Studying and Controlling Chromophore Orientation in Polyelectrolyte Layer-by-Layer Thin Films

By

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B.S. Chemical Engineering
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Studying and Controlling Chromophore Orientation in Polyelectrolyte Layer-by-Layer Thin Films

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ABSTRACT
Many properties such as electrical conductivity, liquid crystallinity, and optical properties depend on specific molecular orientation. Currently, this orientation is achieved using either inorganic crystals or rigorously processed organic materials. This thesis studied a film assembly technique that provides a mechanism for aligning polymeric materials as films are assembled. This eliminates the need for a post-processing alignment step and allows easier film construction.

The fabrication technique for the polymeric thin films is layer-by-layer (LBL) electrostatic assembly. This technique takes advantage of the electrostatic attraction between oppositely charged polyelectrolytes to assemble films. For example, a polyanion and polycation are dissolved in separate aqueous solutions at a given pH and salt concentration. A charged substrate is immersed into one solution, rinsed with water, and immersed in the other solution. This cycle is repeated to assemble films. Typically, the polyelectrolytes in these films are randomly arranged; however, a few researchers have demonstrated that ordered films could be assembled with the LBL technique. We investigated the driving force of this order and how to control it by studying the processing parameters, polyelectrolytes, and surfaces used to assemble ordered LBL films.

For the processing study, two side-chain chromophoric polyanions were used. One, PolyS119, contained sulfonic acid groups while the other, PAZO, contained carboxylic acid groups. These were assembled with four polyamines. The pH of the polyanion solutions was varied to observe its effect on chromophore orientation. Chromophore orientation was measured by FTIR and UV/Visible spectroscopy. From these studies it was determined that stronger electrostatic attraction leads to more orientation; thus, orientation can be controlled by adjusting the strength of the attraction using different pH values since the ionization of the polyelectrolytes changes with the pH. The salt concentration of the solutions has a more subtle effect. The salt can change the ionization of polyelectrolytes in solution, which changes their ionization and influences the electrostatic attraction. Again, it was demonstrated that chromophore orientation could be adjusted by changing the solution conditions.
LBL film structure is influenced by the processing conditions as well as the chemical structure of the polyelectrolytes. Since we studied how processing parameters affect orientation, we also wanted to determine the role of chemical structure. Other research on liquid crystals has shown that the spacer length between the side- and main polymer chain affects rigid side-chain orientation. For this study, a series of polymers of varying spacer length were synthesized. These were then assembled with the same four polyamines used in the previous studies. More orientation with increased spacer length was observed indicating that chromophores with longer spacers have more freedom from the main polymer chain and this allows more orientation. This effect is independent of the polyamine used to assemble the films. Another chemical structure study was changing the location of the charged group from the side-chain chromophores to the polymer main-chain. Two copolymers were synthesized with uncharged side-chain chromophores and a charged main chain. As expected, films assembled with these polyions show much less order compared to the charged chromophore containing polyamions. These results confirm the electrostatic attraction between the chromophore and polyamine is a main driving force for orientation.

In addition to the processing conditions and chemical structure of the polyelectrolytes, these films were constructed onto substrates. The previous studies used bare substrates. A study was undertaken to determine the effect of these substrates on chromophore orientation. The substrates were modified prior to LBL film assembly by self-assembled monolayers and non-chromophore containing LBL films. The substrate does affect the first layer of chromophores and enhances their orientation; however, as the films grow, this enhancement is lost as the subsequent layers adsorb. Other than the first layer, chromophore orientation within LBL films is independent of the type of substrate, which allows a variety of substrates to be used.

Since the main driving force for chromophore orientation is electrostatic attraction, the processing parameters, which all influence this attraction, can control the orientation. In addition, the chemical structures of the chromophore containing polyelectrolytes affect the orientation. A combination of intelligent synthetic design and processing condition selection can result in well-ordered films that would be useful in optical or electronic devices that require specific molecular orientation.
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# Table of Contents

1. Introduction and Background ................................................. 7  
   1.1. Objective ........................................................................... 9  
1.2. Background and Review ....................................................... 9  
   1.2.1. Background on Non-linear Optics ...................................... 10  
   1.2.2. Background of Organic Bulk Ordered Materials (LC and NLO) ....... 12  
   1.2.3. Self-Assembled Ordered Thin Films ................................. 15  
1.3. References ........................................................................... 22  
2. Experimental Setup, Procedures, and Models ............................ 25  
   2.1. Layer-by-Layer Film Assembly ........................................... 25  
   2.2. Materials for the LBL Films .............................................. 26  
   2.2.1. Substrates ..................................................................... 27  
   2.2.2. Polycations .................................................................... 27  
   2.2.3. Polyanions ..................................................................... 29  
   2.3. Film Thickness Measurement ........................................... 32  
   2.4. Orientation Procedures, Measurements, and Models ............... 33  
   2.4.1. Fourier Transform Infrared Spectroscopy (FTIR) ................. 35  
   2.4.1.1 FTIR Setup ................................................................ 35  
   2.4.1.2. Model for FTIR Data .............................................. 37  
   2.4.2. UV/Visible Spectroscopy (UV/Vis) ..................................... 43  
   2.4.2.1 UV/Visible Spectroscopy (UV/Vis) Setup ....................... 44  
   2.4.2.2 Mathematical Models for UV/Vis Data ............................. 45  
   2.4.3. Differences between FTIR and UV/Vis models .................... 49  
2.5. References ........................................................................... 50  
3. Effect of Processing Conditions on Chromophore Orientation ........ 52  
   3.1. Effect of Polyanion pH on Orientation ................................. 55  
   3.1.1. Experimental Procedures ............................................... 59  
   3.1.2. Orientation of PolyS119 or PAZO Films with pH Adjustment ...... 61  
   3.1.4. Discussion of Thickness and pH Trends ............................. 74  
   3.2. Effect of Polycation pH on Orientation .................................. 77  
   3.2.1. Experimental Procedure ............................................... 78  
   3.2.2. Orientation of PolyS119 with Polycations at Neutral pH .......... 78  
   3.2.4. Discussion of Polycation pH Effects ................................. 87  
3.3. Effect of Salt Concentration on Chromophore Orientation ........... 88  
   3.3.1. Experimental Procedures ............................................... 89  
   3.3.2. Effect of Salt Concentration on Chromophore Orientation ... 90  
   3.3.4. Discussion of Salt Effects for PolyS119 and PAZO Films ......... 96  
3.4. Summary and Conclusions on the Effect of Processing Parameters on Orientation ......................................................... 98  
3.5. References ........................................................................... 100  
4. Effect of Polyelectrolyte Chemical Structure on Chromophore Orientation .............................................................. 103  
   4.1. Effects of Ionizable Groups on Chromophore Orientation .......... 104  
   4.2. Effect of Spacer Length on Chromophore Orientation .............. 106  
   4.2.1. Experimental Setup and Synthesis Schemes ....................... 108  
   4.2.2. Thickness and Layer Growth of poly-HABA-n films .............. 111
<table>
<thead>
<tr>
<th>Section</th>
<th>Title</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>4.2.3</td>
<td>Results and Discussion on Spacer Length and Orientation</td>
<td>112</td>
</tr>
<tr>
<td>4.3</td>
<td>Effect of Charge Placement on Chromophore Tilt Angle</td>
<td>115</td>
</tr>
<tr>
<td>4.3.1</td>
<td>Experimental Setup and Synthesis scheme</td>
<td>115</td>
</tr>
<tr>
<td>4.3.2</td>
<td>Results and Discussion on Charge Placement and Orientation</td>
<td>118</td>
</tr>
<tr>
<td>4.4</td>
<td>Conclusions</td>
<td>122</td>
</tr>
<tr>
<td>4.5</td>
<td>References</td>
<td>124</td>
</tr>
<tr>
<td>5.</td>
<td>Effect of Surface on Chromophore Orientation</td>
<td>126</td>
</tr>
<tr>
<td>5.1</td>
<td>Orientation of Chromophores on Bare Substrates</td>
<td>127</td>
</tr>
<tr>
<td>5.1.1</td>
<td>Experimental Procedure</td>
<td>127</td>
</tr>
<tr>
<td>5.1.2</td>
<td>Orientation of PolyS119 after each layer</td>
<td>128</td>
</tr>
<tr>
<td>5.1.3</td>
<td>Orientation of PAZO after each layer</td>
<td>131</td>
</tr>
<tr>
<td>5.2</td>
<td>Effect of Different Substrate Treatments on Chromophore Orientation</td>
<td>133</td>
</tr>
<tr>
<td>5.2.1</td>
<td>Experimental Setup</td>
<td>134</td>
</tr>
<tr>
<td>5.2.2</td>
<td>Results and Discussion on Different Substrate Treatments</td>
<td>135</td>
</tr>
<tr>
<td>5.3</td>
<td>Controlling film deposition on substrates</td>
<td>140</td>
</tr>
<tr>
<td>5.3.1</td>
<td>Experimental Setup</td>
<td>140</td>
</tr>
<tr>
<td>5.3.2</td>
<td>Controlling Film Deposition Results</td>
<td>141</td>
</tr>
<tr>
<td>5.4</td>
<td>Conclusion for Surface results</td>
<td>142</td>
</tr>
<tr>
<td>5.5</td>
<td>References</td>
<td>144</td>
</tr>
<tr>
<td>6.</td>
<td>Second Harmonic Generation Measurements</td>
<td>145</td>
</tr>
<tr>
<td>6.1</td>
<td>Experimental Setup</td>
<td>146</td>
</tr>
<tr>
<td>6.2</td>
<td>Results from SHG Measurements</td>
<td>147</td>
</tr>
<tr>
<td>6.3</td>
<td>Conclusions</td>
<td>148</td>
</tr>
<tr>
<td>6.3</td>
<td>References</td>
<td>149</td>
</tr>
<tr>
<td>7.</td>
<td>Summary, Conclusions, and Applications</td>
<td>150</td>
</tr>
<tr>
<td>7.1</td>
<td>Summary</td>
<td>150</td>
</tr>
<tr>
<td>7.2</td>
<td>Conclusions</td>
<td>151</td>
</tr>
<tr>
<td>7.3</td>
<td>Applications of this Research</td>
<td>151</td>
</tr>
<tr>
<td>7.4</td>
<td>References</td>
<td>154</td>
</tr>
<tr>
<td>Appendix A</td>
<td>FTIR model</td>
<td>155</td>
</tr>
<tr>
<td>Appendix B</td>
<td>UV/Vis model</td>
<td>158</td>
</tr>
</tbody>
</table>
1. Introduction and Background

With the advent of the transistor leading to a large microelectronic economy, there has been a drive to create smaller and smaller devices. A similar evolution has been witnessed for optical and photonic industries. Devices that were originally visible have gone to micro- and nano-scale level. Since many devices depend on specific placement of materials in order to develop specific properties, controlling how the materials are constructed becomes of great concern. A problem develops when trying to specifically control the placement of materials when devices become microscopic or smaller. Self-assembly is one technique that has become popular in research due to its ease and low cost. Self-assembly techniques all involve exploiting a natural driving force to create complex assemblies. Nature has evolved these techniques over millions of years and now science is looking towards these techniques to shrink devices, ease assembly, and enhance device properties. On the nanoscale level, the control of individual molecules becomes necessary to control device properties. This thesis investigated a very simple self-assembly technique as a means to control molecular orientation and optical properties in thin polymeric films. Typically, optically active materials were constructed using inorganic crystals for non-linear optics, fiber optics, photonic materials, and electronic materials usually based on silicon. Unfortunately, crystals are fragile, expensive, and difficult to modify which leads to research into finding organic replacements for inorganic materials. Dopants can be used to enhance properties, but they can affect the crystal lattice and thereby negatively affect the desired crystalline properties. The goal of organic electronic materials research is to find compounds that can be synthesized in large quantity, exhibit properties similar or better than inorganic
crystals, and be physically more robust. Organic chemists have a large toolbox of reactions that can be used and research has been performed to make these replacements and then improve them using chemistry.[1] However, organic crystals have some of the same physical limitations as inorganic crystals such as poor physical stability and processing difficulties. This led researchers to polymers. Polymers have great physical characteristics and processing ability, but they are more difficult to align in a specific orientation due to their large size compared to small-molecule crystalline materials. In order to orient the polymers, many different processing techniques have been used.[2] These processing techniques are typically time-consuming and expensive. Self-assembly (SA) techniques could provide a quick and cheap processing method for ordered thin films. This thesis used one such SA technique called electrostatic layer-by-layer (LBL) assembly to construct oriented thin films.[3, 4] LBL film assembly is being rigorously researched by many groups because of its ability to create functional films by cheap and simple processing methods.[3-6] Many types of materials may be used in LBL assembly as long as they reverse the net charge on the substrate surface upon adsorption. LBL films have been constructed using a variety of materials, but for this research polyelectrolytes are most relevant.[7-13] LBL films are fabricated by dipping a charged surface into a solution of a dissolved oppositely charged species. Ionic bonds form at the surface between the opposite charges. As a layer of polyelectrolyte is deposited, the net charge on the surface is reversed, which reduces adsorption of like charges. The substrate can then be dipped into the oppositely charged polyelectrolyte solution to continue the assembly. Typically, the polyelectrolytes within the films have no preferred orientation; however, studies have demonstrated that the fabrication of LBL films with
specific molecular order is possible for some chromophore-functionalized polyions.[14, 15] Yet, little is known about why these films display this order.

1.1. Objective

We want to understand whether and how these LBL films exhibit chromophore orientation and the driving forces for this orientation. This understanding will be determined by measuring chromophore orientation of films constructed with varying solution processing conditions, different substrates, and new polymers with systematically controlled chemical structures. Several methods of film characterization will be applied to measure chromophore orientation. The processing condition studies will examine the role of polyelectrolyte ionization, excess ions in solution, and substrate effects on chromophore orientation. The effect of polyelectrolyte chemical structure will be explored by tailored chemical synthesis of polymers for LBL assembly. The results will be a set of rules and a general understanding of the influence of polymer architecture, charge density, and processing parameters on orientation of polymer side-chain chromophores in LBL films. The potential applications include electrical conductive, photovoltaic, or optically active films.

1.2. Background and Review

The quest for self-assembled oriented polymer systems has been proceeding for decades. Initially, inorganic crystals were studied and some of these are still in use today. Deficiencies in some aspects of these materials led research into organics, including polymers. As the shift to polymers was being made processing effects took on more importance. Researchers sought to use materials that had better physical properties but
required careful processing of the materials to achieve high degrees of orientation. This led to using self-assembly to construct films with higher degrees of order.

This review will provide an introduction to non-linear optics (NLO) and an overview of different ordered bulk systems such as NLO materials and liquid crystals (LC), and their evolution from inorganic materials to small-molecule organics and finally to macromolecular materials. These were initially all studied as bulk films, typically solvent or spin cast. Also, an overview of ordered thin self-assembled films will be discussed. These films mark the transition to thin films, where processing conditions are used to provide or enhance order in thin films as they are created.

1.2.1. Background on Non-linear Optics
Currently we live in an electronic age. Information is transmitted and stored via electrons and magnets as hard disk drives. The primary material of concern is silicon. Recent years have seen the growth in optics for moving information quickly using light instead of using electrons. Currently, digital signals are converted from an electronic source to optic transmission then back to an electronic signal at the receiver. The electronic signal is then used for processing the information. Eventually, light will become the medium of choice for the processing of information due to the demand for speed in information transmission. The use of light to process and store information will require us to take advantage of non-linear optic properties.

When light strikes a material it can be transmitted through, absorbed by, or reflected off the material. If the light intensity is very strong, a non-linearity can arise with transmitted light. The polarization \( P \) is related to the electric field \( E \) of the light as shown in Equation 1.1.
\[ P = \chi^{(1)} \cdot E + \chi^{(2)} \cdot EE + \chi^{(3)} \cdot EEE + \ldots \] (1.1)

The second-order and higher terms in Equation 1.1 give rise to non-linear properties. The term \( \chi^{(2)} \) is the second-order susceptibility, which is a measure of the second-order non-linear properties of a material. This phenomenon was not observed until the development of lasers that had strong light intensities. Many crystalline materials, such as quartz and lithium niobate (LiNbO₃), exhibit strong non-linearity. These inorganic materials are still used today to generate non-linear effects in optical communication. For inorganic crystals, the NLO properties are thought to arise from electrons not associated with individual nuclei similar to those in metals or semiconductors that allow electrical conduction; thus, inorganic crystals do not need special processing to exhibit NLO behavior. For polymers, NLO properties are derived from their molecular dipolar structure and the arrangement of their chromophores. An electron donating and electron withdrawing groups contacted by a pi-conjugated core constitute the typical organic NLO chromophore. In equation 1.1, for second-order effects to occur, the material dipoles must be aligned in a noncentrosymmetric orientation (Figure 1.1). Stronger dipoles and noncentrosymmetric alignment lead to stronger NLO properties. Second-order effects manifest themselves in the two ways as shown in Figure 1.2. The first is a frequency doubling effect where incident light has its frequency doubled after transmittance. The second is an electrooptic effect where an electric field shifts the phase of the light due to a change in refractive index in response to the electric field. The strength of the NLO signal increases with thickness until the film is thicker than the wavelength of light \[2, 16\]
1.2.2. Background of Organic Bulk Ordered Materials (LC and NLO)

The first organic NLO materials were small-molecule crystals. These were synthesized to have strong dipoles and were oriented by electric field poling. Typically, a film was spin cast. Then, this film was heated and a strong electric field was applied, followed by quenching to "freeze" in the order. This orient the dipoles parallel to the electric field. The poling process can induce non-centrosymmetric order, critical to achieve an NLO
effect. Without poling, centrosymmetry prevails, and NLO signal strength decreases.

The difference between these alignments is shown in Figure 1.3.

\[ \begin{align*}
\uparrow & \quad \downarrow \\
\downarrow & \quad \downarrow
\end{align*} \]

Non-centrosymmetric (net dipole) \quad Centrosymmetric (no net dipole)

**Figure 1.3** Examples of dipole alignment

A major drawback to this technique is the relaxation of the molecules with time or heat leading to decay in the noncentrosymmetric order.[2, 17, 18] Polymers, due to their large size and slow relaxation times, were used to address these limitations. Polymers were first used as a bulk matrix for doping with small NLO molecules. These blends were then poled; however, these films still exhibited orientation decay and phase separation.[19-21] This led to the synthesis of polymers with chromophores attached on either the side- or main-chain. Typically, these polymers have high glass transition temperatures (Tg) to reduce relaxation at room temperature. Again, these were cast and electric field poled. The orientation of these materials was more stable; unfortunately these typically had weaker properties than the small-molecules. Different studies were done with these materials such as blends with small NLO molecules. Some of these materials are shown in Figure 1.4. Most NLO organic materials have a donor, π conjugation, and acceptor configuration similar to those exhibited in Figure 1.4.[2]

These materials have been optimized by many research groups to achieve the strongest NLO effects.
In addition to more acceptable processing properties and physical characteristics, organic materials have been synthesized that possess NLO properties greater than that of the "industry standard" lithium niobate. For example, lithium niobate has an electro-optic coefficient of about 26 pm V\(^{-1}\) while some organics exhibit values as high as 82 pm V\(^{-1}\).[2]

Liquid crystals (LCs) are self-ordering organic systems that exhibit ordered melt phases due to shape anisotropy and packing effects. Commonly studied as small molecules that align to form specific phases, LCs have been used for electro-optic and electro-clinic field response. Again, a driving force for new LC materials was new LC properties and phases as well as improving physical properties and increase domain size. LCs are used extensively in display applications. Typically, the order in LC materials is different from NLO in that it is centrosymmetric. Different alignment techniques are used for LC materials from electric field alignment similar to e-field poling for NLO materials to physical methods such as surface rubbing to align the LCs at the substrate surface. LCs align spontaneously so these alignment techniques are used to achieve large domain sizes rather than induce specific LC phases. Many liquid crystalline materials are rigid rod-
shaped similar to those NLO materials shown in Figure 1.4. Some examples of LC phases are shown in Figure 1.5.[24, 25]

\[
\begin{array}{c}
\text{nematic} \\
\includegraphics[width=0.4\textwidth]{nematic.png}
\end{array} \quad \begin{array}{c}
\text{smectic} \\
\includegraphics[width=0.4\textwidth]{smectic.png}
\end{array}
\]

- liquid crystalline mesogen

**Figure 1.5 – Liquid Crystalline phases**

### 1.2.3. Self-Assembled Ordered Thin Films

Spin or solvent cast bulk films usually have to be aligned using a post-casting treatment. NLO films were constructed via casting and then oriented via an electric field poling. In contrast, LC films can exhibit orientation just from casting but usually these films are annealed to enhance this alignment. These methods are difficult to incorporate into a manufacturing process and have decay in the orientation with time or temperature.

Studies have been performed to fabricate films using a self-assembly process that will align the rigid mesogens (LC or NLO) without post-fabrication treatments. These would allow orientation as the films are constructed as opposed to constructing a randomly oriented film.

One technique used to construct ordered thin films relies on the use of alternating specific chemical reactions on a surface. These reactions can be used to construct rod-like molecules on a substrate. Marks and coworkers were very successful designing a synthetic scheme to build very well-ordered NLO films, one reaction at a time.[26-28]

The scheme grows chromophores one step at a time on a silicon substrate. Although these molecules are very well ordered, this technique has many disadvantages when compared to other types of film assembly. The chromophores constructed are limited by
the types of reactions that can be performed; the construction of films is slow due to the specific conditions required for each reaction; and the films are very thin and their thickness is limited by steric interactions between the rods on the surface. Also, the reactions require 100% yield per cycle to continue to build structures. This technique is best suited as a supplement to the other film construction techniques. For example, chromophores could be constructed onto a substrate and used to aid the alignment of chromophores assembled on top of them. Other methods to self-assemble films eliminate most of the disadvantages of stepwise chemical reactions.

One of the earliest methods to construct films using self-assembly was the Langmuir-Blodgett (LB) technique. [29] Langmuir and Blodgett exploited the tendency of amphiphilic materials to self-assemble at an air-water interface. This material’s hydrophobic tail group prefers the hydrophobic medium of air, while the hydrophilic head group remains submerged in the water phase. These amphiphilic materials are then mechanically compressed by a physical barrier into a two-dimensional solid monolayer on the air-water surface. Raising and lowering a substrate through this layer creates a kinetically frozen, highly ordered film. Figure 1.6 demonstrates the LB film creation process. Well-ordered films can be constructed this way when rigid amphiphilic molecules are used. NLO and LC films have been constructed of small molecules or polymers by using the LB technique. Many researchers have found the LB technique to be useful to construct well-ordered films. Initial work incorporating LC small molecules into LB films was performed by Dörfler and coworkers. [30] Many other groups continued to study LC molecules at the air-water interface and on solid substrates extending this technique to include many functional materials. [31-34] Carpenter and
coworkers used side-chain polymers with liquid crystalline NLO chromophores.[35] These films displayed both LC order and noncentrosymmetric orientation. The first study of NLO chromophores in an LB film were performed by Aktsipetrov et al.[36] This was quickly followed by a number of other researchers studying NLO effects using the LB technique to align the chromophores.[37, 38] This work continues to the present with newly synthesized polymers containing NLO chromophores.[39, 40] All these studies demonstrate the high degree of order achieved using the LB technique; however, researchers have difficulty in fabricating thick and stable films and LB work is time intensive, expensive, and requires special equipment.[29]

![Diagram](image)

**Figure 1.6** – Langmuir-Blodgett film construction

The LB technique has several disadvantages. Only amphiphilic materials can be used to construct LB films, which limits the choice of material incorporated in the film. The construction of the monolayer requires very clean conditions, and it would be hard to
mass-produce devices using LB methods. A self-assembly method that avoids these disadvantages is the LBL technique.

This process was first developed by Iler in 1966. His films were fabricated using ionic components like colloidal silica and alumina, boehmite fibrils, proteins, and polystyrene beads. An electrostatic attraction between the substrate and a positively charged colloid dissolved in an aqueous solution caused it to adsorb on the substrate. Since each of the colloidal materials was covered with surface charge, the adsorbing species created a new surface that had a positive charge. A second negatively charged colloid could be sequentially adsorbed again by electrostatic attraction. Dipping the substrate between these two solutions of negatively and positively charged species built up layers. The layers were the thickness of the particles it was composed of indicating that the adsorption was stopping after the surface was covered. The LBL technique was rediscovered in the early 1990s when Decher and coworkers assembled films of positively and negatively charged rigid bipolar amphiphiles. One charged end of the amphiphile was electrostatically bound to the oppositely charged surface, while the other end created a new surface for sequential deposition of the next charged species. By alternating the oppositely charge bipolar molecules, organic films were deposited with a regular thickness. However if the molecules adsorbed laying flat on the surface as opposed to standing up, the film growth would eventually cease. Only the ends of the molecules were ionized, so when they were laying flat much of the surface was uncharged. As the dipping continued, the surface charge would be decreasing with each layer adsorbed until there was not enough surface charge to electrostatically attract more material. This problematic effect limited the total film thickness that could be achieved,
and small molecules had a tendency to desorb. Using polyelectrolytes instead of small molecules solved this problem. The large number of charged groups on each polyelectrolyte could ionically bond to the oppositely-charged surface preventing desorption while the charge density of the surface stayed approximately constant. This enabled much thicker films to be constructed ad infinitum.

Decher's group extended the LBL system to include polyelectrolytes and combinations of polyelectrolytes and bipolar amphiphiles. They laid the groundwork for processing conditions and materials studied. The ionic strength of the aqueous solutions was varied and its effects on the layers studied. Adding salt proved to thicken the layers. This trend was observed for salt concentrations up to 1 M NaCl. Decher continues to explore the structure and mechanism of polyelectrolyte multilayers assembled by LBL and writes many reviews. At MIT, the Rubner group was quick to realize the commercial advantages of LBL fabrication, and moved quickly towards constructing functional films. Organic light emitting diodes were fabricated by LBL assembly by incorporating conjugated polyelectrolytes into thin films. Using polyelectrolytes like polyaniline and a precursor of poly(phenylenevinylene), Rubner and coworkers pioneered new simpler processing methods for construction of conducting and light emitting films. They have also incorporated functional dyes and observed electrochemiluminescence in LBL films.

A number of groups have constructed NLO active and ordered LBL films. Decher and coworkers first used a NLO chromophore-containing polymer (PAZO) but did not test for a second-harmonic signal. They used other spectroscopic techniques to determine order. Lvov, who has worked with Decher, and coworkers used PAZO and measured
the second harmonic generation (SHG) of the LBL films.[15] SHG is a measure of the noncentrosymmetric order in the films and the strength of the NLO effects. The PAZO films exhibited non-centrosymmetric order only for very thin, 2 layer films. As more layers were deposited, the NLO properties disappeared. Lvov only studied solutions that were not pH adjusted.[15] Other groups followed quickly with NLO active films with different polymers.[14, 52, 53] The studies by Wang et al, Lvov et al, and Laschewsky et al examined very thin films of about 5 bilayers or less and observed decreases in SHG signal as the films grew thicker. Heflin et al and later Roberts et al [54] were able to grow much thicker (~40 bilayer) films with increasing SHG signal as the films grew. No other groups have shown these NLO effects increase with thickness. All groups used side chain polymers and all except Roberts et al and Laschewsky et al had the charged group on the side chain chromophore. The chemical structures used for these studies were very similar to each other as shown in Figure 1.7.

![Chemical structures](image)

**Figure 1.7** - Side chain chromophores used by a) Lvov et al, b) Wang et al, c) Heflin et al, d) Roberts et al, and e) Laschewsky et al

These studies leave many questions unanswered on the mechanism for orientation in LBL films. For example, all these studies use one counter polyelectrolyte, one salt concentration, and one pH value for the polyelectrolyte solutions. The effects of these
processing parameters on NLO order are not considered. Additionally, only two groups observed increasing noncentrosymmetry with increasing layers. Also these side chain polymers have very short spacers separating the side and main chains. The effect of spacer length is unknown. These studies indicate the placement of the charged group on the polymer does not influence the noncentrosymmetric ordering of the chromophores. This thesis will attempt to understand these effects on chromophore orientation and determine the driving forces for this orientation in LBL films.
1.3. References


2. Experimental Setup, Procedures, and Models
This chapter will discuss the various materials and methods used in this research as well as the mathematical models used to interpret the experimental data. The chapter will start with an experimental description of layer-by-layer assembly, which is the method used to construct films. This is followed by descriptions of the substrates and polyelectrolytes for film assembly. Lastly, the film characterization techniques are discussed.

2.1. Layer-by-Layer Film Assembly
The procedure for constructing a layer-by-layer (LBL) film is very straightforward. A substrate is alternately soaked or dipped into positive or negative polyelectrolyte solutions with rinsing between the dipping. For example, the substrate is dipped into polyanion solution allowing deposition onto the surface until there is a net negative charge. At this point no more absorption of polyanion occurs due to charge repulsion with material on the substrate. The substrate is then rinsed and dipped into polycation solution. The polycation is attracted to the negatively charged substrate. Again polycation absorbs until there is a net positive charge on the substrate. Then the rinsing and dipping cycle is repeated to construct the film.

Most films discussed in this work were constructed using a modified Carl Ziess DS50 programmable slide stainer that performs dipping, rinsing, and ultra-sonication on the substrates. A schematic of the slide stainer is shown in Figure 2.1 along with sample immersion solutions. Substrates were exposed first to polycation solution for 10 minutes, followed by 2 minutes of rinsing in several MilliQ water baths, then exposed to polyanion solution for 10 minutes, rinsed, and then the cycle was repeated for a nominal number of layer pairs – 40 layer pairs for most measurements. The pH of the polyanion solutions were varied by the addition of 0.1 M HCl or NaOH and measured using a
Beckman 10 pH meter. The pH of the polycation solutions was usually 3.5. The ultrasonication step removes any loosely bound (physically adsorbed) polyelectrolyte on the surface. The pH of all solutions are determined and adjusted prior to insertion into the slide stainer. Deionized water (resistivity \( \sim 18.0 \, \text{M} \Omega \)) is provided by a Milli-Q DI system and used with its pH unadjusted. Films are kept wet during the dipping process, and after the stainer is finished with its program, the substrates are left soaking in a previously unused rinse until removal from the machine. Different substrates are dipped at the same time to ensure similar solution conditions and films on multiple substrates.

\[ \text{Figure 2.1} - \text{Illustration of slide stainer and dipping procedure} \]

Films that required measurements after each layer were constructed by hand using process similar to the slide stainer: without any ultrasonic. Also these films were dried in a nitrogen stream after each rinse.

2.2. Materials for the LBL Films
For LBL film assembly, three components are essential: substrates, polycations, and polyanions. These will be discussed in detail in this section. All chemicals were purchased through Sigma-Aldrich and used without further purification. The
polyelectrolytes discussed in this section are those used in the construction of thin films. Chemicals used for synthesis for new polymers will be discussed in Chapter 4.

2.2.1. Substrates

Substrates were either polished single crystal (111) silicon wafers, silicon wafers coated with evaporated gold, or glass slides. Silicon wafers and glass slides are rinsed with acetone followed by ethanol, and then they are etched in reactive oxygen plasma for 5 minutes. The plasma cleans the surface and leaves polar groups on the surface and a small negative charge. Evaporated gold wafers are produced by using a polished silicon wafer and evaporating at high vacuum 100 Å of chromium for adhesion then depositing 1000 Å of gold via thermal evaporation. These substrates are rinsed with ethanol prior to use. Prior to use, gold substrates are soaked in a carboxylic acid terminated thiol solution to impart a negative charge on the surface. Since all substrates are negatively charged, they were dipped into polycation solution first.

2.2.2. Polycations

Polycations used in construction of LBL films are poly(diallyldimethylammonium) chloride (PDAC), poly (allylamine hydrochloride) (PAH), branched poly(ethyleneimine) (BPEI), and linear poly (ethyleneimine)(LPEI). Chemical structures of these polycations are shown in Figure 2.2.
PAH, LPEI, and BPEI are called “weak” polycations since their ionization changes with solution pH. The ionization of PDAC does not change due to four covalent bonds on its nitrogen; thus, it is termed a “strong” polycation. Ionization curves of these polycations are shown in Figure 2.3.[2-11]
As can be seen in Figure 2.3, the polycations have unique pKa's. PAH, which contains all primary amines off the main polymer chain, has a pKa of approximately 8.5. BPEI, which contains primary, secondary, and tertiary amines in a ratio of approximately equal percentage, has a pKa of about 7. LPEI consists of all secondary amines on the main chain and has a pKa of around 5\textsuperscript{[1]}. These polymers are soluble over the pH ranges used in the research independent of the degree of ionization. For example, LPEI is soluble in an aqueous solution at a pH of 8.5 even though LPEI is only about 25% ionized at that pH. If polycation solution pH is very basic (~10) then the weak amines will precipitate out of solution.

2.2.3. Polyanions
Two commercially available polyanions were used in construction of LBL films, PolyS119 and poly\{1-[4-(3-carboxy-4-hydroxyphenylazo)-benzenesulfonamido]-1,2-ethanediyl, sodium salt\} (PAZO). Their chemical structures are shown in Figure 2.4.

![Chemical Structures](image)

**Figure 2.4** – Structure of polyanions for LBL films

PAZO has a carboxylic acid for an ionizable group, which has a pKa of about 5; thus, it will be termed a “weak” polyanion. PolyS119 has a sulfonic acid with a pKa of
approximately $-6^{[12]}$ and will be called “strong”. Both these polyanions have strong electron donor and acceptor groups on either end of the azobenzene conjugation. Typically phenols exhibit a pKa from about pH 12 and higher$^{[13]}$. Because of these groups, the phenolic hydrogen could be more acidic. This could present a problem if excess salt is added to the solutions. The salt concentration would need to be doubled if the phenol is deprotonated. In order to determine the pKa of the phenol, solutions of varying pH were made, and their absorbance measured in an UV/Visible spectroscopy experiment. A red shift occurs as the phenol group becomes deprotonated. These results show that for pH values 8.5 and below the UV/Vis absorbances appear the same indicating no deprotonation of the phenol groups. These results are shown in Figures 2.5 and 2.6 and Tables 2.1 and 2.2.

![Graph showing absorbance of PAZO at different pH](image)

**Figure 2.5** – UV/Visible absorbance of PAZO at different pH, 0.01 M solution
<table>
<thead>
<tr>
<th>pH</th>
<th>Wavelength of Maximum PAZO Absorbance</th>
</tr>
</thead>
<tbody>
<tr>
<td>8.5</td>
<td>509 nm</td>
</tr>
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</tr>
<tr>
<td>12.5</td>
<td>557 nm</td>
</tr>
<tr>
<td>13</td>
<td>561 nm</td>
</tr>
</tbody>
</table>

**Table 2.1** – Wavelength Shift of PAZO with pH

A red shift in wavelength starts at pH 8.5 for PAZO and continues increasing to pH 13 and possibly beyond. This indicates a small amount of deprotonation of the phenol at pH 8.5 increasing as the solution becomes more basic. All films are constructed at pH 8.5 or lower so the deprotonation of the phenol should not present at problem.

![Figure 2.6 – UV/Visible absorbance of PolyS119 at different pH, 0.01 M solution](image)

<table>
<thead>
<tr>
<th>pH</th>
<th>Wavelength of Maximum PolyS119 Absorbance</th>
</tr>
</thead>
<tbody>
<tr>
<td>2</td>
<td>537 nm</td>
</tr>
<tr>
<td>3.5</td>
<td>537 nm</td>
</tr>
<tr>
<td>5</td>
<td>537 nm</td>
</tr>
<tr>
<td>7</td>
<td>537 nm</td>
</tr>
<tr>
<td>8.5</td>
<td>537 nm</td>
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</tr>
<tr>
<td>10</td>
<td>537 nm</td>
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<td>11</td>
<td>537 nm</td>
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<td>538 nm</td>
</tr>
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</tr>
<tr>
<td>13</td>
<td>547 nm</td>
</tr>
<tr>
<td>13.4</td>
<td>547 nm</td>
</tr>
</tbody>
</table>

**Table 2.2 – Wavelength Shift of PolyS119 with pH**

A red shift in wavelength starts at between pH 11 and 12 for PolyS119 and continues increasing to pH 13. This indicates a very small amount of deprotonation of the phenol at pH 8.5 increasing as the solution becomes more basic. The red shift is less dramatic in PolyS119 indicating that the pKa of the phenol group is above pH 13. The phenolic proton is much less acidic in PolyS119 than in PAZO probably due to the electron withdrawing of the carboxylic acid.

**2.3. Film Thickness Measurement**

When a new system of polycations and polyanions are initially being studied, film thickness provides a means to study their behavior. Film thickness is used to monitor and study the growth of the LBL films. Film thickness provides clues to the ionization states of the polyelectrolytes and is used in the orientation calculations presented in the following sections. In addition individual layer thickness has been used to determine the orientation of small molecule dyes; however, this technique is not valid for polymers due to the complexity of polymer adsorption and layer thickness[14].

Film thickness is measured via ellipsometry, which uses polarized laser reflection off a substrate to measure thickness. This technique is very accurate (± 3 Å) on submicron films provided the substrate is smooth and reflective. All three substrates, glass, silicon, and gold, work for this measurement. For ellipsometric measurements, a Gaertner L117
instrument equipped with a HeNe laser is used. Substrate values are measured prior to film construction, and these values are used as backgrounds for the measurements. The ellipsometry setup is shown in Figure 2.7.

![Ellipsometry Setup](image)

*Figure 2.7 – Setup of ellipsometry experiments*

2.4. Orientation Procedures, Measurements, and Models

Once the films are constructed and their thickness characterized, films are prepared for the spectroscopy experiments that will allow the determination of chromophore orientation. The LBL process deposits a film on both sides of the substrates. Unfortunately, the models used to determine chromophore orientation assume a film on only one side of the substrate. Therefore, one side of the substrate is cleaned by etching the surface with “piranha” etch, which is a 1:1 mixture of concentrated sulfuric acid and concentrated hydrogen peroxide. This mixture is allowed to soak one side of the substrate for 5 minutes, and then mixture and film are removed by gently wiping the surface. Substrates are rinsed with DI water for 2 minutes to remove any excess film and piranha etch and dried under a nitrogen stream. An example of a substrate before and
after etching is shown in Figure 2.8. As expected the etching of film on one side reduces the absorbance by about 50%.

![Graph showing absorbance vs wavelength for two-sided and one-sided substrates](image)

**Figure 2.8** – Comparison of substrate with film on both sides to one-sided substrate

The chromophore tilt angle can be projected onto a coordinate system as shown in Figure 2.9. If the x-y plane is the substrate, the tilt angle can be calculated by measuring the projection of the chromophore onto the x-y and z-y planes. Using polarized light and changing the incident angles of the light, these two projections can be measured. Then the projection on the third plane, x-z, can be calculated. Once these three projections are determined, the chromophore tilt angle can be calculated. Since the third projection is calculated, the chromophore angle is uniaxial about the z-axis. For example, if one chromophore lying totally in z-y plane with an angle of $\theta_{zy}$ with respect to the x-y substrate plane is compared to one lying in the x-z plane with the same angle, so $\theta_{xz} = \theta_{zy}$, they will be calculated to have the same orientation. Larger the tilt angle $\theta$, the more chromophore orientation the film has.
Figure 2.9 – Diagram of the chromophore tilt angle on a coordinate system and on the substrate

In order to measure two projections, Fourier transform infrared (FTIR) and UV/Visible (UV/Vis) spectroscopy are used. Both of these techniques measure absorption of light by chromophores and have flexibility to vary incident angles of the source beam.

2.4.1. Fourier Transform Infrared Spectroscopy (FTIR)

FTIR allows two measurements to be performed that can measure two projections of the chromophore. The two experiments consist of reflecting the IR beam off the sample while the other transmits it through the sample. FTIR measurement detects individual functional groups in the films.

2.4.1.1 FTIR Setup

FTIR studies were conducted at room temperature using a Nicolet Magna 550 spectrometer equipped with a liquid-nitrogen cooled MCT detector in a purged sample chamber. All measurements were performed with 512 accumulated scans at a resolution of 4 cm⁻¹ and were baseline corrected. For external-reflection absorption measurements a Spectra-Tech Model FT-80 reflection attachment with a fixed 80° angle was used with a
zinc selenide polarizer. The setup of the external reflection experiment is shown in Figure 2.10.

![Diagram of External Reflection FTIR experiment](image)

**Figure 2.10 – External Reflection FTIR experiment**

For external-reflection or grazing angle measurement, a gold-coated silicon wafer is used as the substrate. This measurement is very sensitive and can be used to detect films as thin as 15 Å. Transmission FTIR measurements were performed on thin silicon wafers that are polished on both sides. Silicon wafers, although polished and visible light reflective, cannot be used in an IR reflection experiment due to their nonmetallic surface. Transmission measurement is not as sensitive as reflection measurement due to some IR absorption by the silicon substrate. Figure 2.11 shows how the source beam is polarized, represented by the electric field vector (E), in the two measurements.
The following section will discuss the mathematical model used to interpret and calculate chromophore tilt angles from FTIR data.

2.4.1.2. Model for FTIR Data

As illustrated in Figure 2.11, the two measurements are polarized differently. The measurements only detect covalent bonds that are aligned with the electric field vectors. Therefore, transmission experiment detects the chromophores’ projection onto the substrate plane while reflection experiment detects projections in the plane perpendicular to the substrate. Since FTIR detects the projection of individual transition dipole moments, these absorptions will have to be converted into a projection of the whole chromophore. Figure 2.12 illustrates how the two measurements detect different projections of a sulfonamide group using the O=S=O dipoles. The symmetric O=S=O stretch causes the sulfur and oxygen atoms to move along the direction of the arrow, mostly in the z-direction (Figure 2.12). As drawn in Figure 2.12, the symmetric stretch is perpendicular to the substrate and would absorb strongly in the reflection measurement since the electric field vector is polarized perpendicular in the reflection experiment. The asymmetric stretch is orthogonal to the symmetric stretch and as shown in Figure 2.12
moves parallel to the substrate. This dipole would absorb strongly in the transmission measurement since it detects transitions parallel to the plane of the substrate. The molecule shown in Figure 2.12 is oriented perpendicular to the substrate, but if the molecule is tilted then the two FTIR measurements will detect components of both symmetric and asymmetric transition moments.

\[ \text{Figure 2.12} \quad \text{Diagram of symmetric and asymmetric stretches for the sulfonamides of PAZO and PolyS119} \]

As shown in Figure 2.4, PAZO and PolyS119 are poly (sulfonamides); therefore, the sulfonamide functional group is chosen as the transition dipole to be observed in FTIR spectra. The symmetric stretch of the sulfonamide appears at about 1150 cm\(^{-1}\) and the asymmetric at 1330 cm\(^{-1}\)[15]. Both of these appear as very strong peaks. Polycations used in the LBL films do not have any absorbance in these regions. Also the other functional groups on the polyanions do not interfere with absorbance of the sulfonamide. Figures 2.13 and 2.14 shows sample reflection and transmission spectra of PolyS119 at 1150 and 1330 cm\(^{-1}\).
Figure 2.13 – Sample transmission and reflection spectra of PolyS119 at 1150 cm$^{-1}$

Figure 2.14 – Sample transmission and reflection spectra of PolyS119 at 1330 cm$^{-1}$

The intensities of the poly (sulfonamides) are tabulated from FTIR spectra and are used as input to a model that will calculate chromophore tilt angles.

The LBL film system is modeled as shown in Figure 2.15. The system is treated as a continuum of air/film/substrate/air for transmission and air/film/substrate/film/air for reflection measurements.
Indices of refraction of each layer are used to calculate the incident angles for the reflection experiments. For the polymer film a value of 1.45 is used, for silicon substrates an average refractive index is calculated from the ellipsometric measurements. The LBL film is treated as one uniform material rather than as individual layers. Air has an index of refraction of 1. As light transmits through the model system the incident angle changes as the index of refraction changes with the different layers via Snell’s law (Equation 2.1),

\[ n_1 \sin \psi_1 = n_2 \sin \psi_2 \]  

(2.1)

where \(n_1\) and \(n_2\) are the refractive indices of layers 1 and 2, and \(\psi_1\) and \(\psi_2\) are the incident light angles in the respective layers.

Once the thickness, incident angles, refractive indices, and FTIR intensities are determined for the LBL films, these are input into the model to calculate the orientation of chromophores. The model was proposed by Chollet, et al and later modified by Takenaka\[^{16-19}\]. The beam reflecting off the metallic substrate is different than the beam transmitting through a nonmetallic substrate. This model accounts for this difference by including the frequency-dependent effect on the enhancement factor for reflection.
spectra. Hansen's formulation for optics of thin films is incorporated into the model to calculate these frequency-dependent effects\textsuperscript{[20]}

According to the model, the substrate surface is the x-y plane and the z-direction is normal to the substrate plane (see Figure 2.16). Light is polarized in the x-direction making the absorption intensity in the transmission mode proportional to the x-component of the imaginary part of the complex dielectric constant $\varepsilon_x''$ and the absorption intensity in reflection mode proportional to both the x- and z-components of the imaginary part of the complex dielectric constants $\varepsilon_x''$ and $\varepsilon_z''$.

![Diagram](image.png)

**Figure 2.16** – FTIR model system for the chromophore tilt angle

Therefore, the ratio of transmission-absorption ($A_t$) to reflection-absorption ($A_R$) is related to the dielectric constants in the following manner:

$$\frac{A_t}{A_R} = \frac{\varepsilon_x''}{(m_x\varepsilon_x'' + m_z\varepsilon_z'')}$$ \hspace{1cm} (2.2)

In this equation intensity enhancement factors $m_x$ and $m_z$ along the x- and z-axis respectively are included to account for the different absorption effects caused by the
metallic surface. If the orientation angle ($\theta$) is defined as the angle between the transition dipole moment and the surface normal, equation 2.2 can be rewritten as

$$
\frac{A_t}{A_r} = \frac{\sin^2 \theta}{(2m_x \cos^2 \theta + m_x \sin^2 \theta)}
$$

(2.3)

The appropriate values of $m_x$ and $m_z$ can be calculated from Hansen's formulas for optics of thin films as functions of frequency of the absorption band ($\nu$), the angle of incidence for the source beam ($\Phi$), the film thickness ($h$), and the complex refractive indices of the film and substrate ($n_2$ and $n_3$). In this research, $\Phi$ is 80 degrees, $h$ varies depending on the film, $n_2$ is 1.45 and $n_3$ for the substrates is determined by ellipsometry. Since the asymmetric vibrations ($\alpha$) and symmetric vibrations ($\beta$) vectors form a plane, a third vector ($\gamma$) orthogonal with respect to this plane can be defined (see Figure 3.17). The tilt angle for the third vector ($\gamma$) can be calculated from $\alpha$ and $\beta$ using

$$
\cos^2 \alpha + \cos^2 \beta + \cos^2 \gamma = 1
$$

(2.4)

If the other covalent bonds on the sulfonamide were perpendicular to the plane formed by the O=S=O atoms, then $\gamma$ would be the tilt angle, but there is an angle ($\zeta$) between this plane and the rest of the chromophore (see Figure 3.17). This bond angle is modeled using Chem3D and is 54.5 degrees. By taking this angle into account, the tilt angle ($\theta$) is determined. The tilt angle ($\theta$) is the angle of the first aromatic ring of the azobenzene structure in PAZO and PolyS119 with the substrate plane. The model is solved for $\theta$ using MAPLE V Release 5.1. Appendix A contains a copy of the MAPLE program.
The assumptions made in the model are all chromophores are uniaxial around the surface normal, and the substrate does not influence the orientation of the chromophores. The first assumption of uniaxial orientation is tested by polarizing the FTIR beam in different directions for the transmission measurement. When this experiment is performed, the IR absorption stays constant. The second assumption is tested by constructing films on different substrates and measuring the film thickness on each one. In addition previous work has shown that surface effects only penetrate 5 Å into a monolayer, and the LBL film layers are typically thicker than 5 Å. Given that the assumptions are satisfied, the Takenaka model can be used to determine chromophore orientation in LBL films measured by FTIR.

2.4.2. UV/Visible Spectroscopy (UV/Vis)

One of the drawbacks to using gold and silicon substrates is they do not transmit visible light. In order to measure optical properties of the films, they must be constructed onto glass substrates. Since the films have to be constructed on glass substrates, tilt angle
measurements are performed using UV/Visible (UV/Vis) spectroscopy. Similar to the FTIR experiments, two measurements will be made except instead of a reflection measurement both are transmission through the substrate. Also both measurements are performed on one substrate rather than using two as in the FTIR experiments. Unlike the FTIR, the UV/Vis detects the visible transitions of the whole chromophore. The other polyelectrolytes used in films do not have any visible absorbance.

2.4.2.1 UV/Visible Spectroscopy (UV/Vis) Setup

For the UV/Vis experiments an Oriel helium source lamp is used with an Oriel Instaspec IV CCD detector cooled to 263 K via a thermoelectric cooler to reduce the dark signal. A 1200 lines/mm grating with 170 nm scan width is used to split the source light prior to the detector array. Each spectrum is background corrected in ambient light and compared to a reference spectrum of a blank glass slide. The source light is polarized using sheet polarizer. Each spectrum is a composite of 150 accumulated scans.

In order to get orientation information from UV/Vis, the source light must be polarized, and the substrate tilted toward the incident light. This allows the detection of chromophores in and out of the substrate plane. Unlike the FTIR experiment, in both measurements the light transmits through the substrate, but the source light is polarized in different directions. The s-polarized measurements detect chromophores lying preferentially in the plane of the substrate. The p-polarized measurements detect the chromophores lying perpendicular to the substrate plane. A top-view illustration of the experimental setup is shown in Figure 2.18 where in the p-polarized setup the light is
polarized in the plane of this page and the s-polarized light is polarized perpendicular to this page.

![Diagram of UV/Vis experiments](image)

**Figure 2.18** – Diagram of UV/Vis experiments

The following section will explain the data from the UV/Vis and how this data is converted into chromophore tilt angles.

### 2.4.2.2 Mathematical Models for UV/Vis Data

As illustrated in Figure 2.18, the two measurements are polarized differently. The measurements only detect transitions that are aligned with the electric field vectors. Therefore, the s-polarized experiment detects the chromophores' projection onto the substrate plane while the s-polarized experiment detects projections in the plane perpendicular to the substrate. Since the UV/Vis detects electronic transitions that occur across the whole chromophore, the tilt angle determined will be for the chromophore unlike for the FTIR measurement. The UV/Vis will detect of the visible π-π* transitions of the azobenzene chromophores shown in Figure 2.2. Figure 2.19 illustrates how the two measurements detect different projections of a PAZO chromophore on the substrate.
Figure 2.19 – Diagram of PAZO chromophore on a substrate

As drawn in Figure 2.19, the chromophore transition is represented as the double-headed arrow. The projection of this transition onto the z-axis is detected by the p-polarized measurement. The s-polarized measurement detects the projection onto the substrate or x-y plane. The model will calculate the tilt angle based on the absorption intensity of these two projections.

PAZO and PolyS119 both have π-π* transitions that are in the visible region. These absorptions are shown for PAZO and PolyS119 solutions in Figures 2.5 and 2.6. Sample spectra for PAZO with s- and p- polarization are shown in Figure 2.20.
Figure 2.20 – Polarization dependence of PAZO film

The absorption intensities for the s- and p-polarization are tabulated from the UV/Vis spectra and are used as input to a model that will calculate the chromophore tilt angles.

The LBL film system is modeled as shown in Figure 2.21. The system is treated as a continuum of air/film/substrate/air for the UV/Vis experiments similar to the FTIR transmission experiments except now the substrate is at an angle to the incident beam.
Figure 2.21 – Model System

The indices of refraction of each layer are used to calculate the incident angles for the UV/Vis experiments. For the polymer film a value of 1.45 is used, and for the glass substrate 1.5 is used. The air has an index of refraction of 1. As with the FTIR model, Snell's Law (Equation 2.1) is used to calculate the incident angles at the interface of each layer. These angles are shown in Figure 2.21 as $\delta_i$.

Once the thickness, incident angles, refractive indices, and absorption intensities are determined for the LBL films, these are input into the model to calculate the orientation of the chromophores. This model was also proposed by Chollet, et al and later modified by Kawai and coworkers[16, 17, 21]. Since the substrate is tilted towards the incident light and is polarized, the amount reflected off the substrate surface varies, and this causes the light intensity transmitted through the sample to vary depending on whether it is s- or p-polarization. This model accounts for this difference between the polarizations. The setup for the model is very similar to the FTIR one except this does not include the enhancement factors for a metallic substrate. This model also takes into account the reflection off of the interfacial surfaces. The ratio of the p-polarized absorption ($A_p$) to the s-polarized absorption ($A_s$) is given by

$$A_p / A_s = \frac{n_1 \cos i + n_3 \cos r}{n_1 \cos r + n_3 \cos i} \left( \cos i \cos r + \frac{2n_1^2 n_3 \sin^2 i}{n_2^4 \tan^2 \theta} \right)$$  \hspace{1cm} (2.5)$$

where $n_1$, $n_2$, and $n_3$ are the indices of refraction for the air, film, and substrate (1,1.45, and 1.5, respectively); $i$ is the angle of incidence at the air-film interface (60 degrees); and $r$ is the angle of incidence at the film-substrate interface calculated by Equation 2.1.
This model has the same assumptions as the FTIR model and these assumptions are satisfied by the same measurements. The uniaxial orientation is tested by rotating the polarizer when the substrate is normal to the source light and the other by thickness measurements on different substrates. Again both assumptions are satisfied. Appendix B shows the MAPLE worksheet used to calculate tilt angles.

2.4.3. Differences between FTIR and UV/Vis models

There are two main differences between the FTIR and UV/Vis measurements and models. The FTIR films are constructed onto two substrates, which make the model more complicated. Also the FTIR measures the tilt angle of one functional group. The UV/Vis uses one substrate and measures the tilt angle of the visible chromophore transition. The difference between the tilt angles is shown in Figure 2.22. The FTIR tilt angle ($\Theta_{\text{FTIR}}$) is higher than the UV/Vis tilt angle ($\Theta_{\text{UV}}$) due to the difference in detection methods.

![Diagram of FTIR and UV/Vis Tilt Angles](image)

**Figure 2.22** – Tilt angle measured by FTIR and UV/Vis
2.5. References


3. Effect of Processing Conditions on Chromophore Orientation

There has been considerable interest in constructing self-assembled thin films due to their ease and low cost of fabrication. Applications for these films are very diverse, ranging from simple surface modifications to complex optical devices. Many applications including electrical conductivity, photorefractivity, liquid crystalline, photovoltaic, and nonlinear optical properties (NLO), require specific molecular orientation within the films. If oriented self-assembled films of these materials can be constructed, the cost and time of device manufacture would be decreased significantly. As an example of these applications, a short review of nonlinear optical device manufacture will be discussed and compared to a self-assembly technique.

For NLO device applications, the chromophores must be aligned in a noncentrosymmetric (net dipole) orientation in order to exhibit NLO properties. Typically, NLO devices are painstakingly constructed of inorganic crystalline materials that have inherent electro-optical properties; however, these materials are expensive, fragile, and difficult to process. The combination of polymeric materials and self-assembly techniques improves the mechanical properties and lowers the cost and time to manufacture these films. It also broadens the range of products for which it might be used including thin plastic electronic and optical devices and displays. The polymeric materials have improved physical properties and easier processing than the inorganic compounds currently used, but polymers typically do not exhibit optical properties without an alignment procedure or will have multiple grains of varying alignment.[1-4] Self-assembly techniques could provide this alignment of the optical chromophores while films are being assembled[5]. Polymeric materials were typically spin-cast into films and
oriented post-casting by various methods such as shearing or stretching, heating or cooling steps, and electric field poling, the latter of which is described in detail in Chapter 1[1, 5-7]. These post-casting methods are difficult to incorporate into a continuous, commercially viable process. A potentially better approach involves assembling the film in an oriented state, which eliminates the need for post-processing treatments. One thin film self-assembly technique gaining interest in research is the electrostatic layer-by-layer (LBL) assembly of oppositely charged polyelectrolytes.[8-12] This technique constructs films one layer at a time by alternately immersing a substrate in two solutions of polyelectrolytes with one containing polyanion and the other polycation. Each soaking step adsorbs polyelectrolyte on the surface. With each polyelectrolyte layer deposited, substrate surface charge is reversed prior to soaking in the other solution; therefore, the polyelectrolyte must be able to deposit and cover the surface and present an oppositely charged surface for subsequent adsorption. This technique is cheap and easy; however, it remains a challenge to control the orientation of chromophores within the multilayers.[13-15] The research that has been performed in the area of LBL films revolves primarily around NLO polymers because the NLO effect is relatively easy to detect in a thin film, compared to liquid crystal alignment which is commonly studied for oriented cast films.[8-10, 16-18]

During layer-by-layer assembly, a number of processing parameters affect the film characteristics. The parameters studied in this chapter include pH and salt concentration of the polyelectrolyte solutions and the choice of polyelectrolytes. Research with LBL films has demonstrated film structure is dependent on the processing and solution conditions used in assembly. It has been previously shown that processing conditions
control the growth, porosity, and final thickness of LBL films[19-21]. Additionally processing conditions can determine whether or not the film can be patterned on the substrate and the final roughness of the film[22].

Previous groups have used the LBL procedure to construct NLO active films without requiring any post-processing alignment steps. Thus, noncentrosymmetric films can be assembled, but all of these published results were for films constructed with one pH value, one ionic strength, and one counter-polyelectrolyte[8-10, 17, 18]. Chapter 1 discusses these previous studies in more detail. The effects of these processing conditions on chromophore orientation are unknown but are believed to be very important to control orientation. This chapter will examine the role of these processing conditions on chromophore orientation and determine whether they can be used to control orientation. Solution based processing conditions may allow control and enhancement of orientation that complements the effects of the material structure. This chapter will study the influence of pH and ionic content on chromophore orientation.

The polyelectrolytes used in this chapter are shown in Figure 3.1. These are all commercially available with molecular weights of approximately 50k. Two polyanions were studied that contained different ionizable groups. PolyS119 is a sulfonic acid-containing polymeric dye and the other polyanion is PAZO, which has carboxylic acid groups. Polycations include permanently-charged PDAC, primary amine containing PAH, secondary amine containing LPEI, and BPEI which consists of primary, secondary and tertiary amines. In this chapter, the pH and ionic strength of the polyion solutions will be varied, and the chromophore orientation will be measured to determine how these conditions enhance or hinder this orientation.
Figure 3.1 – Chemical structure of polyanions and polycations used in processing studies

3.1. Effect of Polyanion pH on Orientation

Once dissolved in solution, polyelectrolytes will change their chain conformation and chromophore alignment as their degree of ionization changes. For example, a polyacid in acidic solution will have lower ionization and assume a more loopy conformation due to decreased charge-charge repulsion between repeat units; whereas, in a basic solution it will have higher ionization and increased charge-charge repulsion between the repeat units leading to a flat, expanded conformation on the surface[22, 23]. The behavior for polycations is reversed with respect to pH but results in similar conformational changes. These solution effects are shown in Figure 3.2.

As these different polyelectrolyte conformations deposit onto a charged substrate, they can affect the chromophore orientation in LBL films. Many researchers have studied the effects of pH on LBL films[22-25]. The changes in polyelectrolyte ionization and its effect on conformation are typically observed in layer thickness for non-chromophore
containing polyelectrolytes. As the polyelectrolytes become less ionized, layer thickness increases dramatically due to reduced charge-charge repulsion that results in a more loopy polyion chain contacting the surface at fewer locations along the backbone. Conversely, as polyelectrolytes become more ionized, layer thickness decreases due to increased charge-charge repulsion. The more ionized polyelectrolytes will adsorb in flatter conformations to achieve maximal contact with the oppositely charged surface and minimize charge-charge repulsion. Not only does pH control layer thickness, but also total polyion mass deposited. This mass increase occurs because the loopy polyelectrolyte conformations occupy less surface area per molecule than flat conformations, which leaves more substrate area open for additional adsorption. The illustration in Figure 3.2 diagrams these effects for polyacid adsorption.

**Figure 3.2** – Adsorption diagram for different pH conditions

In this chapter an initial study is discussed which was undertaken to determine what effect, if any, changing pH had on chromophore orientation.

The thickness of LBL films containing side-chain chromophores was initially studied to ensure consistent layer growth, which provides evidence of electrostatic layer-by-layer assembly.[13, 14] All films constructed exhibit linear layer thickness growth after the
initial bilayers are deposited. Even films that were constructed from mixed solvent solutions such as dimethyl acetamide/water still grew linearly as will be demonstrated in subsequent chapters. This linear growth is characteristic of LBL films due to the surface charge reversal behavior described extensively in Chapter 1[13, 14]. PAZO and PolyS119 both behave similarly with respect to pH and film thickness. In fact, they behave like the more typical non-functionalized polyelectrolytes, poly(acrylic acid) (PAA) and sulfonated polystyrene (SPS), respectively, that have been studied extensively by a number of groups[21, 23, 24, 26]. Shown in Figure 3.3 is typical thickness data for PAZO and PolyS119 compared to PAA and SPS with varying polyanion solution pH with the polycation (PDAC) pH held at 3.5.

![Graph](image-url)

**Figure 3.3** – Typical thickness data for PolyS119 and PAZO

As described earlier, when weak polyanion solutions become more acidic, bilayer thickness increases as demonstrated by polyions with carboxylic acid groups (PAZO and PAA). For the strong polyanions, PolyS119 and SPS, their ionization is slightly affected
by the pH range shown in Figure 3.3 yet they show a bilayer thickness increase similar to the carboxylic acid except at a lower pH. Professor Rubner's group at MIT has extensively studied the relationship between pH and layer thickness for the weak polyelectrolytes PAA and PAH. [24, 27] They found that as the pH approaches the polyelectrolyte pKa, layer thickness increases dramatically similar to results demonstrated in Figure 3.3. This layer thickness reaches a maximum near the pKa of the polyelectrolyte. They also found that when a solution is far from the pKa, thinner layers result. Although PolyS119 has a very low pKa, approximately -6, a thickness increase is observed in the pH range shown in Figure 3.3. [28] This is likely due to an increase in the ionic content of the solution to achieve these low pH values. For a pH of 1, the hydrochloric acid concentration is 0.1 molar, which could lead to shielding of the charges on the polyanions leading to thicker layers. This behavior has also been observed in a number of other sulfonic acid containing polymers [29]. Previous studies have shown thickness increase from ionic shielding for the strong polyelectrolytes, SPS and PDAC, at salt concentrations of 0.1M. [21] Data shown in Figure 3.3 demonstrates the effects of polyanion pH on thickness. Similar results would occur using polycations, such as PAH, BPEI, or LPEI, and increasing pH. Polycation pH was held at 3.5 and increased only in limited cases; therefore, film thickness presented throughout this section may be increased further if necessary for a specific application. For the data presented in Figure 3.3, the polycation PDAC only contributes approximately 5 Angstroms in each bilayer because it is fully ionized. Increasing film thickness by changing polycation pH would however incorporate more optically inert material into the films. PAZO solutions are only adjusted down to a pH value of 4 and PolyS119 to 1. These pH limits are
established by polyanion solubility and film growth concerns. When a polyelectrolyte is only slightly ionized other adsorption mechanisms, besides electrostatic attraction, may occur. These mechanisms include hydrogen bonding and hydrophobic attraction.

From the discussion above on layer thickness and ionization of the polyelectrolytes, it is concluded that ionization affects the LBL film architecture. Previous studies have shown that the polyelectrolyte ionization controls the chain conformation, degree of ionic cross-linking, and degree of interpenetration in LBL films. From these studies, it is very likely that the degree of ionization will also influence the chromophore orientation especially since the chromophores contain ionizable groups. Previous research studies on NLO chromophores have hypothesized that the electrostatic attraction between the chromophores and oppositely-charged surface provides the driving force for chromophore orientation. If this hypothesis is true, then varying the polyelectrolyte ionization will vary the electrostatic attraction and chromophore orientation.

Experiments in this section will determine if this hypothesis is correct by varying the pH of the polyelectrolyte solutions.

3.1.1. Experimental Procedures

The films studied for section 3.1.2 and 3.1.3 were all 20 bilayers, with polycation as the first adsorbed layer and polyanion, PolyS119 or PAZO, as the top layer. PolyS119 is a sulfonic acid so it is soluble over a wider pH range than the weaker carboxylic acid containing PAZO. PolyS119 concentrations were at 0.001 Molar (M) and PAZO at 0.01 M based on repeat unit molecular weight and similar to concentrations used in previous studies of LBL films of PAZO and PolyS119.[8, 11, 18] PolyS119 is soluble down to a
pH of 1.0 compared to 4.0 for PAZO. These values set the lower range of pH values studied, and the upper limit is 8.5. At pH above 8.5, the films are too thin to reproducibly observe orientation using FTIR. FTIR films were constructed simultaneously on gold and silicon substrates; whereas, films used in UV/Vis experiments were constructed on cleaned and etched glass slides. Bilayer thickness was measured via ellipsometry on gold, glass, and silicon substrates. All error bars were based on three or more independent samples, and all measurements were performed at least three times on various locations on the substrates. Polycation solution concentration was 0.01 M for all cases. The pH values of polycation solutions (PDAC, PAH, BPEI, and LPEI) were held constant at 3.5 where all are expected to be at least 90% ionized[22], and all films were rinsed using ambient pH rinse water. Films are constructed using the procedure described in Section 2.1. Orientation measurements were made according to procedures described in Section 2.4. Larger chromophore tilt angles indicate more oriented films (Figure 3.4). The measurement of these angles is discussed in detail in Chapter 2. The data throughout this chapter compares tilt angles from FTIR and UV/Vis measurements. As shown in Section 2.4.3, UV/Vis tilt angles are always smaller than the FTIR angles due to the difference in dipoles measured and detection methods for the measurements. FTIR detects individual functional groups whereas UV/Vis measures absorbance of electronic transitions across the chromophore.
3.1.2. Orientation of PolyS119 or PAZO Films with pH Adjustment

The previous section illustrated thickness changes that occur when polyanion pH is adjusted. While thickness can be an important film characteristic, it is not crucial for properties that depend on specific chromophore orientation in polymer films. This section will determine the effects of pH adjustment on chromophore orientation. These experiments will determine whether pH can be used to enhance order in LBL films, which could ultimately lead to cheaper and more robust optical device fabrication. This section will discuss results from two sets of experiments. The first set was performed with polyanion (PAZO or PolyS119) pH adjustment while maintaining polycation pH constant at 3.5, and the second set is similar to the first except with polycation pH at 7. Data will be presented showing FTIR and UV/Vis tilt angles along with film thickness for each polyanion/polycation pair at a specific polyanion pH.

It has been postulated that orientation is the result of electrostatic attraction between the polycation already adsorbed on the substrate and charged chromophores on the polyanion side-chain[8, 9, 11, 18]. Since this theory will be referred to throughout the discussions in this chapter, it will be nicknamed "electrostatic hypothesis." According to this
hypothesis, conditions that allow for maximum attraction between chromophore and substrate should result in higher chromophore tilt angles.

Because the ionization of PolyS119, due to its low pKa, and PDAC, a permanently charged polyion, varies little over the pH range studied and their electrostatic attraction should be constant, PolyS119/PDAC films should not exhibit pH-dependent effects on orientation according to the electrostatic hypothesis. Figure 3.5 plots thickness and orientation data for PolyS119/PDAC films with varying PolyS119 pH. Chromophore tilt angles for PolyS119/PDAC films are constant within error with increasing PolyS119 pH. As the substrate is dipped in PolyS119 solution, PDAC presents a positively charged surface, and PolyS119 is strongly attracted to this surface regardless of pH. Since both polyelectrolytes are highly ionized, there is strong electrostatic attraction between PolyS119 chromophores and PDAC surface in the pH range studied. This leads to approximately constant orientation with increasing PolyS119 pH. As explained earlier, the thickness increase for PolyS119 in acidic solution is most likely due to shielding from the additional ions present from adjusting the pH to such an acidic value, where the concentration of acid is 0.1 molar at pH 1. These ions do not appear to influence the tilt angles measured. A schematic representation of the deposition of PolyS119 onto a PDAC surface is illustrated in Figure 3.6.
Figure 3.5 – Thickness and tilt angle data for PolyS119/PDAC pH-adjusted films

Figure 3.6 – Adsorption of PolyS119 onto PDAC

Since PAZO consists of a carboxylic acid containing chromophore, it would be expected that pH adjustment would affect its electrostatic attraction with the polycation surface, because PAZO has a higher pKa of approximately 5. Figure 3.7 displays tilt angles for PAZO/PDAC films, which slightly increase as PAZO pH becomes more basic. At pH 5, 7, and 8.5 PAZO is approximately 50%, 80%, and 90% ionized, respectively.[30, 31]

This increase in PAZO ionization at pH 8.5 leads to more orientation due to more
electrostatic attraction between PAZO and PDAC. The carboxylic acid pKa is approximately 5 to 5.5 so the tilt angle increase is not dramatic due to the small ionization increase between pH values of 5, 7, and 8.5. Since a stronger attraction between PAZO chromophores and PDAC occurs at basic pH, these results fit the electrostatic hypothesis that higher attraction leads to higher tilt angles. It would be expected that in solutions more acidic than pH 4, there would be a significant decrease in PAZO ionization resulting in a chromophore tilt angle decrease as well. This pH region cannot be studied due to the low solubility of PAZO below pH 4. Figure 3.8 illustrates a schematic representation of the adsorbance of PAZO onto the PDAC surface.

![Graph](image)

**Figure 3.7** – Thickness and tilt angle data for PAZO/PDAC pH-adjusted films
The effects of pH adjustment for PDAC films illustrate the difference between PolyS119 and PAZO chromophores. A highly ionized sulfonic acid (PolyS119) is unaffected by changes in pH when it is coupled with a highly ionized polycation (PDAC) whereas PAZO orientation is affected by its ionization and displays a stronger attraction to the positively-charged surface at higher pH.

PDAC is a fully-charged covalently-bound quaternary amine (Figure 3.1), which allows easy demonstration of polyanion pH effects, since its ionization is constant over the pH ranges studied. Using “weak” polyamines, which vary their ionization with pH, will present different pH effects, because both polyanion and polycation ionization will be affected by the polyanion pH. Figure 3.9 illustrates a schematic representation of the effects of polyanion pH on the deposition of polyelectrolyte layers. As a polycation substrate is soaked in polyanion solution, its ionization is adjusted by the solution pH. For example, a polycation surface soaked in acidic solution will become more ionized compared to one soaked in basic solution. These changes in both polycation and polyanion ionization with pH could greatly affect the chromophore orientation because
the conditions under which there is maximum electrostatic attraction leading to maximum tilt angle, following the electrostatic hypothesis, are the result of achieving the highest charge density possible on the surface and on the polyion in solution.

![Diagram showing the effects of polycation pH on polycation surface](image)

**Figure 3.9** – Effects of Polyanion pH on Polycation Surface

The remaining section will examine chromophore tilt angles using weak polyamines, PAH, BPEI, and LPEI.

Poly (allylamine) hydrochloride (PAH) contains all primary amines off an ethylene backbone. It has a pKa of approximately 8.5 and ionizations of approximately 100%, 95 %, and 85% at pH 3.5, 5, and 7, respectively.[32] From these values, it can be observed that PAH displays little variation in ionization over the pH ranges studied, and should behave similar to the strong polycation PDAC than BPEI or LPEI polycations.

In Figure 3.10, PolyS119/PAH tilt angles are constant within error as polyanion pH increases. These results are similar to PDAC films. Since the highest pH studied is 8.5, approximately the pKa of PAH, it has a high to moderate degree of ionization for the entire pH range studied; thus, PAH behaves as a fully charged polycation like PDAC, at
least with respect to orientation behavior. At pH 8.5, PAH becomes less ionized and displays lower electrostatic attraction to PolyS119, which appears to result in a decrease in tilt angle. Figure 3.11 illustrates the adsorption of PolyS119 on a PAH surface. The strong attraction between polyanion and polycation at any PolyS119 pH leads to a constant orientation as pH increases, similar to the results observed for PDAC films.

**Figure 3.10** – Thickness and tilt angle data for PolyS119/PAH pH-adjusted films

![Graph showing thickness and tilt angle data for PolyS119/PAH films.](image)

**Figure 3.11** – Adsorption of PolyS119 onto PAH

Since PolyS119/PAH films behave like PDAC films, it is expected that PAZO/PAH would also be similar to those with PDAC. PAZO/PAH films (Figure 3.12) display a
slightly increasing tilt angle with increasing pH similar to PDAC results. Since PAH ionization is approximately constant, the strongest electrostatic attraction occurs when the PAZO acid groups are fully ionized in basic solution. Again, these results are consistent with the ES theory. Figure 3.12 illustrates the adsorbance of PAZO onto a PAH surface.

![Graph showing thickness and tilt angle data for PAZO/PAH pH-adjusted films.](image)

**Figure 3.11** – Thickness and tilt angle data for PAZO/PAH pH-adjusted films

![Diagram showing adsorption process.](image)

**Figure 3.12** - Adsorption of PAZO onto PAH
PDAC and PAH both behaved as strong polycations when polyanion pH is controlled. PAH has a relatively high pKa of 8.5, which allows it to behave as a fully ionized polycation over the pH range of this study. It is expected that weaker polyamines with pKa lower than PAH should behave differently than PDAC and PAH. Branched poly(ethyleneimine) (BPEI) contains a mixture of primary, secondary, and tertiary amines in a branched structure. It has a pKa of approximately 7 and ionizations of approximately 85%, 70%, and 35% at pH 3.5, 5, and 8.5, respectively.[33-35] From these values, it can be observed that BPEI has a broad ionization curve over the pH ranges studied and should have a strong influence on electrostatic attraction and chromophore orientation.

Unlike PDAC and PAH films which show no variation in chromophore tilt angle with PolyS119 pH, PolyS119/BPEI films, shown in Figure 3.13, tilt angles show an increase with decreasing PolyS119 pH. BPEI has a pKa of about 7; therefore as the pH decreases the BPEI surface becomes more ionized during PolyS119 adsorption while, as shown for PolyS119/PDAC and PAH films, PolyS119 ionization undergoes very little change. This increase in BPEI ionization strengthens the electrostatic attraction between PolyS119 in solution and the BPEI surface. This effect is illustrated in Figure 3.14. These films exhibit the lowest tilt angle at PolyS119 pH 8.5 indicating that in basic solution there is less electrostatic attraction between the BPEI surface and PolyS119.
Figure 3.13 – Thickness and tilt angle data for PolyS119/BPEI pH-adjusted films

Figure 3.14 – Adsorption of PolyS119 onto BPEI

For PolyS119/BPEI films, the higher electrostatic attraction occurred in acidic solutions when BPEI was more ionized. Part of the results is due to PolyS119 being highly ionized over the pH range studied. On the other hand, PAZO ionization varies with pH more than PolyS119, so different results are expected for PAZO/BPEI films.
Results for PAZO/BPEI films are shown in Figure 3.15, and these films have tilt angles with the lowest occurring at pH 7. This results from the competition between decreasing BPEI (amines) and increasing PAZO (carboxylic acid) ionizations as pH increases; thus, in the acidic region, BPEI has a higher ionization and compensates for lower PAZO ionization. As the pH increases, BPEI ionization decreases resulting in lower tilt angles as demonstrated above for PolyS119/BPEI films. In the basic region, PAZO has more charge and compensates for decreased BPEI surface ionization; however, the change in PAZO ionization between pH 7 and 8.5 is slight, approximately 80 to 90% respectively[30, 31, 36], whereas the change in tilt angle is significant. There may be another mechanism for the PAZO/BPEI films causing this tilt angle increase. For example, some of the chromophores are adsorbing to the positively-charged amines, others may be influenced through dipole-dipole interactions to also align in the same direction similar to interactions within liquid crystals. Another aligning mechanism may be hydrogen bonding between the amines and terminal hydroxy groups on PAZO. The behavior of these films is illustrated in Figure 3.16.

![Figure 3.15 - Thickness and tilt angle data for PAZO/BPEI pH-adjusted films](image)
The last polycation considered was linear poly (ethyleneimine) (LPEI), which is similar to BPEI, but unlike BPEI, LPEI contains only secondary amines on a linear polymer chain. It has a pKa of approximately 5 and ionizations of approximately 65%, 45%, and 25% at pH 3.5, 7, and 8.5, respectively.[37, 38] LPEI has the lowest pKa of the polycations studied which should influence the pH value where maximum electrostatic attraction occurs.

PolyS119/LPEI films (see Figure 3.17) show similar behavior to those constructed with BPEI. Chromophore tilt angles increase as the pH becomes more acidic, and these results occur for the same reasons given for PolyS119/BPEI films. PolyS119 ionization changes little over this pH range while the LPEI is more ionized at low pH. This leads to the maximum electrostatic attraction occurring around pH 2 well below the pKa of LPEI. The adsorption of PolyS119 onto a LPEI substrate is illustrated in Figure 3.18.
Figure 3.17 – Thickness and tilt angle data for PolyS119/LPEI pH-adjusted films

![Graph showing thickness and tilt angle data for PolyS119/LPEI pH-adjusted films]

Figure 3.18 – Adsorption of PolyS119 onto LPEI

For PolyS119/LPEI films, the higher electrostatic attraction occurred in acidic solutions where LPEI was more ionized, and part of this attraction resulted from PolyS119 being highly ionized over the entire pH range studied.

Figure 3.19 displays the results for PAZO/LPEI films, which have a tilt angle increase with decreasing PAZO pH. LPEI has a lower pKa of approximately 5 compared to 7 for BPEI. This difference causes the tilt angle increase with pH decrease to be more dramatic. The decrease in LPEI ionization at higher pH decreases the electrostatic attraction between PAZO chromophores and the LPEI surface. LPEI films do not display
the same tilt angle increase at pH 8.5 as BPEI films. The ionization of LPEI is so low at pH 8.5 it provides little help in orienting chromophores and cannot aid other ordering mechanisms like BPEI. Having a fully charged LPEI substrate allows the strong electrostatic attraction to occur, but once this ionization is removed there is little driving force for orientation. These effects are diagrammed in Figure 3.20.

![Graph showing thickness and tilt angle data for PAZO/LPEI pH-adjusted films.](image)

**Figure 3.19** – Thickness and tilt angle data for PAZO/LPEI pH-adjusted films

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**Figure 3.20** - Adsorption of PAZO onto LPEI

3.1.4. Discussion of Thickness and pH Trends
Each trend observed in the previous section from FTIR data is confirmed with UV/Vis data, and, as expected, UV/Vis tilt angles are smaller than FTIR angles due to differences in the measurements as explained in detail in Chapter 2. FTIR measures the dipole of one functional group while UV/Vis measures the dipole of the visible chromophore transition.[39, 40]

The pH adjustment results demonstrate that the strength of the electrostatic attraction between polyanion and polycation controls the chromophore orientation, and the results validate the ES theory that stronger attraction leads to greater orientation. Differences in tilt angles between PolyS119 and PAZO are due to differences in their ionization at a given pH. The ionization of PolyS119, a polyanion with a very low pKa (~6)[41], varies little over the pH range studied; therefore, it has little effect with pH changes on chromophore orientation in LBL films. On the other hand, the degree of ionization of the polycations determines the chromophore tilt angle for PolyS119 films; thus, for PolyS119 films constructed with higher pKa polycations (PDAC and PAH), the orientation does not vary with pH because the electrostatic attraction is approximately constant. For PolyS119 films constructed with lower pKa polycations (BPEI and LPEI), the chromophore orientation decreases with decreasing polycation ionization (basic pH) because the electrostatic attraction decreases. The PolyS119 experiments can be viewed as controls because its ionization is not changing. These provide a good basis to examine the effects of the polycations on chromophore orientation.

The ionization of PAZO, a polyanion with a pKa of about 5, can affect the chromophore orientation in LBL films, unlike PolyS119, due to its changing degree of ionization. This change combined with the polycation degree of ionization affects chromophore
orientation as films are constructed. For PAZO films constructed with higher pKa polycations (PDAC and PAH), the orientation slightly increases with increasing PAZO ionization or higher pH, because the polycations have approximately constant ionization. For PAZO films constructed with lower pKa polycations (BPEI and LPEI), chromophore orientation and electrostatic attraction depend more on the polyamines ionization.

PAZO/BPEI films show a decreasing tilt angle with decreasing BPEI ionization, and these films display an increase in tilt angle at pH 8.5. The rationale for this increase is secondary interactions such as hydrogen bonding, ionic condensation, or dipole-dipole interactions combined with high PAZO ionization resulting in a tilt angle increase.

PAZO/LPEI films have higher electrostatic attraction, therefore orientation, in acidic solution due to the ionization increase of LPEI. Note that we cannot observe orientation behavior below pH 4 where it would be expected that the decrease in PAZO ionization would cause a decrease in tilt angle similar to that observed for LPEI in basic solutions. At pH 4, the PAZO is still approximately 40% ionized[30, 31] so there is a decrease in chromophore tilt angle observed and there is not a large increase in PAZO ionization as the pH increases from 4 to 8.5. As demonstrated by PAZO/PDAC films, the tilt angle increase caused by the increase in PAZO ionization is slight compared to the polyamine ionization effects. Also as the PAZO becomes less ionized the carboxylic acid groups can participate in hydrogen bonding which as a secondary effect may increase orientation.

A secondary effect of changing polyanion pH is thickness changes. Since both PolyS119/PDAC and PAH films have little orientation variation with PolyS119 pH, film thickness can be varied using pH without affecting the chromophore orientation. In
actuality, this thickness change results from an increase in ionic strength of the solutions and is not truly a pH affect; however, the thickness behavior discussed for PolyS119 occurred as a result of adjusting the solution pH. PAZO/PDAC and PAH films have more orientation at PAZO pH 8.5. At this pH, films are thinner. All BPEI and LPEI films have more orientation in acidic solution.

This section explored the effects of polyanion pH changes on chromophore orientation while holding the solution pH of the polycations constant and at an acidic value of 3.5. The next section will study the effects on chromophore orientation of increasing the polycation pH to neutral conditions.

3.2. Effect of Polycation pH on Orientation

Previous results demonstrated the large effect polycations, especially weak polyamines, have on chromophore orientation since this orientation depends on the strength of the electrostatic attraction between polyanion and polycation. All previous films were constructed with polycation pH held at acidic (3.5) pH where they are all highly ionized in solution.[22] In order to further study the effect of polycation on chromophore orientation, films are constructed with polycation solutions at neutral pH. Since this pH is closer to the pKa of the polycations, there will be more polycation adsorbed per layer compared to films at pH 3.5 for the reasons given in Section 3.2. Near its pKa, a polycation will assume a more three-dimensional loopy conformation, which results in a thicker layer as it adsorbs. This pH effect is similar to thickness effects described previously for polyacids in acidic solution. As the polycation solution approaches its pKa, the layer thickness increases dramatically as observed by Shiratori and Rubner, and these films will adsorb more polycation per layer.[24] This adsorption effect is
represented schematically in Figure 3.27. Since PDAC is fully ionized at all pH, it is expected that no thickness and possibly no orientation change will be observed with pH adjustment.

**Figure 3.27** – Adsorption of weak polycation at neutral pH compared to pH 3.5

### 3.2.1. Experimental Procedure

These films are constructed in the same way as those in Sections 3.1 and 3.2 except polycation solution pH is held constant at pH 7. Only acidic conditions are studied for PolyS119 since, as described earlier, its ionization varies little with pH. These films were only studied via UV/Vis spectroscopy, but based on previous experiments similar trends would be observed via FTIR measurements.

### 3.2.2. Orientation of PolyS119 with Polycations at Neutral pH

Since PDAC and PolyS119 ionization changes little in these pH ranges, it would be expected that changing the PDAC pH to 7 would have no affect on chromophore orientation in PolyS119/PDAC films. Indeed, this is observed in Figure 3.28 where there
is little difference, within experimental error, between the tilt angles for the two sets of experiments. PDAC is a permanently charged, quaternary amine and its ionization is unaffected by pH.

**Figure 3.28** – Tilt angle and thickness data for PolyS119/PDAC with PDAC at pH 7 compared to PDAC at pH 3.5

PAZO/PDAC films with PDAC at pH 7, shown in Figure 3.29, also exhibit little variation in tilt angles. Previous PDAC films had slightly increasing tilt angle with increasing pH due to increasing PAZO ionization, which led to greater electrostatic attraction between chromophore and PDAC. These slight differences between the films are within the error of previous experiments so it is difficult to observe differences. The differences in tilt angles probably result experimental error introduced by difficulty in adjusting solution pH to neutral without using buffered solutions. This may result in lower chromophore tilt angles.
The pKₐ of PAH is approximately 8.5, so the pH of the PAH solutions are below the pKₐ when adjusted to pH 7, and PAH will be more ionized than other polycations. At pH 7 PAH is approximately 85% ionized compared to about 100% at pH 3.5. [32] Films constructed with PolyS119/PAH with neutral PAH solution exhibit a decreasing tilt angle with increasing PolyS119 pH (see Figure 3.30). Previously PolyS119/PAH films at pH 3.5 had tilt angles that varied little with polyanion pH. Also tilt angles for pH 7 films are lower than angles for the pH 3.5 films. Why this new trend is observed is not clear because it would be expected that results would be similar to pH 3.5. The trend is likely caused by the decreasing ionization of PAH as the PolyS119 solution becomes less acidic, and when PAH pH is increased to pH 7, more PAH is deposited on the substrate with each dipping cycle making this trend more visible than for films with less PAH. This could change how the PolyS119 adsorbs leading to the trend seen, but the electrostatic attraction between PAH and PolyS119 should be approximately constant over the pH range studied; however, the surfaces of the neutral pH films are rougher than
those from acidic PAH solution indicating it could be a physical change in the actual surface that influences the orientation. The lower tilt angles could be caused by neutral pH being closer to the pKa of PAH, which is 8.5. By being closer to the pKa, PAH would be less ionized or undergo conformation changes leading to less electrostatic attraction with the chromophores.

Figure 3.30 – Tilt angle and thickness data for PolyS119/PAH with PAH at pH 7 compared to PAH at pH 3.5

For PAZO/PAH films (Figure 3.31) tilt angles at PAH pH 7 decrease initially and then level off at higher PAZO pH. The increase in tilt angle that was observed previously (PAH pH 3.5) at basic PAZO pH was not observed with PAH at pH 7. PAZO/PAH films with neutral PAH initially follow the same trend as earlier, pH 3.5 films with decreasing tilt angle in acidic PAZO solution but then tilt angles for PAH pH 7 films level off compared to increasing for pH 3.5 films. As with PolyS119 films, the PAH pH 7 films have lower tilt angles than the pH 3.5 films probably for the same reasons. As the PAZO ionization increases, the tilt angles do not increase due to the loss of PAH ionization at basic pH. For some reason, having PAH at pH 7 counteracts the increasing PAZO
ionization. It appears the ionization of PAH results in stronger electrostatic attraction when paired with less ionized PAZO rather than in the opposite situation of more ionized PAZO and less ionized PAH. Adsorbing more PAH on the surface and at a neutral pH makes the films appear to be constructed from the “weaker” polyamines.

![Graph showing thickness and tilt angle data](image)

**Figure 3.31** – Tilt angle and thickness data for PAZO/PAH with PAH at pH 7 compared to PAH at pH 3.5

Because of their higher pKa, PDAC and PAH behaved as stronger polycations in previous sections compared to the other polycations, BPEI and LPEI. BPEI has a pKa of approximately 7 and is less ionized at neutral pH than PAH; however, since BPEI is equally composed of primary, secondary, and tertiary amines it has multiple pKa values. Secondary and tertiary amines have pKa lower than pH 7 so a significant portion of BPEI will have lower charge density. For example at neutral pH, BPEI has an ionization of approximately 50% compared to 85% at pH 3.5.[33-35]

Figure 3.32 displays the data for PolyS119/BPEI films. They show a constant tilt angle with PolyS119 pH indicating approximately constant electrostatic attraction compared to
decreasing angles with pH 3.5 BPEI solutions. Previously, the pH 3.5 films displayed a decrease in tilt angle as pH became more basic due to decreasing ionization of BPEI. Overall films at BPEI pH 7 have slightly higher tilt angles than those constructed from pH 3.5. This effect is in contrast to PAH films and may be caused by the pKa difference between the polycations.

![Graph](image)

**Figure 3.29** – Tilt angle and thickness data for PolyS119/BPEI with BPEI at pH 7 compared to BPEI at pH 3.5

Again, the behavior of PAZO/BPEI films differs significantly from PolyS119/BPEI. PAZO/BPEI films with neutral BPEI (Figure 3.33) have decreasing tilt angles with increasing PAZO pH similar to films at pH 3.5 except at PAZO pH 8.5 where earlier films had an increase in tilt angle. This behavior is similar to LPEI films studied earlier and is more expected since as pH increases the BPEI is becoming less ionized. At PAZO pH 8.5, the neutral films do not increase their chromophore tilt angles indicating the loss of ionization on the BPEI decreases the electrostatic attraction similar to the PAZO/PAH films. The trends are similar, and tilt angles are about equal for these two sets of BPEI
films. Similar to PAH films, it appears depositing more polyamine results in trends where the amine ionization has stronger influence on orientation.

Figure 3.33 – Tilt angle and thickness data for PAZO/BPEI with BPEI at pH 7 compared to BPEI at pH 3.5

Similar to BPEI, LPEI also contains amine groups but only secondary. This gives LPEI a lower pKa of approximately 5; therefore, it will be less ionized than either PAH or BPEI in neutral solution. For example at neutral pH, LPEI has an ionization of approximately 45% compared to 65% at pH 3.5. [37, 38] Thus far, PAH films had lower and BPEI films had about the same tilt angles when assembled using neutral solutions. PolyS119/LPEI neutral films show an approximately constant tilt angle with increasing pH. These results are unlike pH 3.5 films where the chromophore tilt angle decreased with increasing pH. These results are shown in Figure 3.30. The larger amount of LPEI may be less influenced by changes in pH or there may be other effects occurring in these films that create a constant attraction between the surface and chromophores. It is

84
assumed that at higher pH this effect may disappear with the larger decrease in LPEI ionization.

The trend with different polycations appears to be if the solution is at pH lower than the pKa as the case for PAH there is less orientation. If the solution pH is approximately the same as polycation pKa similar to BPEI, the orientation is unaffected by the polycation pH. Lastly when the pH is higher than the pKa as is the case of LPEI, the orientation is unchanged. These results apply to films with PolyS119, which has an approximately constant ionization over the pH range studied.

![Graph showing tilt angle and thickness data for PolyS119/LPEI with LPEI at pH 7 compared to LPEI at pH 3.5.](image)

**Figure 3.30** – Tilt angle and thickness data for PolyS119/LPEI with LPEI at pH 7 compared to LPEI at pH 3.5

Unlike PAZO/BPEI films, which exhibit varying tilt angles with pH, neutral LPEI films show approximately constant angles. PAZO/LPEI films at LPEI pH 7 (Figure 3.34) have a roughly constant chromophore tilt angle at all PAZO pH unlike films at LPEI pH 3.5 where increasing PAZO ionization lead to decreasing chromophore tilt angles. This constant tilt angle behavior was observed for the PolyS119/LPEI films as well except for
the PAZO films even at basic pH, where LPEI is less ionized, the tilt angles are approximately constant.

With carboxylic acid containing PAZO, different behavior is observed with the individual polycations, but when the polycation pH is increased to neutral, similar trends to PolyS119 films are observed. Neutral PDAC and PAH have lower chromophore tilt angles when compared to those assembled in acidic solution. PDAC films are affected by this pH adjustment due to the variable ionization of PAZO. Apparently, there is a stronger electrostatic attraction in acidic solution where the PAZO is less ionized. This behavior is understandable for PAH, which is more ionized in acidic solution, but is confusing for the strongly ionized PDAC. The weaker polycation BPEI exhibits slightly higher tilt angles for neutral solution and similar trends to acidic solution. Neutral PAZO/LPEI films have approximately constant tilt angles with pH and are similar in degree to those assembled from acidic LPEI solution.

Similar to PolyS119 films, when the pH is above the polycation pKa lower tilt angles result as demonstrated by PAH. If the pH is approximately equal to the pKa or higher as is the case for BPEI and LPEI, then there is little difference in tilt angle between the films.
3.2.4. Discussion of Polycation pH Effects

For a fully ionized polycation such as PDAC, no difference would be expected and that was observed for PDAC films. The ionization is constant for PDAC, which results in a constant electrostatic attraction with the polyanions. The results and explanations become much more complicated for the weak polycations, PAH, BPEI, and LPEI due to their varying ionization with pH.

The weak polyamines seem to follow a tilt angle trend based on pKa when their solutions are at neutral pH. For PAH with a pKa of 8.5, chromophore tilt angles for films assembled from neutral solution are lower than for pH 3.5 films. For BPEI, which has a pKa of about 7, the chromophore tilt angles at pH 7 are approximately the same as at pH 3.5. Even though the ionization of BPEI changed, the electrostatic attraction between it and polyanions did not. LPEI has a pKa of about 5 and its films also have similar tilt angles at pH 7 than pH 3.5. The trend appears to be at pH conditions near or above the pKa, for example BPEI and LPEI films, similar tilt angles result from an increase in
solution pH, but when the pH is below the polycation pKα, for example PAH films, lower tilt angle films are assembled. Why the pH affects each polycation differently is unknown because one would expect them all to behave similarly.

3.3. Effect of Salt Concentration on Chromophore Orientation

Varying pH is one way to affect polyelectrolyte solution conformation, which leads to different chromophore orientation; however, pH variation does not affect the ionization of strong polyelectrolytes. Additionally, solution pH can change over time from exposure to air and other contaminants. Another method to change polyelectrolyte conformation is changing the ionic strength of the medium by adding excess ions in the form of salt.

Typically when excess ions are added to polyelectrolyte solutions behavior similar to pH effects occurs in regard to polymer conformation.[20, 21] The excess ions help to “shield” the charges on the polyelectrolytes, which leads to different conformations and chromophore alignments in solution. As shielded polyelectrolytes deposit from these solutions onto a substrate, they result in different chromophore orientations. The more a polyelectrolyte is shielded the more loopy its deposition.

Again, effects of polymer conformation can be observed by studying layer thickness. The effect of salt concentration on thickness will give an indication of polyelectrolyte conformation in solution and provide insights to its conformation as it adsorbs. These may help to explain differences in chromophore orientation within LBL films constructed at varying salt concentrations.

As salt concentration increases, the polymer chains in solution effect a more three dimensional coil due to the decrease in charge-charge repulsion between the segments of
the chain. In effect, the ions "shield" the charges, and this leads to thicker layers (see Figure 3.35). Eventually as salt concentration is increased to high values, polymer will precipitate of solution due to the high shielding. Charge shielding with salt ions is analogous to protonation of weak polyacids with acidic solutions. Orientation results similar to those for pH are expected. On the other hand, this case is different from that of pH because the polycation on the substrate surface are affected differently by ions than by pH. This ionic content may change the effective polycation pKa. In pH studies, the combined effects of polyanion and polycation ionization played a role in the chromophore orientation due to electrostatic attraction within the films. The salt concentration studies attempt to separate these effects by determining the role of polyanion shielding on chromophore orientation.

![Diagram of varying salt concentration in solution and films](image)

**Figure 3.35** – Illustration of varying salt concentration in solution and films.

### 3.3.1. Experimental Procedures

Films studied for section 3.2.2 and 3.2.3 consisted of 20 bilayers, with polycation as the first adsorbed layer and polyanion, PolyS119 or PAZO, as the top layer. PolyS119 and PAZO were dissolved into aqueous solution, and then NaCl was added to a specific concentration. The pH of the solutions was then adjusted to neutral using dilute solutions.
of hydrochloric acid or sodium hydroxide. Due to the highly ionizable nature of its sulfoinic acid, PolyS119 will stay soluble at a higher salt concentration than PAZO, up to 0.2M NaCl. Polycation solution (PDAC, PAH, BPEI, and LPEI) pH values were held constant at 3.5 where all are expected to be at least 65% ionized based on pKa values, and all films were rinsed using ambient pH rinse water. Films were constructed using the technique described in Section 2.1, and the same concentrations were used as in the above sections. The orientation within these films was studied with FTIR measurements.

3.3.2. Effect of Salt Concentration on Chromophore Orientation

Salt is added to only polyanion solutions, and how this affects the polycation substrate is unknown. It is expected that, similar to pH variation results, films will have the highest tilt angle in conditions where the electrostatic attraction between chromophore and substrate is greatest, and shielding could hinder this attraction.

PolyS119/PDAC films, shown in Figure 3.36, display little variation in tilt angle with salt concentration. Even as PolyS119 is shielded by the excess ions, the electrostatic attraction between chromophore and substrate is constant. A reasonable cause maybe an exclusion of the salt ions as PolyS119 adsorbs, which has been observed by other groups for non-chromophoric polyions.[13-15] This leads to the same electrostatic attraction between chromophore and substrate as if there was no salt added to the solution and resulting in little tilt angle variation with salt concentration. This behavior is similar to the results of pH adjustment, where the strong polyelectrolytes (PDAC and PolyS119) had constant electrostatic attraction.
Figure 3.36 – Thickness and tilt angle data for PolyS119/PDAC salt-added films

PAZO/PDAC films (Figure 3.37) have a slightly higher tilt angle with lower salt concentration. It would be expected that PAZO/PDAC films would be unaffected by salt like the PolyS119/PDAC films because the ionization of these polyions is unchanged by the increasing ionic content. It is unknown what mechanism would result in a lower tilt angle for these films although the changes are small and almost within the experimental error.

Figure 3.37 – Thickness and tilt angle data for PAZO/PDAC salt-added films
Previously for pH adjustment studies, PolyS119/PAH films behaved as if PAH was a strong polyelectrolytes similar to PDAC. Like salt-added PDAC films, PolyS119/PAH films (Figure 3.38) show little variation with salt concentration similar to the trend observed with pH adjustment. This occurs due to same reasons given above for PolyS119/PDAC films. There is strong electrostatic attraction between highly ionized PAH and PolyS119 regardless of salt concentration or pH condition of the polyanion solution.

![Graph showing thickness and tilt angle data for PolyS119/PAH salt-added films](image)

**Figure 3.38** – Thickness and tilt angle data for PolyS119/PAH salt-added films

PAZO/PAH films (Figure 3.39) also show a slight tilt angle decrease with salt concentration. Like the case for PolyS119 salt-added films, these results are similar to PAZO/PDAC films. Again, it would be expected that these films would behave similar to PolyS119/PAH films. The PAZO ionization must be affected by the ionic content in a way that decreases its electrostatic attraction to the surface.
PolyS119/PAH and PDAC films assembled from salt solutions demonstrate that shielding has little affect on the strongly ionized PolyS119; therefore, any measurable change in chromophore tilt angles will have to be generated by differences in the polycations behavior with excess ions present rather than by any change in PolyS119. PolyS119/BPEI films with varying salt concentration have increasing tilt angle with increasing salt concentration. At pH 7, BPEI (pKa ~7) has lower ionization than PDAC or PAH (pKa ~8.5). Based on the PAH film results, it would be expected that BPEI films would have the same orientation with increasing salt concentration. This is not the case because the addition of salt ions to solution shifts the pKa of BPEI higher resulting in more polycation surface charge. This effect of changing pKa with excess ions has been studied extensively for surfaces and micelles.[42-44] Polyelectrolyte pKa value changes as high as 1 pKa unit have been observed with the addition of salt ions to polyelectrolyte solution. This effect is especially pronounced for weaker polyamines like BPEI and LPEI. This causes BPEI to become more ionized as salt concentration increases which leads to more orientation at higher ionic content. The shielding state of PolyS119 has
little effect on orientation in films with BPEI as observed for PAH and PDAC films. At salt concentration of 0.2M, PolyS119 becomes sufficiently shielded to adversely affect the electrostatic attraction resulting in lower tilt angles and lower film thickness.

Figure 3.40 - Thickness and tilt angle data for PolyS119/BPEI salt-added films

PAZO/BPEI salt-added films decrease in tilt angle at low salt concentrations and then increase. This initial decrease is caused by a similar mechanism observed in the PDAC and PAH films. The initial salt concentration lowers the electrostatic attraction between PAZO and the surface. As the salt concentration increases, BPEI ionization increases as seen for PolyS119/BPEI films, and the tilt angles increase. The addition of salt ions to the solutions shifts the BPEI pKa higher leading to higher degree of ionization, which as shown for the pH-adjusted films, has a larger influence on orientation than changes to PAZO ionization.
Figure 3.41 – Thickness and tilt angle data for PAZO/BPEI salt-added films

PolyS119/LPEI films (see Figure 3.42) with varying salt concentration have increasing tilt angle with increasing salt concentration just like PolyS119/BPEI films and for similar reasons. This trend is similar to the BPEI films but appears slightly different in the data due to differences between BPEI and LPEI’s ionization curves. As the salt (ion) concentration increases, the pKa of LPEI increases causing an increase in ionization. Since LPEI has a lower pKa, a higher salt concentration is needed to change its ionization compared to BPEI.

Figure 3.42 – Thickness and tilt angle data for PolyS119/LPEI salt-added films
PAZO/LPEI (see Figure 3.43) films behave similarly to BPEI films with an initial decrease in tilt angle followed by an increase as salt concentration rises. As the salt concentration increases, LPEI ionization increases leading to stronger electrostatic attraction with PAZO.

![Graph](image)

**Figure 3.43** – Thickness and tilt angle data for PAZO/LPEI salt-added films

### 3.3.4. Discussion of Salt Effects for PolyS119 and PAZO Films

The previous sections established the electrostatic attraction between chromophores and substrate dictates the tilt angles measured. As with the pH adjustment results, differences between PolyS119 (sulfonic acid) and PAZO (carboxylic acid) are due to their respective charged groups. The electrostatic attraction of PolyS119 to positively charged substrate is less affected by salt ions than PAZO. PolyS119 is only measurably affected by salt concentrations of 0.2M. Films with the strong polycation, PDAC, demonstrate these results. PolyS119/PDAC films have little change in tilt angle with increasing salt concentration. Both polyelectrolytes are shielded by the salt ions as evidenced by the increasing film thickness with increasing salt concentration [20, 21]; however, the shielding has no affect on the electrostatic attraction between the polyelectrolytes.
PolyS119/PAH films display similar behavior to PDAC films because PAH has a high pKa (~8.5) resulting in a polycation that appears to be fully ionized like PDAC. When PolyS119 films are assembled with lower pKa polycations, BPEI and LPEI, different results than PAH and PDAC are observed because BPEI and LPEI surface ionization are affected by salt ions. PolyS119/BPEI and LPEI films have slightly higher tilt angles with increasing salt concentration. BPEI and LPEI both have the ability to change ionization in high ionic content solutions. This allows the substrate to be more ionized and have increased electrostatic attraction with the chromophores. As shown in the pH adjustment sections, greater attraction leads to higher tilt angles.

Films with PAZO behave much differently than PolyS119 because PAZO is not as strongly ionized. The salt ions affect the electrostatic attraction of the PAZO chromophores as shown by PAZO/PDAC films. These have lower tilt angles with increasing salt concentration caused by shielding of the PAZO chromophores. The PDAC surface does not appear to be shielded in PolyS119 films so it should not be shielded during the assembly of PAZO films either. Again, PAZO/PAH films behave in a similar fashion to those with PDAC because PAH has a high pKa. PAZO/BPEI and LPEI demonstrate results from competing effects. As the salt concentration increases PAZO chromophores become shielded and their electrostatic attraction to the substrate is weakened. At the same time, the increasing salt concentration is causing the polycations to increase their ionization by increasing their pKa through ionic interactions. These competing effects cause the films to possess a minimum tilt angle where the electrostatic attraction between the chromophores and polycation surface is weakest. This is similar to trends exhibited by PAZO/BPEI films that were pH adjusted.
3.4. Summary and Conclusions on the Effect of Processing Parameters on Orientation

Previous research has hypothesized that the chromophore orientation in layer-by-layer films results from electrostatic attraction between charged side-chain chromophores and positively charged substrates[8-11, 18]. To test this hypothesis, the first section of this chapter examined the effects of varying chromophoric-polyanion pH on orientation in the LBL films. Changing the polyanion pH not only influences the polyanion in solution but affects the polycation adsorbed on the substrate surface as well; therefore, the choice of polycation plays as an important role as the polyanion pH. Results from this section demonstrated that the electrostatic attraction between chromophores (polyanion) and substrates (polycation) does control the chromophore orientation. Chromophores have the largest tilt angles in films constructed with the maximum amount of attraction between the polyanion and polycation, which occurs when there is a maximum amount of ionization for the given polyelectrolyte pair. For example, tilt angles vary little when PolyS119, a sulfonated polyelectrolyte, is assembled with a strongly charged polycation such as PDAC or PAH, because the ionizations of the polyelectrolytes are approximately constant over the pH range studied. When weakly charged (or less ionized) polycations, such as BPEI or LPEI, are paired with PolyS119, their degree of ionization controls the amount of electrostatic attraction and thereby the chromophore tilt angles.

Results from the section on the effect of changing polycation pH demonstrated the influence of polycation pKa on achieving the most electrostatic attraction between polyelectrolytes. If the polycation solution pH is above the polycation pKa, higher tilt angles result from the decreased ionization, but if the pH is below this pKa then the tilt angles remain unchanged. These studies illustrate that the ionization of the polycation as
well as the chromophore ionization controls the electrostatic attraction and hence the orientation. The pH of both solutions affects both polyelectrolytes and the chromophore orientation.

Changing pH is not the only way to influence the electrostatic attraction. Ionic solutions can be used to shield the charge on polyelectrolytes and affect the ionization of the polyamines. Polyelectrolyte pairs that had small variation in tilt angles with pH changes show similar behavior in ionic solutions, even though thickness measurements exhibit considerable charge shielding occurring. At the length scale of the electrostatic attraction, the ions must be excluded by the attraction of the polyelectrolytes.

Lastly, there are strong differences in behavior between the two polyanions studied. PolyS119 is unaffected by processing conditions due to a low pKa on its sulfonic acid groups. In contrast, PAZO is more affected by processing conditions like pH because its pKa is higher (~5) because of its carboxylic acid groups. This illustrates a difference in chemical structure affecting chromophore orientation. These differences will be examined further in Chapter 4.
3.5. References


40. Kawai, T., J. Umemura, and T. Takenaka, Molecular-Orientation in Lb Films of Azobenzene-Containing Long-Chain Fatty-Acids and Their Barium Salts Studied


4. Effect of Polyelectrolyte Chemical Structure on Chromophore Orientation

Chapter 3 studied the effects of pH and ionic content on the chromophore orientation in layer-by-layer electrostatic films. It was demonstrated that by varying these parameters the chromophore tilt angle can be controlled, and this control was based on the electrostatic attraction between the negatively-charged side-chain chromophore and polycation. The previous chapter studied two chromophoric polyanions, PAZO and PolyS119, shown in Figure 4.1.[1-3] Both polymers contain an ionizable group at the end of the chromophore, which allows electrostatic assembly (Figure 4.1). Other researchers have hypothesized that one mechanism for the assembly of ordered LBL films using chromophoric polymers is the attraction between the ionized chromophore being attracted to the deposited polycation surface.[1, 3-5] If this hypothesis is correct, then changing the polymer architecture specifically the location of the charged groups should impact the orientation achieved through layer-by-layer (LBL) assembly. This chapter will study the key chemical structural parameters that influence chromophore orientation.

Other research groups have constructed LBL films containing non-linear optical (NLO) chromophores. Typically, these were polymers that were either commercially available, previously studied using cast films, or water-soluble versions of previously studied polymers that were similar in structure to examples displayed in Figure 4.1[1, 3-6]. There have been no published reports of targeted chemical synthesis to study the effects of the chemical structure of chromophore containing polymers used for LBL films; however, we can draw upon the analogy of side-chain thermotropic liquid crystal (LC)
polymers in considering order within the layers. Since previous research in liquid crystalline materials has shown different LC orientations occur at different spacer lengths, there probably will be orientation differences in chromophore orientation with chemical structure in LBL films as well.

New polymers were synthesized to study the effects of chemical structure on chromophore orientation. PAZO and PolyS119 (Figure 4.1) have charged groups at the end of their side-chain and have a short spacer between the polymer main-chain and side-chain chromophore. This chapter will examine the effect of increasing spacer length on orientation and the position of the charged group on the polymer. These parameters are illustrated in Figure 4.1 in the schematic. These new polymers were incorporated into LBL films using the same processing conditions studied in Chapter 3. This will help to differentiate processing effects from polymer structure properties.

![Chemical structures](image)

**Figure 4.1** – Side chain chromophores used by a) Lvov et al, b) Wang et al, c) Heflin et al, d) Roberts et al, and e) Laschewsky et al and a generic polyanion[1, 3-6]

### 4.1. Effects of Ionizable Groups on Chromophore Orientation

Chapter 3 studied the effects of pH and salt concentration on PolyS119 and PAZO orientation. These polymers, shown in Figure 4.1, are structurally similar except for their
charged group. PolyS119 is a sulfonic acid (pKa ~6) compared to the carboxylic acid (pKa ~5) containing PAZO.[7-9] Because of its low pKa, PolyS119 ionization changes only slightly over the pH range studied, from 1 to 8.5, whereas PAZO, which was studied in the range of 4 to 8.5, ionization varies from approximately 50% at pH 5 to 90% at pH 8.5.[9] This difference is most noticeable in films constructed with the polycation PDAC (Figure 4.2). PDAC is fully ionized and its ionization is unaffected by pH, so the difference between the ionizable groups of PAZO and PolyS119 can be observed without influence from the polycation ionization.

![Figure 4.2 - Chemical Structure of PDAC polycation](image)

Figures 3.5 and 3.7 in Chapter 3 display tilt angle results for PolyS119/PDAC and PAZO/PDAC films, respectively. At most pH, PolyS119 is fully ionized which results in little tilt angle variation, but PAZO is not; therefore in acidic solution, PAZO has less charge on its chromophores than PolyS119 and less orientation due to weaker electrostatic attraction with the PDAC substrate. Overall, PAZO and PolyS119 films have about the same maximum tilt angles so the strength of the acid only determines pH effects on orientation not the overall resulting tilt angles.

Since PolyS119 and PAZO are very similar structurally, differences between these charged groups are easily observed. Other polymers with different charged groups are expected to follow this trend depending on their degree of ionization unless their
chemical structure allows for other non-electrostatic interactions such as hydrogen bonding. Two of the polymers shown in Figure 4.1 contain quaternary-amine ionized groups similar to PDAC. It would be expected that their orientation would be unaffected by pH conditions.

4.2. Effect of Spacer Length on Chromophore Orientation

Previous work with side-chain liquid crystals has shown orientation depends on spacer length between the polymer main-chain and rigid side-chain mesogens. These films were typically constructed by spin or solvent casting. Typically, there is an optimum spacer length for specific phases. If the spacer is too short, the mesogens do not have enough freedom from the main chain to display LC phases. On the other hand if it is too long, the mesogens have too much freedom and do not align in a specific phase[10]. These effects are shown in Figure 4.3. How the spacer length affects orientation in LBL films is unknown, but it may be similar to LC effects. The studies of NLO layer-by-layer films mentioned previously all examined polymers with very short (a couple of methylene units) spacers. The research groups who studied these films did not study or comment on the effect of chromophore decoupling from the polymer main-chain.[1, 3-6]

![Figure 4.3](image)

**Figure 4.3** – Spacer length effects for liquid crystal polymer films
It is known that small-molecule chromophores, those not attached to a polymer, can order in LBL films, but the construction of these films is more difficult than polynomials due to the larger aspect ratio and lower charge density per molecule.\cite{11,12} These small molecules can lay flat on the surface eliminating surface normal orientation. These also can desorb more readily than polynomials. A comparison of orientation differences between LBL films constructed of polymeric side-chain chromophores and small-molecule chromophores has not been performed but can be speculated on. A polymer has many charged groups; therefore, its adsorption is not dependent on a small number of electrostatic interactions like the small molecules. A schematic illustration of the adsorption of small molecules, which can be thought of as having infinite spacers or total freedom, is shown in Figure 4.4. Since materials used in LBL films must contain at least two charged groups in order to exhibit consistent layer growth, the small molecules are displayed with charges on the ends of a long conjugated molecule similar to boladi-ions used by Decher and co-workers. \cite{11,12} These molecules have relatively large regions of non-ionizable groups. As these molecules deposit, there is coverage of surface charge by uncharged portions because some lay flat on the surface, and this reduces the surface charge density as the layers grow. Eventually, no more material will deposit because there will not be enough surface charge\cite{12}. Polymers usually do not have this problem because there are charged groups that do not contact the surface, which keeps the surface charge density approximately constant. Some groups have used small molecules successfully but most have trouble depositing thicker films.\cite{13-15}
4.2.1. Experimental Setup and Synthesis Schemes

The synthetic scheme was designed to minimize synthetic steps. Since both FTIR and UV/Vis measurements were shown in Chapter 3 to provide a method of determining orientation, the importance of having an unusual optical property, such as non-linear behavior, is reduced. The polymer synthesized does not have to be NLO active but still should have a strong dipole, be rigid, and similar in structure to the polymers featured in Chapter 3 and in Figure 4.1.

The chromophore chosen was purchased from Sigma-Aldrich. Hydroxy-azobenzoezoic acid (HABA) is shown in Figure 4.5. HABA has functionality that allows relatively easy modification. The hydroxy functional group will be used to attach methylene (CH₂) spacers through ether linkages. Spacer lengths of 2, 6, and 10 methylene units are used. Before the spacers are attached to the chromophores, the spacers are attached to polymerizable acrylate groups. Once the spacer is attached to the chromophore, it can be polymerized via solution free-radical polymerization. The synthesis scheme is shown in Figure 4.5 with all relevant reaction conditions.
Figure 4.5 – Synthesis scheme for poly-HABA-n polymers

All products were washed with water and extracted three times via chloroform/water and finally purified via flash chromatography using acetone/hexane as an eluant. All structures were verified using NMR and IR. After monomer polymerization, polymers were purified by THF dissolution and precipitation in methanol and again, structures were verified by NMR and molecular weight determination by gel permeation chromatography (GPC) using THF and polystyrene standard. The molecular weights of all polymers were about 5000 g/mol; therefore, there are only about 10 repeat units, but this is enough to observe polymer-like behavior, even though they are more like oligomers, in LBL films.

Films are constructed and characterized using the procedures outlined in Chapters 2 and 3. Since poly-HABA-n does not have a unique functional group visible in IR,
UV/Visible spectroscopy was used to determine tilt angles. The carboxylic acid does not display clearly in FTIR because of asymmetric stretch overlap with other groups such as methylene C-H stretches. Also, the carbonyl group will exist in three forms: acid, anion, and salt complex with polycation which while informative are difficult to resolve; therefore, UV/Vis is the best measurement option, and previous results in Chapter 3 established that trends were measurable with either IR or UV/Vis.

Since poly-HABA-n polymers are only soluble in very basic solutions (pH >10), a solvent mixture of 50% dimethylacetamide (DMAC) and 50% pH 8.5 water was used to dissolve the polymers. This solubility issue is due to the hydrophobic nature of the polymer. Poly-HABA-n concentrations were 0.01 Molar based on repeat unit molecular weight, as were the polycation solutions. Films were assembled onto glass substrates and were 20 bilayers thick. Since the glass surface was assumed to have a negative charge, polycation was first deposited followed by poly-HABA-n. The pH values of polycation-water solutions (PDAC, PAH, BPEI, and LPEI) were held constant at 3.5 where all are expected to be at least 70% ionized, and all films were rinsed using ambient rinse deionized water. The polycations used in these studies are shown in Figure 4.6. Films are constructed using the procedure described in Section 2.1. Orientation measurements were made according to procedures described in Section 2.4.
4.2.2. Thickness and Layer Growth of poly-HABA-n films
Since a mixture of water and DMAC is used as a solvent, and growth of LBL films constructed from this mixture is unknown, thickness was measured with each layer. The growth of sample films of poly-HABA-2 is shown in Figure 4.7. These films grow in a linear manner similar to films constructed from water only solutions. This linear growth indicates constant thickness of the polyanion and polycation layers, which is a sign of electrostatic attraction being the dominant mechanism for film growth.[11, 12] Films of poly-HABA-6 and poly-HABA-10 show similar growth behavior.
4.2.3. Results and Discussion on Spacer Length and Orientation

The previous section demonstrated the growth of the poly-HABA-n films and confirmed that they appear to growth by electrostatic attraction. Since Chapter 3 established that one mechanism for chromophore orientation in LBL films is this attraction, the poly-HABA-n films were measured to determine the effect of the methylene spacer width between the polymer main-chain and the side-chain chromophore. Based on the above description of liquid crystals, it is expected that longer spacers will result in higher tilt angles while too long may lead to a decrease.

Results for poly-HABA-n films are displayed in Figures 4.8, 4.9, 4.10, and 4.11. The films all show an increasing orientation with increasing spacer length; therefore, a chromophore decoupled from the polymer main-chain has more orientation. This effect is seen with all polycations. More freedom (longer spacer) allows chromophores to align more perpendicular to the substrate. It is expected that this effect would level off at even higher spacer lengths similar to the results described above for non-polymeric
chromophores because once the side-chain gains enough freedom from the main-chain, any additional spacer length does not supply significant decoupling. How the aqueous/organic solvent mixture affects polycations on the surface is unknown, but since the solution is at pH 8.5 it is expected that the weak polycations (PAH, BPEI, LPEI) would have less charge. The thickness data indicates that the electrostatic attraction is still present in the organic/aqueous solvent. As shown in Chapter 3, the choice of polycation made a large difference in chromophore orientation. Since poly-HABA-n is a carboxylic acid containing polymer like PAZO (displayed in Figure 4.1), it is expected that similar behavior would be seen as PAZO with varying polycation, pH, and salt concentration.

![Graph showing UV/Vis tilt angles for poly-HABA-n/PDAC films with varying spacer length](image)

**Figure 4.8** – UV/Vis tilt angles for poly-HABA-n/PDAC films with varying spacer length.
**Figure 4.9** – UV/Vis tilt angles for poly-HABA-n/PAH films with varying spacer length

**Figure 4.10** – UV/Vis tilt angles for poly-HABA-n/BPEI films with varying spacer length

**Figure 4.11** – UV/Vis tilt angles for poly-HABA-n/LPEI films with varying spacer length
4.3. Effect of Charge Placement on Chromophore Tilt Angle

The polyelectrolytes previously used for NLO films typically had the ionizable group on the end of the chromophore for example, the polyions A, B, and C in Figure 4.12. Later, research groups constructed polymers like D and E (Figure 4.12) where the ionizable group was closer to or on the polymer main-chain. These groups observed no difference in optical properties due to the charge placement indicating that the chromophores align by dipole and other intermolecular interactions. These studies demonstrate that electrostatic attraction may not be the only aligning mechanism, and for the NLO materials, they can align through other mechanisms, such as dipole interactions, hydrogen bonding, and other intermolecular and intramolecular forces as seen in cast films. Again to test the effect of charge placement, polymers had to be synthesized.

Figure 4.12 – Side chain chromophores used by a) Lvov et al, b) Wang et al, c) Heflin et al, d) Roberts et al, and e) Laschewsky et al and a generic polyanion[1, 3-6]

4.3.1. Experimental Setup and Synthesis scheme
The purpose of these experiments is to determine the difference between a charged group on the side-chain chromophore compared to one on the polymer main-chain. Since charged side-chain chromophoric polymers are commercially available, these polymers are a combination of an uncharged side chain chromophore and a charged polymer main chain. The Disperse Red #1 chromophore is purchased from Sigma-Aldrich; then, attached to the acrylate group via esterification.[16] These polymers have a fixed spacer of 2 methylene units. The acrylate groups are synthesized similar to the scheme in Section 4.2.1. Then they are attached as shown in Figure 4.13. The disperse red monomers are random co-polymerized with acrylic acid monomer. Two polymers are synthesized by varying the percentage of acrylic acid monomer in the polymerization. PDR1_AA50 has 50 percent acrylic acid, and pDR1_AA80 has 80 percent acrylic acid.
Figure 4.13 – Synthesis scheme for pDR1-AA50 and pDR1-AA80 polymers

All products were extracted three times in water/chloroform and purified via flash chromatography. Products were verified using NMR and IR. After the polymerization, polymers are purified by dissolving into THF and precipitating in methanol and verified by NMR and molecular weight determination by gel permeation chromatography (GPC). The molecular weights of all polymers were approximately 6000 g/mole.

Films are constructed and characterized using the procedures outlined in Chapter 2. Both FTIR and UV/Vis are used to determine tilt angles. For FTIR measurements, the terminal nitro (NO2) functional group is observed. This absorbance has no interference from other groups present on the polyelectrolytes.[17]
Due to the quantity of acid groups, these polymers are water-soluble over a range of pH values. All polyelectrolyte concentrations were at 0.01 M, and these concentrations were based on repeat unit molecular weight. Films were constructed onto glass, gold, and silicon substrates and were 20 bilayers thick. The glass substrates were used for UV/Vis measurements while the gold and silicon substrates were for IR characterization as detailed in Chapter 2. Polycation was first adsorbed and polyanion as the top layer was deposited. The pH values of polycation solutions (PDAC, PAH, BPEI, and LPEI) were held constant at 3.5 where all are expected to be at least 70% ionized, and all films were rinsed using ambient pH rinse water. Chemical structures of the polycations used in these studies are shown in Figure 4.8. Films are constructed using the procedure described in Section 2.1. Orientation measurements were made according to procedures described in Section 2.4.

**4.3.2. Results and Discussion on Charge Placement and Orientation**

If electrostatic attraction controls the orientation, then it would be expected that uncharged chromophores would exhibit less orientation than charged ones because the charged chromophores would be drawn towards the charged surface and when the next layer was deposited, drawn upwards. The uncharged chromophores would randomly align without this strong directing force. Random tilt angles would be measured for a film of uncharged chromophores that are much lower than those observed for charged chromophores. If there were another mechanism present that aligns the chromophores, then comparable tilt angles between uncharged and charged chromophores would be measured.
Results for pDR1_AA50 polymers with different polycations are displayed in Figures 4.14 through 4.16. All films have tilt angles of approximately 30 degrees for both FTIR and UV/Vis, and a 30-degree angle is near the angle of a randomly ordered film. These films confirm the expectation that having an uncharged chromophore results in less orientation. These are randomly aligned chromophores indicating no preferred orientation unlike results observed with the other side-chain, charged chromophores. Since the polymer main-chain is attracted to the surface, uncharged chromophores are free to align individually which results in the random order displayed. All the pDR1_AA50 films show a decrease in tilt angle with increasing pH. This is an effect of increasing ionization on the main-chain leading to increased attraction of the polymer to the surface. If the polymer main-chain is strongly attracted to the surface, the chromophores are more randomly aligned because the main-chain flexibility is reduced when it is attracted to the substrate.

Figure 4.14 - Tilt angles for pDR1_AA50/PDAC films
Results for pDR1_AA80 polymers with different polycations are displayed in Figures 4.17 through 4.19. These films behave similarly, in that the tilt angles are approximately 30-degrees, to the pDR1_AA50 films. The pDR1_AA80 films are more affected by pH adjustment because of the larger amount of carboxylic acid groups, which causes an enhancement in the attraction of the main-chain to the surface. As the pH increases, the
main-chain is more strongly attracted to the substrate, resulting in chromophores having less freedom to align themselves via a secondary interaction.

**Figure 4.17** - Tilt angles for pDR1_AA80/PDAC films

**Figure 4.18** - Tilt angles for pDR1_AA80/PAH films
4.4. Conclusions

Films constructed with carboxylic acid containing polymers are more affected by processing conditions than those with a sulfonic acid. These effects correlate to the pKa of the acid group, which controls the ionization at different pH values. A lower pKa leads to more ionization at any pH value and consequently less change in orientation with pH. These results were demonstrated with PAZO and PolyS119 polyions. This indicates that depending on the conditions of assembly different ionizable groups can be used without creating detrimental effects on the orientation. This allows more charged polymers to be used in ordered LBL films.

A set of polymers with varying methylene spacer-length between the side-chain and main-chain were synthesized and assembled with various polycations. All films exhibit an increasing tilt angle with increasing spacer length. These results demonstrate that the more freedom a chromophore has the more orientation it can assume. It can be concluded if a polymer exhibits more orientation with longer spacers then this trend will
continue into LBL film assembly. Also this study showed that a longer spacer than
normally used for LC polymer research was beneficial demonstrating a difference
between bulk and thin LBL films.

To study the effect of charge position, two random co-polymers were synthesized with an
acrylic acid backbone and also assembled into films with various polycations. It was
observed that moving the charged group to the backbone resulted in less orientation then
having it on the side chain chromophore; thus, the electrostatic attraction is necessary to
construct a more oriented film. These films also demonstrate a stronger attraction of the
polymer main-chain to the polycation surface leads to a more substrate parallel (lower tilt
angle) orientation because secondary ordering mechanisms are inhibited by the main-
chain. This study demonstrates a limitation on the LBL technique for assembling ordered
films. If the side-chain moieties must be aligned, then they must contain charged groups
to assist that alignment.

This chapter demonstrates that the chemical architecture of the polyions used in ordered
LBL films plays an important in determining the orientation. With this knowledge, a
more ideal chromophoric polymer can be designed and optimized for maximum
orientation in LBL films. The ideal polymer would contain side-chain chromophores that
have terminal, strongly ionizable groups and would be decoupled from the polymer main-
chain by a spacer of ten or more methylene units.

Chapter 3 examined the effects of pH adjustment and salt addition on the chromophore
orientation. This chapter establishes the connection between chemical structure and
orientation. There is one more general area for LBL films to be examined, which is the
effect of the surface or substrate on the chromophore orientation.
4.5. References


5. Effect of Surface on Chromophore Orientation

Chapters 3 and 4 studied the effects of processing parameters and chemical structure on the chromophore orientation for 20-bilayer films. Since these films were deposited with linear thickness growth and constant layer thickness, it was assumed that each layer on average had the same chromophore orientation. This chapter will investigate the effect of substrates and surfaces on the chromophore tilt angle to determine if the assumption made in previous chapters was correct. In addition, this chapter will determine if the choice of substrate or substrate pre-treatments can further enhance the orientation of a LBL film especially when coupled with the knowledge gained in previous chapters of the effects of processing and chemical structure parameters. If the orientation is independent of the surface, then oriented films may be deposited on any surface depending on the properties necessary such as transparency, flexibility, or strength to name a few.

Other research groups examined LBL films that were constructed onto bare glass substrates in order to study the films’ optical properties, and their published reports exhibit NLO active LBL films with very thin films of a few bilayers but this NLO orientation disappears with subsequent film deposition[1-3]. This ordering may be due to a substrate effect, which disappears as subsequent layers are deposited. This leads to a study in this chapter where chromophore orientation is measured as additional layers are deposited.

Previous results for more general layer-by-layer films on bare substrates showed that the once a few bilayers are deposited on the substrate the films behave independent of the substrate.[4, 5] Those films started with polycation then polyanion since the glass surface is assumed to have a negative charge due to static electricity and silanol groups.
This effect has been observed in previous chapters for the 20-bilayer films. The films characterized by IR spectroscopy were deposited on both silicon and gold substrates, and little difference between the two was observed in terms of layer thickness.

Another surface treatment besides using different substrate materials is modifying the charge density of the surface using polyions or self-assembled monolayers (SAMs). SAMs are small molecules that will react with the glass surface and self organize such that the terminal charged group becomes a new surface.[6] On these new surfaces, LBL films can be assembled.

5.1. Orientation of Chromophores on Bare Substrates

UV/Vis measurement is sensitive enough to be able to detect individual layers, and then calculate chromophore tilt angles from these data. Another study was undertaken to watch the orientation of the chromophores change as the films grew and more layers were added. Tilt angles were measured at 1 bilayer up to 6 bilayers. This study will determine if the final, 20-bilayer orientation is less than the initial chromophore orientation.

5.1.1. Experimental Procedure

Films were constructed as those in earlier sections with polycation pH held constant at 3.5. All films are characterized by UV/Vis spectroscopy. First, a layer of polyamine is adsorbed, and subsequently the polyanion, PAZO or PolyS119, was deposited and a UV/Vis spectrum collected. Every full bilayer was PolyS119 or PAZO on top whereas the half bilayers are polycation as the top layer. The substrates were glass slides that were first cleaned using sulfuric acid and hydrogen peroxide, rinsed with deionized water (Milli-Q), and oxygen plasma etched to remove any organic material and create a silanol surface. Chemical structures for the polyelectrolytes are shown in Figure 5.1. PolyS119
films were deposited from pH 2 and 8.5 solution to determine if there was a difference in chromophore orientation with film thickness for these very thin films, and PAZO films were deposited from pH 5 and 8.5 solutions for the same reasons.

Figure 5.1 – Polyanions and polycation used in surface treatment study

5.1.2. Orientation of PolyS119 after each layer

Results for PolyS119/PDAC at pH 2 are shown in Figure 5.2. These chromophores alternate tilt angles with the dipping cycles, but there is not any discernable trend as the film grows. The initial chromophore tilt angles are slightly higher compared to the 20-bilayer angles. Also, no consistent change is observed when PDAC is deposited onto the PolyS119 layers. For these films, the chromophore orientation appears independent of layer number and thickness after a few bilayers, but there is a measurable increase for the first two bilayers. Since PolyS119 and PDAC are strong polyelectrolytes, it would be expected that after a few layers the electrostatic attraction would become constant as the layer thickness becomes linear by 6 bilayers the film is growing linearly with constant layer thickness for both polyelectrolytes. Since these films are assembled on glass

128
substrates, their thickness was not measured, but a constant UV/Vis absorbance was observed indicating constant mass deposited per layer for the PolyS119.

**Figure 5.2** – Tilt angle data for PolyS119/PDAC pH 2 at each half-bilayer

In Figure 5.3 tilt angle results for PolyS119/PDAC films at pH 8.5 are displayed. Again, there appears no consistent trend with the different layers adsorbing, and the chromophore tilt angle is higher after two bilayers then decreases. These films are significantly thinner than those assembled at pH 2, but both films behave similarly.

**Figure 5.3** – Tilt angle data for PolyS119/PDAC pH 8.5 at each half-bilayer
To test whether the polyamine ionization changes the initial chromophore orientation, films were constructed with LPEI instead of PDAC. Results for PolyS119/LPEI films at pH 2 are shown in Figure 5.4. At 1.5 bilayers where the top layer is LPEI, the highest tilt angles are measured similar to the PDAC film results. These tilt angles do not vary as much likely due to their increased thickness compared to PDAC films. Since more polymer is deposited per layer, the subsequent layers are more consistent because the charge density on the surface is more consistent. A consistent charge density results in more uniform electrostatic attraction, which is one driving force for alignment.

![Graph showing UV/Vis Tilt Angle vs PolyS119/LPEI Bilayers](image)

**Figure 5.4** – Tilt angle data for PolyS119/LPEI pH 2 at each half-bilayer

In Figure 5.5 results for PolyS119/LPEI films at pH 8.5 are displayed. These films fluctuate more than pH 2 films probably due to the decreased ionization of LPEI at pH 8.5. These films also display higher tilt angles than a 20-bilayer film. It would be expected that these films would show lower tilt angles compared to the pH 2 films, but that is not the case. In this case it could be chromophores deposited in a thinner layer show more orientation at least initially.
5.1.3. Orientation of PAZO after each layer

Results for PAZO/PDAC at pH 5 are shown in Figure 5.6. These chromophores alternate tilt angles with each layer much more than the PolyS119 films. There is not any discernable trend as the film grows; however the average orientation must increase later in the films. The difference between PAZO and PolyS119 is ionization. The PAZO is less ionized and provides lower charge density on the surface initially. This causes the initial growth to be less consistent as evidenced by the tilt angles varying widely.
In Figure 5.7 the results for the PAZO/PDAC films at pH 8.5 are shown. These films exhibit an increase in tilt angles probably due to the stronger ionization of PAZO that is adsorbing compared to pH 5 films. Note to that these films still have variation in the chromophore tilt angle with every adsorbed layer, but this variation is much smaller than for the pH 5 films.

![Graph showing UV/Vis Tilt Angle vs. PAZO/PDAC pH 8.5 Bilayers](image)

**Figure 5.7** – Tilt angle data for PAZO/PDAC pH 8.5 at each half-bilayer

PAZO/PDAC films demonstrate the effect of PAZO ionization on the initial chromophore tilt angles because the PDAC ionization is unaffected by pH. It is expected that PAZO/LPEI films will behave differently since LPEI ionization will change depending on pH.

Results for PAZO/LPEI at pH 5 are shown in Figure 5.8. These films have a steady increase in chromophore tilt angle with increasing bilayers. These films do shown a decrease at 1.5 bilayers when LPEI is adsorbed onto the first PAZO layer. This may be what Lvov and co-workers observed in their research where the NLO signal disappeared after the initial PAZO deposition.[2] PAZO/LPEI films at pH 8.5 could not be studied
because their UV/Vis absorbance was below the detection limit. These films are very thin and at least initially, do not deposit very uniformly.

Figure 5.8 – Tilt angle data for PAZO/LPEI pH 5 at each half-bilayer

Neither the PolyS119 nor PAZO films show any consistent change in tilt angle with the deposition of polyanion or polycation indicating the orientation measured is an average of each layer.

5.2 Effect of Different Substrate Treatments on Chromophore Orientation

The first surface treatment studied is self-assembled monolayers. These are small molecules, typically with high aspect ratios, have surface reactive groups on one end and a terminal group that can be charged on the other. For glass substrates that are plasma treated to create Si-OH (silanol) on the surface, three types of silanes are used. The most reactive silanes are trichlorosilanes followed by trimethoxy and then triethoxysilanes. An example of SAMs is shown in Figure 5.9.[6, 7]
Another surface treatment used was constructed by the LBL technique. This is composed of sulfonated polystyrene (SPS) and either PDAC or LPEI for polycations (Figure 5.2). These films are assembled with 2.5 bilayers starting with polycation as the first layer and last layer. These films will have an approximately constant charge density on the surface compared to a bare glass substrate. This will allow immediate linear thickness growth of the chromophoric LBL films.

5.2.1. Experimental Setup
These films are constructed and characterized using the procedures explained and discussed in Chapter 2. The polycation solutions are held at a constant pH of 3.5. Due to its sensitivity, UV/Vis measurements are used to determine the chromophore tilt angles so all films are assembled onto glass slides.

To construct monolayers, silanes are dissolved into toluene at a concentration of 0.05M. Water will react with silanes so toluene is chosen because of its very low water solubility. The toluene/silane solution is heated to 45°C, and the clean glass substrates are soaked in
the heated solution for 15 minutes. After 15 minutes, a small amount of glacial acetic acid is added to catalyze the reaction. The substrates are then removed and rinsed with acetone, ethanol, and water[7]. As substrates are rinsed with water, it is easy to see the change in water contact angle that has occurred. The methyl-terminated SAMs do not wet (high contact angle), and water bounces off the substrate. The amino-terminated SAMs have a surface that wets less than a blank glass slide due to the lack of alcohol groups in the SAM surface. Before use, the amino groups were protonated by dipping the slide in pH 3.5 water solution.

Substrates coated with SPS/PDAC or SPS/LPEI layers are constructed similar to the procedures used to make LBL films. Bare, plasma cleaned glass slides are dipped first in polycation, rinsed, and then dipped into SPS (polyanion) solution until 2.5 bilayers are constructed with the top layer being polycation (LPEI or PDAC). These precursor layers have a thickness of approximately 40 Å.

PolyS119 polyanion solutions are held constant at pH 2. This results in thicker films that are easier to characterize. The polyanions and polycations used in this study are shown in Figure 5.1.

5.2.2. Results and Discussion on Different Substrate Treatments
This section will present results for four substrate treatments: methyl-terminated SAMs, amino-terminated SAMs, 2.5 bilayers of SPS/LPEI, and 2.5 bilayers of SPS/PDAC. The chromophore tilt angle is measured after each layer of polyelectrolyte is deposited on top of these treatments. The methyl-terminated SAM prevented adsorption of the polyelectrolytes so no tilt angle measurements were performed for these films. Methyl-
terminated SAMs have been used as surfaces for LBL films previously but require hydrophobic interactions between adsorbing the polyelectrolyte and surface to create a charged surface.[8] The methyl-terminated SAMs may be used in future research as a method to control deposition of the polyelectrolytes. In contrast to the methyl-terminated SAMs, the amino-terminated SAM presents a positively-charged surface for polyelectrolyte deposition. After reacting the SAM on the slide, PolyS119 is adsorbed on the positive surface. These films did not have deposition problems like the methyl-terminated films. Figures 5.10 and 5.11 show the chromophore tilt angles for an amino-terminated silane surface after deposition of each half bilayer. Both PDAC and LPEI films have higher PolyS119 tilt angles with the initial layers, and these angles decrease with adsorption of polycation layers. Other research groups studying non-linear optical orientation also observed this behavior. They measured higher non-linearity at low numbers of bilayers and the alignment decreased with polycation adsorption.[1, 2] At higher bilayers, the tilt angle change between polyanion and polycation dipping steps is small because the UV/Vis measurement detects all of the chromophores in a film, which is large compared to one layer.
Figure 5.10 – Tilt angle for PolyS119/PDAC films at PolyS119 pH 2 on amino-terminated monolayers where half bilayers are PolyS119 adsorption steps

Figure 5.11 – Tilt angle for PolyS119/LPEI films at PolyS119 pH 2 on amino-terminated monolayers where half bilayers are PolyS119 adsorption steps

SAMs require a chemical reaction on the substrate to assemble and use organic solvents to ensure proper coverage. This limits their usefulness to substrates that can be correctly functionalized for the attachment reaction. An easier way to functionalize and introduce
charge to the substrate is to use LBL films. For this study, a thin LBL film consisting of non-chromophore polyelectrolytes, SPS with PDAC or LPEI (shown in Figure 5.1), will be assembled on the surface.

Chromophore tilt angles for films on SPS/PDAC or SPS/LPEI substrates are shown in Figures 5.12 and 5.13. Again like the amino-SAM results, these films have higher tilt angles initially but these angles decrease as more layers are deposited. For the SPS/PDAC treatment (Figure 5.5), there is a steady decrease in chromophore tilt angle as opposed to the "flipping" seen for the amino-terminated SAMs and SPS/LPEI treatments. Since SPS and PDAC are highly ionized, this decrease is likely caused by a decrease in surface charge density as chromophores adsorb. Compared to SPS, PolyS119, while similarly sulfonated, has more uncharged molecular surface area. Once 2 bilayers of PolyS119/PDAC are adsorbed, the surface charge density recovers leading to an increasing tilt angle. The PolyS119/LPEI film actually shows a tilt angle increase with adsorption of LPEI unlike previous films, which displayed a decrease when the polycation adsorbs. LPEI helps to align the chromophores more perpendicular to the substrate.
Figure 5.12 – Tilt angle for PolyS119/PDAC films at PolyS119 pH 2 on (SPS/PDAC)$_{2.5}$ films where half bilayers are PolyS119 adsorption steps

Figure 5.13 – Tilt angle for PolyS119/LPEI films at PolyS119 pH 2 on (SPS/LPEI)$_{2.5}$ films where half bilayers are PolyS119 adsorption steps

These results demonstrate that substrate treatments have little effect on the overall orientation especially after several bilayers are applied. For thicker films, the orientation is independent of the substrate, which allows a large choice of substrate materials that can be used and tailored to meet other requirements.
5.3. Controlling film deposition on substrates
In addition to using monolayers to change the surface properties of a substrate, they can
be used to control where the film deposits on the surface. Many interesting devices, such
as photorefractive systems, thin-film transistors, and waveguides, would require the
ability to control the placement of the film as well as the orientation within the film. This
section discusses preliminary results for controlling where the film grows on the substrate
surface.

5.3.1. Experimental Setup
Since the methyl-terminated SAM resisted adsorption, it could be used to control
adsorption on the substrate. SAMs can be patterned by the micro-contact printing
procedure shown in Figure 5.14. A master is etched into a silicon wafer similar to the
technique used in microelectronics industry. Polydimethylsiloxane is poured onto this
master and cured leaving an imprinted pattern on a polymer stamp. Carboxylic acid
terminated thiol is spread on the polymer stamp surface. The stamp is placed onto a gold
substrate and then removed. This patterns the thiol on the gold substrate with bare gold
in the other areas. The substrate is then dipped into a solution containing penta-ethylene
glycol terminated thiol. This thiol will resist deposition of charged material. After
stamping, a 5-bilayer SPS/PDAC film is constructed onto the substrate using the
techniques described earlier. Then, the functional film is grown.[8, 9] The films
described in the following section are 20 bilayers using LPEI as the polycation at a pH
value of 5. PolyS119 is used as the polyanion.
5.3.2. Controlling Film Deposition Results
An example of PolyS119/LPEI is shown in Figures 5.15 and 5.16. PAZO and PolyS119 have very good selectivity, which results in very good patterns. Because these patterns refract light, the chromophore orientation cannot be measured, but it is expected to be the same as a continuous film.

Figure 5.14 – Micro-contact printing technique

Figure 5.15 – Optical micrograph of PolyS119 pH 5/LPEI pH 5 patterned film
Figure 5.16 – AFM micrograph of PolyS119 pH 5/LPEI pH 5 patterned films

5.4. Conclusion for Surface results
The substrate can increase orientation in the first layer, but this effect does not continue into subsequent layers. These results could be used to incorporate layers to refresh the surface charge. For example, several layers of PolyS119/Polycation could be adsorbed followed by SPS/PDAC to recharge the surface. These results would be similar to those of the SPS/PDAC precursor layers. Then more PolyS119 could be deposited with this cycle repeating. One drawback to this method would be a decrease in functional material incorporated into the film. This study also demonstrates the independence of a thicker film on substrate effects. This knowledge allows oriented films to be assembled on any substrate that can support the LBL technique. To date, LBL polymer films have been
assembled on a variety of substrates including flexible polymers, conducting indium-tin oxide glass, and mica surfaces just to name a few.

The surface can be used as a template to control film deposition. The PolyS119 and PAZO functional polyanions can be patterned using micro-contact printing. These patterning results could be optimized for device prototype manufacture.
5.5. References


6. Second Harmonic Generation Measurements

All the previous studies used FTIR and UV/Vis measurements to determine orientation. These are first-order measurements in that they can determine the tilt angle for a chromophore but cannot determine the direction the chromophore is aligned; thus, it is unknown if the orientation measured is noncentrosymmetric (net dipole). A centrosymmetric type of alignment can be exploited for a number of applications including electrical and optical devices; however, for second-order non-linear optical (NLO) applications the films must exhibit a net dipole. Second-harmonic generation (SHG) is used to measure the strength of the non-linearity of a material and determines the degree of noncentrosymmetric alignment of the chromophores. This will determine the strength of the NLO properties in the films. The differences between these SHG and FTIR/UV/Vis measurements are shown in Figure 6.1 for an ordered, centrosymmetric film.

![Sample film diagram]

- Chromophore

FTIR and UV/Vis
Measure high orientation

Second Harmonic Generation
Measures no noncentrosymmetric orientation and has no signal

**Figure 6.1** – Differences between FTIR and UV/Vis absorbance and SHG absorbance.
Other researchers have used SHG to detect noncentrosymmetry in LBL films that contained NLO active polymers. Five studies were published in 1997 and 1998.[1-5] Of these, three studies used very thin, less than 5 bilayer, films and saw decreases in noncentrosymmetric order with film deposition. Most observed a “flipping” of the chromophores when a top layer of polycation was added which was discussed in Chapter 5. This effect is illustrated in Figure 6.2.

![Diagram showing noncentrosymmetric orientation](image)

**Figure 6.2** – Loss of noncentrosymmetric orientation as layers are added (chromophores “flip”)

As the films grew the initial noncentrosymmetric orientation was lost. The other two studies had an increase in SHG signal as the films grew without any loss of orientation. The first two studies, Lvov et al and Heflin et al, were repeated with thick and thin films to measure SHG in LBL films and reproduce their results using PAZO and PolyS119 polyanions. The goal was to correlate the SHG measurements to the FTIR and UV/Vis results and compare noncentrosymmetric to centrosymmetric order in the films.

### 6.1. Experimental Setup

The second-order NLO coefficients \( (d_{33}) \) of the self-assembled films and spin-coated, poled films were measured by second-harmonic generation using 1.064 μm laser radiation. The measurements were carried out on a Q-switched Nd:YAG laser (Quantel
660A). The SHG signal, selected with an interference filter at 0.532 μm, was detected by a photomultiplier tube and measured with a boxcar integrator. A Y-cut quartz crystal was used as the reference. By comparing the SHG intensity from the LBL films to the quartz crystal, the orientation of the chromophores and strength of the NLO properties can be determined[3]. This setup is the same used by Wang et al and the measurement performed by a coauthor of their paper, Ke Yang at the University of Massachusetts-Lowell.

6.2. Results from SHG Measurements
All the samples present in earlier chapters were tested for SHG signals. Over 250 samples were tested yet none exhibited a SHG signal. These include numerous samples constructed using the exact conditions and materials presented by Heflin et al and Lvov et al.[2, 5, 6] Also, other conditions were copied from other references substituting PolyS119 and PAZO polyanions for the polyanions used in those references. In order to try and enhance the NLO effects, films were constructed using pH 13 solutions of PAZO/PDAC and PolyS119/PDAC. At this high pH, the phenolic hydrogen on the polyanions is deprotonated, which makes the hydroxyl anion a very strong electron-donor group.[7] This deprotonation has been shown to increase NLO properties for a variety of chromophores.[7, 8] In addition, several films constructed previously were soaked in pH 13 water for 20 minutes to try to detect a SHG signal from the films. Both these efforts failed to produce any signal. Films at thin as one bilayer and as thick as 30 bilayers were also tested to no avail. Although, we are measuring orientation with the FTIR and UV/Vis experiments, there is not any noncentrosymmetry in these films, which was demonstrated by other groups.
Films of PolYS119, PAZO, and pDR1_AA## that were spin-coated and electric-field poled did display relatively strong SHG signals so these polymers can align to produce noncentrosymmetric order. Since only two groups have reported detecting SHG signal in thicker films, it must be difficult to get a noncentrosymmetric order reproducibly using the LBL method. Also, not all the research groups are performing the same measurements on the samples. For example, some measure the decrease in energy of the 1.064 μm laser to observe the generation of a second-harmonic signal rather that detect the 0.532 μm wavelength like Wang et al.[3, 5, 6] It is unknown if one method is more sensitive, but some researchers believe the most accurate measurement requires detection of the 0.532 μm wavelength.

6.3. Conclusions
Although the films display order as evidenced by the FTIR and UV/Vis data, none of the LBL films studied have a SHG signal. The LBL assembly can provide centrosymmetric order to a film based on electrostatic attraction between the polyelectrolytes; however, this results in the chromophores pointing up and down in approximately equal numbers preventing the creation of a noncentrosymmetric order, which negates the second-order NLO properties. The LBL technique is best utilized to provide centrosymmetric order and is not suited for non-linear optical work.
6.3 References

7. Summary, Conclusions, and Applications

7.1 Summary

Processing conditions play a very important role in controlling orientation. The chromophore orientation is controlled by the electrostatic attraction between the chromophore (negatively charged) and polycation. Conditions that affect the polyelectrolyte ionization will impact the orientation. For example, sulfonic acid containing polyanions are unaffected by pH conditions and salt concentration because of the very low pKa of the acid group; however, the polycations used with these polyanions can be affected by these parameters. Additionally, the pH and salt concentration can be varied for a given polyanion/polycation pair to generate more orientation. Generally, the highest tilt angles occur when the polycations are fully ionized.

The surface has little effect on chromophore orientation for LBL films once the first bilayer is deposited. The subsequent layers are not influenced by the substrate but by the previous layer. This allows a wide variety of substrates to be used and constructing ordered films is not limited to specific ones. Although, the surface does not affect orientation, it can be used to control the deposition of the functional polyanions via self-assembled monolayers and micro-contact printing.

In addition to processing parameters, the chemical structure of the side chain polymers containing chromophores is important. Polymers were synthesized to study specific structural characteristics. Results on three new polyanions demonstrated that longer spacers between the polymer main and side chain result in more chromophore orientation. Also, chromophoric polyanions were synthesized with uncharged side-chain
chromophores and charged groups on the main-chain instead of the side-chain. These polymers exhibited random alignment with no preferred order in LBL films. The longer spacer and charged side chain chromophore lead to more orientation. The results observed for structural changes are independent of processing conditions and polycations. The combination of specific processing conditions and specific synthesis can greatly enhance the chromophore orientation in these LBL assembled films. These results will lead to intelligently engineering polymers for use in the LBL technique.

7.2 Conclusions

This research has shown that orientation can be controlled via processing conditions, and polyelectrolytes can be designed to increase chromophore orientation in layer-by-layer films. The combination of processing conditions with specific synthesis allows well-ordered, centrosymmetric films to be grown in an all-aqueous assembly technique; however, achieving noncentrosymmetric orientation for NLO active films is elusive. Other applications aside from NLO applications that require well-ordered films would be better suited for LBL assembly.

7.3 Applications of this Research

Since constructing noncentrosymmetric films is very difficult, potential applications for this work would likely be in other areas than nonlinear optical devices. A few specific areas include electrical conductivity, liquid crystalline displays, optical switches, and photovoltaic cells. One potential use would be constructing all-organic thin film transistor (TFT). A TFT consists of a semiconducting surface, gate (G), source (S), and drain (D) electrodes, and a hole transport layer. Examples of an organic hole transport and semiconducting material are different types of polythiophenes including
poly(sexithiophene). Side chain polythiophenes have been shown to have high hole conductivity when ordered in specific fashion.[1-4] The construction of a TFT is shown in Figure 7.1. The semiconductor (type of polythiophene) is spin cast onto a flexible plastic substrate. On top of this a patterned film the electrodes consisting of conducting polyaniline are grown using layer-by-layer assembly and patterned using polymer-on-polymer (POP) stamping.[5-9] POP is similar to micro-contact printing except the stamp is covered with a polymer rather than a thiol or silane. The polymer used to resist adsorption similar to the ethylene glycol terminated thiols. Filling in and covering the polyaniline electrodes would be a LBL film of side chain poly(thiophene). This film would have to be oriented along the side-chains to have high hole mobility and constructed with a spacer and the charged group on side chain to enhance this orientation. The polythiophene solution would have 0.1 M salt concentration and be layered with LPEI since these conditions provide the highest chromophore tilt angles. These would induce strong electrostatic attraction, which would enhance the orientation. TFT are used in active-matrix displays to turn on and off the individual pixels and are currently constructed using photolithographic techniques in a complex procedure that does not allow flexible substrates to be used.
Figure 7.1 – Construction of thin-film transistor using LBL assembly

The future directions of this work should be toward constructing devices and finding new applications for LBL assembly. The fundamentals of LBL becoming well understood, and the push for commercial products has begun.
7.4 References


Appendix A- FTIR model

The following code is for MAPLE. This calculates the tilt angles for the chromophores based on FTIR absorbance intensities.

FTIR program
To calculate the tilt angles from IR data for multilayer films from Chollet et al, Takenaka et al, and Josephine Cheung, et al
For each orientation (transmission or grazing) the numbers will be calculated for k=0 and k=0.1

Phi is the grazing angle, wave is the wavenumbers, h is the height of the films, nfilm is the index of refraction of the films

restart;phi:=80.0;wave:=1150.0;h:=64.0e-8;ATex:=.00043;ARex:=.00085;
Nair is the index of refraction for air, and nznse is the index of refraction for the IR window
> nair:=1.0;nznse:=3.899-.157*i;nfilm:=1.5;
> i := sqrt(-1.0);
Convert grazing angle to radians
> pie:=3.14159;
> phirad:=phi*pie/180.0;
Calculate index of refraction for Gold
> a:=32.246-3.31e-2*wave+1.31e-5*wave^2-1.77e-9*wave^3;
> b:=92.3674-8.07e-2*wave+2.96e-5*wave^2-3.84e-9*wave^3;
> nplat:=-156-3.369*i;
Calculate Index of Refraction for Film for k=0 and k=0.1
> k1:=0.0;k2:=0.1;
> nfilm1:=nfilm+k1*i;nfilm2:=nfilm+k2*i;
Calculate angles through each layer for TRANSMISSION
>
> tphiair:=0.0; tphifilm1:=arcsin(nair/nfilm1*sin(tphiair)); tphisub1:=arcsin(nair/nznse*sin(tphiair)); tphifilm2:=arcsin(nair/nfilm2*sin(tphiair)); tphisub2:=arcsin(nair/nznse*sin(tphiair));
Calculate q values and beta values for TRANSMISSION at k=0 and k=0.1
>
> tqair:=-cos(tphiair)/nair;tqfilm1:=-cos(tphifilm1)/nfilm1;tqsub1:=-cos(tphisub1)/nznse;tqfilm2:=-cos(tphifilm2)/nfilm2;tqsub2:=-cos(tphisub2)/nznse;
>
> tbetaair:=-h*pie*nair*wave*cos(tphiair);tbetafilm1:=-h*pie*nfilm1*wave*cos(tphifilm1);tbetasub1:=-h*pie*nznse*wave*cos(tphisub1);tbetafilm2:=-h*pie*nfilm2*wave*cos(tphifilm2);tbetasub2:=-h*pie*nznse*wave*cos(tphisub2);
Calculate angles through each layer for GRAZING
>
> gphiair:=phirad;gphifilm1:=arcsin(nair/nfilm1*sin(gphiair));gphisub1:=arcsin(nair/nplat*sin(gphiair));gphifilm2:=arcsin(nair/nfilm2*sin(gphiair));gphisub2:=arcsin(nair/nplat*sin(gphiair));
Calculate q values and beta values for GRAZING at k=0 and k=0.1

\[
g_{qair}:=\cos(\phi_{qair}/n_{air}); g_{qfilm1}:=\cos(\phi_{qfilm1}/n_{film1}); g_{qsub1}:=\cos(\phi_{qsub1}/n_{plat}; g_{qfilm2}:=\cos(\phi_{qfilm2}/n_{film2}); g_{qsub2}:=\cos(\phi_{qsub2}/n_{plat});
\]

\[
\begin{align*}
g_{betaair}=& 2\times h \times \pi \times \sin(\phi_{air}) \times \cos(\phi_{film1}); g_{betafilm1}:=2\times h \times \pi \times \sin(\phi_{film1}) \times \cos(\phi_{air}); g_{betafilm1}:=2\times h \times \pi \times \sin(\phi_{film1} \times \cos(\phi_{air}); g_{betafilm1}:=2\times h \times \pi \times \sin(\phi_{film1} \times \cos(\phi_{air}); g_{betafilm1}:=2\times h \times \pi \times \sin(\phi_{film1} \times \cos(\phi_{air});
\end{align*}
\]

Now calculate the Matrix M for transmission using the betas and q's from above for k=0 and k=0.1

\[
t_{1m11}:=\cos(t_{betafilm1}); t_{1m12}:=1.0 \times i \times \sin(t_{betafilm1})/t_{qfilm1}; t_{1m21}:=1.0 \times i \times \sin(t_{betafilm1})/t_{qfilm1}; t_{1m22}:=\cos(t_{betafilm1});
\]

\[
t_{2m11}:=\cos(t_{betafilm2}); t_{2m12}:=1.0 \times i \times \sin(t_{betafilm2})/t_{qfilm2}; t_{2m21}:=1.0 \times i \times \sin(t_{betafilm2})/t_{qfilm2}; t_{2m22}:=\cos(t_{betafilm2});
\]

Calculate Matrix M for grazing angle for k=0 and k=0.1 using betas and q's above

\[
g_{1m11}:=\cos(g_{betafilm1}); g_{1m12}:=1.0 \times i \times \sin(g_{betafilm1})/g_{qfilm1}; g_{1m21}:=1.0 \times i \times \sin(g_{betafilm1})/g_{qfilm1}; g_{1m22}:=\cos(g_{betafilm1});
\]

\[
g_{2m11}:=\cos(g_{betafilm2}); g_{2m12}:=1.0 \times i \times \sin(g_{betafilm2})/g_{qfilm2}; g_{2m21}:=1.0 \times i \times \sin(g_{betafilm2})/g_{qfilm2}; g_{2m22}:=\cos(g_{betafilm2});
\]

Calculate absorbance for transmission for both k values

\[
tb1:=\Re(\cos(t_{phsub1}/nn_{znse})/(\cos(t_{phsub1}/nair));
\]

\[
tb2:=\Re(\cos(t_{phsub2}/nn_{znse})/(\cos(t_{phsub2}/nair));
\]

\[
tc1:=(t_{1m11}+t_{1m12} \times t_{qsub1}) \times t_{qair}+(t_{1m21}+t_{1m22} \times t_{qsub1});
\]

\[
tc2:=(t_{2m11}+t_{2m12} \times t_{qsub2}) \times t_{qair}+(t_{2m21}+t_{2m22} \times t_{qsub2});
\]

\[
td1:=(\abs(2.0 \times t_{qair}/tc1))^2;
\]

\[
td2:=(\abs(2.0 \times t_{qair}/tc2))^2;
\]

Calculate absorbance for grazing angle for both k values

\[
rb1:=(g_{1m11}+g_{1m12} \times g_{qsub1}) \times g_{qair};
\]

\[
rb2:=(g_{2m11}+g_{2m12} \times g_{qsub2}) \times g_{qair};
\]

\[
r_{c1}:=g_{1m21}+g_{1m22} \times g_{qsub1};
\]

\[
r_{c2}:=g_{2m21}+g_{2m22} \times g_{qsub2};
\]

\[
r_{d1}:=rb_{1-c1}/(rb_{1-c1});
\]

\[
r_{d2}:=rb_{2-c2}/(rb_{2-c2});
\]

Calculate absorbances TA and RA

\[
TA1:=tb_{1 \times td1};
\]

\[
TA2:=tb_{2 \times td2};
\]

\[
RA1:=(\abs(rd_{1-c1}))^2;
\]

\[
RA2:=(\abs(rd_{2-c2}))^2;
\]

Calculate ratio of m/xz from grazing angle theory

\[
with(linalg): Q1:=array([[1+rd2], [-1.0 \times g_{qair} \times (1-nd2)]]);
\]

\[
M1:=array([[g_{2m11}, g_{2m12}], [g_{2m21}, g_{2m22}]])
\]

\[
N1:=inverse(M1);
\]

\[
Q2:=evalm(N1 \times Q1);
\]

\[
E:=(\abs(Q2[2,1]))^2;
\]

156
> Ez:=(abs(nair*sin(gphiair)*Q2[1,1]/nfilm2))^2;
> Ratio:=Ex/Ez;
Calculate Transmission and Reflectance (grazing) absorptions to get mx+mz
> AT:=log(TA1/TA2);
> AR:=log(RA1/RA2);
Calculate AR/AT or mx+mz
> sum1:=AR/AT;
> mz:=sum1/(1+Ratio);mx:=sum1-mz;
Calculate Tilt angle from Experimental Data
>
> test1 := pie/2.0;

> for ang from 1.5750795 by -0.001 to 0.0 do
>   err1:=abs(sin(ang)^2/(2.0*mz*cos(ang)^2+mx*sin(ang)^2)-ATex/ARex);
>   if (err1<0.01) then break fi od;
> ti:=ang*180.0/pie;

> alpha:=ti*pie/180.0;beta:=69.0*pie/180.0;

> gamma1:=(arccos(sqrt(1-(cos (alpha))^2-(cos(beta))^2)))*180.0/pie;
Appendix B – UV/Vis model

The following code is used to calculate chromophore tilt angles from UV/Vis absorbance intensity. This worksheet is used with MAPLE.

Program to calculate tilt angles from UV/Vis data

\[
\text{nair}:=1.0; \text{nfilm}:=1.45; \text{nglass}:=1.49; \text{angle}:=60.0; \text{Ap}:=0.00921; \text{As}:=0.00747; \\
\text{iangle}:=\text{angle} \times 3.14159/180.0; \\
\text{rangle}:=\arcsin(\text{nair}/\text{nfilm} \times \sin(\text{iangle})); \\
\text{denom1}:=\text{nair} \times \cos(\text{iangle})+\text{nglass} \times \cos(\text{rangle}); \\
\text{numer1}:=\text{nair} \times \cos(\text{rangle})+\text{nglass} \times \cos(\text{iangle}); \\
\text{alpha}:=\cos(\text{iangle}) \times \cos(\text{rangle}); \\
\text{beta}:=2.0 \times \text{nair}^3 \times \text{nglass} \times (\sin(\text{iangle}))^2; \\
\text{chi}:=\left(\frac{\text{Ap}}{\text{As}}\right)/(\text{denom1}/\text{numer1}); \\
\text{theta}:=\arctan\left(\sqrt{\left(\frac{1}{\text{nfilm}^4}\right) \times (\text{beta}/(\text{chi}-\text{alpha}))}\right); \\
\text{tiltangle}:=\text{theta} \times 180.0/3.14159;
\]