lie largely in the plane of the substrate and therefore have a large tilt angle relative to the surface normal. Thus in general, the thickness contributions of the PAH and PCBS are equivalent.

There are several competing effects regarding $\chi^{(2)}$ as the polycation pH is increased. The amount of PCBS adsorbed upon each layer deposition is increased and the average tilt angle of the chromophores away from the direction of the net polar order (perpendicular to the substrate) appears to decrease. Both of these would tend to increase the $\chi^{(2)}$ value. However, as we have reported previously in the study of varying the polyanion and polycation pH values simultaneously, thicker layers of the NLO-active polymer lead, in fact, to decreased $\chi^{(2)}$ values. This is because the chromophores within the "bulk" of the monolayer tend towards random orientation. This effect works towards a decreased $\chi^{(2)}$ value at the higher PAH pH value. It is clear from Table 3.4.1 that this effect is dominant.
Table 3.4.1: Results for PAH pH 7 and pH 10 films. Tilt angle measurements were not performed on pH 7 {1,5,10,40} bilayer samples. $\chi^{(2)} (37^\circ)$ is the susceptibility considering a chromophore tilt angle of 37°.

<table>
<thead>
<tr>
<th>PAH pH</th>
<th>Number Bilayers</th>
<th>Thickness ±10%, (nm)</th>
<th>Absorbance ±0.0005</th>
<th>$\chi_{eff}^{(2)}$ ±20% (10⁻⁹ esu)</th>
<th>Tilt Angle $\psi$</th>
<th>$\chi^{(2)} (\psi)$ (10⁻⁹ esu)</th>
<th>$\chi^{(2)} (37^\circ)$ (10⁻⁹ esu)</th>
<th>$\chi^{(2)} (65^\circ)$ (10⁻⁹ esu)</th>
</tr>
</thead>
<tbody>
<tr>
<td>10</td>
<td>1</td>
<td>9.2</td>
<td>0.0150</td>
<td>2.0</td>
<td>43°</td>
<td>4.1</td>
<td>5.7</td>
<td></td>
</tr>
<tr>
<td>10</td>
<td>5</td>
<td>46</td>
<td>0.1250</td>
<td>0.76</td>
<td>47°</td>
<td>1.2</td>
<td>2.1</td>
<td></td>
</tr>
<tr>
<td>10</td>
<td>10</td>
<td>92</td>
<td>0.2400</td>
<td>0.55</td>
<td>56°</td>
<td>0.48</td>
<td>1.5</td>
<td></td>
</tr>
<tr>
<td>10</td>
<td>20</td>
<td>184</td>
<td>0.5700</td>
<td>0.43</td>
<td>37°</td>
<td>1.2</td>
<td>1.2</td>
<td></td>
</tr>
<tr>
<td>10</td>
<td>40</td>
<td>368</td>
<td>1.1700</td>
<td>0.39</td>
<td>27°</td>
<td>1.8</td>
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<tr>
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<td>1</td>
<td>0.21</td>
<td>0.0055</td>
<td>79</td>
<td>27°</td>
<td>1.8</td>
<td>32</td>
<td></td>
</tr>
<tr>
<td>7</td>
<td>5</td>
<td>1.1</td>
<td>0.0270</td>
<td>21</td>
<td></td>
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<td>2.1</td>
<td>0.0540</td>
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<tr>
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<td>20</td>
<td>4.2</td>
<td>0.1205</td>
<td>8.4</td>
<td>65°</td>
<td>3.4</td>
<td>3.4</td>
<td></td>
</tr>
<tr>
<td>7</td>
<td>40</td>
<td>8.4</td>
<td>0.1990</td>
<td>5.3</td>
<td></td>
<td></td>
<td>2.1</td>
<td></td>
</tr>
</tbody>
</table>
Figure 3.4.12 shows the nonlinear susceptibilities $\chi^{(2)}_{\text{eff}}, \chi^{(2)}_{zzz}(37^\circ)$ and $\chi^{(2)}_{zzz}(65^\circ)$, labeled “chi(2),” “chi(2)zzz(37),” and “chi(2)zzz(65),” respectively. We observe the same trend we reported previously for the case of simultaneous pH variations. The susceptibilities approach an asymptotic value as a function of the number of bilayers. The contribution of surface SHG and the lack of interpenetration of the first few layers serve to artificially inflate the “true” susceptibility of the film. The excess contribution from the first few layers becomes negligible after the film has acquired enough thickness. This trend is an indication that each successive bilayer produces equivalent interpenetration, but it does not reveal when that equilibrium was reached.

In order to verify this asymptotic value, we calculate $\chi^{(2)}_{\text{eff, ISAM}}$ using the slope of the square root of SHG per bilayer for the samples from Figure 3.4.7, since the slope represents the contribution per bilayer, separately from surface and interface effects. Since eq. 3.3.24 has already been applied to the charted data, eq. 3.3.26 becomes

$$\chi^{(2)}_{\text{eff, ISAM}}(\omega) = \frac{1}{\sqrt{\frac{1}{4} I_{2 \omega, \text{ref}}}} \frac{slope}{I_{bl, \text{ISAM}}},$$  

(3.4.3)

where $I_{bl, \text{ISAM}}$ is the physical pathlength per bilayer given by eq. 3.3.2. For the PAH pH \{7, 10\} series respectively, the slopes are {0.21, 0.94} \(\text{a.u./bl}\), the bilayer thickness are {0.21, 9.21} \(\text{nm/bl}\), and the values of $I_{2 \omega, \text{ref}}$ are {548, 488} \(\text{a.u.}\). Accordingly $\chi^{(2)}_{\text{eff, ISAM}}$ for the pH 7 series is 3.1x10^{-9} esu, and $\chi^{(2)}_{\text{eff, ISAM}}$ for the pH 10 series is 0.33x10^{-9} esu. The disparity between the $\chi^{(2)}_{\text{eff, ISAM}}$ values for the pH 7 series illustrates that the asymptote has not yet been reached, as is evident in Figure 3.4.12, and the values for the pH 10 series are in excellent agreement. Accordingly, the values of the zzz-component of the $\chi^{(2)}$ tensor for these films are calculated to be $\chi^{(2)}_{zzz}(65^\circ) = 1.2x10^{-9}$ esu for the pH 7 series, and $\chi^{(2)}_{zzz}(37^\circ) = 0.84x10^{-9}$ esu for the pH 10 series.
Figure 3.4.12: Nonlinear susceptibilities $\chi^{(2)}$, $\chi^{(2)}_{zzz}(37^\circ)$ and $\chi^{(2)}_{zzz}(65^\circ)$, labeled “chi(2),” “chi(2)zzz(37)” and “chi(2)zzz(65),” respectively, for pH variations for which they apply. The susceptibilities asymptotically approach a true value for the film. Surface SHG and the lack of interpenetration for the first few layers causes the susceptibility to be artificially inflated. The artificial inflation becomes negligible as film thickness is increased.
3.4.3 Impact of the Choice of Polycation

We further explored the role of the polycation within the NLO ISAM film by replacing PAH with other polycations. We used separately poly(diallyldimethyl ammonium chloride) (PDDA) and poly (L-Lysine) (PLL), illustrated in Figure 3.4.13 which compares all three cations addressed in this thesis. PLL is Poly[imino[(1S)-1-(4-aminobutyl)-2-oxo-1,2-ethanediyl]] (9Cl), and PDDA is 2-Propen-1-aminium, N,N-dimethyl-N-2-propenyl-, hydroxide, homopolymer (9Cl). The weight average molecular weight was $100,000 \text{ g/mol} < M_w < 200,000 \text{ g/mol}$ for PDDA as purchased from Aldrich, and $70,000 \text{ g/mol} < M_w < 150,000 \text{ g/mol}$ for PLL as purchased from Sigma. The pKa value for PLL is 11, compared to 8.7 for PAH. Figures 3.3.14 and 3.3.15 illustrate the short-range conformation of PDDA and PLL, respectively, in the absence of external forces. PDDA tends to have similar conformation as PAH with a slightly smaller radius of curvature, while PLL tends to form a twisted, or helical, structure.

![Figure 3.4.13: Cations used in ISAM film fabrication to study the effect of cation choice.](image-url)
Figure 3.4.14: Twelve repeat units of PDDA in the absence of external forces, illustrating a tighter conformation than PAH. The radius of curvature in (a) is approximately 15 Å. Only carbons and nitrogens are shown.
Figure 3.4.15: Ten repeat units of Poly(L-Lysine) in the absence of external forces. PLL appears to possess a short-range conformation of a small radius helix.
Films made with each of these polycations showed linear growth of absorbance with number of bilayers demonstrating that a constant rate of PCBS deposition per bilayer was achieved, as shown in Figure 3.4.16. However, Figure 3.4.17 reveals that after the first bilayer, the SHG intensity remained essentially constant as the number of bilayers was increased. Thus, although PCBS is well incorporated into ISAM films with PDDA and PLL, net polar ordering is not achieved with these polycations as it is with PAH. These data suggest we have a surface SHG component as well as a glass-film interface component. It is possible that the first layer retains a net orientation since it is so near the glass surface, or that the final layer possesses a net orientation that is lost upon subsequent layer adsorption.

We speculate that hydrogen bonding may play a role in the orientational stability of the films. The primary amines on PLL and PAH are capable of forming hydrogen bonds while the quaternary amines on PDDA are not. The location of the hydrogen-bonding group in reference to the backbone may also be a governing factor. The amine group on PAH is separated from the backbone by just one methyl group while the amine on PLL is separated from the backbone by four methyl groups, making a much larger distance between the amine and the backbone. The hydrogen-bonding group will be more mobile in films made with PLL, thereby allowing chromophores to orient in a more random fashion. The strong dependence of the $\chi^{(2)}$ on the nature of the NLO-active polycation is an important observation for the development of ISAM NLO films. While the usage of polycations other than PAH failed to produce good $\chi^{(2)}$ films, they did produce high-quality ISAM films, which reveals their potential in other applications such as LEDs, photovoltaics and electrochromic devices.
Figure 3.4.16: The absorbance of one film (one side of the sample) as a function of the number of bilayers. Linear relation shows constant chromophore deposition throughout the growth of the film which is also indicative of constant film growth.
Figure 3.4.17: $\sqrt{I_{2i\omega}}$ as a function of number of bilayers. After the first bilayer, the SHG intensity remains essentially constant as the number of bilayers is increased. Net polar ordering is not achieved with these polycations as it is with PAH.
3.5 Conclusions

In continuing efforts to develop a full understanding of the structure of ionically self-assembled monolayers and, in particular, its relation to polar ordering and $\chi^{(2)}$, we have systematically studied the effect of varying the NLO-inactive polycation. Using PAH as a polycation with PCBS as the active NLO polyanion, we have found that increasing the polycation pH from 7 to 10 yields an increase in the bilayer thickness of a factor of 45. While the average chromophore tilt angle away from the preferred direction is decreased and the total SHG intensity is increased for the higher pH value, the $\chi^{(2)}$ value is significantly deceased due to the random orientation of chromophores within the thicker PCBS layers, and increased PAH layer thickness. We have also found that the polycations PDDA and PLL do not exhibit bulk $\chi^{(2)}$ effects, suggesting that hydrogen bonding plays a vital role in obtaining the polar order.


CHAPTER 4

INCORPORATION OF MONOMER CHROMOPHORES

Due to the nature of the formation of ISAM films consisting of two polymers, the NLO-active polyelectrolyte must have chromophores oriented in opposite directions in order to provide binding to the preceding and following oppositely-charged layers as previously discussed in Chapter 2, and illustrated in Figure 2.1.2. The opposing dipole orientations cancel one another and lead to an overall reduction in the $\chi^{(2)}$ of the film. In addition, polyelectrolyte-based ISAM films suffer from lack of orientation of chromophores within the bulk of a monolayer as discussed in Chapter 3. In attempts to overcome these issues, we have fabricated ionically self-assembled films of a distinctly different structure. These films contain dianionic NLO chromophores, as opposed to polyelectrolytes with NLO sidechains. This type of film has the potential to increase the nonlinear optical susceptibility by increasing the net orientation and decreasing the bilayer thickness. We also studied the effects of complexing dianionic chromophores with cyclodextrins in order to improve orientation and increase solubility. Finally, we examined the incorporation of monomer chromophores containing ionic and covalent bonding sites. This is a novel technique that is in its infant stage, yet has produced exciting results.
4.1 Incorporation of Dianionic Molecules\textsuperscript{107,108}

In order to overcome the issues of opposing chromophore orientation and random intralayer bulk chromophore orientation, we have fabricated ionically self-assembled films incorporating dianionic NLO chromophores. Similar films incorporating amphiphiles between polyion layers have successfully been demonstrated to grow on the same time scale as polymer-polymer ISAM films, but no nonlinear optical effects were demonstrated.\textsuperscript{109,110} The use of a chromophore with two distinct ionic functionalities provides a method for directing the orientation of the chromophore as it is adsorbed.

An example of a dianionic chromophore is the dye Mordant Orange 10 (from Aldrich) depicted in Figure 4.1.1. Mordant Orange 10 is benzoic acid, 2-hydroxy-3-methyl-5-[[4-[(4-sulfophenyl)azo] phenyl]azo], disodium salt (9CI). The sulfonic acid moiety has a pKa near zero while that of the carboxylic acid is 5. Thus, at pH 3, the sulfonic acid will be ionized while the carboxylic acid will remain neutral. When the substrate is immersed in a Mordant Orange aqueous solution at pH 3, the sulfonate will be preferentially adsorbed towards the preceding polycation layer. Subsequent immersion in the polycation solution at pH 7 will lead to ionization of the carboxy groups, allowing adsorption of the next polycation layer.

\begin{center}
\begin{tabular}{c}
Mordant Orange 10 \\
\text{C}_{20}\text{H}_{14}\text{N}_{4}\text{Na}_{2}\text{O}_{6}\text{S} \\
\text{Mol. Wt.: 484.4}
\end{tabular}
\end{center}

\textbf{Figure 4.1.1:} Dianionic molecule Mordant Orange 10. The sulfonic acid moiety has a pKa near zero while that of the carboxylic acid is 5.
The structure obtained by such a procedure, illustrated schematically in Figure 4.1.2.b, is expected to possess a much larger net polar orientation than that of Figure 4.1.2.a. A typical absorbance spectrum for a Mordant Orange / PAH film is shown in Figure 4.1.3. The absorbance at 532 nm is stronger for Mordant Orange than for PCBS, but not enough to adversely reduce the SHG efficiency for these films.

In order to improve orientation of the dianionic chromophores as well as their solubility in solution, β-cyclodextrins (Aldrich) were incorporated into the Mordant Orange solution at a molar concentration of 0.16 M. Cyclodextrins are a family of cyclic oligosaccharides that have been of increasing interest due to their ability to easily complex with rod-like molecules (rotaxanes) and chain or ring-like molecules (catananes). The molecules form a conical cylinder whose interior region is lined by hydrogen atoms and glycosidic oxygen bridges. β-cyclodextrin comprises 7 glucopyranose repeat units, as shown in Figure 4.1.4.b, and has an inner diameter of 7.8 Å at the larger opening. When in aqueous solution, the apolar cavity is filled with energetically unfavored water molecules which are easily substituted by guest molecules, which are less polar than water. This is the basis for “molecular encapsulation.” Figure 4.1.5 shows a three-dimensional view of a β-cyclodextrin-encapsulated Mordant Orange 10 molecule. Of particular interest is that the solubility of the guest increases since the cyclodextrin is in general very soluble in aqueous solution. Additionally, complexation of β-cyclodextrins in this manner may aid in chromophore alignment by filling up empty space between the chromophores and physically forcing them into a more upright position, as illustrated in Figure 4.1.4.a.
Figure 4.1.2: Schematic representation of (a) a polymer chromophore layer between two PAH layers, and (b) a dianionic chromophore layer between two PAH layers. The polymer-polymer ISAM films suffer from competitive chromophore orientation at the upper interface, as well as random orientation within the bulk of the chromophore layer.
Figure 4.1.3: Typical absorbance spectrum for Mordant Orange / PAH film. Peak absorbance occurs at 380 nm. Absorbance at SHG wavelength (532 nm) is small enough so as not to adversely affect the SHG efficiency for these films.
Figure 4.1.4: (a) Schematic representation of improved chromophore orientation due to complexation with β-cyclodextrin. (b) β-cyclodextrin is comprised of 7 glucopyranose repeat units.
Figure 4.1.5: Three-dimensional views of β-cyclodextrin-encapsulated Mordant Orange 10 molecule. Hydrogens are not shown.
Shown in Figures 4.1.6 and 4.1.7 are the results of studies of Mordant Orange 10 films with and without complexation with \( \beta \)-cyclodextrin. Two comparisons are made in this study with the pH and molarity of PAH held constant at 7 and 10 mM, respectively. The first study involves the comparison of Mordant Orange films at pH 7 with and without \( \beta \)-cyclodextrin complexation. The second study involves variation of the pH of the \( \beta \)-cyclodextrin-complexed Mordant Orange solution. The molarity of Mordant Orange was varied from 0.5 mM to 1 mM. The layers were allowed to adsorb for 5 minutes each, with the exception of a 10 minute initial layer adsorption.

Figure 4.1.6 shows that the films grew thicker with increased bilayer adsorption. Importantly, Figure 4.1.7 reveals that neither study resulted in a growth of SHG with increased number of bilayers. Because the outermost monolayer of Mordant Orange is only tethered to the preceding PAH layer by a single ionic bond for each molecule, each chromophore can by dissociated during the following immersion into PAH. The Mordant Orange molecule may either be removed from the film entirely or subsequently readsorb with opposite orientation. The Mordant Orange films also suffered from an inconsistency in SHG across the slides. This could possibly due to a lack of self-healing which is a well known feature of polymer-polymer ISAM films, and is not expected to be as efficient in films containing monomeric species.

Additional studies were performed on Mordant Orange prior to the establishment of the SHG measurement procedure used so far in this thesis. Originally, one side of the substrate was removed by polishing, and the single-sided ISAM samples were characterized by measuring the SHG intensity as a function of the intensity of the fundamental at a constant 45° incident angle. Comparison of the quadratic fit to the data leads to a determination of the effective second-order nonlinear susceptibility. When we initiated studies of ISAM films with only a few layers, the signal was weak enough that interference of SHG from the films with surface SHG from the opposite air-glass interface was observable. In order to obtain a good fit to the data, we incorporated an interference fringe technique for single-sided samples that eventually led to the
**Figure 4.1.6:** Single-side absorbance for Mordant Orange studies. Films grew thicker with increased bilayer adsorption.
Chapter 4  Incorporation of Monomer Chromophores

Figure 4.1.7: $\sqrt{I_{2\omega}}$ as a function of number of bilayers for Mordant Orange studies. Films failed to exhibit growth of SHG with increased number of bilayers. Each datum is an average over the measurements of 2 separately fabricated samples.
simpler technique for double-sided samples. This technique provides illustrative proof of eq. 3.3.24 which states that the SHG of one side of a double-sided film is one-fourth the SHG generated by the constructive interference of two sides.

Figure 4.1.8 shows the SHG signal as a function of the incident angle for a 2-bilayer Mordant Orange 10 / PAH ISAM sample from which one side of the film has been removed. The fringes with non-zero minima result from interference of the SHG from the film with the SHG from the air-glass interface on the opposite side. The lower curve in the figure shows the SHG signal from a bare glass slide. Because the air-glass interface is inherently noncentrosymmetric, it also possesses a non-zero $\chi^{(2)}$ and generates second harmonic. The two air-glass interfaces on the bare slide create an SHG signal with maximum ~10 counts in the vicinity of 45° incident angle. This corresponds to a second harmonic electric field amplitude, proportional to the square root of the SHG, of 1.5 counts$^{1/2}$ for each of the glass-air interfaces. The fringes for the sample with a film on one side can then be interpreted as a field amplitude of 9.5 counts$^{1/2}$ from that side and 1.5 counts$^{1/2}$ from the opposite side. This results in an SHG maximum of 121 counts $[(9.5+1.5)^2]$ and a minimum of 64 counts $[(9.5-1.5)^2]$, in excellent agreement with the data.

Incorporation of $\beta$-cyclodextrin (Figure 4.1.4) causes an increase in solubility of Mordant Orange 10 at pH 3 from $10^{-4}$ M to $10^{-3}$ M. Figure 4.1.9 shows this results in a two-fold increase of SHG intensity. Incorporation of $\beta$-cyclodextrin did not resolve the issue of failure of Mordant Orange to exhibit growth of SHG with the number of bilayers. However, the results offer potential for incorporation of cyclodextrins in polymer-polymer films and in other type of films that may be used for purposes other than second harmonic generation.
**Figure 4.1.8:** SHG interference fringe pattern for a single-sided film. Upper curve shows interference fringes from a Mordant Orange 10 / PAH ISAM sample of 2 bilayers, from which one side of the film has been polished off. The fringes with non-zero minima result from interference of the SHG from the film with the SHG from the air-glass interface on the opposite side. The lower curve in the figure shows the SHG signal from a bare glass slide.
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**Figure 4.1.9:** SHG Interference fringes for β-cyclodextrin maximum solubility study. β-Cyclodextrin causes an increase in solubility of Mordant Orange 10 at pH 3 from $10^{-4}$ M to $10^{-3}$ M. This results in a two-fold increase of SHG intensity.
4.2 Hybrid Covalent / Ionic Self Assembly

In continuing efforts to develop a self-assembled organic structure for use in electro-optic devices, we have recently introduced a novel technique involving monomer chromophores that improves polar ordering and $\chi^{(2)}$. This technique involves covalently attaching the chromophore at only one of its ends, providing a preferential polar orientation, then ionically attaching the subsequent cationic layer. For initial studies of this procedure, we chose a chromophore that met the requirements for hybrid covalent / ionic assembly and that was commercially available at a low cost. The molecule is Procion Red MX-5B, shown in Figure 4.2.1.a, and also shown incorporated into an ISAM layer in Figure 4.2.1.b. This molecule has a very low molecular first-order molecular hyperpolarizability ($\beta$ in eq. 1.3.4), yet has exhibited a second-order susceptibility that rivals any reported polymer-polymer ISAM film.

![Figure 4.2.1: Schematic illustration of (a) Procion Red MX-5B molecule, and (b) Procion Red MX-5B between two PAH layers illustrating the tendency to form thin (sub-nanometer), highly oriented bilayers.](image-url)
When a film with a PAH outer layer is immersed in a Procion Red (PR) solution, the triazine ring on Procion Red (PR) can covalently react with the PAH amines. This occurs preferentially at PR pH values greater than the pKa (9) of PAH. When a film with an upper layer of PR is immersed in PAH, protonated amines of PAH can electrostatically attach to the PR sulfonates, preferentially occurring at pH<9. Procion Red / PAH films were fabricated using 25 mM Procion Red at pH 10.5, and 10 mM PAH at pH 7. These layers were allowed to adsorb for 10 minutes each.

The absorbance spectrum for the thickest film in this study is shown in Figure 4.2.2. It is obvious that Procion Red (PR) absorbs significantly at the second harmonic wavelength (532 nm). Unfortunately, a specially designed photomultiplier tube (PMT) is necessary to measure wavelengths greater than 600 nm. Incorporation of such a PMT is in progress. Utilizing eq. 3.3.22 in the same manner as in Section 3.3.2, we calculate that the films have ~100% relative SHG conversion efficiency. However, the coherence length \( l_c = 1/\Delta k \) of these films is unknown, so the assumptions of \( \Delta k L/2 < 2 \) used in Section 3.3.2, although likely, may not be valid for these films. A smaller value of coherence length could result in different SHG conversion efficiencies for films thicker than the ones presented here. To illustrate this point, Figure 4.2.3, generated by Mathematica 4.0, shows the SHG conversion efficiency as calculated from eq. 3.2.22 for a non-SHG-absorbing film (red, solid line), and a hypothetical film with 1.0 single-side absorbance at the SHG wavelength (blue, dashed line). If the quantity \( \Delta k L/2 \) in eq. 3.3.22 is greater than 3, the SHG conversion efficiency, relative to an equivalent non-SHG-absorbing film would climb rapidly as shown by the black, dash-dot line. For the Procion Red films in this thesis, the SHG conversion efficiency remains near 100% until reaching that value where the conversion efficiency of a non-absorbing film is zero. This is quite an interesting phenomenon of second-order nonlinear optics. For two films with the same wave-vector mismatch \( \Delta k \), as the film thickness is near a value \( L \approx 6 p l_c \), where \( p \) is an integer, an SHG-absorbing film will exhibit greater conversion efficiency than a non-SHG-absorbing film, as illustrated in Figure 4.2.4 for a film with 1.0 single-side absorbance. Future study is warranted in order to characterize the susceptibility for the films that have greater number of bilayers.
**Figure 4.2.2:** Typical absorbance spectrum for Procion Red / PAH film. The peak at 523 nm is used to monitor film growth. Absorbance at SHG wavelength (532 nm) is not large enough to adversely effect the SHG efficiency for films in this study.
**Figure 4.2.3:** SHG conversion efficiency plots, generated by Mathematica 4.0, as calculated from eq. 3.2.22. Shown is a non-SHG-absorbing film (red, solid line), and a film with 1.0 absorbance at the SHG wavelength (blue, dashed line) to illustrate SHG conversion efficiency of thicker films. The absorbance of the 30-bilayer film at 532 nm is 0.16. Also shown is the SHG conversion efficiency of the SHG-absorbing film relative to the non-SHG absorbing film (black, dash-dot line).
Figure 4.2.4: SHG conversion efficiency plots, generated by Mathematica 4.0, as calculated from eq. 3.2.22. Shown are a non-SHG-absorbing film (red, solid line), and a film with 1.0 absorbance at the SHG wavelength (blue, dashed line) to illustrate the SHG conversion efficiency phenomenon. For two films with the same wavevector mismatch $\Delta k$ and film thickness near a value $L \approx 6p\lambda_c$, where $p$ is an integer, an SHG-absorbing film will exhibit greater conversion efficiency than a non-SHG-absorbing film.
Figure 4.2.5 shows the absorbance as a function of the number of bilayers. The linearity demonstrates that uniform deposition is obtained in each adsorption step. The square root of the SHG as a function of the number of bilayers is shown in Figure 4.2.6. The square root of the SHG increases linearly with the number of bilayers, demonstrating preferential polar orientation of the PR molecule and sustained orientation as additional layers are added. Further, the SHG remained constant across the length of the film as shown in Figure 4.2.7. There is less error in the SHG measurement of the Procion Red study than for the cation study largely due to refinement of the multi-stage system.

The results of calculations of the effective second-order nonlinear optical susceptibilities, along with as film thickness and absorbance data are presented in Table 4.2.1. Figure 4.2.8 shows the trend of the second-order nonlinear optical susceptibility, without accounting for SHG absorption. From the SHG data as well as the susceptibility trend, we can hypothesize that SHG conversion efficiency is not a large factor. However, further study is warranted before any trend can be established with full confidence. If the SHG conversion is not a factor, then the Figure 4.2.8 shows that the effective susceptibility asymptotically approaches a value $\chi^{(2)}_{\text{eff.ISAM}}$ that rivals the best polymer-polymer ISAM film we have fabricated and tested, despite the small molecular hyperpolarizability $\beta$ of Procion Red. As with the Cation study, we expect the asymptotic value in Figure 4.2.8 to match the value of $\chi^{(2)}_{\text{eff.ISAM}}$, utilizing the analysis presented in Section 3.4.2, using eq. 3.4.3. For this data, $l_{bl,ISAM} = 0.55$ nm, $I_{2\omega,ref} = 557$ a.u., and slope (of SHG versus number of bilayers) = $0.83 \sqrt{\text{a.u.}/\text{bl}}$, resulting in $\chi^{(2)}_{\text{eff.ISAM}} = 4.6 \times 10^{-9}$ esu. This is in excellent agreement with the asymptotic value shown in Figure 4.2.8, revealing Procion Red / PAH films with a large number of bilayers, fabricated with solutions of 25 mM Procion Red at pH 10.5, and 10 mM PAH at pH 7, will exhibit a second-order nonlinear optical susceptibility $\chi^{(2)}_{\text{eff.ISAM}} = 4.5 \times 10^{-9}$ esu.
Figure 4.2.5: Absorbance of one film (one side of the sample) as a function of the number of bilayers. Linear relation shows constant chromophore deposition throughout the growth of the film which is also indicative of constant film growth.
Figure 4.2.6: \( \sqrt{I_{2\omega}} \) as a function of number of bilayers. The square root of SHG increases linearly with the number of bilayers, demonstrating preferential polar orientation of the Procion Red molecule and sustained orientation as additional layers are added.
Figure 4.2.7: Interference fringe patterns for three positions along the sample. Data are offset for the purpose of distinguishing the three positions which are 1 cm apart. The SHG intensity offset for positions \{1,2,3\} are \{0, 2000, 4000\} a.u., respectively. Each datum is an average of 50 measurements.
Table 4.2.1: Results for Procion Red / PAH films.

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<th>Number Bilayers</th>
<th>Thickness ±10%, (nm)</th>
<th>Absorbance ±0.0005</th>
<th>$\chi_{\text{eff}}^{(2)}$, ±20% (10⁻⁹ esu)</th>
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<tr>
<td>1</td>
<td>0.55</td>
<td>0.0018</td>
<td>34</td>
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<tr>
<td>5</td>
<td>2.8</td>
<td>0.0097</td>
<td>8.1</td>
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<td>10</td>
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<td>5.9</td>
</tr>
<tr>
<td>20</td>
<td>11</td>
<td>0.0575</td>
<td>5.4</td>
</tr>
<tr>
<td>30</td>
<td>17</td>
<td>0.0845</td>
<td>4.9</td>
</tr>
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</table>
Figure 4.2.8: Nonlinear susceptibilities $\chi^{(2)}_{\text{eff}}$ for Procion Red / PAH films. As with the PCBS / PAH films, the susceptibilities asymptotically approach a true value of $\chi^{(2)}_{\text{eff}}$ for the film.
4.3 Conclusions

By replacing polymer chromophores with monomer chromophores, we have significantly reduced competitive dipole orientation and eliminated randomly oriented chromophores in the bulk of the anion layer inherent in films produced exclusively with polyelectrolytes. We found that films fabricated with this hybrid covalent / ionic technique exhibit an effective $\chi^{(2)}$ that rivals the best polymer-polymer ISAM film. The first-order molecular hyperpolarizability $\beta$ is very low for Procion Red, suggesting that incorporation of high $\beta$ molecules may result in significant improvement of $\chi^{(2)}$. Further, the SHG remained constant across the length of the film, showing that the hybrid covalent / ionic self-assembly does not suffer from the film morphology problems apparently inherent with dianionic chromophores. This is likely due to the chromophores being locked in place to the subsequent layer by covalent bonding. Future studies will incorporate usage of a specialized PMT that can detect light in the non-absorbing region of the Procion Red films.
107 P. J. Neyman, M. T. Guzy, S. Shah, H. Wang, H. W. Gibson, K. E. Van Cott, R. M. Davis, C. Figura, J. R. Heflin,


CHAPTER 5

CONCLUSIONS

This thesis has presented an investigation into a novel technique for the fabrication of nanometer scale organic multilayer films for use in nonlinear optical (NLO) applications. Ionically self-assembled monolayer (ISAM) films are an assemblage of oppositely charged polymers built layer by layer through coulombic attraction utilizing an environmentally friendly process to form ordered structures that are uniform, molecularly smooth and physically robust. In addition to NLO properties, this study has provided valuable information into the structure of the ISAM films, which was presented as a secondary goal of this thesis.
In continuing efforts to develop a full understanding of the structure of ionically self-assembled monolayers and, in particular, its relation to polar ordering and $\chi^{(2)}$, we systematically studied the effect of varying the NLO-inactive polycation as described in Chapter 3. The films presented in this thesis were fabricated using a 10 mM solution of PCBS at pH 7, and a 10 mM solution of PAH at varied pH. Using PAH as a polycation with PCBS as the NLO-active polyanion, we have found that increasing the polycation pH from 7 to 10, while keeping the polyanion pH fixed at pH 7, yielded an increase in the bilayer thickness of a factor of 45. While the average chromophore tilt angle away from the preferred direction was decreased and the total SHG intensity was increased for the higher pH value, the $\chi^{(2)}$ value was significantly deceased due to the random orientation of chromophores within the thicker PCBS layers, and to the larger fraction of PAH content relative to PCBS.

There are several competing effects regarding $\chi^{(2)}$ as the polycation pH is increased. The amount of PCBS adsorbed upon each layer deposition is increased and the average tilt angle of the chromophores away from the direction of the net polar order (perpendicular to the substrate) appears to decrease. Both of these would tend to increase the $\chi^{(2)}$ value. However, as we have reported previously in the study of varying the polyanion and polycation pH values simultaneously, thicker layers of the NLO-active polymer lead in fact to decreased $\chi^{(2)}$ values. This is because the chromophores within the "bulk" of the monolayer tend towards random orientation. This effect works towards a decreased $\chi^{(2)}$ value at the higher PAH pH value. The effective nonlinear optical susceptibility is the $\chi^{(2)}$ that results from all the components in the susceptibility tensor. While the susceptibility which determines the usefulness of the material is that along the axis (zzz) normal to the substrate. $\chi^{(2)}_{\text{eff}}$ for the pH 7 series was determined to be $3.1 \times 10^{-9}$ esu, and $\chi^{(2)}_{\text{eff}}$ for the pH 10 series was $0.33 \times 10^{-9}$ esu. The largest susceptibility determined for polymer-polymer ISAM films was for the PCBS / PAH variation with both at 10 mM and pH 7, and was found to be $\chi^{(2)}_{zzz} = 1.2 \times 10^{-9}$ esu, which is 64% of the $\chi^{(2)}$ of quartz.
We have also found that the use of polycations PDDA and PLL with PCBS does not lead to bulk $\chi^{(2)}$ effects, suggesting that hydrogen bonding plays a vital role in obtaining polar order. Films made with each of these polycations exhibited linear growth of absorbance with number of bilayers demonstrating that a constant rate of PCBS deposition per bilayer was achieved. However, after the first bilayer, the SHG intensity remained essentially constant as the number of bilayers was increased. Thus, although PCBS was well incorporated into ISAM films with PDDA and PLL, net polar ordering was not achieved with these polycations as it was with PAH. It is possible that the first layer retains a net orientation since it is so near the glass surface, or that the final layer possesses a net orientation that is lost upon subsequent layer adsorption.

We speculate that hydrogen bonding may play a role in the orientational stability of the films. The primary amines on PLL and PAH are capable of forming hydrogen bonds while the quaternary amines on PDDA are not. The location of the hydrogen-bonding group in reference to the backbone may also be a governing factor. The amine group on PAH is separated from the backbone by just one methyl group while the amine on PLL is separated from the backbone by four methyl groups, making a much larger distance between the amine and the backbone. The hydrogen-bonding group will be more mobile in films made with PLL, thereby allowing chromophores to orient in a more random fashion. While the usage of polycations other than PAH failed to produce good $\chi^{(2)}$ films, they did produce high-quality ISAM films, which reveals their potential in other applications such as LEDs, photovoltaics and electrochromic devices.

These studies aided in developing a picture of the structure of ISAM films, described largely in Chapter 2. There is increasing evidence that ISAM layers are quite interpenetrated rather than stratified. When the film is immersed in a dipping solution, the phase at the surface of the film is altered due to the solution parameters; thus, the degree of interpenetration is also altered. The pH of the dipping solution also dictates the degree of ionization of the polyelectrolytes as well as the free ion concentration, which increases with decreased pH of the anionic solution, and increases with increased pH of the cationic solutions. We refer to the free ion concentration as the concentration of ions of opposite charge to the polyelectrolyte in solution. With decreased electrostatic exclusion volume due to decreased cation solution pH, for instance, the polymer
obtains more degrees of freedom, thus higher configurational entropy and more negative $\Delta G$ of adsorption which results in increased adsorption as well as more loopy polymer conformation. This can result not only in a thicker adsorbed layer due to increased diffusion layer thickness and increased polymer looping and dangling from that layer, but also greater interpenetration into the previously adsorbed layers due to increased reptation (snake-like motion) afforded by the more loopy polymer conformation of previous layers and increased configurational entropy of the penetrating polymer chains. Therefore, for a polyelectrolyte, the thickness of the adsorbed layer is largely controlled by the two competing effects of electrostatic exclusion modeled by the electric double-layer, and the electrostatic exclusion volume about the ionic groups. While increased free ion concentration increases the ability for polymer chains to intermingle and form thicker layers due to an increased electrostatic exclusion zone around the polymer sidechain ionic groups, it also serves to govern the thickness due to a macroscopic electronic screening illustrated by the electric double-layer model. These models and vantage points help to demonstrate the complexity of ISAM films. The set of models presented helps to provide a better understanding of the morphology of ISAM films.

In attempts to overcome the drawbacks of polymer-polymer ISAM films, we incorporated monomer chromophores in place of polymer chromophores, as presented in Chapter 4. One type of monomer-polymer film we studied contained the dianionic NLO chromophore Mordant Orange 10 which contains as sulfonate and one end, and a carboxy at the other end. The sulfonic acid moiety has a pKa near zero while that of the carboxylic acid is 5. Thus, at a pH of 3, the sulfonic acid will be ionized while the carboxylic acid will remain neutral. When the substrate is immersed in a Mordant Orange aqueous solution at pH 3, the sulfonate will be preferentially adsorbed towards the preceding polycation layer. Subsequent immersion in the polycation solution at pH 7 will lead to ionization of the carboxy groups, allowing adsorption of the next polycation layer. The structure of such a film is expected to possess a much larger net polar orientation than a polymer-polymer film.
In order to improve orientation of the dianionic chromophores as well as their solubility in solution, β-cyclodextrin was incorporated into the Mordant Orange solution. Cyclodextrins are a family of cyclic oligosaccharides that have been of increasing interest due to their ability to easily complex with rod-like molecules (rotaxanes) and chain or ring-like molecules (catananes). The molecules form a conical cylinder whose interior region is lined by hydrogen atoms and glycosidic oxygen bridges. β-cyclodextrin comprises 7 glucopyranose repeat units, and has an inner diameter of 7.8 Å at the larger opening. When in aqueous solution, the apolar cavity is filled with energetically unfavored water molecules that are easily substituted by guest Mordant Orange molecules, which are less polar than water.

Two comparisons were made in this study. For both, the pH and molarity of PAH were held constant at 7 and 10 mM, respectively. The first study involved the comparison of Mordant Orange films at pH 7 with and without β-cyclodextrin complexation. The second study involved variation of the pH of the β-cyclodextrin-complexed Mordant Orange solution. For both, the pH and molarity of PAH were held constant at 7 and 10 mM, respectively. The molarity of Mordant Orange was varied from 0.5 mM to 1 mM for both studies, and the molarity of β-cyclodextrin was 0.16 M. These layers were allowed to adsorb for 5 minutes each, with the exception of the initial layer which was allowed to adsorb for 10 minutes.

The films grew thicker with increased number of bilayers for all films, but neither study resulted in a growth of SHG with the number of bilayers. Because the outermost monolayer of Mordant Orange is only tethered to the preceding PAH layer by a single ionic bond for each molecule, each chromophore can by dissociated during the following immersion into PAH. The Mordant Orange molecule may either be removed from the film entirely or subsequently reabsorb with opposite orientation. The Mordant Orange films also suffered from an inconsistency in SHG across the slides. This could possibly due to a lack of self-healing which is a well known feature of polymer-polymer ISAM films, but is not expected to be as efficient in films containing monomeric species.
The incorporation of β-cyclodextrin caused an increase in solubility of Mordant Orange 10 at pH 3 from $10^{-4}$ M to $10^{-3}$ M. This resulted in a two-fold increase of SHG intensity. Incorporation of β-cyclodextrin did not resolve the issue of failure of Mordant Orange to exhibit growth of SHG with the number of bilayers. However, the results offer potential for incorporation of cyclodextrins in polymer-polymer films and in other types of films that may be used for purposes other than second harmonic generation.

Finally, we examined the incorporation of monomer chromophores containing ionic and covalent bonding sites. This novel hybrid covalent / ionic deposition technique is in its infant stage, yet has produced exciting results. By replacing polymer chromophores with monomer chromophores, we have significantly reduced competitive dipole orientation and eliminated randomly oriented chromophores in the bulk of the anion layer inherent in films produced exclusively with polyelectrolytes. We found that films fabricated with this hybrid covalent / ionic technique exhibit a $\chi^{(2)}$ that rivals the best polymer-polymer ISAM film. The effective nonlinear optical susceptibility $\chi_{\text{eff,ISAM}}^{(2)}$ of the Procion Red / PAH film studied here was $4.6 \times 10^{-9}$ esu. The first-order molecular hyperpolarizability $\beta$ is very low for Procion Red, suggesting that incorporation of high $\beta$ molecules may result in significant improvement of $\chi^{(2)}$. Further, the SHG remained constant across the length of the film, showing that the hybrid covalent / ionic self-assembly does not suffer from the film morphology problems apparently inherent with dianionic chromophores. This is likely due to the chromophores being locked in place to the subsequent layer by covalent bonding. Future studies will focus on methods for increasing the $\chi^{(2)}$ of films fabricated using the hybrid / ionic fabrication technique.
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