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ABSTRACT

The fabrication and characterization of highly-ordered thin films made from an amphiphilic, regioregular (RR) polythiophene (PT) derivative are described. The effects of structural conformation and order on materials properties and reactivity are discussed. High optical-quality films of poly(3-(11-(2-tetrahydropyranyloxy)undecyl)thiophene) (PTHPUDT) were prepared by the Langmuir-Blodgett (LB) technique. The amphiphilic nature of the polymer affords layer-by-layer deposition and the formation of multilayer films of head-to-head and tail-to-tail, Y-type structure. X-ray diffraction (XRD) studies indicate the formation of a semi-crystalline film with bilayer separations of ~30 Å. Anisotropic optical absorption in the plane of the film signifies that the thiophene backbones are preferentially oriented along the dipping direction. Further, polarized light microscopy studies reveal that these films are highly birefringent.

The nonlinear optical properties of PTHPUDT films were explored. Optical second harmonic generation (SHG) studies of multilayer films provide information regarding both the thiophene orientation within the film and the anisotropic distribution of chromophores in the surface plane. The third-order nonlinear optical response of the polymer films was probed using z-scan methods. Analysis of the resulting z-scan data yielded values consistent with previous studies on PT-based polymer systems. However, even with relatively low intensities incident on pristine PTHPUDT polymer films, the required power to
achieve a nonlinear response in the film is sufficient to produce photoinduced changes in the original polymer. Although our observations pertain specifically to PTHPUDT, our results may extend to the broader class of PT-based materials more generally. These observations put into question whether the nonlinear optical susceptibility values of PT-based materials currently being reported in the literature result from pristine polymers or from their photoconverted products.

The chemistry occurring in the ordered films was examined. Large differences in both the thermal reactivity (thermochromism) and physical properties (solvatochromism) of the films were observed after heat-treatment.

Taken together, this data offers strong evidence of highly-ordered films. As such, PTHPUDT is a model polymer system with potential of elucidating the connection between polymer morphology and physical properties in materials that are otherwise subject to a sufficiently complex distribution of morphologies that such a correspondence is precluded.

Keywords: Langmuir-Blodgett; polymer; thin films; second harmonic generation; Z-scan
DEDICATION

This thesis is dedicated to my parents who taught me the value of education and who made countless sacrifices, so that I could have the opportunities they did not have. Their love and support have encouraged me throughout my studies.
ACKNOWLEDGEMENTS

A big thank you goes to my Senior Supervisor, Dr. Gary W. Leach, who gave me the opportunity to work in his lab during my undergraduate and graduate studies. I have always appreciated his teaching, advice and valuable guidance during my graduate program. I would also like to thank the members of my Supervisory Committee, Dr. Vance Williams and Dr. Hogan Yu for all of their assistance and helpful discussions. I wish to acknowledge Dr. Steven Holdcroft for his beneficial suggestions and for the use of his laboratory equipment. I would also like to thank Dr. Z-G. Ye for the utilization of his polarized light microscope, Dr. Jianfei Yu for synthesizing PTPUDT, Dr. Johan Foster for his aid with chromatography experiments, Ms. Monica Szczepina for help with NMR experiments and Ms. Gisela Schulz for assistance with quantum yield measurements.

I want to thank all of my friends and colleagues with whom I have worked over the years. I have tremendously enjoyed my graduate experience because of all of you. Particular thanks go out to all the members of the Leach lab for their friendship especially Dr. Thomas Johansson and Ms. Karen Chan for all of their hard work and late nights, Dr. Greg Cetnarowski for useful dialogues and Dr. Claire McCague for reviewing this thesis. I would also like to recognize members of Dr. Holdcroft’s group for their assistance and friendship over the years.
I would also like to thank Simon Fraser University, 4D Labs and the Natural Sciences and Engineering Research Council for their financial support.
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GLOSSARY

\( \alpha \)  
Absorption coefficient

\( \beta \)  
Nonlinear molecular hyperpolarizability tensor

\( \chi^{(n)} \)  
N'th order nonlinear susceptibility tensor

\( \chi_i^{(3)} \)  
Imaginary component of \( \chi^{(3)} \)

\( \chi_k^{(3)} \)  
Real component of \( \chi^{(3)} \)

\( \varepsilon \)  
Dielectric constant

\( \phi \)  
Azimuthal rotation angle

\( \gamma \)  
Nonlinear index of refraction

\( \eta \)  
Complex index of refraction

\( \eta' \)  
Real part of the index of refraction

\( \kappa \)  
Imaginary part of the index of refraction

\( \lambda_{\text{max}} \)  
Wavelength of maximum absorption

\( \mu \)  
Electron mobility

\( \pi_c \)  
Collapse pressure

\( \pi \text{CPs} \)  
\( \pi \)-conjugated polymers

\( \theta \)  
Angle between the surface normal and the molecular z' axis

\( \rho \)  
Resistivity

\( \sigma \)  
Conductivity

\( t \)  
Crystallite size

\( \omega_0 \)  
Radius of the beam at the beam waist

\( \psi \)  
Relative amplitude change

\( B \)  
Nonlinear absorption coefficient

\( \Delta \)  
Relative phase change

\( \Phi \)  
Fluorescence quantum yield

\( \Omega \)  
Ohm
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<td>( \Delta T_{p-v} )</td>
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<td>( A_0 )</td>
<td>Critical area</td>
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<td>AFM</td>
<td>Atomic force microscopy</td>
</tr>
<tr>
<td>ATR</td>
<td>Attenuated total reflection</td>
</tr>
<tr>
<td>( c )</td>
<td>Speed of light</td>
</tr>
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<td>CAP</td>
<td>Chemically amplified photolithography</td>
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<td>CaF(_2)</td>
<td>Calcium fluoride</td>
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<td>FTIR</td>
<td>Fourier transform infrared spectroscopy</td>
</tr>
<tr>
<td>HOMO</td>
<td>Highest occupied molecular orbital</td>
</tr>
<tr>
<td>( I )</td>
<td>Current</td>
</tr>
<tr>
<td>( I_i )</td>
<td>Intensity of light</td>
</tr>
<tr>
<td>IC</td>
<td>Internal conversion</td>
</tr>
<tr>
<td>( I_c, I_s )</td>
<td>The measured quantities in ellipsometry</td>
</tr>
<tr>
<td>IR</td>
<td>Infrared spectroscopy</td>
</tr>
<tr>
<td>ISC</td>
<td>Intersystem crossing</td>
</tr>
<tr>
<td>ITO</td>
<td>Indium tin oxide</td>
</tr>
<tr>
<td>LB</td>
<td>Langmuir-Blodgett</td>
</tr>
</tbody>
</table>
\( L_{\omega}, L_{2\omega} \) Local field factor tensors (Fresnel coefficients) at the incident field and at the SH field

LUMO Lowest unoccupied molecular orbital

MG Malachite green

NLO Nonlinear optical

NMR Nuclear magnetic resonance spectroscopy

\( N_s \) Number of adsorbate molecules on the surface

OLEDs Organic light-emitting diodes

\( P \) Polarization

PDI Polydispersity index

PFTT Poly(9,9-dihexylfluorene-alt-2,2'-bithiophene)

PMMA Poly(methyl methacrylate)

PMT Photomultiplier tube

PT Polythiophene

PTHPET Poly(3-(2-(2-tetrahydropyranyloxy)ethyl)thiophene)

PTHPUDT Poly(3-(11-(2-tetrahydropyranyloxy)undecyl)thiophene)

P3ATs Poly(3-alkylthiophenes)

P3HT Poly(3-hexylthiophene)

\( R \) Resistance

\( R_{\text{sheet}} \) Sheet resistance

RR Regioregular

\( S_o \) Size of the far field aperture

SC Spin-cast

SFG Sum frequency generation

SHG Second harmonic generation

SVA Solvent vapour annealing

\( T^2 \) Measure of the quality of fit between the generated theoretical data and the experimental data in ellipsometry

TEM Transmission electron microscopy

2D Two-dimensional

2D-FFT Two-Dimensional Fast-Fourier Transform

2PA Two photon absorption
<table>
<thead>
<tr>
<th>Abbreviation</th>
<th>Description</th>
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<tbody>
<tr>
<td>THP</td>
<td>Tetrahydropyranyl</td>
</tr>
<tr>
<td>TR</td>
<td>Transfer ratio</td>
</tr>
<tr>
<td>UV-vis</td>
<td>Ultraviolet-visible spectroscopy</td>
</tr>
<tr>
<td>$\nu$</td>
<td>Voltage</td>
</tr>
<tr>
<td>VR</td>
<td>Vibrational relaxation</td>
</tr>
<tr>
<td>XRD</td>
<td>X-ray diffraction</td>
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</table>
CHAPTER 1: INTRODUCTION

1.1 Subject and Motivation of the Study

Polymers are substances whose molecules have large molecular weights and are composed of covalently bonded repeating monomer units. They include both naturally occurring polymers such as proteins and cellulose, as well as synthetic polymers often referred to as "plastics". Synthetic polymers are produced on an industrial scale for a wide variety of applications including packaging, tubing, coatings and clothing.

One interesting class of polymers, known as conjugated polymers (CPs) or conducting polymers, is distinguished by the repeating pattern of alternating single and double bonds between carbon atoms along the polymer backbone. The interest in conjugated polymers began in 1963, when Weiss et al.\(^1\) reported high conductivity in oxidized iodine-doped polypyrrole (Figure 1) with reported values as high as 0.03 S/cm. However, this group's work was "lost" until recently. In the 1970's Shirakawa accidentally prepared a glittering silvery film of trans-polyacetylene (Figure 1), the first polyacetylene capable of conducting electricity,\(^2\) followed by Heeger and MacDiarmid's discovery that this polymer underwent a 12 order of magnitude increase in conductivity when oxidatively doped.\(^3\), \(^4\) For their efforts, Heeger, MacDiarmid and Shirakawa received the 2000 Nobel Prize in Chemistry for "The discovery and development of conductive organic polymers."
Figure 1: The structures of 1) polypyrrole, 2) trans-polyacetylene (left), cis-polyacetylene (right), 3) acridine orange and 4) (p-phenylene vinylene).

While much of the interest in conjugated polymers focused on their conducting properties, far less attention was shown in their luminescence properties, most likely because of the very weak photo-luminescence of polyacetylene, the most widely studied conducting polymer. In the 1950s Bernanose et al.\textsuperscript{5-8} first produced light from organic materials.
(electroluminescence) by applying high alternating current electric fields to thin crystalline films of materials such as acridine orange (Figure 1). However, the small electrical conductivities of such materials resulted in limited light output. Modern work with electroluminescence began with the work of Burroughes et al.\textsuperscript{9} on (p-phenylene vinylene) (Figure 1) where a high efficiency (0.05 % quantum yield of luminescence) green light emitting polymer device was fabricated. The increased conductivity of modern conductive polymers means enough power can be put through such devices at low voltages to generate practical amounts of light. This has led to CPs finding increasing use as the active media in emerging technologies such as organic light-emitting diodes\textsuperscript{10} (OLEDs) and flat panel displays, as well as organic field-effect transistors\textsuperscript{11} (FETs). Because of their unique electrical, optical, and luminescent properties, \( \pi \)-conjugated polymers (\( \pi \)CPs) have been incorporated as photoactive and electroactive layers in these devices.

The optical properties of materials can change in response to an electric field (electro-optics). This can manifest itself as a change of the absorption, for example with the creation of an absorption band at some wavelengths giving rise to a colour change (an electro-chromic effect), or in a change of the refractive index. The change in the refractive index can be linearly proportional to the electric field (Pockels effect) or proportional to the square of the electric field (Kerr effect).\textsuperscript{12} Electro-optical phenomena find use in devices such as optical switches. An optical switch enables signals in optical fibers to be selectively switched from one circuit to another. One type of optical switch, a "photonic"
switch, exploits a material's nonlinear properties to physically switch light by steering.

The extensive use of fiber optics in communications systems is revolutionizing data processing and communications technologies to include components based on optics rather than electronics. Nonlinear optical (NLO) polymeric materials are strong candidates for emerging photonic data processing technologies. Organic materials are especially promising candidates for NLO devices since their optical and electronic properties can be tuned and tailored by chemical modification. Among organic materials, πCPs, such as polythiophene (PT) and its derivatives, have attracted significant attention due to their large and fast nonlinear optical responses making them particularly attractive for high bandwidth applications. In addition, they can be produced as high quality thin films, an essential quality for use in many devices. Basic research into the properties of candidate materials such as their third-order optical nonlinearities is ongoing.

The third-order optical nonlinearities of PT-based derivatives have been previously studied with a variety of techniques, including degenerate four-wave mixing, sensitive to the square of third-order nonlinear susceptibility \( \chi^{(3)} \), photon-induced absorption, providing information regarding the imaginary part of \( \chi^{(3)} \), and the z-scan technique capable of providing information on the sign and magnitude of the third-order nonlinearity. These studies have primarily focused on determining the origin of \( \chi^{(3)} \) or on measuring the magnitude of the nonlinear susceptibility in the vicinity of the single-photon absorption
These studies have provided a wide distribution of $\chi^{(3)}$ values, ranging from $\sim 10^{-4}$ - $10^{-12}$ electrostatic units (esu).

All carbon based polymers were regarded as insulators until the work of Weiss et al. The search for conducting polymers that combine the advantages of a polymer with the electrical properties of a metal continues. However, several challenges still need to be overcome. They include an increase in the stability of CP's if they are to be used in the marketplace as well as a further reduction in the cost of such polymers. Combined with their ease of processability, the electrical, luminescent, linear and nonlinear optical properties of conducting polymers make them attractive candidates for the long-term replacement of existing technologies and for new niche applications.

With this great potential has come considerable effort to understand and control the physical properties of these polymer systems. The extent of molecular organization in these polymer systems has been shown to be vital in determining their luminescent and conducting abilities and hence their efficacy as device materials. Efforts to control the level of organization have included the development of synthetic strategies for regiochemical control that provide primarily head-to-tail (HT) couplings of monomer units (Figure 2) and afford low-energy planar conformations, greater conjugation lengths and enhanced conductivities. Polymers that contain primarily HT couplings are referred to as regioregular (RR). In contrast, polymers that contain a mixture of the possible couplings are called regioirregular (RIR). RR polymers are able to pack with a higher degree of crystallinity in the solid state than do their RIR
analogs, giving rise to smaller band gaps and higher carrier mobilities.\textsuperscript{23-28} Irregularly substituted polythiophenes have structures where unfavorable head-to-head (HH) couplings cause a sterically-driven twist of thiophene rings, resulting in a loss of conjugation.

\begin{center}
\includegraphics[width=\textwidth]{figure2.png}
\end{center}

**Figure 2:** Possible regiochemical couplings of a 3-alkylthiophene.

Importantly, it has also been demonstrated that the structure and orientation of the crystalline domains formed in spin-cast (SC) films of poly(3-hexylthiophene) (P3HT) have a dramatic influence on their charge carrier mobilities.\textsuperscript{29} In that paper, the transport properties of the ordered microcrystalline domains in P3HT were probed. In samples with high regioregularity and low molecular weight, the preferential orientation of ordered domains was with the (001) axis normal to the film and the (010) axis in the plane of the film. However, the diffraction pattern also displayed large amorphous areas indicating the presence of vast non-crystalline regions. In contrast, in samples with low regioregularity and high molecular weight, the crystallites preferentially oriented with the (001) axis in the plane and the (010) axis normal to the film.
lamellae were found to adopt two different orientations, either parallel or normal to the substrate, the mobilities of which were found to differ by more than two orders of magnitude. It is not clear what differences between the two materials is responsible for the observed change in orientation. It may be related to the degree of regioregularity, the molecular weight, the processing conditions, or some other factor.

Nevertheless, conventional solution-casting techniques of these polymers lead to the formation of distributions of crystalline domains with varying properties, depending on the extent of crystallinity, the packing within the domains, the relative domain orientations, as well as the complex morphologies inherent to non-crystalline regions. As a result, the detailed structural properties of πCP-based thin films have remained difficult to characterize and control.

Kim and Swager have examined the intrinsic spectroscopic properties of poly(p-phenylene-ethynylene) Langmuir films by varying chain conformation and interpolymer interactions through changes in mechanical force imparted by a Langmuir trough. Specific tailoring of functional group properties to synthesize amphiphilic polymers (polymers possessing a water soluble polar group attached to a nonpolar moiety) which preferentially order at the air-liquid interface has also been examined. The introduction of polar functionalities into poly-alkylthiophenes in the proximity of the thiophene chain or in the pendant alkyl groups has permitted the fabrication of Langmuir-Blodgett (LB) structures of various architectures, without the requirement for dilution with other amphiphiles. Likewise, the characterization of Langmuir films of amphiphilic, bithiophene-
based RR polymers have shown that they form large, highly-ordered domains, distinct from the dramatically lower degree of crystallinity evidenced in less regioregularly coupled polymers.\textsuperscript{35}

The task of unravelling the connection between polymer conformation and physical properties in systems of complex morphology represents a significant challenge. One potentially useful strategy to impart morphological control over large areas is the use of external forces to control molecular order. The approach used in this thesis is to use the LB trough (a device used to study amphiphilic molecules at the air-liquid interface, and to transfer monolayers onto solid substrates) to build mono-molecular polymer films consisting of a narrow distribution of morphologies by restricting the molecules to the air-water interface and by exerting mechanical control over them. The degree of molecular order in these films is due not only to intermolecular interactions within the film (as for SC or drop-cast (DC) films), but also from those forces inherent to the interface and from those under external (mechanical) control. The goal of this project is to resolve the connection between structural orientation and physical property in thin films of a model polymer system. The polymer under investigation must exhibit a hydrophilic/hydrophobic balance at the air-water interface and be able to form a monolayer using the LB trough. The polymer should also be RR to increase the likelihood of forming highly-ordered domains in the mono-molecular film and be able to undergo chemistry that can be examined in a highly oriented film.
One important example of a \( \pi \)CP with attractive properties is poly(3-(2-(2-tetrahydropyranyloxy)ethyl)thiophene) (PTHPET), which has potential lithographic applications due to its ability to be patterned with micron resolution via chemically amplified photolithography (CAP).\(^{36}\) In this process, the tetrahydropyranyl (THP) group is photochemically converted to a hydroxyl group by acid catalysis, changing the polymer’s solubility (Figure 3). Here we describe studies on a more amphiphilic analog of this polymer, RR PTHPUDT (Figure 4). This polymer is comprised of a hydrophobic PT chain with hydrophilic THP groups that terminate the pendant alkyl chains. Here we show that a well-ordered monolayer of PTHPUDT can be formed at the air-water interface and that this layer can be deposited into highly-ordered multilayer films of high optical-quality by the LB technique.\(^{37}\) Further, these films display significantly red-shifted absorption features consistent with planar conformation and a high degree of conjugation. These films offer the possibility of examining the detailed chemistry responsible for photo-deprotection and structure/property relationships in well-ordered and highly structured environments.

![Figure 3: Acid catalyzed elimination of dihydropyran from PTHPET.](image)

\[ \text{Figure 3: Acid catalyzed elimination of dihydropyran from PTHPET.} \]
In what follows, we describe the structure/property relationships of LB films of PTHPUDT and compare their properties to less-well-ordered films of approximately equivalent absorbance formed via spin- and drop-cast techniques. The thesis is organized as follows: Chapter 2 describes the theoretical concepts that form the basis of the experiments performed. Chapter 3 discusses the methods of film deposition and the experimental apparatus used to carry out these studies. Following this, we present the results of our Langmuir film, Langmuir-Blodgett film and spin-cast film characterization studies including surface wettability, absorbance, luminescence, optical microscopy, X-ray diffraction, atomic force microscopy and conductivity measurements. Chapter 4 includes a nonlinear optical surface second harmonic generation (SHG) analysis. When two waves of equal frequencies induce a third wave at double the frequency, this three wave mixing process is called SHG. Our analysis shows that there exists well-defined order in the films and allows us to confirm the orientation of the polymer within the film, as well as discussing the third-order
nonlinear optical properties. Chapter 5 is concerned with the thermal reactivity and physical properties that occur in the thin films, as well as transmission electron microscopy experiments.

In Chapter 6, the work is summarized, and future directions of this project are discussed.
CHAPTER 2: THEORY

In this chapter, we describe the theoretical concepts that form the basis of the experiments performed. The methods of film preparation are explored. Following this, the characterization methods including absorption and photoluminescence spectroscopy, ellipsometry, X-ray diffraction, atomic force microscopy, conductivity, nonlinear optical spectroscopy, and the z-scan technique are discussed.

2.1 Film Preparation

2.1.1 Langmuir Films

The effect of surfactants on water surfaces have been known since ancient times. In the eighteenth century B.C., Babylonians practiced their spiritual rituals by observing the effects of oils spread on water. The first scientific interest in mono-molecular layers was shown by Benjamin Franklin. He observed that one teaspoon of oil spread onto a pond had a calming influence over half an acre of water. Franklin reported his findings to the Royal Society of London in 1774.

Langmuir films are composed of surface-active materials (surfactants) confined at the boundary between two different phases, for example, at the air-liquid interface. Surfactants are amphiphilic molecules, that is, they consist of a
hydrophilic polar water soluble group attached to a hydrophobic water insoluble hydrocarbon chain. Hydrophilic groups are attracted to polar media, and the forces acting on them are predominantly Coulombic. In contrast, hydrophobic groups are much less water soluble and the forces acting on them are mainly van der Waals in nature. Amphiphilic molecules are trapped at the air-liquid interface because they possess two different types of bonding within the one molecular structure.

When surfactants are dissolved in a non-aqueous volatile solvent, such as chloroform (CHCl₃), and then deposited onto the surface of a water subphase, the solvent evaporates leaving the molecules oriented at the air-liquid interface. The hydrophilic “head” group is pulled into the aqueous phase, while the hydrophobic “tail” group points into the air. A monolayer only forms on the surface if there is an amphiphilic balance in the molecule, that is, a good balance between the hydrophilic and hydrophobic parts. If the hydrophobic “tail” group is too short (not hydrophobic enough) then the molecule will be pulled into the water subphase. On the other hand, if the hydrophilicity is insufficient, the molecules form multi-layer films on the surface.

Sweeping a barrier over the water surface causes the molecules to come closer together and eventually form a packed ordered monolayer (Figure 5). The film that results from this method is known as a Langmuir film.
In the bulk of a liquid, the molecules are attracted to each other by van der Waals forces. This causes each molecule to be pulled equally in all directions by neighbouring liquid molecules, resulting in a net force of zero. However, at the surface, the molecules are pulled into the subphase since they are not attracted as intensely by molecules in the air. Thus, all of the molecules at the surface are subject to a downward force of molecular attraction, which can only be balanced by the resistance of the liquid to compression. This effect gives rise to surface tension.

Surface tension is defined as the amount of work needed to expand the surface isothermally by a unit area. Since surface-active molecules have a tendency to accumulate at interfaces, this favours the expansion of the interface and lowers the surface tension. The reduction in surface tension relative to a clean interface is known as the surface pressure. This makes it possible to
monitor the surface pressure as a function of the area occupied per molecule, provided that the number of molecules deposited on the surface is known.

The characteristics of a monolayer on the water surface are studied by measuring the changes in surface tension as the monolayer is compressed. The pressure is recorded using a Wilhelmy plate (a strip of chromatography paper) attached to a microbalance. The plot of surface pressure versus area occupied per molecule is known as a “pressure-area isotherm.” The plot is called an isotherm since compression takes place at a constant temperature. The shape of the isotherm is characteristic of the molecules that make up the film and reflects intermolecular interactions and adsorbate-subphase interactions.

Molecular dimensions and the shape of the molecule can be determined from the pressure-area isotherm. When the monolayer is in a two-dimensional (2D) “solid” or “liquid” phase, the molecules are relatively well oriented. The critical area \( A_0 \) can be determined by extrapolating the slope of the phase under investigation to zero pressure, which is the point at which this line crosses the x-axis. This is the hypothetical interfacial area occupied by one molecule in the condensed phase at zero pressure. Taking a typical fatty acid molecule like stearic acid \( \text{CH}_3(\text{CH}_2)_{16}\text{COOH} \) as an example, the molecular area determined in this manner is 18 - 23 Å² (Figure 6). Such an area corresponds to the cross sectional area of a hydrocarbon chain, which suggests that the compressed monolayer consists of closely-packed, vertically-oriented chains.
The maximum pressure to which a monolayer can be compressed without the expulsion of molecules from the Langmuir film is known as the collapse pressure ($\pi_c$). It depends on the molecule, the temperature, the rate of compression, and the conditions to which the film has been subjected. At $\pi_c$, the film loses its monomolecular form, and the molecules are ejected out of the monolayer into either the subphase or superphase.

It is important to study the isotherm of the monolayer since information regarding how molecules pack at the interface, and how stable the monolayer is at the collapse pressure can be obtained. The quality of the film can be improved by “pressure annealing” the film. This term refers to compressing the film, but never past $\pi_c$, then opening the barriers again, and repeating the

**Figure 6:** Pressure-Area isotherm for stearic acid, showing the critical area and the collapse pressure..
process of compression and opening. This procedure encourages more efficient packing of the molecules.

2.1.1.1 The Langmuir-Blodgett (LB) Technique

LB films consist of monolayers assembled in a repeating pattern onto a solid substrate (Figure 7). As a solid hydrophobic substrate is lowered onto a monolayer-covered water surface held at constant surface pressure, it penetrates through the Langmuir film. The Langmuir film then attaches itself to the substrate, coating it with a monolayer. After the deposition of the first layer, further layers are deposited on each successive pass of the substrate through the air-water interface. If the direction of the meniscus at the water-substrate boundary follows the direction of the substrate movement, deposition will occur.
Figure 7: Deposition of a two-layer film onto a hydrophobic substrate: A hydrophobic substrate moving toward a monolayer covered water surface (top left); deposition of the first monolayer (top right), deposition of the second monolayer (bottom left); completed two-monolayer film (bottom right). The resulting film is a Y-type film with a head-to-head and tail-to-tail type of architecture.

2.1.2 Spin-Coating

Spin-coating is the most widely used technique to deposit a thin, uniform film onto a flat substrate (Figure 8). An excess quantity of solution is placed onto the center of a substrate, which is then spun at high speeds (typically around 2000 rpm, depending on the properties of the solution as well as the substrate). Centripetal acceleration causes the polymer solution to spread out with fluid being spun off the edges of the substrate. Rotation is continued in order to
remove excess solvent and to thin the film close to its desired thickness. The final film thickness and properties of the coated film depend both on the characteristics of the polymer solution (viscosity, solvent volatility, percent solids, surface tension, etc.) and also on the parameters chosen for the spin process (rotational speed, acceleration, and fume exhaust).

Figure 8: Deposition of a spin-coated film: Polymer solution being placed onto the center of a substrate (top); rotation of the substrate to remove excess solvent (middle); thin film close to its desired thickness (bottom).
2.2 Characterization Techniques

2.2.1 Absorption and Photoluminescence Spectroscopy

Most absorption spectroscopy of conjugated polymers is based on $\pi - \pi^*$ electronic transitions and $\pi^* - \pi$ transitions for emission spectroscopy. When a polymer is electronically excited, several photo-physical processes can occur including fluorescence, phosphorescence, or radiationless decay (Figure 9). If the photon emission occurs between states of the same spin state (e.g. $S_1 \rightarrow S_0$) this is termed fluorescence. If the spin state of the initial and final energy levels are different (e.g. $T_1 \rightarrow S_0$), the emission is called phosphorescence. Fluorescence is statistically much more likely than phosphorescence, the lifetimes of fluorescent states are very short ($1 \times 10^{-5}$ to $10^{-9}$ seconds) and phosphorescence somewhat longer ($1 \times 10^{-4}$ seconds to minutes or even hours).
Figure 9: Jablonski diagram showing absorption (A), fluorescence (F), phosphorescence (P), internal or external conversion (IC/EC), intersystem crossing (ISC), vibrational relaxation (VR), singlet ground state (S$_0$), first excited singlet state (S$_1$), and the first triplet excited state (T$_1$).

Three nonradiative deactivation processes are also indicated, including internal conversion (IC), intersystem crossing (ISC) and vibrational relaxation (VR). Internal conversion is the radiationless transition between energy states of the same spin state. Intersystem crossing is a radiationless transition between different spin states. Vibrational relaxation is the most common nonradiative pathway. It occurs very quickly ($<$1 x 10$^{-12}$ seconds) and results in the electronic excitation's being converted into vibrational and rotational motion within the molecule and its surroundings through collisions. This means that many excited state molecules never emit any light because other molecules that are present "steal" the energy before photo-emission processes can occur.
The difference between positions of the maxima of the absorption and emission spectra is termed the Stokes shift. Stokes fluorescence is the emission of longer-wavelength energy by a molecule that has absorbed photons of shorter wavelengths. Light is absorbed by molecules, causing electrons to become excited to a higher electronic state. The electrons remain in the excited state, depending on the fluorescence lifetime of the material, and then return to the ground state. Energy is emitted during the electrons' return to the ground state. Emitted light always has a longer wavelength than the absorbed light because of limited energy loss by the molecule prior to emission (Figure 10).

The Frank-Condon principle states that optical transitions are "vertical", meaning electronic transitions occur so rapidly ($10^{-15}$ sec) that the framework of nuclear coordinates cannot follow and that all internuclear distances and angles are preserved in the excited state. This means that the energies of vibrational and rotational transitions do not change during the optical transition. They only do so after the optical transition has occurred to minimize the total energy of the new electron configuration. Therefore, if the molecule is to move to a new vibrational level during the electronic transition, this new vibrational level must be instantaneously compatible with the nuclear positions and momenta of the vibrational level of the molecule in the original electronic state. The quantum-mechanical formulation of this principle is that the intensity of a vibronic transition is proportional to the square of the overlap integral between the vibrational wavefunctions of the two states that are involved in the transition.
Figure 10 illustrates the Franck-Condon principle for vibronic transitions in a molecule with Morse-like potential energy functions in both the ground and excited electronic states. The molecule starts out in the $v'' = 0$ vibrational level of the ground electronic state and upon absorbing a photon of the necessary energy, makes a transition to the excited electronic state. The electron configuration of the new state may result in a shift of the equilibrium position of the nuclei constituting the molecule. In the simplest case of a diatomic molecule, the nuclear coordinate axis refers to the internuclear separation. The vibronic transition is indicated by a vertical arrow due to the assumption of constant nuclear coordinates during the transition. The probability that the molecule can end up in any particular vibrational level is proportional to the square of the (vertical) overlap of the vibrational wavefunctions of the original and final state. In the electronic excited state molecules quickly relax to the lowest vibrational level (Kasha's rule), and from there can decay to the lowest electronic state via photon emission. The Franck-Condon principle is applied equally to both absorption and fluorescence, and leads to an approximate mirror symmetry shown in Figure 10 (right). The vibronic transitions are drawn as narrow, equally spaced lines. Equal spacing between vibrational levels is the case for the parabolic potential of simple harmonic oscillators. Thus, optical transitions can produce vibrational fine structure and these optical transitions occur between wavefunctions that have vibrational and rotational contributions (sub-levels).
Figure 10: Franck-Condon principle energy diagram.\textsuperscript{40} Since electronic transitions are very fast compared with nuclear motions, vibrational levels are favoured when they correspond to a minimal change in the nuclear coordinates. The potential wells are shown favouring transitions between $v' = 0$ and $v = 4$. The blue line corresponds to absorption and the green line corresponds to fluorescence. On the right is a schematic representation of the absorption and fluorescence spectra corresponding to the energy diagram on the left. The symmetry is due to the equal shape of the ground and excited state potential wells.

The efficiency of the fluorescence process is measured by the fluorescence quantum yield ($\Phi$), which is defined to be the ratio of the number of photons emitted to the number of photons absorbed:
According to the law of conservation of energy, the maximum fluorescence quantum yield is 1.0 (100 %), meaning that for every photon absorbed there is an emitted photon.

The quantum yield of luminescence can be determined via two methods. The first is the comparative method of Williams et al.\textsuperscript{41} which involves the use of well-characterized standard samples with known \( \Phi \) values. In this method, solutions of the standard and test samples with the same absorbance at the same excitation wavelength are assumed to absorb the same number of photons. The ratio of the integrated fluorescence intensities of the two solutions, recorded under identical conditions, yield the ratio of the quantum yield values. Since the \( \Phi \) of the standard solution is known, \( \Phi \) of the test sample is readily calculated. A limitation of this method is the assumption that the emission from the sample is isotropic in all directions. Measuring \( \Phi \) of an anisotropic sample, such as a film, is quite difficult since its emission intensity can have an angular dependence.

The second method does not rely on standard samples, but rather on calculating the number of photons that are absorbed and emitted in the sample using an integrating sphere. An integrating sphere is a spherical enclosure coated with a highly reflective inner surface such that the reflected light from the film enters the sphere and bounces around the inner surface until it reaches the detector. The main reasons for using an integrating sphere are to efficiently measure the combined diffuse and specular reflectance, to measure the

\[
\Phi = \frac{\# \text{photons}_\text{emitted}}{\# \text{photons}_\text{absorbed}}
\]
reflectance when the sample is inhomogeneous, or to measure the reflectance of samples that reflect in preferred directions by collecting light in all directions. This method was used to acquire the luminescent efficiency of PTHPUDT LB and SC films.

The use of an integrating sphere to monitor the \( \Phi \) of thin films of conjugated polymers has been previously reported.\textsuperscript{42, 43} The experimental setup described by Greenham \textit{et al.}\textsuperscript{39} is shown in Figure 11. Two experiments are carried out: 1) The excitation light blocking filter is removed and the photomultiplier tube (PMT) signal is measured with no sample in the integrating sphere (thus, measuring the number of incident excitation photons from 520 nm – 900 nm). 2) The PMT signal is recorded with the excitation beam directly hitting the sample in the integrating sphere, with the blocking filter present (thus measuring the photoluminescence signal due to both primary and secondary excitation from 520 nm – 900 nm).\textsuperscript{44}
Figure 11: Experimental setup for integrating sphere measurements of $\Phi$ according to Greenham et al.\textsuperscript{39} The baffle prevents direct illumination of the PMT.

These experiments yield the total number of incident excitation photons and the number of photoluminescence photons. To obtain the $\Phi$, the number of excitation photons absorbed is required.\textsuperscript{42} This is achieved by measuring the external transmittance (equivalent to the sum of the internal transmittance and reflectance) of the sample, at the excitation wavelength (520 nm in this case), in a conventional spectrometer. The fraction of excitation photons absorbed is equivalent to (1 - external transmittance).
2.2.2 Contact Angle Determination

Contact angle measurements are invaluable for understanding the hydophilicity or hydrophobicity of a surface. When a drop of liquid is added onto a solid substrate the degree of wetting is related to the contact angle (Figure 12). The point where the three phases meet is referred to as the three-phase contact point. At this point, there are three force vectors, the solid-vapour ($\gamma_{SV}$), the liquid-vapour ($\gamma_{LV}$), and the solid-liquid interfacial tension ($\gamma_{SL}$). The angle between the interfacial tension vectors ($\gamma_{SL}$ and $\gamma_{LV}$) is the contact angle $\theta_c$.

![Diagram of contact angle](image)

$$\gamma_{SV} = \gamma_{SL} + \gamma_{LV}\cos\theta_c$$

**Figure 12**: Force balance at the three-phase contact point.\(^{45}\)

2.2.3 Ellipsometry

When a beam of light from a transparent medium (air) strikes a second transparent medium (a thin film) it can be reflected from the air-film interface or it can enter the second medium. The light that enters the new medium changes
direction according to Snell’s Law and the speed of the beam is reduced and in some cases the light can be absorbed (Figure 13). The angle between the incident beam and the sample normal ($\theta_i$) is equal to the reflected angle ($\theta_r$).

![Diagram of light refraction](image)

**Figure 13**: A beam of light entering a medium with a different index of refraction.

Light that enters the material is refracted to the angle ($\theta_i$) given by Snell’s Law:

$$n_i \sin \theta_i = n_r \sin \theta_r$$

(2)

The refractive index ($n$) is a measure of how much the speed of light has been reduced and is defined as the ratio of the speed of light ($c$) in a reference medium (vacuum) to the speed of light in the medium itself ($v$):
\[ n = \frac{c}{v} \]  \tag{3}
	his number is typically greater than one meaning that the higher the index of a material, the more the light is slowed down.

One of the most common methods to measure the index of refraction of a material is attenuated total reflection (ATR). However, in ATR the wavelength is fixed and as such this is not an ideal method for measuring the refractive index over a large wavelength range. A more suitable technique for determining the properties of surfaces and thin films over a broad wavelength range is spectroscopic ellipsometry. It permits the simultaneous determination of several optical constants including the refractive index, extinction coefficient, reflectance and transmittance. Material characteristics such as the sample thickness and composition can also be elucidated.

Spectroscopic ellipsometry is a sensitive technique that measures the change in the polarization state as well as the intensity of light reflected from the surface of a film. Linearly polarized light changes state to elliptically polarized light when reflected from a surface. Viewed end on, in the direction of light propagation, the electric vector of the light appears to describe an ellipse. The relative phase change (\( \Delta \)) and the relative amplitude change (\( \Psi \)) introduced by reflection from the surface are related to the values of the measurable light intensity quantities in this experiment (\( I_s \) defined in (4) and \( I_c \) defined in (5)) and are usually plotted as a function of wavelength..
\[ I_s = \sin 2\Psi \sin \Delta \]

\[ I_c = \sin 2\Psi \cos \Delta \]

The reflection of a linearly polarized beam of light from the surface of a material producing an elliptically polarized beam of light is shown in Figure 14. The incident beam of light and the surface normal define a plane called the plane of incidence. The electric field vector of the incident beam (\(\vec{E}\)) is comprised of two perpendicular components: the one parallel to the plane of incidence is referred to as being \(p\)-polarized, while the other that is perpendicular to the plane of incidence is referred to as being \(s\)-polarized. The notation of \(p\) and \(s\)-polarized light originates historically from the German words for parallel (parallel) and perpendicular (senkrecht). These waves are referred to as the \(p\)-wave and \(s\)-wave. This \(p\)-\(s\) coordinate system is used to describe the resulting ellipse of polarization.
Figure 14: The reflection of a linearly polarized beam of light from the surface of a material producing an elliptically polarized beam of light.

The incident light is linear with both $p$- and $s$- components. The reflected light has undergone amplitude and phase changes for both $p$- and $s$- polarization components and ellipsometry measures these changes. The phase and amplitude variables ($\Delta$ and $\Psi$) are related to the ratio of Fresnel reflection coefficients, $R_p$ and $R_s$ for $p$- and $s$-polarized light and therefore to the refractive index, according to (6):

$$\tan(\Psi) e^{i\Delta} = \frac{R_p}{R_s}$$  \hspace{1cm} (6)
The values of $\Delta$ and $\Psi$ are the real and imaginary parts of the complex ratio $\frac{R_P}{R_S}$, where $R_P$ and $R_S$ represent the total reflection coefficients for the $p$- and $s$-wave, respectively.

The data analysis procedure used to extract the physical parameters of the sample involves several steps. The first step is to measure the values of $\Delta$ and $\Psi$ as a function of wavelength from a sample. Then an optical model describing the sample structure that accounts for all the layers in the sample is created using available modelling software. Each layer is estimated with a thickness and optical constants. If these values are unknown, their values are estimated for the purpose of a preliminary calculation. The model is used to calculate the predicted response from Fresnel's equations. Theoretical data from the optical model that corresponds to the experimental data are generated. The generated data are then compared to the experimental data and the unknown parameters are varied to try and produce a “best fit” to the experimental data. Regression algorithms are used to vary the unknown parameters and minimize the difference between the generated and experimental data.

Care has to be taken to ensure a physically sensible result is found by comparing the results of the spectroscopic ellipsometry fit with experimental results from different corroborating methods. For example, the thickness of the material obtained from the best fit via spectroscopic ellipsometry should be compared to that obtained from AFM or profilometer measurements to ensure self-consistency.
The optical constants derived from such a fitting routine describe how light interacts with a material. For substances that absorb as well as refract, a complex index of refraction \( \tilde{\eta} \) can be defined (7). This complex refractive index is a representation of the optical constants of the material. The real part \( \eta \) is an indication of the amount of refraction which takes place for light passing from one medium to another. In other words, it describes the velocity of light in a material in accord with (3). The imaginary part \( \kappa \) indicates the amount of absorption loss at a particular wavelength as a wave propagates through a material, or how fast the amplitude of the wave decreases. It is also referred to as the extinction coefficient. The extinction coefficient is directly related to the absorption of a material, and thus, to the absorption coefficient \( \alpha \), via the wavelength of light \( \lambda \) (8).

\[
\tilde{\eta} = \eta - i\kappa \tag{7}
\]

\[
\alpha = \frac{4\pi\kappa}{\lambda} \tag{8}
\]

The microscopic molecular properties of the polymer can be related to the macroscopic film properties through the refractive index, film polarizability and density using the Lorentz-Lorenz equation (9), where the index of refraction of a material \( n \) is related to its temperature \( T \), pressure \( P_r \) and molar volume \( M_r \).

\[
n \approx \sqrt{1 + \frac{3M_rP_r}{RT}} \tag{9}
\]
The Lorentz oscillator model\textsuperscript{46} offers a simple description of the interactions between an atom and an electric field. Lorentz considered the atom as a mass (the nucleus) connected to another smaller mass (the electron) by a spring. The spring would be set into motion by an electric field interacting with the charge of the electron. The field would either attract or repel the electron, causing the spring to stretch or compress.

The Lorentz force acting on a bound electron in a material depends on the effective electromagnetic field. The effective electric field ($E_{\text{eff}}$) acting on a molecule at a space-time position ($r,t$) in a polarisable medium with polarization ($P$) is given by:\textsuperscript{47}

$$E_{\text{eff}}(r,t) = E(r,t) + \frac{4}{3} \pi P(r,t)$$

(10)

where $E$ is the external, applied electric field. The induced polarization of the system ($P$) is given by:

$$P(r,\omega) = N_s p(r,\omega)$$

(11)

where $N_s$ is the number density of molecules in the system, $p$ is the induced polarization of each individual molecule at angular frequency ($\omega$). The induced polarization of the system is related to the electric field by:

$$P(r,\omega) = \chi_r(\omega)E(r,\omega)$$

(12)
where $\chi_e$ is the electric susceptibility. The relative dielectric permittivity ($\varepsilon$) is related to $\chi_e$ via:

$$\tilde{\eta}^2 = \varepsilon(\omega) = 1 + 4\pi\chi_e(\omega) \quad (13)$$

where $\tilde{\eta}^2$ is the square of the complex index of refraction. Since $\chi_e(\omega) = N\alpha(\omega)$, where $\alpha$ is the mean polarizability, the following must hold:

$$\tilde{\eta}^2 = \varepsilon(\omega) \approx 1 + 4\pi N\alpha(\omega) \quad (14)$$

Thus, it is clear from the preceding equation that the index of refraction increases as the number density of molecules increases. The polarizability of a molecule describes the interaction of an electron cloud with an applied electric field. Molecules with delocalized electrons have larger polarizabilities because their electron clouds exhibit larger polarization changes in response to an electric field. Molecules with larger dipole moments and polarizabilities have higher indices of refraction. Thus, the polarizability of a molecule is directly related to its refractive index. The real part of the index of refraction ($\eta$) is given by:

$$\eta(\omega) = R\sqrt{\varepsilon(\omega)} \quad (15)$$

where $R$ refers to the real part of the square root of the dielectric permittivity, while the imaginary part ($\kappa$), is given by:

$$\kappa(\omega) = I\sqrt{\varepsilon(\omega)} \quad (16)$$
where $I$ refers to the imaginary part of the square root of the dielectric permittivity. Thus, the real part of $\alpha$ is related to the refractive index, while the imaginary part of $\alpha$ is related to the absorption.

2.2.4 X-ray Diffraction

2.2.4.1 Bragg’s Law

Interference occurs among the waves scattered by the atoms in a crystalline or semi-crystalline film when exposed to X-rays. The electron density of the atoms in the material scatter the incoming radiation, resulting in a diffraction pattern. Destructive interference occurs most often; however, if the path difference of the scattered X-rays is a whole number of wavelengths, then constructive interference can occur. This is described by Bragg’s Law:

$$2d \sin \theta = n\lambda$$

(17)

where $d$ is the interlayer spacing of the layers, $\theta$ is the incident angle of the photons in degrees, and $\lambda$ is the wavelength of the X-rays (1.5418 Å). The geometry used to derive Bragg’s Law is shown in Figure 15.
Figure 15: The geometry used to derive Bragg's Law.

The conditions that are necessary to make the phases of the beam coincide are that the angle of the incident beam must be equal to the angle of the reflected beam in Figure 15. The incident beams are in phase and parallel to each other up to the point that the first layer is impinged at atom z. At this point the second beam continues into the second layer of the film where it is scattered by atom b. The extra distance that the second beam travels is \((ab + bc)\) if the two
beams are to continue travelling adjacent and parallel. This extra distance must be an integral \( m \) multiple of the wavelength for the phases of the two beams to be the same:

\[
m\lambda = ab + bc
\]  

(18)

If \( d \) is considered the hypotenuse of the right angle triangle \( zab \) in Figure 15, trigonometry can be used to relate \( d \) and \( \theta \) to the distance \( (ab + bc) \):

\[
ab = d \sin \theta
\]  

(19)

Because \( ab = bc \), (18) becomes:

\[
m\lambda = 2ab
\]  

(20)

and by substituting (19) into (20) we have:

\[
m\lambda = 2d \sin \theta
\]  

(21)

and Bragg’s Law has been defined. Thus, constructive interference of diffracted X-rays from ordered structures can be employed to determine the repeat unit distances and extent of order.

2.2.5 Atomic Force Microscopy

A schematic representation of the atomic force microscope (AFM) is shown in Figure 16. It shows a laser beam emanating from a laser diode reflecting off a flexible spring-like cantilever. In contact mode AFM, the tip is within a few Å of the surface. As the tip is raster scanned over the surface it is deflected as it moves over the surface. The reflected laser light is collected in a quadrant position-sensitive photodetector, which measures the deflection and twist of the cantilever. In constant force mode, the deflection from the cantilever
is an input into a feedback circuit that moves the scanner up or down in the z direction responding to the topography by keeping the cantilever deflection constant. The image is generated from the motion of the piezoelectric tube scanner. The speed of scanning is limited by the response time of the feedback circuit.

To obtain molecular resolution images the AFM must be operated in constant height mode. With atomically flat samples, the cantilever deflections are small and the feedback circuit is not used. The image is generated from the cantilever deflections in the position sensitive photodetector. Constant height mode is also essential for recording real time images of changing surfaces, where a high scan speed is essential.

Figure 16: A schematic diagram of the AFM.
2.2.6 General Description of a Laser

“Laser” is an acronym for light amplification by stimulated emission of radiation. A laser is an electro-optical device that produces coherent radiation. A laser consists of a gain medium inside an optical cavity with mirrors at both ends. The gain medium is pumped by an external energy source (for example by a flash lamp or by another laser) that supplies energy into the laser beam. The pumping promotes the electrons into excited states creating a population inversion. Some of the electrons drop to the ground state spontaneously releasing a photon. These photons stimulate other excited electrons to emit photons with the same energy, in the same direction and in phase with the original (Figure 17).

![Figure 17: The process of stimulated emission. Stimulated emission occurs when an electron in an excited state senses the electromagnetic field of an external photon. The atom oscillates with the applied field and this oscillation causes the excited electron to decay to the ground state. The emitted photon is in phase and in the same direction as the stimulating photon.](image-url)
The light waves build in strength and are amplified as they are repeatedly made to pass through the gain medium by reflecting off mirrors at either end of the laser cavity. At this point the amount of stimulated emission due to light that passes through the cavity is larger than the amount of absorption in the gain medium, and thus, the light is amplified. Eventually the laser begins to lase (Figure 18). Typically, one of the two mirrors is partially transparent (output coupler) and it is out of this mirror that the amplified beam emerges.
1) Pump off

Laser material

Mirror

Mirror with partial transmittance

2) Pump on

3) Pump on

4) Pump on

5) Pump on

Figure 18: The lasing of a laser. In step 2, the gain medium is pumped and stimulated emission occurs as excited electrons drop to the ground state and photons are emitted. In step 3, photons reflect off the mirrors and cause other electrons to emit. In step 4, there is a chain reaction and the laser begins to lase. In step 5, the laser is fully lasing.

2.2.7 The Electronic Structure of Materials

2.2.7.1 Inorganic Semiconductors

In a metal, the individual atomic orbitals overlap to form extended orbital structures. With so many orbitals spaced together in a given range of energies, they form a continuous band of energies (Figure 19). The highest occupied band is called the valence band (VB), while the lowest unoccupied band is called the
conduction band (CB). The difference in energy between these bands is called the band gap. The conductivity of a metal results from either the valence or conduction band being only partially filled, or due to the band gap being very small.

![Energy vs Band gap diagram](image)

**Figure 19:** A band picture describing the difference between a metal, semiconductor and insulator.

In pure inorganic semiconductors at room temperature, the number of thermally excited charge carriers is small. These pure semiconductors have high electrical resistivities, and therefore low electrical conductivities. In order to increase their conductivity, semiconducting materials are doped with impurity atoms. Even very small controlled additions of impurity atoms can make very large differences to the conductivity of a semiconductor.

For example, silicon is a group IV element and has four valence electrons per atom. At absolute zero, the valence band of pure silicon is completely filled.
At finite temperatures, the only charge carriers are the electrons in the conduction band and the holes in the valence band that arise due to the thermal excitation of electrons into the conduction band. These charge carriers are called *intrinsic* charge carriers, and there are equal numbers of electrons and holes. Pure silicon is therefore an example of an intrinsic semiconductor (Figure 20 left).

![Energy Diagram](Image)

**Figure 20:** An intrinsic semiconductor (left), an *n*-type extrinsic semiconductor (middle), and a *p*-type extrinsic semiconductor (right).

If a small number of atoms of a group V element, such as phosphorus, are added to the silicon as substitutional atoms in the lattice, additional valence electrons are introduced into the material because each phosphorus atom has five valence electrons. These additional electrons are only weakly bound to their parent impurity atoms and even at very low temperatures these electrons can be promoted into the conduction band of the semiconductor. This is often
represented schematically in band diagrams by the addition of donor levels just below the bottom of the conduction band. The dotted line represents the existence of additional electrons which can be easily excited into the conduction band. Semiconductors that have been doped in this way will have a surplus of electrons, and are called \textit{n}-type semiconductors. In such semiconductors, electrons are the majority carriers (Figure 20 middle).

If a group III element, such as aluminium, is substituted for some of the atoms in silicon, there will be a deficit in the number of valence electrons in the material. This introduces electron accepting levels just above the top of the valence band and causes more holes to be introduced into the valence band. Hence, the majority charge carriers are positive holes in this case. Semiconductors doped in this way are termed \textit{p}-type semiconductors (Figure 20 right).

Doped semiconductors (either \textit{n}-type or \textit{p}-type) are known as extrinsic semiconductors. The activation energy for electrons to be donated by or accepted to impurity states is usually so low that at room temperature the concentration of majority charge carriers is similar to the concentration of impurities. In an extrinsic semiconductor, there is a contribution to the total number of charge carriers from intrinsic electrons and holes, but at room temperature, this contribution is often very small in comparison with the number of charge carriers introduced by the controlled impurity doping of the semiconductor.\textsuperscript{48}
2.2.7.2 Organic Semiconductors

A simple free-electron molecular orbital model provides the minimum elements for quantitatively describing a conductor, semiconductor or insulator built up of a linear chain of atoms such as in polyacetylene, which has alternating single and double bonds.\(^49\) If the length of the molecule \((L)\) is described by the number of atoms in the chain \((N)\) separated by a distance \((d)\), the total length of the chain is \((N-1)d \approx Nd\) for a large number of atoms. According to the quantum mechanical model for a free particle in a one-dimensional box, the wavefunctions correspond to a ladder of eigenvalues:\(^49\)

\[
E_n = \frac{n^2 \hbar^2}{8mL^2} = \frac{n^2 \hbar^2}{8m(Nd)^2}, \text{ with } n = 1, 2, 3, \ldots
\] (22)

where \(\hbar\) is Plank’s constant, \(m\) is the mass of an electron, and \(n\) is the quantum number. If the \(\pi\)-electrons from the \(N\) \(p\)-orbitals of the carbon chain are filled into this ladder with two electrons per molecular orbital, the energy of the highest occupied molecular orbital (HOMO) is:

\[
E_{\text{HOMO}} = \frac{(\frac{N}{2})^2 \hbar^2}{8m(Nd)^2}
\] (23)

and that of the lowest unoccupied molecular orbital (LUMO) is:

\[
E_{\text{LUMO}} = \frac{(\frac{N}{2} + 1)^2 \hbar^2}{8m(Nd)^2}
\] (24)

The difference in energy between the HOMO and LUMO is:
for large $N$. This is illustrated in Figure 21, which shows that increased conjugation leads to a shift to longer wavelengths (a bathochromic shift) and a smaller band gap. For an isolated double bond (C=C) that only has two $\pi$ orbitals, one bonding and one anti-bonding, the $\pi - \pi^*$ electronic transition occurs from the highest energy occupied bonding orbital ($\pi$ bonding) to the lowest energy unoccupied orbital ($\pi$ anti-bonding). When two double bonds are conjugated, the four $p$ atomic orbitals combine to form four $\pi$ molecular orbitals, two that are bonding and two that are anti-bonding. Increased conjugation brings the HOMO and LUMO orbitals closer, decreasing the band gap. Thus, less energy is required to promote the electron from the HOMO to the LUMO, and the wavelength that provides this energy increases correspondingly with increasing polymer conjugation. Since the band gap is predicted to decrease as the polymer length increases in accord with (25), CPs with macroscopic dimensions would be predicted to behave as conductors, like metals which possess a small band gap. However, CPs behave like semiconductors.
Figure 21: Illustration of how increased conjugation brings the HOMO and LUMO orbitals closer together.

The wavelength of the absorption must increase as the length of the molecule increases. However, there is a limit at which point increasing conjugation does not lower the band gap any further. This contradiction arises from Hückel’s theory, which describes the sigma bonds in CPs as being tightly bound and immobile. In contrast, the nature of the \( \pi \)-molecular orbitals including all of the p-orbitals of the carbon atoms along the chain of conjugated double bonds causes the \( \pi \)-electrons to be delocalized over the entire chain. The electrons are thus predicted to be spaced out evenly along the entire chain, meaning all of the bonds are predicted to be equal. However, in CPs, not every
bond is the same, since every second bond has some double bond character. It was Peierls who first described a small conformational distortion that had the effect of increasing the size of the band gap rendering CPs to be semiconductors or insulators.\(^{50}\)

Before a current can flow along the molecule, one or more electrons must be either added or removed in a process known as doping. Doping can take place either by the addition of electrons (a reduction reaction) or by the removal of electrons (an oxidation reaction) from the system (Figure 22). Then, if an electric field is applied the added electrons or holes will be able to move along the polymer chain, and so an electric current will flow.

\[
\begin{align*}
n\text{-type doping} & \quad \leftrightarrow \quad + e^- \quad Polymer \quad - e^- \quad p\text{-type doping} \\
\text{reduction} & \quad \text{oxidation}
\end{align*}
\]

**Figure 22:** Controlling the electrical properties of conjugated polymers via simple redox chemistry.

Oxidative doping (or p-doping), can be achieved using a halogen element such as iodine (26) or FeCl\(_3\),\(^{51-53}\) while reductive doping (or n-doping) is possible using an alkali metal (27). It is the doped polymer that is responsible for the charge carriers and not the counter ions due to their very low mobility.\(^{49}\)
The increase in the conductivity of organic polymers upon doping was initially explained with the analogous mechanism of generation of charge carriers in doped inorganic semiconductors. It was assumed that upon p-type or n-type doping, electrons were removed from the top of the VB or added to the bottom of the CB, respectively. The discovery that the conductivity of \( \pi \)-conjugated polymers (\( \pi \) CPs) is associated with spinless charge carriers rather than unpaired electrons (carriers with spin \( \frac{1}{2} \)) indicated that the nature of these carriers is different from conventional semiconductors. New models were required to explain the conductivity of these polymers. The polaron-bipolaron model was used to explain the doping behaviour of these polymers.\(^{54-56}\)

For the case of (p-doping) \( I_2 \) abstracts an electron from one of the \( \pi \)-bonds, and forms \( I_j^- \). An example of this process is shown for the tridecene molecule in Figure 23 (step 1). Removal of the electron is linked with a structural change of the polymer that typically extends over several adjacent monomer units. The tridecene chain is now positively charged and is termed a radical cation or polaron (step 2). The remaining electron of the double bond from which an electron was removed (shown as a black circle in step 2) moves by pairing with an adjacent electron. As a result, the double bond successively moves along the chain (steps 2-5). The resulting radical cation (polaron) is localized.
because of its electrostatic attraction to the $I^-_i$ counterion with low mobility. A high concentration of counterions is needed so that the polaron can move in the field of close counterions.$^{49}$ The polaron migration is shown in steps 6-9. Charge conduction in the molecule occurs under an applied electric field.
Figure 23: Step 1 shows the creation of a polaron by oxidation of tridecene with iodine (grey circle) followed by movement of the double bond (steps 2-5). The migration of the cation along the chain at high dopant levels (steps 6-9). Charge conduction of the molecule occurs under an applied electric field.
If another electron is removed from the already oxidized polymer two things can happen: this electron may come from a different segment of the polymer chain, creating another independent polaron, or if the second removed electron is the unpaired electron of the polaron, a bipolaron is formed (steps 1-2 Figure 24). A high concentration of counterions is needed so that the bipolaron can move in the field of close counterions (step 3). The two positive charges of the bipolaron do not move independently but move together as a pair. The migration of the positive charges is shown in steps 3-5. Charge conduction in the molecule occurs under an applied electric field.
Figure 24: The formation of a bipolaron (steps 1-2) and its migration along the chain under an applied electric field (steps 3-5).

The molecular structures of a polaron and bipolaron in P3ATs are shown in Figure 25.
In polythiophenes, the equilibrium geometry of the ground state is different from that in the ionized state. For example, in the equilibrium state of P3ATs, the geometry is benzenoid-like, while in the ionized state the geometry is quinoid-like (Figure 25). The energies involved in the ionization process of a molecule are depicted in Figure 26. A vertical Franck-Condon-like ionization process requires an energy, $E_{\text{VERT}}$. If the geometry relaxes while in the ionized state, the relaxation energy, $E_{\text{REL}}$ is recovered. Going from the ground state to the relaxed ionized state can also be conceived in the following way: first, the geometry of
the molecule in the ground state is distorted such that the molecule adopts the equilibrium geometry of the ionized state. This costs a distortion energy, $E_{\text{DIST}}$. This distortion leads to an upward shift of the HOMO and a downward shift of LUMO. If we then proceed to the ionization of the distorted molecule, it requires the energy, $E_{\text{IDIST}}$. 
Figure 26: Illustration of the energies involved in a molecular ionization process. $E_{\text{IVERT}}$ is the vertical ionization energy, $E_{\text{REL}}$ is the relaxation energy gained in the ionized state, $E_{\text{DIST}}$ is the distortion energy that must be paid in the ground state in order that the molecule adopts the equilibrium geometry of the ionized state, and $E_{\text{IDIST}}$ is the ionization energy of the distorted molecule.\textsuperscript{56}

It is energetically favourable to have a geometry relaxation in the ionized state if the quantity $E_{\text{IVERT}} - E_{\text{DIST}}$ ($= \Delta e$) is larger than $E_{\text{DIST}}$. In a polymer, the vertical ionization process, $E_{\text{IVERT}}$, results in the creation of a hole at the top of the valence band. In an organic polymer chain, it can be energetically favourable
to localize the charge that appears on the chain and to have, around the charge, a local distortion (relaxation) of the lattice. This process causes the presence of localized electronic states in the band gap due to a local upward shift ($\Delta e$) of the HOMO and downward shift of the LUMO (Figure 27b). If $\Delta e$ is larger than the necessary energy to distort the lattice locally around the charge, $E_{DIST}$, a polaron can form.

Figure 27: The energy band diagram of a) an undoped P3AT, b) at $\sim 0.1 \%$ doping level with polaron states in the band gap, c) at a few percent doping level with the appearance of bipoarhon states. This is an energy level picture of what is happening in Figure 23 and Figure 24.

A neutral P3AT with the benzenoid structure is depicted as “P” in Figure 25 and its energy level diagram is shown in Figure 27a. The band gap is $\sim 2.2$ eV, and this polymer is categorized as a semiconductor. The band gap is too large for electrons to transfer from the valence to the conduction band at room
temperature. Upon the removal of an electron from the polymer chain via the doping process, a local distortion to the quinoid structure occurs (P'' in Figure 25). The resulting radical cation is referred to as a polaron (Figure 27b). The formation of the polaron induces two new intermediate states (bonding and antibonding) within the band gap. The unpaired electron occupies the bonding (low energy) state, giving the polaron a spin of $\frac{1}{2}$.

As oxidation continues, if the second removed electron is the unpaired electron of the polaron, a bipolaron is formed (BP$^{2+}$ in Figure 25). The bipolaron states lie further from the band edges (Figure 27c). The lower energy state of the bipolaron is empty; thus, the species has a zero spin. At a doping level of a few percent, bipolarons predominate, and there are only a few polarons. Bipolarons are believed responsible for the electronic conduction characteristics of doped poly(3-alkylthiophenes) (P3ATs), thus, the charge carriers in conducting P3ATs have zero spin.

Bredas et al.$^{56}$ have compared the energy required to form a bipolaron with the energy needed to form two polarons. They show that the distortion energy to form one bipolaron is roughly equal to that to form two polarons. However, the decrease in ionization energy is much greater for the case of the bipolaron. This is the reason that one bipolaron is thermodynamically more stable than two polarons, despite the Coulomb repulsion between two similar charges.
In addition to charge conduction along the polymer chain, charge conduction between polymer chains can occur. Bredas et al.\textsuperscript{57} have proposed a model to account for the conductivity by charge hopping between different polymer chains. Interchain hopping of bipolarons accounts for the spinless conductivity of P3ATs. The process involves one of the two charges transferring to an adjacent chain, and the instantaneous description is of two polarons on adjacent chains. If the second charge follows the first, the bipolaron has moved from one chain to the other and has surmounted an energy barrier equal to the stabilization energy of the bipolaron.\textsuperscript{58}

\begin{figure}[h]
\centering
\includegraphics[scale=0.5]{bipolaron_hopping}
\caption{Interchain hopping of a bipolaron in P3ATs.}
\end{figure}

The transport of charge carriers in conjugated polymers is controlled by their mobility. The main components that contribute to carrier transport are \textit{intra}-chain and \textit{inter}-chain mobility. Bipolarons are believed responsible for the
electronic conduction characteristics of doped P3ATs along the polymer chain, with charge hopping responsible for transport from one chain to another. The conductivity is limited in the respect that the electrons must somehow move between different polymer molecules. Thus, the polymer must be well-ordered and packed efficiently to minimize the distance that the electrons must move.

Conjugated polymers, when processed from solutions, form complicated structures. In this environment the charge transport is limited by the most difficult hopping processes. Previous studies on the charge transport of P3HT FET structures have shown a two order of magnitude higher mobility when the polymer is highly RR and the $\pi-\pi$ stacking direction (010) corresponds to the in-plane direction rather than when the polymer is less RR and the (010) direction is normal to the film (Figure 29). This is consistent with the in-plane FET mobility reflecting a more efficient $\pi-\pi$ transport between different polymer chains rather than transport via alkyl chain hopping mechanisms.
Figure 29: RR P3HT with the (001) axis oriented normal to the substrate and the (010) axis parallel to the substrate (top). In this orientation, there is a two order of magnitude larger in-plane charge carrier mobility than in RIR P3HT, which has the (010) axis oriented normal to the substrate and the (001) axis parallel to the substrate (bottom).

2.2.8 Electrical Conductivity

Ohm’s Law (28) relates the voltage ($V$), current ($I$) and the resistance ($R$) of a material via:

$$V = IR$$  \hspace{1cm} (28)

The resistance of a material per unit length is known as the resistivity ($\rho$). It is defined in (29), where $R$ is the resistance in Ohms, $l$ is the length of the sample and $Area$ is the cross-sectional area. It indicates whether a material is a
conductor or an insulator. The conductivity \( \sigma \) is the reciprocal of the resistivity (30) and has units of Seimens/m (Seimen, \( S = \Omega^{-1} \)) but many times conductivity is also represented with units of Seimens/cm.

\[
R = \frac{\rho l}{Area}
\]

(29)

\[
\sigma = \frac{1}{\rho}
\]

(30)

The conductivity depends on how many charge carriers (electrons) are present in a material and their mobility (31), where \( n \) is the number of electrons, \( \mu \) is their mobility, and \( e \) is the charge on an electron. For example, in a metal, the valance and conduction bands can overlap. Since this band is partly filled and partly empty regardless of the temperature, there is little or no resistance to the flow of current. Thus, metals exhibit a high electrical conductivity.

\[
\sigma = n\mu e
\]

(31)

Increasing the temperature of a metal leads to a decrease in the electrical conductivity. This occurs because as the particle velocity increases, the number of collisions between particles increases. These collisions reduce the net flow of charge, reducing the conductivity.

Insulators have large band gaps and current can only flow when electrons are excited from the valence to the conduction band. With a large band gap, so few electrons are found in the conduction band that the electrical conductivity will be very low. The conductivity of polymers can vary from that of an insulator to
that of a conductor, depending on the size of the band gap, the number of charge carriers, and their mobility. The conductivity of PTHPUDT films will be examined using the two- and four-point probe techniques.

2.2.8.1 Two-Point Probe Method

In the two-point probe technique, two sharp probe tips made from tungsten are attached to separate arms and positioned very close (3.3 mm) to each other. A small voltage is applied across the probes and the resistance (called the spreading resistance) is measured. If the contact area of the probes is made small enough, the largest component of the measured resistance arises from the current crowding in the immediate vicinity of the probe tip. In this case the relationship becomes:

\[ R_{\text{sheet}} = \frac{\rho}{2a} \]  

where \( R_{\text{sheet}} \) is the measured spreading resistance (Ohms), \( \rho \) is the resistivity (\( \Omega \cdot cm \)) and \( a \) is the radius of the contact area of the probe (cm). This expression is an oversimplification. In practice, bulk samples whose resistivity is well documented are measured and then \( a \) is calculated. It is also rare for the contact areas of the probes to be truly circular or the same size. The resistivity is sensed in a volume that approximates a hemisphere with radius \( a \). If there is a resistivity gradient through the volume, then corrections need to be made for this. Corrections are also needed if the volume is distorted because of the proximity of
an insulator or a region of much higher conductivity, such as a buried layer. Several procedures have been developed to address these corrections.\textsuperscript{60,61}

\begin{figure}
\centering
\includegraphics[width=\textwidth]{two_point_probe.png}
\caption{A schematic diagram of the two-point probe experimental setup with \(s\) as the distance between the equally spaced probes, \(t_h\) the thickness, \(L\) the length and \(w\) the width of the film, respectively.}
\end{figure}

### 2.2.8.2 Four-Point Probe Method

A simple non-destructive tool for measuring the resistivity of a material is the four-point probe technique. It consists of four equally spaced tungsten wires that contact the sample (Figure 31). A known current is made to flow between the outer wires, while the voltage between the two inner wires is measured. Since little, if any, current flows between the two inner wires, there are no errors due to contact resistance. Thus, the four-point probe technique provides a more accurate measurement than the traditional two-point probe technique. One potential pitfall of the four-point probe technique is that the probes must be able
to make Ohmic contact with the material which can be difficult if the material is soft and easily scratched off the substrate by the metal probes.

Figure 31: A schematic diagram of the four-point probe experimental setup with $s$ as the distance between the equally spaced probes and $t_h$, $L$ and $w$ as the thickness, length and width of the film, respectively.

For a semi-infinite sample, the resistivity ($\rho$) is given by: \[ \rho = 2\pi s \frac{V}{I} \] (33)

However, practical samples have a finite size. For the case of a thin 2D-conducting sheet the current is assumed to be completely confined to the film layer with thickness $t_h$ where and $t_h << s$ (which is the case for all of the four-point probe measurements in this thesis). In such a case, it is convenient to
define the sheet resistance $R_{\text{sheet}}$ with units of $\frac{\Omega}{\text{square}}$, where the square refers to any sized area along the surface. So the resistance of a square is independent of the size of the square. This is the resistance of a bar of material of unit length and width, with thickness $t_h$. If $t_h$ is known then:

$$\rho = R_{\text{sheet}} t_h \quad (\Omega \cdot \text{cm}) \quad (34)$$

and for a 2D-sheet:

$$R_{\text{sheet}} = \left( \frac{\pi}{\ln 2} \right) \frac{V}{I} = 4.53 \frac{V}{I} \left( \frac{\Omega}{\text{square}} \right). \quad (35)$$

Combining the last two equations we get:

$$\rho = 4.53 t_h \frac{V}{I} \quad (\Omega \cdot \text{cm}) \quad (36)$$

Finally, in order to account fully for a sample of finite size, two other correction factors must be included, a diameter correction factor $^{64}$ ($CF_d$) which depends on the $\frac{L}{w}$ ratio, and a thickness correction factor ($CF_{t_h}$) $^{62}$ which depends on the $\frac{t_h}{s}$ ratio. The bulk resistivity and sheet resistance for a real sample are expressed in final form as:
The conductivity is the inverse of the resistivity as described by (30).

The substrate used for the conductivity measurements was indium tin oxide (ITO). Indium oxide is a semiconductor, but is not a very conducting material since it lacks free electrons. If it is doped with 5-10 % tin by weight, this adds the free electrons to make ITO a conductor. Another feature of ITO that makes it an attractive semiconducting material is that thin films of ITO are transparent. The ITO used in this thesis had a measured sheet resistance of 4.2 ± 0.1 Ω/square.

2.2.9 Origin of Nonlinear Optical Spectroscopy

Nonlinear optics describes the interaction of light in nonlinear media, that is, in a material whose polarization or dipole moment per unit volume (\(\vec{P}\)) responds nonlinearly to the applied electric field component (\(\vec{E}\)) of light. This can be represented by a Taylor series:

\[
\vec{P} = \chi \vec{E} + \chi^{(2)} \vec{E}^2 + \chi^{(3)} \vec{E}^3 + \chi^{(4)} \vec{E}^4 + \ldots \tag{39}
\]

where \(\chi\) is the linear dielectric susceptibility of the medium, and \(\chi^{(2)}, \chi^{(3)}, \chi^{(4)}\) are the second, third and fourth higher order susceptibilities. The susceptibility of
a material describes its response to an applied field. In most everyday applications, the induced polarization only depends on the electric field strength and the linear susceptibility term, since the nonlinear response of a material is orders of magnitude smaller than the linear one \( \chi^{(2)} \approx 10^{-7} \chi^{(1)} \text{ esu} \). This nonlinearity is typically only observed at very high light intensities such as those from pulsed lasers.

If the electric field \( \vec{E} \) is represented as a plane wave (a constant frequency wave whose wavefronts are infinite parallel planes of constant amplitude normal to the phase velocity vector) by:

\[
\vec{E} = \sum_m \vec{E}_m = \sum_m e_m A_m \exp(i(\omega_m t - k_m r))
\]  

(40)

where \( e \) is the electric vector, \( A \) is the amplitude, \( \omega \) is the laser frequency, \( t \) is the time, \( k \) is the wave vector and \( r \) is the direction of wave propagation, an infinite number of waves of nonlinear polarization, \( \vec{P}_{\text{nonlinear}} \), can arise:

\[
\vec{P}_{\text{nonlinear}}(\omega) = \hat{\chi} : \vec{E}_1 \vec{E}_2 \vec{E}_3 \ldots \vec{E}_n
\]  

(41)

at frequencies \( \omega = \sum_{m=1}^{n} \omega_m \). The factor that determines the macroscopic nonlinear response of the medium is the spectral component of a tensor of \( (n+1) \) rank \( \hat{\chi}^n \):

\[
\hat{\chi}_{jk...n+1}^{(n)}(\omega = \omega_1 \pm \omega_2 \pm \ldots \pm \omega_n) = N < \hat{\beta}_{jk...n+1}^{(n)}(\omega) > L(n)
\]  

(42)

where \( < \hat{\beta}_{jk...n+1}^{(n)}(\omega) > \) is the molecular hyperpolarizability tensor averaged over the molecular orientation distribution, and \( L(n) \) is a factor accounting for local field
effects associated with dipole-dipole interaction between $N$ species in a molecular ensemble.\textsuperscript{66}

The second-order polarization ($\tilde{P}^{(2)}$) is quadratic in the electric field, $\tilde{P}^{(2)} = \tilde{\chi}^{(2)} : \tilde{E}\tilde{E}$. The second-order susceptibility ($\tilde{\chi}^{(2)}$), is a third-rank tensor which gives rise to second-order optical effects, quadratic in the electric field. These $\tilde{\chi}^{(2)}$ effects are only possible in media that lack a center of inversion symmetry. In a material with inversion symmetry, the following is true:

\begin{equation}
\tilde{P}^{(2)} = \tilde{\chi}^{(2)} : \tilde{E}\tilde{E} \quad (43)
\end{equation}

Since both the polarization and the electric field are vector quantities, by definition, their signs must be reversible in a material possessing inversion symmetry. The following must also hold:

\begin{equation}
-\tilde{P}^{(2)} = \tilde{\chi}^{(2)} : -\tilde{E} \cdot -\tilde{E} \quad (44)
\end{equation}

which can be simplified to:

\begin{equation}
-\tilde{P}^{(2)} = \tilde{\chi}^{(2)} : \tilde{E}\tilde{E} \quad (45)
\end{equation}

Thus, $\tilde{P}^{(2)} = -\tilde{P}^{(2)}$ only when $\tilde{\chi}^{(2)} = 0$. The same is true for all even order susceptibilities. In centrosymmetric media, all even-ordered susceptibilities are zero; as such, any nonlinear optical processes generated by an even-order nonlinear polarizability are forbidden (Appendix III). This symmetry property can be very useful. Even-order nonlinear optical effects can be used to investigate surfaces and interfaces since the interface between two centrosymmetric media lacks inversion symmetry. This means that any nonlinear optical phenomena
induced by an even order nonlinear polarizability will only arise at the interface, giving information only about the interfacial region without contributions from the bulk.

In situations where the macroscopic second-order surface nonlinear susceptibility \( \tilde{\chi}_s^{(2)} \) is large because of the presence of adsorbed molecules, contributions from the substrate and local field effects can be ignored and the susceptibility written as an averaged sum of the second-order nonlinear molecular hyperpolarizabilities \( \tilde{\beta}^{(2)} \) of the adsorbed species:

\[
\tilde{\chi}_s^{(2)} = N_s \langle \tilde{\beta}^{(2)} \rangle
\]  

(46)

where \( N_s \) is the number of adsorbate molecules on the surface and the brackets denote an average taken over all adsorbate orientations. Thus, given information regarding the molecular hyperpolarizabilities, measurement of the surface susceptibility can indicate the averaged molecular orientation. The polarization dependence of the surface second harmonic response can be used to extract the elements of the second-order nonlinear susceptibility tensor \( \tilde{\chi}^{(2)} \), and thereby, used to obtain orientation information.

The molecular hyperpolarizability tensor \( \tilde{\beta} \) describes the second-order nonlinear molecular properties (47). Using perturbation theory, one can express the components of \( \tilde{\beta} \) in terms of molecular energies and wavefunctions. \( \tilde{\beta}_{ijk} \) is the tensor element referenced to the molecular coordinate axes \( i, j, \) and \( k \); \( \omega \) is the laser frequency, \( \hbar \omega_{ng} \) is the difference in energy between the excited state.
and the ground state; $\Gamma_{ng}$ is the lifetime of the excited state; $r_{ng}^i$ is the transition dipole matrix element between states $n$ and $g$ along the molecular $i$-axis. The notation $\pm$ is used to denote the in-phase (real) and out-of-phase (imaginary) components of $\hat{\beta}$.

$$\hat{\beta}_{qk} + \hat{\beta}_{kj} = -\frac{e^3}{4\hbar^2} \sum_{n,n'=g}^N \left( r_{g'n}_{n'}^{k} r_{ng}^{i} r_{ng}^{k} + r_{g'n}_{n'}^{i} r_{ng}^{k} r_{ng}^{i} \right)$$

$$\times \left[ \frac{1}{\omega_{n'g} - 2\omega + i\Gamma_{n'g}^{n'}} \left( \frac{1}{\omega_{ng} + \omega - i\Gamma_{ng}^{n'}} - \frac{1}{\omega_{ng} - \omega + i\Gamma_{ng}^{n'}} \right) \pm \frac{1}{\omega_{n'g} - 2\omega - i\Gamma_{n'g}^{n'}} \left( \frac{1}{\omega_{ng} + \omega + i\Gamma_{ng}^{n'}} - \frac{1}{\omega_{ng} - \omega - i\Gamma_{ng}^{n'}} \right) \right]$$

$$+ \left( r_{g'n}_{n'}^{i} r_{ng}^{k} r_{ng}^{i} + r_{g'n}_{n'}^{k} r_{ng}^{i} r_{ng}^{i} \right)$$

$$\times \left[ \frac{1}{(\omega_{ng} - \omega + i\Gamma_{ng}^{n')(\omega_{ng} - 2\omega + i\Gamma_{ng}^{n'})} \pm \frac{1}{(\omega_{ng} - \omega - i\Gamma_{ng}^{n')(\omega_{ng} - 2\omega - i\Gamma_{ng}^{n'})} \right]$$

$$+ \left( r_{g'n}_{n'}^{i} r_{ng}^{k} r_{ng}^{i} + r_{g'n}_{n'}^{k} r_{ng}^{i} r_{ng}^{i} \right)$$

$$\times \left[ \frac{1}{(\omega_{ng} + \omega - i\Gamma_{ng}^{n')(\omega_{ng} + 2\omega - i\Gamma_{ng}^{n'})} \pm \frac{1}{(\omega_{ng} + \omega + i\Gamma_{ng}^{n')(\omega_{ng} + 2\omega + i\Gamma_{ng}^{n'})} \right]$$

The complexities involved in the calculation of $\hat{\beta}$ from (47) are obvious. In order to simplify this expression, we assume that in aromatic compounds the $\pi$-electronic structure is the sole contributor to $\hat{\beta}$ in the UV-vis region. An electronic structure calculation can be used to obtain the energies and wavefunctions of the molecule. If $\hat{\beta}$ has resonances at the fundamental and doubled frequencies, (47) can be further simplified by considering only the terms that are resonantly enhanced.

The most important features of the molecular second harmonic response can be obtained with a simple two-level model where only the ground and a single excited state (the state responsible for the optical transition near the
wavelength of interest) are considered (Figure 32). In this case, the second harmonic wavelength is in resonance with a transition in the molecule. This is an ideal situation since resonant enhancement of the SHG can be obtained at a wavelength where there is virtually no absorption of the incident laser power. SHG measurements which utilize resonances at twice the laser frequency also have the advantage of avoiding the problems of photobleaching, fluorescence and burning. A quantitative analysis of the hyperpolarizability allows the determination of its dominant components which can be related to the measured $\chi^{(2)}$ components to extract the molecular orientation parameters (Appendix II).

![Figure 32: A molecular resonance at the second harmonic wavelength.](image)

### 2.2.9.1 Surface Second Harmonic Generation

Optical second harmonic generation can be used as a tool to investigate surface and interface structure, providing information regarding adsorbate
orientation.\textsuperscript{72, 73} This technique takes advantage of the inherently asymmetric environment of the interface formed between two bulk phases of matter. When the two bulk phases are both centrosymmetric, the noncentrosymmetric interface between them possesses a second-order surface nonlinearity ($\hat{\chi}_s^{(2)}$)

$$\vec{P}^{(2)} = \hat{\chi}_s^{(2)} \vec{E}^{(2)}$$  \hspace{1cm} (48)

which can give rise to interface-specific, second-order, nonlinear optical effects. These $\hat{\chi}_s^{(2)}$ effects are only possible in media that lack a center of inversion symmetry (Figure 33).

\begin{figure}[h]
\centering
\includegraphics[width=0.5\textwidth]{figure33.png}
\caption{The lack of a center of inversion symmetry at the air-substrate interface.}
\end{figure}

Let us consider two plane waves with electric field components given by:
where $\vec{k}_j$ is a wave vector and $\vec{r}$ is the direction of wave propagation. If the two plane waves enter a material that has a non-zero $\chi^{(2)}$, they induce a nonlinear polarization within the medium:

$$\vec{P}^{(2)} = \chi^{(2)} : \vec{E}_1 \vec{E}_2 = \vec{P}_{2\omega_1} + \vec{P}_{2\omega_2} + \vec{P}_{\omega_1 + \omega_2} + \vec{P}_{\omega_1 - \omega_2} + \vec{P}_0$$

where $\vec{P}_0$ is a constant polarization of the medium induced by high electric fields.

Polarization at double the frequencies $\vec{P}_{2\omega_1}, \vec{P}_{2\omega_2}$ and also at $\vec{P}_{\omega_1 + \omega_2}$ (sum frequency generation (SFG)), and $\vec{P}_{\omega_1 - \omega_2}$ (difference frequency generation (DFG)) can lead to a re-radiation of light at these frequencies.

When the frequencies of the two waves are equal, they induce a third wave at double the frequency. This three wave mixing process is called second harmonic generation, SHG. In SHG the incident light is converted to its second harmonic. This means, for example, that two photons at 800 nm can combine and produce one 400 nm photon. The frequency of the light has been doubled, but the energy is conserved as the total energy of the two red photons should be identical to the energy of the blue one.

Consider an intense laser beam of frequency $\omega$ incident from media 1 at an angle $\theta_i$ with respect to the surface normal and the reflected SH output is detected (Figure 33). The SH signal at frequency $2\omega$ is given by:
where \( I_\omega \) is the intensity of the incident beam, \( T \) is the laser pulse width, \( A \) is the area of the laser spot on the surface, \( \varepsilon_i \) is the dielectric constant of medium 1, \( \theta_i(2\omega) \) is the SH reflection angle, and \( \hat{\chi}^{(2)} \) is the effective nonlinear susceptibility. The effective nonlinear susceptibility has the form: \(^{74}\)

\[
\hat{\chi}^{(2)} \rightarrow L \left( \frac{\varepsilon_{2\omega} \cdot L_{1\omega}}{\varepsilon_{1\omega} \cdot L_{1\omega}} \right) \]  

(53)

where \( \hat{\varepsilon}_{\omega} \) and \( \hat{\varepsilon}_{2\omega} \) are the unit polarization vectors at the respective frequencies, and \( L_{\omega} \) and \( L_{2\omega} \) are local field factor tensors at the incident field and at the SH field. The local field factor tensors are also known as Fresnel coefficients, and they are corrections to the incident laser fields and to the SH field generated at the interface. These Fresnel factors take into account the reflection, refraction and enhancement of fields due to the presence of the interface (Appendix IV).

### 2.2.10 The Z-scan Technique

The z-scan technique is a sensitive single-beam method that can be used to measure both the size and magnitude of the nonlinear index of refraction (\( \gamma \)) and the nonlinear absorption coefficient (\( B \)) for a wide variety of materials. The z-scan method is based upon the \( \hat{\chi}^{(3)} \)-related self-lensing (focusing or defocusing) effects that occur when a sample is subjected to high peak intensity light as it is moved along the optic axis from \(-z\) to \(+z\) through the focus of a laser
beam in the direction of laser propagation through a finite aperture in the far field (Figure 34). The value of the intensity-dependent nonlinear refractive index can be extracted from the resulting variation in transmission. For example, if a material under investigation has a nonlinear refractive index and a thickness smaller than the diffraction length of the focused beam, it can be regarded as a thin film with a variable focal length. In regions of relative low intensity, the transmittance remains constant as the substrate moves from \(-z\) to \(+z\), toward the focus. As the sample nears the focus, the beam irradiance (power per unit area) increases, leading to self-lensing. For a sample characterized by positive self-lensing, positioning the sample prior to the focus causes the beam to diverge at an aperture positioned in the far field, thus decreasing the measured transmittance through the aperture. As the film passes through the focus, the positive self-lensing causes the beam to narrow and focus at the far field aperture, increasing the transmittance. When the film is again far from the focus (+z) in a region of relative low intensity, the transmittance once again becomes constant with sample position. In the absence of other effects, the resulting normalized transmission curve appears as a characteristic dispersion-type line shape.
Figure 34: The Z-scan technique.

A prefocal transmittance minimum (valley) followed by a postfocal transmittance maximum (peak) is a z-scan signature of a positive refractive nonlinearity (Figure 35). Negative nonlinear refraction, produces a peak-valley configuration. A very useful feature of the z-scan technique is that the sign of the nonlinear index is immediately obvious from the data.
Figure 35: An idealized example of nonlinear refraction in a z-scan experiment. The red curve corresponds to a negative phase shift (self-defocusing) while the blue curve corresponds to a positive phase shift (self-focusing).

For an optical material capable of nonlinear refraction and absorption, the nonlinear refraction and absorption coefficients, $\gamma$ and $B$ are defined by:

$$n(I_i) = n_0 + \gamma I_i$$  \hspace{1cm} (54)

$$\alpha(I_i) = \alpha_0 + BI_i$$  \hspace{1cm} (55)

where $n$ is the index of refraction, $n_0$ is the linear refractive index, $\alpha$ is the absorption, $\alpha_0$ is the linear absorption coefficient and $I_i$ is the intensity of light. Both $\gamma$ and $B$ can be either positive or negative corresponding to the possibility of self-focusing or defocusing in the case of $\gamma$ and nonlinear absorption or saturable absorption in the case of $B$. 

80
The third-order nonlinear susceptibility \( \chi^{(3)} \), is a complex quantity with the real \( \chi^{(3)}_R \) and imaginary \( \chi^{(3)}_I \) components related to the nonlinear refraction and absorption coefficients, respectively:

\[
\chi^{(3)} = \chi^{(3)}_R + i\chi^{(3)}_I \tag{56}
\]

\[
\chi^{(3)}_R = n_0^2 \varepsilon_0 c \gamma \tag{57}
\]

\[
\chi^{(3)}_I = \frac{n_0^2 \varepsilon_0 c^2 B}{\omega} \tag{58}
\]

where \( \varepsilon_0 \) is the permittivity of free space, \( c \) is the speed of light, and \( \omega \) is the optical frequency of the laser. Thus, measuring the nonlinear refraction and absorption coefficients gives the third-order nonlinear response of a material.

In order to determine \( \chi^{(3)}_R \), one must first estimate \( \gamma \) via (59). First, the normalized transmittance profile of the film is obtained and the experimentally determined magnitude of the peak-to-valley transmission \( \Delta T_{p-v} \) is measured from the z-scan trace. Then, knowing the size of the far field aperture \( (S_o) \), one calculates the magnitude of the on axis phase shift \( \Delta Z \). The sign of the phase shift is immediately apparent from the z-scan trace: a peak-valley shape corresponds to a negative phase shift, while a valley-peak shape corresponds to a positive phase shift. Next, the time-averaged index change \( \Delta n(t) \) is established knowing the wavevector \( (k = \frac{2\pi}{\lambda}) \) where \( \lambda \) is the wavelength of the laser beam, and the effective sample length \( (L_{eff}) \). The effective sample length is determined by measuring the experimentally determined value of the linear
absorption coefficient obtained from absorption measurements on the LB films. Finally, $\gamma$ is calculated knowing the Area and Power of the laser beam at the focus.

$$\Delta T_{p-v} \approx 0.406(1 - S_g)^{0.25} |\Delta Z| \text{ for } |\Delta Z| \leq \pi$$  \hspace{1cm} (59)

$$\Delta n(t) = \frac{\Delta Z(t)}{kL_{\text{eff}}}$$  \hspace{1cm} (60)

$$L_{\text{eff}} = \frac{(1 - \exp^{-\alpha_0 L})}{\alpha_0}$$  \hspace{1cm} (61)

$$\gamma = \frac{\Delta n(t) \text{Area} \sqrt{2}}{\text{Power}}$$  \hspace{1cm} (62)

Because the absorptive and refractive contributions to the far field beam profile (and hence to the z-scan transmittance profile) are coupled, it is also possible to extract the sign and magnitude of the nonlinear absorption coefficient ($B$) from z-scan measurements directly. When the aperture is removed ($S_a = 1$), the z-scan trace becomes insensitive to beam distortions, and is only a function of the effects of nonlinear absorption/saturation. For a temporally Gaussian pulse, the resulting transmittance can be expressed in terms of the peak irradiance in the following summation.\textsuperscript{76}
\[ T(z, S = 1) = \sum_{m=0}^{\infty} \left[ -q_0(z) \right]^m \left( m + 1 \right)^{1/2} \]  

where, \( q_0(z) = \frac{B I_0 L_{\text{eff}}}{(1 + \left( \frac{z}{z_0} \right)^2)} \)  

Equation (65) describes the transmittance profile expected to result from the coupled effects of nonlinear refraction and absorption in the general case, where \( \Delta Z \) is the nonlinear phase shift due to the nonlinear refraction, \( x = \frac{z}{z_0} \) indicates the dimensionless relative position from the beam waist, and \( \rho \) represents the ratio of the imaginary to real part of the third-order nonlinear susceptibility:

\[ T = 1 + \frac{2(-\rho x^2 + 2x - 3\rho) \Delta Z}{(x^2 + 9)(x^2 + 1)} \]  

\[ \rho = \frac{x^{(3)}_i}{x^{(3)}_k} = \frac{B}{2k\gamma} \]  

Because both the closed and open aperture analyses require knowledge of the beam’s spatial characteristics to determine \( \gamma \) and \( B \), the radius \( \omega_0 \) of the beam

\[ \omega_0 = \frac{k \omega_0^2}{2} \]  

\( k \) is the propagation constant of the laser in vacuum, \( \omega_0 \) is the radius of the beam at the beam waist, and \( I_0 \) is the irradiance of the laser beam at the waist. To extract \( B \), the open aperture z-scan traces can be fit using (63) and (64).
at the beam waist is extracted by fitting the experimentally determined z-scan data from standard samples of known nonlinear response or from samples known to possess no nonlinear absorption effects. In the absence of nonlinear absorption effects, $\rho$ reduces to zero, allowing one to extract $\omega_0$ directly from the best fits of the data to (65).
CHAPTER 3: CHARACTERIZATION OF PTHPUDT THIN POLYMER FILMS

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In what follows, we describe the structure/property relationships of LB films of PTHPUDT. The methods of film deposition and the experimental apparatus used to carry out these studies are examined. Following this, we present the results of our Langmuir film, LB film and SC film characterization
studies including surface wettability, absorbance, luminescence, optical microscopy, XRD, atomic force microscopy and conductivity measurements.

3.1 Experimental

3.1.1 Design and Rational

The process used to select a model polymer system began by considering which materials would be able to form a monolayer on the LB trough. A material must possess both a water-soluble polar moiety and a hydrophobic functionality, usually an alkyl chain, in order to take shape as a monolayer at the air-water interface. Thus, the hydrophilic and hydrophobic components of various polymers were assessed in order to gauge the amphiphatic balance. Some of the molecules under consideration are shown in Figure 36. All of the molecules in the library shown were synthesized by past group members in the lab of Dr. Steven Holdcroft. The polymers P3HT, PDHBT, COOH polymer, NH₂ polymer, CH₂OH polymer, and DiHxd COOH polymer were synthesized by Dr. Yuning Li. Dr. Jianfei Yu synthesized PTHPUDT-EDOT, PTHPET, and PTHPUDT.³⁶ Stearic acid was purchased from Aldrich. All of the materials were used as received.
Figure 36: The polymers considered as possible model systems.
Poly(3-hexylthiophene) (P3HT) and poly(dihexylbithiophene) (PDHBT) lack a hydrophilic group and were unable to form a monolayer at the air-water interface. These polymers had a tendency to form “islands” of material interspersed between clear open areas where no surfactants had accumulated on the surface of the trough. Next, a series of bithiophene-based polymers including poly(3,4-dihexylthiophene)3’ or 4’phenylcarboxylicacid thiophene (COOH polymer) and similar derivatives (NH2 polymer and CH2OH polymer) were investigated. These polymers have hydrophobic alkyl chains attached to a thiophene subunit and a hydrophilic moiety on the adjacent thiophene subunit. These polymers spread out onto the surface of the trough but we could not deposit them onto solid substrates as mono-molecular films. Several explanations were considered. Compared with stearic acid (CH3(CH2)16COOH), both the bithiophene-based polymers and stearic acid possess a hydrophilic carboxylic acid group. The alkyl chains in these polymers were only six carbons in length, far shorter in comparison to the alkyl chain length of stearic acid. It is well known that on the surface of the trough, it is the van der Waals forces between the alkyl chains that tend to hold individual fatty acid molecules together as a group. The lower degree of hydrophobicity on the part of the polymers may have precluded the deposition of organized multilayers. In addition, these bithiophene-based polymers were not RR and as such may not have been able to pack efficiently into organized films.

To resolve the question of whether the lack of hydrophobicity of the alkyl chains precluded the deposition of organized multilayers, poly(3, 4-
dihexadecylthiophene-3' or 4'phenylcarboxylicacid thiophene) (DiHxd COOH polymer in Figure 36) was examined. However, this polymer was regioirregular and did not form ordered films just like its dihexyl-chained analogue, COOH polymer.

A series of THP containing polymers including poly(3-(2-(2-tetrahydropyranloxy)ethyl)thiophene) (PTHPET), poly(3-(11-(2-tetrahydropyranloxy)undecyl)thiophene-3,4-ethylenedioxythiophene) (PTHPUDT-EDOT) and poly(3-(11-(2-tetrahydropyranloxy)undecyl)thiophene) (PTHPUDT) were also examined. These polymers were considered as possible model candidates since the hydrophilic THP functionality was directly connected to a long hydrophobic alkyl chain, in much the same fashion as stearic acid. PTHPET dissolved into the subphase when compressed under pressure, while PTHPUDT-EDOT formed "islands" on the surface of the trough. PTHPUDT, by contrast, was not forced into the subphase when compressed, nor did it form any "islands".

The synthesis of PTHPUDT has been discussed in detail previously.36 PTHPUDT was synthesized from its corresponding brominated monomer using the Grignard cross coupling reaction according to the general method described by McCullough et al.78 (Appendix I)

Amphiphilic monolayer and multilayer films have been studied using linear and nonlinear optical methods. Samples were prepared using spin-coating and the LB techniques, respectively. The details of the sample preparation are given below.
3.1.2 Sample Preparation

3.1.2.1 Amphiphilic Mono-Molecular Films

Water quality and purity were important aspects in the process of monolayer formation and its subsequent transfer onto a solid substrate. The pH of the water and the presence of different ions and contaminants have been shown to affect film quality dramatically. Thus, the Milli-pore water surface was cleaned thoroughly via aspiration until the increase in surface pressure upon compression of the barriers was less than 0.1 mN/m.

Polymer solutions of the amphiphilic molecules were prepared by dissolving 5 mg of polymer in 5 mL of spectroscopic grade CHCl₃. LB films were made by adding 75 μL of polymer solution drop-by-drop evenly across a fresh and clean Milli-pore water subphase (18.2 MΩ-cm resistivity) in a computer-controlled, Nima 600 series LB trough with a Wilhelmy plate pressure sensor. The solvent was allowed to evaporate for 5 minutes before compression began. The monolayer of amphiphilic molecules was compressed at a rate of 10 cm²/min. Surface pressure-area isotherms were used to infer the structural transitions of the polymer from an expanded "gas phase" to a "liquid phase" film. Polymer films were deposited onto hydrophobic glass substrates.

Glass substrates were made hydrophobic via the LB deposition of one monolayer of ferric stearate (Fe⁺³(CH₃(CH₂)₁₆COO⁻)₃) onto clean substrates such as glass microscope slides, calcium fluoride (CaF₂) or fused silica prisms at a surface pressure of 35 mN/m. The glass microscope slides and the fused silica
prisms were thoroughly cleaned by immersion into a fresh “piranha bath” consisting of a 3:1 volume ratio of 95% sulphuric acid and 30% hydrogen peroxide. This cleaning procedure was done in the fumehood using a face shield and hand protection because of the very corrosive nature of the “piranha bath.” Next, the substrates were repeatedly washed with distilled, deionized water in order to activate the hydroxyl groups of silica and increase its hydrophilicity. The CaF₂ prisms were washed with CHCl₃, followed by ethanol, acetone, and copious amounts of distilled deionized water. A piranha bath was not employed with this substrate since it can etch the surface resulting in a pitted surface.

The Langmuir film was held for 5 minutes at the target pressure before dipping was commenced. The film was then transferred onto a substrate under pressure control at a surface pressure of 17.5 mN/m, when the isotherm was nearing its steepest portion. The films were deposited at a dipping rate of 10 mm/min using the vertical dipping mechanism of the trough. Y-type films with a head-to-head and tail-to-tail repeating architecture were deposited onto the substrates. The efficiency of polymer transfer onto the substrate was determined by recording the transfer ratio (TR):

$$TR = \frac{\text{area of the monolayer removed from the subphase at constant pressure}}{\text{area of substrate immersed in water}}$$  \hspace{1cm} (67)
3.1.2.2 Spin-Cast (SC) Films

Amphiphilic films were also prepared by spin-casting solutions onto solid substrates. The cleaning procedure for the substrates was the same as for the LB films. The polymers under investigation were dissolved in spectroscopic grade CHCl$_3$ or ethanol respectively. Solutions were deposited onto either glass microscope slides or right angled prisms. A specially designed prism holder was used to hold right angle prism substrates onto which polymer solutions were deposited. The prism was spun using a small motor whose current was adjusted to the desired spin speed. The spin speed was calibrated with a strobe light. With all of the substrates, the spin speed was set to 2000 rpm and the substrates were spun for 30 seconds. The surface coverage (number of molecules on the surface) was varied by spin-coating solutions with different concentrations of solute. The surface coverage was examined using linear absorption UV-vis measurements and with the aid of an optical microscope. Surface coverage reproducibility was estimated to be ± 10 % via UV-visible spectroscopy. Film thickness was measured using contact mode atomic force microscopy or with the aid of a profiliometer.

3.1.3 Instrumentation

Mono- and multilayer films fabricated at variable temperatures employed an RM6 Lauda recirculating water bath attached to the trough to control the temperature of the water subphase. UV-vis absorption spectra were obtained from a Cary 3E (Varian) spectrophotometer. Contact angle measurements were
conducted using a digital AST Optima contact angle apparatus (AST products, Inc., Billerica, MA) via deposition of 1 - 2 μL of water onto the films from a 10 μL syringe. Polarized light microscopy images were acquired using an Olympus BX60 microscope with crossed polarizers. Films approximately 1 cm² in size were examined with 10 x magnification providing images 1 mm² in dimension. The resolution limit with 10 x magnification is 1.10 μm. Ellipsometry measurements were conducted with a Horiba Jobin Yvon UVISEL UV-Visible-NIR: Ex-Situ Phase Modulated Spectroscopic Ellipsometer. Fluorescence measurements were conducted on polymer solutions, SC and LB-deposited films using a Photon Technology International (PTI) Quantamaster Model QM1 and Ratiomaster Model RC-M photomultiplier detection system. Atomic force microscopy (AFM) studies were carried out using a Thermomicroscopes Explorer scanning probe microscope system with an 8 μm Z-linearized dry scanner and a 2 μm tube scanner. AFM measurements were taken to assess the overall quality of the films, to determine film thickness and to obtain high resolution contact mode images in order to investigate film crystallinity. Film thickness measurements were obtained by scratching a portion of the film from the substrate and measuring the height of the unperturbed film in comparison to the region where the film had been removed.

Low angle X-ray diffraction (XRD) experiments were carried out using a RAPID (Rigaku) X-ray diffractometer with a copper target (λ₀ = 1.542 Å) and an image plate detector. Intermolecular distances and van der Waals radii calculations from space-filling models were carried out with the program
Molecular Modeling Basic Revision 2.38 published by ChemSW Software Inc.
The two-point probe electrical conductivity measurements were conducted on a Solartron electrochemical interface Model S1 2187 on films deposited on evaporated gold (thickness 20 nm) on glass microscope slides. A razor blade was used to scratch a channel along the substrate 30 μm in width (the width of which was measured with a profilometer). The thickness of the films deposited on top of the gold was also measured with a profilometer. The four-point probe experimental setup was calibrated with 280 nm-thick ITO (obtained from Merck Display Technologies Ltd.) deposited on a glass substrate using a Princeton Applied Research Potentiostat/Galvanostat Model 263A and a Keithley 2000 Multimeter. The surface profile measurements illustrated in this manuscript were conducted with a KLA-Tensor Alpha-Step IQ Surface Profilometer. Thermogravimetric Analysis (TGA) was carried out on a Thermogravimetric Analyzer Model TGA-50. Solvatochromic measurements were conducted using an Ocean Optics USB 2000 handheld spectrophotometer with a USB-ISS UV-vis light source. Differential Scanning Calorimetry experiments were performed on a Perkin Elmer DSC 7, with a heating rate of 10 °C/min.

3.2 Langmuir-Blodgett (LB) Isotherms

Langmuir films of PTHPUDT were formed at the air-water interface of the LB trough by the addition of a 1.0 mg/mL solution of PTHPUDT in CHCl₃. The barriers of the trough were compressed and the resulting surface pressure-area isotherms obtained at various temperatures were recorded. One such isotherm
is displayed in Figure 37. The shape of the isotherms was very reproducible and subject to small changes with temperature. The isotherm shows an initial increase in surface pressure at a molecular area (here considered as an area per repeat unit of the polymer) corresponding to approximately 20 Å$^2$. The surface pressure rises at a moderate rate with decreasing area until a surface pressure of approximately 30 mN/m is attained, at which point, the rate of increase in surface pressure with barrier compression decreases dramatically. This plateau region of the isotherm continues until a surface pressure $\sim$43 mN/m is reached. Further barrier compression leads to a much faster rate of surface pressure increase until evidence of film collapse appears beyond surface pressures $\sim$55 mN/m.
Figure 37: LB trough surface pressure vs area isotherm for PTHPUDT at room temperature. The inset shows the structure of the polymer under investigation, PTHPUDT.

Analysis of the first increase in surface pressure shows that the area per repeat unit when extrapolated to zero pressure corresponds to $\sim 18 \, \text{Å}^2$. Given that the tetrahydropyranyl moiety is hydrophilic, one might expect this zero pressure area to be dictated by the THP functionality. Space-filling models indicate that the THP moiety has a diameter of $\sim 5.1 \, \text{Å}$, and that the zero-pressure area per repeat unit is consistent with the THP moiety being anchored into the water subphase and having some freedom to rotate. This area per repeat unit is consistent with a situation in which the plane of the PT chain lies parallel to the water surface with every pendant alkyl chain and THP group oriented toward the water subphase.
Analysis of the second rise in surface pressure shows an area per repeat unit of ~8 Å² when extrapolated to zero pressure – roughly half of that corresponding to the first increase. It is possible that an increase in surface pressure from ~30 mN/m to ~43 mN/m leads to a change in the conformation of the polymer at the water surface. The polymer geometry could transition from an orientation where the thiophene backbone lies face-on to the water surface to one in which the plane of the polymer backbone lies perpendicular (edge-on) to the water surface with every second THP group anchored into the subphase, consistent with a substantially smaller area per repeat unit. Indeed, as others have reported, variations of angle between the thiophene ring plane and the water surface are responsible for variations in the area per repeat unit of this magnitude. Attempts to deposit mono and multilayer films at surface pressures of ~43 mN/m were unsuccessful since in such an end-on conformation, the molecules lose their amphiphilic nature. The inability to deposit organized monolayers at such high pressures is consistent with this observation.

Temperature-dependent studies of the isotherm behavior show that as the temperature of the subphase is decreased, the area per repeat unit undergoes a small decrease as well, but the general shape of the isotherms remain unchanged.

3.3 Surface Compressibility

The 2D compressibility \( C_s \) of a monolayer at any area is defined by:\textsuperscript{80,81}
\[ C_s = -\frac{1}{\text{Area}} \left( \frac{\partial \text{Area}}{\partial \pi} \right)_T \approx -\frac{1}{\text{Area}} \left( \frac{\Delta \text{Area}}{\Delta \pi} \right)_T \]  \quad (68)

where \( \pi \) is the surface pressure. It can be calculated directly from the slope of the pressure-area plot. It is more convenient to use the reciprocal of \( C_s \) when the properties of surface films are discussed. This is called the surface compressional modulus \((C_s^{-1})\) and it has units of mN/m. For a clean surface, the modulus is zero since no surface active materials are present on the water surface. As the amount of surfactant increases, so does the modulus. \( C_s^{-1} \) depends on the state of the film, being greater for more condensed films.

The macroscopic 2D-compressibility can be deduced from the pressure-area isotherm if the mean area per molecule of the compression isotherm and the applied surface pressure are known. The macroscopic compressibility is determined from the negative slope of the pressure-area isotherm at the deposition pressure using (68) \( (C_s^{-1} = 142.3 \pm 0.1 \text{ mN/m}) \). This compressibility value is a measure of the average mechanical properties of the Langmuir film.

\( C_s^{-1} \) values are used to categorize Langmuir film phases and phase behaviour. Figure 38 shows the \( C_s^{-1} \) as well as the pressure-area isotherm plotted as a function of the surface area on the LB trough for stearic acid. When the barriers of the trough are relatively open \((250 \text{cm}^2 - 150 \text{ cm}^2)\) stearic acid molecules are far apart. The LB trough barriers can close a great deal with little or no change in the surface pressure. Thus, the film is very compressible, and as such the inverse compressibility is very small \((\sim 0 \text{ mN/m})\). However, when the
surface area reaches \( \sim 140 \text{ cm}^2 \), small changes in the surface area cause the surface pressure to rise considerably. At this point, the film is less compressible than when the barriers were wide open. Thus, the value of \( C_s^{-1} \) rises and the molecules are said to behave like a “liquid”. When the surface area reaches \( \sim 110 \text{ cm}^2 \), very small changes in the surface area cause drastic changes in the surface pressure. The film exhibits very little compressibility and as a result the value of \( C_s^{-1} \) rises and reaches a maximum. At small surface areas the film behaves like a “solid”. Further compression leads to a collapse of the film. This occurs at a collapse pressure of \( \sim 50 \text{ mN/m} \).

![Graph showing \( C_s^{-1} \) and Langmuir-Blodgett pressure-area isotherm](image)

**Figure 38:** The \( C_s^{-1} \) (blue) as well as Langmuir-Blodgett pressure-area isotherm (red) plotted as a function of the surface area on the LB trough for stearic acid.

After the initial deposition of the PTHPUDT polymer solution onto the water surface, when no external pressure from the moveable barriers is applied,
the molecules behave as a 2D-gas and $C^{-1}_s$ is $\approx 0$ mN/m. Figure 39 shows $C^{-1}_s$ plotted as a function of the area per repeat unit. The steepest portions of the pressure-area isotherm conform to the regions of the film on the LB trough that are the most compressed. As the LB trough barriers slowly close, some ordering of the film takes place, and the film begins to act like a 2D-liquid. Since the LB film is deposited onto a solid substrate at 17.5 mN/m, at that surface pressure the film behaves like a 2D-compressed liquid. As the barriers continue to close the surface pressure increases from $\sim 30$ mN/m to $\sim 43$ mN/m. This can be envisioned as a change in the conformation of the film on the surface of the trough. The increase in pressure may lead to a change in the conformation of the polymer at the water surface from a geometry in which the plane of the polymer backbone lies perpendicular (edge-on) to the water surface with every THP group anchored into the subphase to one in which every second THP group is anchored into the subphase. This would allow the surface to compress over a large area range without a substantial increase in the surface pressure. Once converted to this state, further barrier compression leads to a rapid increase in the surface pressure, meaning the film is not very compressible. When the surface pressure nears the collapse pressure ($\pi_c$), the second steep increase in $C^{-1}_s$ takes place. A well-compressed film is usually characterized by a steep and linear relationship between surface pressure and molecular area.
Figure 39: The surface compressional modulus ($C_s^{-1}$) of PTHPU DT plotted as a function of the area per repeat unit ($\AA^2$).

Table 1: General values of the $C_s^{-1}$ for a typical fatty acid monolayer, the 2D-state of the surface as well as the values of $C_s^{-1}$ for a Langmuir film of PTHPU DT.

<table>
<thead>
<tr>
<th>Monolayer</th>
<th>$C_s^{-1}$ Fatty acid (mN/m)</th>
<th>$C_s^{-1}$ PTHPU DT LB film (mN/m)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Clean surface</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>Liquid expanded</td>
<td>12.5 - 50</td>
<td>12.5 - 50</td>
</tr>
<tr>
<td>Liquid compressed</td>
<td>100 - 250</td>
<td>&gt; 150</td>
</tr>
<tr>
<td>Solid</td>
<td>500 - 2000</td>
<td>not reached</td>
</tr>
</tbody>
</table>

It should be noted that the films never achieved the “solid phase” ordering on the trough. Since at pressures greater than 55 mN/m, the $\pi_c$ was reached. At $\pi_c$, the forces exerted on the film are too great for it to be confined in just two dimensions. Molecules are ejected out of the monolayer into the superphase and off the sides of the trough. The collapsed film consists of large areas of
uncollapsed monolayer interspersed with “mountain ridges” or “hair-like structures” where multilayers had been crushed together (buckeled) to form bulky aggregates.

3.4 Transfer Ratios

Attempts to transfer monolayers onto hydrophilic substrates met with limited success. Deposition (transfer) ratios for multilayer films showed inconsistent transfer. Leclerc et al.\textsuperscript{82} reported similar findings on P3AT derivatives with a perfluorinated group attached directly to the thiophene ring. The ineffective deposition was explained in terms of the strong hydrophobic nature of the material, which caused the polymer to peel from the substrate upon immersion into the water subphase.

In contrast to our attempts to deposit onto hydrophilic substrates, monolayers of PTHPUDT readily transferred via the vertical dipping mechanism of the trough onto hydrophobic glass substrates. Deposition was monitored by two means: the first was by noting the advancing and receding water contact angles as the substrate passed through the monolayer-covered water surface, and the second was by the creation of a high optical-quality pink/purple film on the previously clear substrate. Monitoring the transfer ratios confirmed an LB film of Y-type architecture (Figure 7 bottom right). A Y-type film is a one where deposition occurs on each subsequent pass of the substrate through the air-water interface. Upon the first downstroke of a hydrophobic substrate through the water surface, the hydrophobic portion of the surfactant deposits on the
surface of the substrate with the hydrophilic segment of the surfactant oriented away from the substrate. With the first upstroke, deposition of an additional monolayer occurs via interaction of the hydrophilic film and polar head groups of the monolayer (Figure 7). At the conclusion of the upstroke, the outside of the film is coated with the hydrophobic portion of the surfactant. Thus, a Y-type film consists of a head-to-head and tail-to-tail type of architecture. It should be noted that the head-to-head and tail-to-tail notation used here describes the Y-type film architecture and should not be confused with the coupling between monomer units which is 95% head-to-tail.

Deposition ratios for the PTHPU DT polymer multilayer films are similar to those of simple fatty acid multilayer films. The measured deposition ratios were 1.0 ± .2 and indicated deposition on both the up- and down-strokes, consistent with a Y-type film structure (Figure 40). The resulting film is of high optical-quality and is shown in Figure 41.
Figure 40: Transfer ratio vs the number of deposited monolayers for a 100-layer PTHPUDT LB film.
3.5 Contact Angle Measurements

In order to deposit Y-type architectures, one requires considerable hydrophobicity of the surface film on the down stroke (advancing water contact angles ~90° or greater) and a hydrophilic film (receding water contact angle << 90°) for deposition on the up stroke. The observed deposition behavior is consistent with the hydrophilic nature of the THP groups and the hydrophobic nature of the alkyl chains and thiophene backbones in adjacent layers. Aqueous
contact angle measurements support this view. Our measurements provide contact angles of \( \sim 85^\circ \) for multilayer films, where one expects the final layer deposited to expose a hydrophobic film (Figure 42, top). As a hydrophobic film passes down through a monolayer covered air-liquid interface, the exterior of the film is coated with a hydrophilic layer (Figure 12 top right). If the monolayer is removed from the surface of the trough, it may be possible to determine the water contact angle for the hydrophilic moiety on the exterior of the LB film. However, similar experiments conducted on fatty acid molecules showed evidence of previously deposited monolayers peeling off the substrate. Thus, instead of a direct measurement of the water contact angle of the hydrophilic exterior, it is estimated visually by viewing the meniscus formed at the substrate surface as the substrate is withdrawn from the water subphase. In this way, the receding aqueous contact angle is visually estimated to be \( \sim 35^\circ \). In addition, the water contact angles of spin-cast films (where the polymer is expected to have a different and broader distribution of orientations) are substantially lower (\( \sim 70^\circ \)) than the LB deposited films (Figure 42, bottom).
Figure 42: Contact angle image for a drop of water on the surface of a 100-layer LB film (top) and on a SC film of approximately the same thickness (bottom).
3.6 Optical Absorbance

Further confirmation of layer-by-layer deposition was obtained by monitoring the optical absorbance of films of various thickness. The maximum absorbance of each film was plotted against the number of transferred layers (Figure 43) and a linear correlation was found, consistent with the near unity transfer ratios observed for both the up- and down-strokes. The error in the absorbance was estimated from the variation of the absorption from several films of equivalent thickness, while the uncertainties in the transfer ratios was used as a measure of the error in the transferred monolayers.

![Graph showing absorbance vs transferred monolayers.](image)

**Figure 43:** Absorbance vs number of transferred PTHPUDT layers.

In addition to the observation of a linear increase in film absorption with film thickness, anisotropic behavior was observed via polarized UV-vis
absorbance experiments. It was established that the absorption of the polymer film depended on the electric vector of the incident beam. The absolute value of the absorbance was more than twice as large with the electric vector of the incident beam parallel to the dipping direction rather than when it was perpendicular to it (Figure 44). The observed dichroic ratio of ~2.2 indicates an anisotropic orientation of molecules. The maximum wavelength of absorption was also different in the two orientations: 550 nm with light polarized parallel to the dipping direction versus 525 nm with light polarized perpendicular to the dipping direction. This type of observation has been previously described\textsuperscript{34, 83-85} for highly oriented systems and is attributed to a difference in conjugation length with orientation, meaning that alkyl chains from segments of polymers with greater conjugation lengths are preferentially oriented along the dipping direction compared to segments of polymers with shorter conjugation chains.
Figure 44: UV-visible absorption spectra (normalized) for a 30-layer LB film of PTHPUDT with the electric vector parallel to the dipping direction (black); with the electric vector orthogonal to the dipping direction (red).

Similar measurements performed on the SC films yielded no differences in the polarized UV-vis absorbance, indicating an isotropic distribution of polymer orientations in the plane of the film. In contrast to the LB film, the maximum wavelength of absorption was 520 nm for the SC film. Figure 45 shows how the absorption profile differs for PTHPUDT depending on the method of solid state deposition and when in solution. The more red-shifted absorption maximum of the LB film indicates a lower $\pi - \pi^*$ transition energy compared to the SC film. Thus, the LB technique affords better molecular control over the PTHPUDT polymer, forming organized structures with low band gaps and with anisotropic orientations of polymer chains, compared to other film preparation techniques.85
Figure 45: UV-visible absorption spectra (normalized) of a 200-layer LB film of PTHPUDT (black); of a SC film of PTHPUDT (red); and of a solution of PTHPUDT (blue).

In contrast to the absorption spectrum of PTHPUDT in solution, the spectra of both the LB and spin-cast films show structured absorption. For the SC film, four peaks are observed at 484 nm, 520 nm, 550 nm and at 598 nm. For the LB film, four peaks are also observed at 486 nm, 524 nm, 555 nm and 597 nm. The spectral positions of these features show a good correspondence between the two films. One possible explanation for the structured absorption appearing in Figure 45 is that the peaks may correspond to vibrational fine structure (2.2.1), resulting from a vibrational progression. In such a scenario, the vibrational modes of the excited electronic state ($\pi^*$) are being probed. The energy level separation between the peaks is $\sim 1288$ cm$^{-1}$, consistent with the C-
C inter-ring stretch between two thiophene subunits along the main chain. This mode has been assigned based on IR studies of P3ATs and appears at \sim 1260 cm\(^{-1}\) in the ground electronic state.\(^{86}\) Since the \(\pi-\pi^*\) electronic excitation in polythiophenes is known to be characterized by a transition dipole directed along the thiophene chain, changes in the electronic distribution upon excitation may be expected to result in vibrational excitation of these inter-ring stretch modes.

### 3.7 Luminescence

LB films of PTHPUDT were weakly luminescent. The magnitudes of the fluorescence signals from both SC and LB deposited films of PTHPUDT are similar to those of regioregular SC films of P3HT. However, they are relatively small compared to films of other materials of comparable thickness that have been examined. In particular, photon count rates of the PTHPUDT film luminescence were one to two orders of magnitude smaller than those from films of poly(9,9-dihexylfluorene-alt-2,2'-bithiophene) (PFTT) (Figure 46) since this molecule contains the highly luminescent fluorene moiety.\(^{87}\)
The results of fluorescence studies carried out on SC and LB deposited films are presented in Figure 47. The excitation wavelength for the emission spectra of the SC and LB films was 520 nm. The LB film emission maximum (746 nm) is red-shifted ~18 nm with respect to the SC film emission maximum (728 nm). The LB film shows two features: a shoulder at 665 nm, and a peak at 746 nm. The SC film exhibits two features: a shoulder at 662 nm, and a peak at 728 nm.

**Figure 46:** The structure of PFTT.
In the solid state, the absorption and emission wavelength maxima of PTHPUDT films are red-shifted with respect to their solution counterparts, but the quantum yield of luminescence (Φ) was greatly reduced (Table 2). The absorption maximum of PTHPUDT in solution was 449 nm; in the SC film, it was 520 nm; while in the solid state LB film, it was ~550 nm. The emission maximum in solution was at 614 nm, with a Φ of $39 \pm 4\%$\textsuperscript{87}. In the SC film, the emission maximum was 728 nm; while in the LB film, the emission maximum is at 746 nm. Both the SC and LB films were very weakly emitting (Φ < 4 %). In comparison, P3HT, when dissolved in THF exhibits a Φ of $41 \pm 4\%$, and when deposited as a spin-cast film, possesses a Φ < 4 %.\textsuperscript{87}
Table 2: The absorption and emission wavelength maxima and quantum yield of fluorescence for PTHPUDT in solution and when cast as a film.

<table>
<thead>
<tr>
<th>PTHPUDT</th>
<th>Absorption $\lambda_{\text{max}}$(nm)</th>
<th>Emission $\lambda_{\text{max}}$(nm)</th>
<th>$\Phi$(%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>solution</td>
<td>449</td>
<td>614</td>
<td>39</td>
</tr>
<tr>
<td>SC film</td>
<td>520</td>
<td>728</td>
<td>&lt; 4</td>
</tr>
<tr>
<td>LB film</td>
<td>550</td>
<td>746</td>
<td>&lt; 4</td>
</tr>
</tbody>
</table>

The optical absorbance and fluorescence properties of PTHPUDT thin films have been investigated. The absorption red-shift on going from a solution to a film in P3ATs has been previously attributed to the planarization of the polymer backbone which results in additional $\pi$-conjugation.\(^8\) Several models suggest possible explanations for the observed decrease in the luminescence on going from a solution to a film. They include exciton splitting, the creation of excimers, aggregate formation, or other non-radiative decay pathways.

Any interpretation of the optical properties of thin films must take into account the high concentration environment of the surface, and the possibility of formation of dimers and higher aggregates.\(^8^8\) For example, molecular aggregation occurs in a variety of solutions,\(^8^9-9^2\) in Langmuir-Blodgett films,\(^9^3\) in phospholipid vesicles,\(^9^4, 9^5\) and on fused silica surfaces.\(^9^6\) The interpretation of the absorbance, fluorescence and dynamics of these physically bound dimers is based on the theory of exciton splitting.\(^9^7-1^0^0\)

The photoexcitation of an isolated conjugated polymer chain in a dilute solution creates only one singlet intrachain electronic species.\(^1^0^1\) In a film, where there is a high concentration of polymer molecules and several polymer chains are in contact, photoexcitation can result in the creation of weakly emissive
interchain species (aggregates) that are the major cause of quenched luminescence in fully conjugated polymers such as poly(p-phenylenevinylene) (Section 2.2.7.2). ¹⁰¹

An excimer (excited dimer) is a dimeric molecule formed from two species, one of which is in an excited state. This intermolecular singlet excited state complex is emissive. This excimer cannot be directly excited since the ground state of the dimer is dissociative. One example of a molecule that forms excimers is pyrene. In the emission spectrum of pyrene, the broad, red-shifted peak that develops with increasing concentration, is attributed to excimers. ¹⁰² This phenomenon has also been observed in rigid-rod conjugated polymers. ¹⁰³

These aggregate and excimer states are induced by strong intramolecular interactions between two or more molecules (or polymer units). ⁸⁷ The optical properties of bound dimers or higher aggregates can be described by the monomeric wavefunctions that have been perturbed through their mutual interactions. ⁸⁸ For the case of a dimer, this perturbation results in the formation of two excited electronic states (Figure 48). The resulting shift in the absorption spectrum may be towards either the red or blue, depending on the geometry of the aggregates, which determines the aggregate transition moment. For molecules with a parallel orientation (Figure 48, left) the lower energy excited state is dipole forbidden since an optical transition is allowed only for a non-zero transition moment. The result is a blue-shift in the absorption spectrum, while the emission is forbidden, causing the quantum yield of luminescence to be reduced. If the dimers have a head-to-tail orientation (Figure 48, middle), the result is a
red-shifted absorbance and fluorescence spectrum. For nonparallel dimers (Figure 48, right), both excited states have nonzero transition moments, and so both are optically allowed. This leads to band splitting in the form of both red and blue-shifted features in the optical absorption spectrum and red-shifted fluorescence. The fluorescence spectra of these aggregate states are red-shifted compared to isolated molecules due to fast internal conversion.

Figure 48: Exciton splitting in dimers with different geometries. Dipole allowed transitions are indicated with solid arrows, while dipole forbidden transitions are indicated with dashed arrows. Orientations of the monomer transition dipoles are represented by the short arrows. An optical transition is only allowed for a non-zero transition moment.

The photoexcitation and deactivation mechanisms in conjugated polymers are not fully understood. Photoexcitation can lead to the emission of light, as a result of the formation of excitons followed by recombination of an electron and a
hole leading to the release of a photon. To understand the photoluminescence process in solution and in the solid state, the different nonradiative decay paths of the generated excitons need to be investigated. Theander et al.\textsuperscript{104} have characterized two polythiophenes, poly(3-(2,5-octyldiphenyl)-thiophene) (PDOPT) and poly(3-(4-octylphenyl)-2,2'-bithiophene) (PTOPT), with respect to their photoluminescence properties both in solution and when deposited as spin-cast films (Figure 49). The photoluminescence yield of PDOPT is similar in solution (37 %) and in a spin-cast film (24 %). This was attributed to the separation of the polymer backbones in the film, since the phenyl ring is turned out of the plane of the thiophene backbone. Separating the chains gives an emitting species that is the same as in the solution, and no aggregate formation takes place in the film.

\begin{figure}
\centering
\includegraphics[width=\textwidth]{polymers.png}
\caption{The structure of the polymers PDOPT and PTOPT.}
\end{figure}
For PTOPT, the photoluminescence yield decreases from 27 % to 4 % on going from solution to the solid state. The lower number of sidechains in PTOPT makes the average distance between the polymer backbones shorter. This implies that the transport of excitons should increase as the distance between the donor and acceptor decreases. As the distance between main chains decreases, there should be an increase in the formation of weakly emitting excimers.

The most efficient nonradiative decay path for oligothiophenes in solution is intersystem crossing (ISC) from the singlet to the triplet state. However, there are additional nonradiative decay routes present in films such as quenching at traps and weakly luminescent excimers. Depending on the separation of the chains, the interchain hopping of these excitons will vary, and so will the probability of finding the traps.

3.8 Optical Microscopy

We have examined 88-layer PTHPUDT LB films via optical microscopy. The anisotropic nature of the film was confirmed upon observing the films between crossed polarizers. No light was seen to pass through the system and a dark field of view was present when the polarizer and analyzer were positioned at right angles to each other. However, with the addition of an 88-layer PTHPUDT film between the crossed polarizers, a uniform colour (a measure of the optical retardation) was observed over the entire film. A $\frac{1}{4}$ accessory plate was
inserted into the optical path in order to improve the contrast. The resultant colour change was subsequently interpreted with the help of a polarization colour chart. As the specimen was rotated relative to the polarizers, the intensity of the polarization colour varied cyclically, from zero (extinction) up to a maximum after a 45° rotation and back down to zero after a 90° rotation.

Reitzel et al.\textsuperscript{35} have also examined one monolayer-thick LB films of bi-thiopehene based regioregular polymers via optical microscopy. Domains up to 1 mm in length were observed when the films were examined through crossed polarizers. The 88-layer PTHPUDT LB films exhibit uniform optical retardation across the entire film. This indicates that at the length scale being examined (1 mm\(^2\)), the films are homogeneous. From this, one can infer that domain sizes in PTHPUDT films are at least 1 mm\(^2\).

The directions associated with the film birefringence were determined with the aid of the wave plate and found to be parallel/perpendicular to the LB dipping direction (high index parallel to the dipping direction.) Optical retardation values were measured at individual points throughout the film and then used to calculate the size of the \textit{in-plane} birefringence at 23 °C and 550 nm. The birefringence was found to be of magnitude 0.56 and constant across the film. SC films showed no evidence of \textit{in-plane} anisotropy.

Upon cooling the film to -180 °C followed by heating to 30 °C, the film was found to exhibit uniform optical retardation. However, when heated to 50 °C under a constant flow of N\(_2\), complete extinction occurred in the film. As the stage was rotated through 360 °, only a dark field of view was observed,
indicating a loss of anisotropy. This behavior can be attributed to the loss of in-plane anisotropy in the film, and has been linked to alkyl chain melting processes.\textsuperscript{105}

3.9 Ellipsometry

Spectroscopic ellipsometry measures the change in the polarization state as well as the intensity of light reflected from the surface of a film to provide information regarding film thickness and index of refraction. The relative phase change ($\Delta$) and the relative amplitude change ($\Psi$) introduced by reflection from the surface (the quantities determined by an ellipsometer) are related to the values of the measurable quantities in this experiment ($I_s(4)$ and $I_c(5)$). These variables are related to the ratio of Fresnel reflection coefficients, $R_p$ and $R_s$ for $p$- and $s$-polarized light and therefore to the refractive index.

In order to extract physical parameters of the sample such as optical constants, $I_s$ and $I_c$ are plotted versus the wavelength. Then an optical model describing the sample structure that accounts for all the layers in the sample is created. Theoretical data from the optical model that corresponds to the experimental data are generated. The generated data are then compared to the experimental data and the parameters in the optical model are varied to try to produce a "best fit" to the experimental data. Regression algorithms are used to vary the unknown parameters and minimize the difference between the generated and experimental data. Data fitting consists of minimizing the mean-
square deviation $\chi^2$ (here referred to as $T^2$) between calculated and measured ellipsometric parameters $\Delta$ and $\Psi$.\textsuperscript{106}

$$T^2 = \sum_{i=1}^{l} \sum_{j=1}^{M} \left[ \left( \Psi_{\text{calc}}(\lambda_i, \varphi_j) - \Psi_{\text{measure}}(\lambda_i, \varphi_j) \right)^2 
+ \left( \Delta_{\text{calc}}(\lambda_i, \varphi_j) - \Delta_{\text{measure}}(\lambda_i, \varphi_j) \right)^2 \right] / (2N - P - 1) \tag{69}$$

where the sum is taken over all measured wavelengths ($\lambda_i$) and angles of incidence ($\varphi_j$); $P$ is the number of unknown material parameters and $N$ is the number of experimental data points. The closer the mean square error is to zero, the less error there is between the calculated and measured ellipsometric parameters.

Figure 50 shows the ellipsometric data as well as the best fit to this data assuming a simple model for the film. The model consists of a bottom layer assumed to be a layer of voids (if the substrate or layer are assumed to be porous, void space is treated like a chemical material). Above this layer was placed a 0.2 mm-thick SiO$_2$ layer. The optical parameters associated with these layers were provided with the analysis software and were not varied. In order to account for in-plane film birefringence, the program requires a layer of polymer to be placed on top of the SiO$_2$ with three orthogonal indices of refraction, two for the in-plane axes and one for the out-of-plane axis. Twenty-six parameters are varied to obtain the fit. The first is the total thickness of the three layers. An initial guess value of the thickness was that measured from a multilayer PTHPU DT LB film via AFM. Eight parameters corresponding to the dispersion equation are used to fit each orthogonal index of refraction, for a total of twenty-
four parameters. The angle of incidence is the final fitting parameter that is varied. Varying the angle of incidence changes the reflectance, and path length of the film. Since some samples are more sensitive at certain angles of incidence, the sensitivity of the sample can be maximized by varying the incident angle. While the number of parameters in this fit may seem excessive and could potentially lead to erroneous results, the fitting procedure is subject to several constraints, including the positions and intensities of electronic resonances appearing in the real and imaginary parts of each of the refractive index components. The resulting data is also checked in order to confirm that it is physically reasonable and is consistent with results obtained from polarized light experiments. The wavelength dependence is determined via the instrument monochromator. A more detailed description of the model, the dispersion equation used to fit the data and the fitted parameters is included in Appendix V.

The film thickness associated with the best fit is found to be 249 ± 23 nm which is compatible with the experimentally determined thickness of 225 ± 15 nm, for a 150-layer LB film determined by scratching the film and measuring the depth of the scratch with an AFM. The data fit well over the entire spectral range by this simple model.
**Figure 50:** $I_s$ (blue squares) and $I_c$ (red squares) vs wavelength (nm) for a PTHPUDT LB film and their fits, $I_s$ (blue line) and $I_c$ (red line).

From this model, the imaginary ($\kappa$) and real ($\eta$) parts of the refractive index along the *in-plane* directions (arbitrarily assigned as $x$, $y$), and along the surface normal ($z$) are determined (Figure 51, Figure 52). From this, the resulting *in-plane* film birefringence is determined. The value of the birefringence at 532 nm obtained from the ellipsometry measurements is found to be $\sim0.51$, in very good agreement with the value obtained from the polarized light microscope using a green filter.
Figure 51: The imaginary part of the refractive index ($\kappa$) as a function of wavelength along the $x$-direction (red), $y$-direction (green), and $z$-direction (purple). The $x$-direction corresponds to the dipping direction. The in-plane refractive index (blue) and the overall fit for the imaginary part of the film refractive index (black) are plotted as a function of the wavelength.
Figure 52: The real part of the refractive index ($\eta$) as a function of wavelength along the x-direction (red), y-direction (green), and z-direction (purple). The x-direction corresponds to the dipping direction. The in-plane refractive index (blue) and the overall fit for the real part of the film refractive index (black) are plotted as a function of the wavelength.

The absorption and dispersion curves correspond to the imaginary and real parts of the refractive index. The real part of the refractive index decreases near the peak of the absorption and begins to increase again on the higher energy side of the peak (black curve in Figure 52). In the regions of the spectrum where the material does not absorb, the real part of the refractive index increases with the frequency.

The microscopic molecular properties of the polymer can be related to the macroscopic film properties through the refractive index, film polarizability and density using the Lorentz-Lorenz equation (9). The in-plane birefringence contains information about how the polymer has oriented in the film and about
the polarizability of the molecule. In Figure 51, the wavelength of maximum absorption ($\lambda_{\text{max}}$) along the x-direction is $\sim$560 nm, along the y-direction is $\sim$470 nm, and along the z-direction is $\sim$505 nm. For the overall fit for the film, the $\lambda_{\text{max}}$ is 540 – 560 nm, consistent with polarized light experiments in Section 3.6. The $\lambda_{\text{max}}$ in the x-direction implies that this direction is parallel to the dipping direction and that the alkyl chains from segments of polymers with greater conjugation lengths are preferentially oriented along this direction. It is well known that polythiophene is more polarizable along its thiophene backbone than in any other direction. This would mean that along the x-direction there should be a larger polarizability and a correspondingly greater index of refraction. The data are consistent with this view and shows an approximately 30% larger index of refraction in the x-direction as compared with the y-direction, consistent with polarized light microscopy experiments in the absence of a polarizer.

3.10 X-ray Diffraction

The results of our X-ray analysis of a 100-layer LB film of PTHPUUDT are shown in Figure 53. The XRD pattern shows the existence of three peaks appearing at 2.93°, 5.87°, and 8.97°. These have been assigned to the first-, second-, and third-order peaks of the repeating interlayer spacing.
Figure 53: X-ray diffraction pattern from a 100-layer PTHPUDT LB film. The inset shows a magnified image of the (002) and (003) peaks in the film.

The XRD pattern of a SC film of equivalent thickness shows three peaks at 2.81°, 5.81°, and 8.65° (Figure 54). These peaks represent a \( d \)-spacing normal to the surface of the substrate. It is worth noting that much thicker, heat-treated SC films have shown up to sixth-order diffraction peaks, as well as peaks at 19.5° and 23° resulting from chain crystallization and \( \pi \)-stacking, respectively.
The similarity of the XRD patterns for the LB and SC films might imply that the films possess the same molecular architecture. However, heat-treatment studies show vastly different pre- and post-heating behaviour. Figure 55 shows the XRD of the LB film before and after heat-treatment. Note the disappearance of the second- and third-order peaks. In contrast, Figure 56 shows that heat-treating a SC film of equivalent thickness leads to the appearance of up to fifth-order peaks and a $\pi$-stacking peak. The substantially different XRD patterns of the heat-treated films imply a different architecture.
Figure 55: X-ray diffraction pattern from a 100-layer PTHPUDT LB film before heating (blue trace); room temperature diffraction pattern after heating at 50 °C for 20 minutes under vacuum (red trace). The inset shows a magnified image of the (002) and (003) peaks in the film before heating.
Figure 56: X-ray diffraction pattern from a SC film of PTHPUDT before heating (blue trace); room temperature diffraction pattern after heating at 50 °C for 20 minutes under vacuum (red trace). *Much thicker, heat-treated SC films have shown a peak at 23° resulting from π-stacking.

Assuming an all trans, fully extended side chain with adjacent thiophenes possessing coplanar conformations, the theoretical interlayer spacing of PTHPUDT is computed to be 42 Å. This is considerably larger than the observed experimental interlayer spacing of ~30 Å. Interdigitation of the THP containing side chains would be unexpected due to the 5.1 Å diameter of the THP moiety. Rather, the interlayer d-spacing in the LB film is more likely a reflection of the bilayer repeat distance and is consistent with the interlayer spacing obtained from ball-and-stick models where each thiophene unit has its THP containing side chain oriented in the same direction, while the thiophene backbone remains planar and parallel to the substrate (Figure 57). Note that such a film structure would not be expected to give rise to a π-stacking
diffraction peak since $\pi$-stacking would only occur between adjacent thiophene planes in each bilayer and no extended order at this length scale would develop.

![Diffraction peak diagram](image)

**Figure 57:** The experimentally determined architecture of an LB film of PTHPUDT on a hydrophobic substrate

It is worth noting that previous work on RR, amphiphilic PTs has shown *edge-on* conformation of the thiophene chains with respect to the surface. However, these studies have focused on bithiophene-based polymers with a hydrophilic and hydrophobic pendant group on each thiophene sub-unit.$^{35}$
Under these circumstances, it is not altogether surprising that films such as these would yield edge-on architectures. Edge-on architectures in the case of PTHPUDT, however, would provide hydrophilic THP moieties oriented both toward and away from the water surface. Such an orientation of the polymer chain would tend to preclude deposition in the “head-to-head and tail-to-tail” fashion, which produces the Y-type LB film structure observed here.

For the SC film, the $d$ spacing has been previously attributed to the repeat distance between two successive lamellar-type structures with tilted side chains (Figure 58).$^{36}$

![Figure 58: The order found in a SC film of PTHPUDT on a hydrophilic substrate.](image-url)
The different heat-treatment behaviour between the LB and SC films reflects the different architectures that must be present in the films.

3.11 Molecular-Resolution Atomic Force Microscopy

A freshly cleaved sheet of mica (the substrate on which the atomic force microscopy experiments were conducted) was used as a standard to check both the force constant of the cantilever, as well as the operating condition of the atomic force microscope (AFM). AFM studies were subsequently conducted on a 20-layer-thick film of PTHPUDT, LB-deposited onto a freshly cleaved sheet of mica on which one monolayer of ferric stearate had been deposited. Internal sensor images from mica and the LB film are shown in Figure 59. Also shown are the results of a two-dimensional fast-fourier transform (2D-FFT) analysis of each film. A fourier transform converts a function from one representation to another. The FFT algorithm decomposes a function in terms of a sum of sinusoidal basis functions of different frequency. Here, a 2D-FFT is used to help identify elements of surface periodicity. It should be noted that 2D-FFT filtering is often used to eliminate noise from uniform patterned images; however, no such filtering was done in this case, and all of the AFM images shown consist of raw, unfiltered data. The data demonstrate that a hexagonally-packed arrangement was observed for both mica and the LB films, with an experimentally determined lattice spacing of 5.3 Å ± 0.2 Å for mica, consistent with previously published values and 4.6 Å ± 0.6 Å for the LB film. In Figure 59 the LB AFM image is of
the top surface of the film expected to consist of the terminal thiophene groups of PTHPUDT.

**Figure 59:** AFM contact mode internal sensor image of a freshly cleaved sheet of mica (top left), 2D-FFT image of mica (top right), internal sensor image of a 20-layer LB film deposited on a sheet of mica on which one monolayer of ferric stearate has been deposited (bottom left) and a 2D-FFT image of the LB film (bottom right).

In order to confirm that the observed features were real, and not artifacts of the tip, the images were rotated during scanning to make sure the features
moved accordingly. The lattice spacing of both the mica and the LB film were obtained by scanning the films both in the forward (0°) and reverse direction (180°) and then averaging the lattice spacing values obtained from the 2D-FFT of the raw contact mode AFM images. This method helps to mitigate the effects of thermal drift, as well as confirming that the image being obtained is an accurate representation of the surface.

Crystalline domains in fatty acid LB films have been previously observed with molecular resolution AFM.\textsuperscript{108, 109} For example, LB films of cadmium arachidate (Cd\textsuperscript{+2}[CH\textsubscript{3}(CH\textsubscript{2})\textsubscript{18}COO\textsuperscript{-}]\textsubscript{2}) on mica have been shown to possess lattice spacings of 4.6 - 4.8 Å ± 0.2 Å.\textsuperscript{108} In the films of cadmium arachidate, the 4.6 - 4.8 Å distance between nearest neighbours results from a combination of the attractive forces from the packing of the alkyl chains and from the repulsion of the head groups, which results in the observed distances between terminal methyl groups.

The packing in the PTHPUDT polymer film is different from that found in the fatty acids films. The distance between nearest neighbours in the LB film of PTHPUDT is not just due to the packing of the alkyl chains and repulsion of the head groups, but also from the packing of the thiophene subunits, since these subunits are directly connected to each other via covalent bonds. It is these thiophene subunits that are observed in the AFM images in Figure 59. The square drawn in Figure 60 shows the nearest-neighbour distances and next-nearest-neighbour distances measured from Figure 59. This square contains two atoms and, thus, the area per molecule would be half of the area of this
square. The area per molecule derived from the LB AFM images corresponds to \( \sim 16 \text{ Å}^2/\text{molecule} \), consistent with the critical area from the LB isotherm data (18 Å\(^2\)/molecule). Figure 60 shows a cartoon representation of the hexagonal structure that is observed for the LB film of PTHPUDT. To our knowledge, this is the first observation of molecular-resolution AFM of a P3AT polymer showing the ordered terminal thiophene subunits on a mica substrate.

Figure 60: The hexagonal structure extracted from the contact mode AFM image of the LB film of PTHPUDT (left). The 4.6 Å close contact distance results from the alkyl chain packing. A cartoon picture of the hexagonal pattern observed in the AFM image of the PTHPUDT LB film (right).

It was not possible to obtain molecular resolution images from the SC films. SC films of PTHPUDT appeared rougher and showed inhomogeneous defects including aggregations in magnified AFM images.
Reitzel et al.\textsuperscript{35} have previously measured the macroscopic compressibilities of bi-thiophene based regioregular polymers from the negative slope of the Langmuir-Blodgett compression isotherms. These polymers possess a hydrophilic and hydrophobic pendant group on each thiophene sub-unit, leading to an \textit{edge-on} conformation of the thiophene chains with respect to the surface of the LB trough. The macroscopic compressibilities were compared to the microscopic compressibilities obtained from grazing angle synchrotron X-ray diffraction experiments. These diffraction experiments were used to elucidate the \textit{in-plane} structure of the Langmuir monolayer at a surface pressure of 30
mN/m. Their results indicate that the macroscopic compressibility (~4 - 7 m/N) is an order of magnitude larger than the microscopic compressibility (~0.6 m/N). From this result, it was inferred that the crystalline domains on the surface of the trough were separated from one another by amorphous regions. Compression of the monolayer affected mainly the amorphous domain boundaries, while the crystalline domains remained virtually unchanged. Thus, the domain boundaries on the trough are considered soft, while the crystallites are considered hard.

Given the analogous amphiphilic nature of the bi-thiophene based polymers and PTHPUDT on the surface of the LB trough, their regioregularity, comparable molecular weights, and similar $C_{25}^{\infty}$ values, it is reasonable to infer similar structural behaviour on the surface of the LB trough. PTHPUDT LB films are found to have a similar macroscopic compressibility (~6 - 10 m/N). It is possible for similar domains to form in a monolayer of PTHPUDT, and for these domains to compress as the LB tough barriers sweep across the surface.

Reitzel et al.\textsuperscript{35} were unable to image any \textit{in-plane} structure of their one monolayer-thick LB film surfaces with molecular resolution using AFM, rationalized as a result of the disordered state of the terminal alkyl chains. Instead, they used grazing angle synchrotron X-ray diffraction experiments to measure the size of \textit{in-plane} microscopic domains. They obtained a crystallite size corresponding to ~40 Å. We have examined 20-layer PTHPUDT LB films via AFM and obtained molecular resolution images (Figure 59). This indicates that the terminal thiophene groups are ordered. The AFM images of PTHPUDT show that the crystalline domains being imaged are at least the size of the scan
shown in Figure 59 (100 Å x 100 Å). Thus, the domain size is ~2.5 times larger than that obtained by others on RR P3AT polymers.

The differences in the size of the domains may be attributed to epitaxial deposition in the LB film, where each ordered layer deposits in such a manner that it takes on the lattice structure and orientation of the previous deposited layer. The lattice spacing observed in the AFM images suggests there is well-defined order 20-layers from the surface of the substrate, while optical microscopy studies show large uniform domains across the entire substrate. In contrast, Reitzel et al.\textsuperscript{35} measured domain sizes of Langmuir films using XRD studies on a floating monolayer. However, there is inherently more motion associated with the surface of water, than in a deposited film. They have also obtained optical microscopy images of one-monolayer LB films deposited onto hydrophilic substrates. These images show vastly different sized domains separated by cracks. The larger, more uniform domains observed in PTHPUDT LB films suggests a more-ordered structure than that present in other RR P3AT polymers.

### 3.12 Electrical Conductivity

Conjugated polymers (CPs) are known as conducting polymers. The increased conductivity of modern conductive polymers means enough power can be put through light emitting polymer devices at low voltages to generate practical amounts of light. This has led to CPs finding increasing use as the
photoactive and electroactive layers in organic light-emitting diodes\textsuperscript{10} (OLEDs) and flat panel displays, as well as organic field-effect transistors\textsuperscript{11} (FETs).

To investigate the conductive properties of PTHPUOT, electrical conductivity measurements were conducted on LB and SC films of PTHPUOT using both the two- and four-point probe techniques. In order to calibrate our four-point probe experimental setup, the sheet resistance of ITO (a standard) was determined and compared to the value obtained by the supplier. Figure 62 shows Ohmic behaviour of the ITO substrate. This resistance data was used to determine the sheet resistance ($R_{\text{sheet}}$) according to (38). The sheet resistance values we obtained ($4.6 \pm 0.1 \frac{\Omega}{\text{square}}$) were approximately 10\% larger than those from the supplier ($4.2 \pm 0.1 \frac{\Omega}{\text{square}}$).
Figure 62: Voltage (V) vs current (A) behaviour of an ITO substrate.

In its pristine form, PTHPUUDT is expected to be a semiconductor, as discussed in Section 2.2.7.2. By doping the polymer, its conductivity is expected to increase markedly. The conductivity of pristine LB films was too small to be measured. In order to become conducting, the films had to be doped. FeCl$_3$ was dissolved in nitromethane up to a concentration of 0.2 M. The films were doped by immersion into the FeCl$_3$ solution and the reaction was complete in a few minutes (Figure 63). There is a strong likelihood of a charge transfer reaction occurring since the polymer can donate an electron (be oxidized) to FeCl$_3$. 
Figure 63: Schematic representation of the doping process in PTHPUDT with FeCl$_3$.

The normalized UV-vis absorption spectra of a LB film before and after doping are shown in Figure 64. For the LB film of PTHPUDT, the peaks between 500 and 650 nm are attributed to the $\pi - \pi^*$ transition. After doping, there is an onset of two new peaks. The first is near 800 nm and the second is a broad featureless absorption with a maximum at $\sim$1500 nm, in the near IR. These two peaks are believed to be the optically-induced electronic transitions involving charge carrying bipolaronic states.\textsuperscript{110-113} The peaks at 318 nm and 367 nm correspond to the absorption of FeCl$_4^-$, the counter-anion of doped polymers.\textsuperscript{51-53} The polymer possesses a smaller absorbance in the visible region of the spectrum after doping. The decrease in the absorption in the visible region can be attributed to the chemical reaction of the polymer with the dopant.\textsuperscript{114} (Figure 63)
Figure 64: The change in absorption profile from before doping (black squares) to after doping (red squares). The appearance of a broad peak in the near IR after doping is shown in the inset.

The optical properties of the film before and after doping are summarized in Table 3. All of the traces have been normalized to the pristine LB film before doping. The films exhibit similar transmittances at 400 nm, while at 700 nm the oxidized film has a larger absorption. The pristine polymer is pink/purple in colour, while after doping, it becomes bluish/grey. The location of the peaks in the UV-vis spectra and the colour of the films before and after doping are consistent with previously published results on films of P3HT.36
Table 3: Optical properties before and after doping an LB film of PTHPUDT with FeCl$_3$.

<table>
<thead>
<tr>
<th></th>
<th>%T (at 400nm)</th>
<th>%T (at $\lambda_{\text{max}}$)</th>
<th>%T (at 700nm)</th>
<th>Color</th>
</tr>
</thead>
<tbody>
<tr>
<td>neutral neutral</td>
<td>74</td>
<td>0</td>
<td>95</td>
<td>pink/purple</td>
</tr>
<tr>
<td>oxidized</td>
<td>60</td>
<td>71</td>
<td>58</td>
<td>blue/grey</td>
</tr>
</tbody>
</table>

The conductivity of the doped film was then measured with the four-point probe apparatus. There was good Ohmic contact between the probes and the film as can be seen from the linear voltage versus current profile of Figure 66. The average resistance was measured both parallel and perpendicular to the dipping direction across the whole film. The resistance was $\sim$20 % greater in the direction parallel to the dipping direction than perpendicular to it (Table 4). This also means that the conductivity is $\sim$20 % greater in the perpendicular direction than in the parallel direction. This observation is consistent with the polarized light experiments that showed a greater absorption parallel to the dipping direction, explained due to the polymer backbones being primarily oriented in this direction (Figure 44). The proposed mechanism for conduction is by charge hopping between different polymer chains, where an electron can jump between localized states on adjacent polymer chains.$^{49}$ This hopping must occur to a greater extent perpendicular to the chains, that is, in the direction perpendicular to dipping (Figure 65).
Figure 65: Charge hopping parallel and perpendicular to the dipping direction.
Figure 66: Voltage (V) vs current (A) behaviour of an LB film doped with FeCl₃.

Table 4: Anisotropic conductivity in 100-layer LB films of PTHPUDET doped with 0.2 M FeCl₃ in nitromethane.

<table>
<thead>
<tr>
<th></th>
<th>Avg R (Ω)</th>
<th>Thickness (m)</th>
<th>CFₐ</th>
<th>CFm</th>
<th>Rs (Ω/square)</th>
<th>ρ (Ωm)</th>
<th>σ (S/cm⁻¹)</th>
<th>% Difference</th>
</tr>
</thead>
<tbody>
<tr>
<td>Perpendicular</td>
<td>13115</td>
<td>0.0000001</td>
<td>4.5324</td>
<td>1</td>
<td>59443</td>
<td>0.0059</td>
<td>1.7</td>
<td>18</td>
</tr>
<tr>
<td>Parallel</td>
<td>15756</td>
<td>0.0000001</td>
<td>4.5324</td>
<td>1</td>
<td>71415</td>
<td>0.0071</td>
<td>1.4</td>
<td></td>
</tr>
</tbody>
</table>

The two-point probe technique was also used to measure the conductivity of the LB and SC films. The substrates used in this experiment were glass microscope slides onto which a 20 nm-thick layer of gold had been evaporated. The surface was scratched with a razor blade to provide a channel onto which the polymer could be deposited. The resistance of the gold film measured with the two probes on the same side of the scratch was ~17 Ω ± 2Ω. However, with the two probes on either side of the scratch, an infinite resistance was measured meaning that there was no contact between the probes. The conductivity of LB
and SC films were investigated following deposition onto scratched substrates and doping with iodine vapour. The Ohmic nature of the film was confirmed upon observing a linear voltage versus current relationship. Finally, the conductivity of the films was determined and plotted as a function of the time following dopant introduction (Figure 67). The time it takes for the “onset” of the conductivity is a reflection of how long it takes the iodine vapour to interact with the film. Once the film became conductive it maintained this level of conductivity for the duration of this experiment (20 minutes). The film also changed colour from pink/purple to grey upon interaction with iodine vapour. Since the two-point probe technique is not expected to be as accurate as the four-point probe method, only the order of magnitude and relative conductivity values obtained were considered relevant. The conductivity of 100 % RR P3HT was measured in the same way and compared to literature values\textsuperscript{115} as a standard (Table 5).
Figure 67: Conductivity (S/cm) vs the time (seconds) after the addition of dopant. The red line corresponds to the SC film, while the blue line corresponds to the LB film.
Table 5: The doped conductivity (S/cm) and sheet resistance ($\frac{\Omega}{\text{square}}$) for P3HT and PTHPUDT films. a) literature value$^{115}$, b) using the two-point probe, c) using the four-point probe, d) measurement parallel to the dipping direction, e) measurement perpendicular to the dipping direction.

<table>
<thead>
<tr>
<th>Polymer</th>
<th>Conductivity (S/cm)</th>
<th>Sheet Resistance ($\Omega$/square)</th>
</tr>
</thead>
<tbody>
<tr>
<td>P3HT$^a$</td>
<td>110</td>
<td></td>
</tr>
<tr>
<td>P3HT (SC)$^b$</td>
<td>100</td>
<td></td>
</tr>
<tr>
<td>PTHPUDT (SC)$^b$</td>
<td>6</td>
<td></td>
</tr>
<tr>
<td>PTHPUDT (LB)$^b$</td>
<td>2</td>
<td></td>
</tr>
<tr>
<td>PTHPUDT (LB)$^{c,d}$</td>
<td>1.4 ± 0.3</td>
<td>71400 ± 7140</td>
</tr>
<tr>
<td>PTHPUDT (LB)$^{c,e}$</td>
<td>1.7 ± 0.4</td>
<td>59400 ± 5140</td>
</tr>
</tbody>
</table>

The conductivity values of P3HT from literature$^{115}$ and the value from the two-point probe method are quite close. It should be noted that the conductivity values for PTHPUDT are about two orders of magnitude smaller than those obtained for P3HT. As previously discussed in Section 2.2.7.2, conjugated polymers, when processed from solutions, form complicated structures where ordered microcrystalline domains are rooted in an amorphous environment. In this environment the charge transport is limited by the most difficult hopping processes and is therefore dominated by the disordered matrix resulting in low charge carrier mobilities.$^{29}$ Previous studies on the charge transport of P3HT FET structures have shown a two order of magnitude higher mobility when the polymer is highly RR and the $\pi - \pi$ stacking direction (010) corresponds to the in-plane direction rather than when the polymer is less RR and the (010) direction is normal to the film (Figure 29).$^{29}$
In the X-ray diffraction image plate intensity pattern of spin-cast RR P3HT, fifth-order peaks normal to the substrate are observed, which we attribute to the distance between two successive lamellar-type structures (Figure 68). Parallel to the substrate are peaks ascribed to $\pi-\pi$ interactions. The observed large in-plane FET mobility in P3HT reflects the efficient $\pi-\pi$ transport between different polymer chains.\textsuperscript{29}

Figure 68: The XRD pattern for RR P3HT spin-cast onto a glass microscope slide (top left). The (001) direction is normal to the substrate, while the (010) direction is parallel to the substrate.

The XRD image plate intensity pattern of a 100-layer LB film of PTHPUDT is shown in Figure 69. In order to obtain this pattern, we rocked the sample in order to remove any peaks resulting from reflections from the glass substrate.
As a result, the intensity spreads out normal to the substrate. The most intense spot nearest the surface is not due to the sample but is attributed to the direct beam hitting the image plate. Third-order peaks are observed normal to the substrate, consistent with the spacing of a bilayer type structure. In contrast to P3HT, no peaks ascribed to $\pi-\pi$ interactions parallel to the substrate are observed. The lower conductivity of PTHPUDT may result from its limited in-plane $\pi-\pi$ interactions.

Figure 69: The XRD pattern for RR PTHPUDT on deposited on a hydrophobic glass microscope slide (top left). The (001) direction is normal to the substrate, while the (010) direction is parallel to the substrate.
It is not altogether surprising that the conductivity of PTHPUDT is smaller than that of P3HT. In PTHPUDT, the charge transport does not occur via $\pi-\pi$ interactions. Charge transport along the alkyl chain is improbable because of the large 3 nm bilayer distance. The ordered architecture present in the LB films appears to present an inherent barrier to charge transport. In spin-cast films of P3HT, the most difficult hopping processes limit charge transport. Charge hopping can occur from domain to domain, with the conductivity limited by the amorphous areas between the domains.

The values for the conductivity of the LB and SC films of PTHPUDT using the two-point probe are essentially the same, within experimental error. This result is surprising in that the X-ray diffraction pattern of the SC film has shown a $\pi$-stacking peak, whereas that particular peak is absent in the LB film’s diffraction pattern. The $\pi-\pi$ stacking direction in SC films of PTHPUDT (010) corresponds to the same in-plane direction as discussed previously for the P3HT FET structures exhibiting large mobilities. The conductivity of the PTHPUDT SC films is therefore attributed to the same $\pi-\pi$ transport mechanisms observed in SC P3HT films. The absence of a $\pi$-stacking peak in the diffraction pattern of PTHPUDT LB film means that the conductivity is not due to $\pi-\pi$ transport. It may be that the limited charge transport in these films is due to charge hopping between chains.

The four-point probe measurements on the LB films are also very close but do show a directional dependence consistent with our previous optical microscopy observations presented earlier (Section 3.6). However, the two- and
four-point probe experimental values should not be directly compared. Since the two methods use different dopants, either iodine vapour or FeCl$_3$, it is not possible to rule out what effect, if any, the nature of the dopant has on the conductivity.

3.13 Conclusions

The structure/property relationships of Langmuir-Blodgett and spin-cast films are compared using PTHPUDT as a model polymer system because of its amphiphatic balance at the air-water interface. Our data suggest that the thiophene backbone of the polymer lies parallel to the surface with its pendant alkyl groups oriented normal to the surface. This contrasts with other regioregular bithiophene-based amphiphilic PTs that possess a hydrophilic and hydrophobic pendant group on each thiophene sub-unit, leading to an edge-on conformation of the thiophene chains with respect to the water surface.$^{35}$ LB films constructed from PTHPUDT form highly-ordered multilayer structures. Layer-by-layer deposition affords Y-type architectures that possess considerable in-plane anisotropy as demonstrated by anisotropic optical absorption, emission, ellipsometry, and conductivity measurements. The anisotropy results from a difference in conjugation length with orientation, meaning that alkyl chains from segments of polymers with greater conjugation lengths are preferentially oriented along the dipping direction compared to segments of polymers with shorter conjugation chains.
PTHPUDT LB films are of high optical-quality and show uniform optical retardation over the entire film. The directions of the in-plane birefringence are found to be parallel and perpendicular to the LB dipping directions, with the high index parallel to the dipping direction. Domains at least 1 mm$^2$ in size are observed via optical microscopy. The domains are not separated via cracks, nor is there a distribution of sizes as observed in other RR P3AT systems. The different behaviour is attributed to better ordering in the LB films of PTHPUDT.

PTHPUDT films possess a highly-ordered structure according to XRD measurements. Heat-treatment leads to a reduction in the number of diffraction peaks for the LB film, and the opposite for spin-cast films. This implies that a different architecture must be present in the different deposition methods. A hexagonally packed arrangement is observed via molecular resolution atomic force microscopy. Microscopic domains (100 Å x 100 Å) are observed in a 20-layer LB film, dramatically larger than those observed using XRD studies of a floating monolayer. The differences in the size of the domains is ascribed to epitaxial growth in the LB film, where each ordered layer deposits in such a manner that it takes on the lattice structure and orientation of the previous deposited layer. This leads to well-defined order 20-layers from the surface of the substrate. On the contrary, there is inherently more motion associated with the surface of water, than what is found in a deposited film. The semiconducting LB films become conducting upon doping with FeCl$_3$ or I$_2$. They exhibit anisotropic conductivity consistent with the deposition behavior inferred from optical microscopy observations. The smaller conductivity of PTHPUDT with
respect to P3HT results from the absence of $\pi - \pi$ transport mechanisms. Charge transport along the PTHPUUDT alkyl chain is unlikely on account of the 3-nm bilayer repeat unit distance. Thus, the highly-ordered architecture in the LB films presents an inherent barrier to charge transport.
CHAPTER 4: NONLINEAR OPTICAL SPECTROSCOPY

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The Second Harmonic Generation experiments and results from the first paper and the Z-scan experiments and results from the second paper form the basis of this chapter. J. Mattu conducted the experiments and analyzed the results, while Dr. Johansson assisted with the SHG and Z-scan experimental setup and with the writing of the fitting programs used to interpret the results.

4.1 Optical Second Harmonic Generation

Nonlinear optics describes the interaction of light in nonlinear media in accordance with (39). In most everyday applications, the induced polarization of a material only depends on the electric field strength and the linear susceptibility term. There is always a nonlinear response but it is typically orders of magnitude
smaller than the linear one. Nonlinear effects are typically only observed at very high light intensities such as those from pulsed lasers. Nonlinear optics gives rise to optical phenomena such as SHG, which can be used as a tool to investigate surface and interface structure and to provide information regarding adsorbate orientation.

4.1.1 Experimental Setup

Optical SHG measurements of PTHPUDT deposited onto hydrophobic glass substrates were carried out using the regeneratively amplified output of a mode-locked titanium:sapphire oscillator. A detailed schematic of the setup is shown in Figure 70. The output from a 6 W continuous-wave Nd:YVO$_4$ laser (Coherent, Verdi) was used to pump a mode-locked Ti:sapphire oscillator (Spectra Physics, Tsunami 3960) which produced a 82 MHz pulse train, tunable from 750 to 850 nm. A portion of this pulse train was then amplified in a Ti:sapphire chirped pulse regenerative amplifier (Positive Light, Spitfire) which was itself pumped by an intracavity frequency-doubled, Q-switched Nd:YLF laser (Positive Light, Merlin) operated at a 1 kHz repetition rate. This system can produce 100 fs pulses with energy of 1 mJ, tunable from 750 to 850 nm. Since pulses of such high peak intensity can lead to photochemical damage of the films under investigation, only a fraction (typically < 50 mW) of the available laser power was employed during these studies.

The polarization of the incident pulses was controlled by passing them through a quartz, zero-order, half-wave plate (CVI laser). Finally, the beam was
passed through an interference filter prior to striking the interface of interest in order to filter any second harmonic light that may be generated at previously encountered mirror interfaces or in the quartz half-wave plate.

Figure 70: General description of the experimental setup.

The fundamental and second harmonic light were then passed through a spectral filter to block the fundamental wavelength, then into a Glan-Taylor polarizer (CVI laser) for polarization selection and finally focused onto the
entrance plane of a 0.25 m monochromator (CVI Laser, Digikrom 240). The resultant, spectrally filtered light from the monochromator was collected with a photomultiplier tube (Hamamatsu, R212) whose analogue signal was processed with a boxcar integrator (Stanford Research Systems, SR 245). The signals produced in this way are processed with a computer.

Film nonlinear susceptibility measurements were accomplished on LB-deposited PTHPUDT films using an external reflection geometry. External reflection measurements were made by monitoring the polarized SHG intensity from a 100-layer LB-deposited film as a function of the azimuthal rotation angle ($\phi$) of the sample (Figure 71, Figure 72). Four polarization configurations corresponding to s- and p-polarized input and second harmonic output beam polarizations were implemented ($s_{in}$-$s_{out}$, $p_{in}$-$s_{out}$, $s_{in}$-$p_{out}$, and $p_{in}$-$p_{out}$).

As we previously described in Section 2.2.3, the incident beam of light and the surface normal define a plane called the plane of incidence. The electric field vector of the incident beam ($\vec{E}$) is comprised of two perpendicular components. The component parallel to the plane of incidence is referred to as being $p$-polarized, while the component perpendicular to the plane of incidence is referred to as being $s$-polarized. These waves are referred to as the $p$-wave and $s$-wave. Thus, the various input-output polarization combinations refer to the polarization of the incident and output waves. The $s_{in}$ polarization refers to the input light being polarized perpendicular to the plane of incidence. This causes the dipole moment of the molecules at the interface to oscillate in that direction. The output polarization, $s_{out}$, refers to the oscillating dipoles emitting light
polarized perpendicular to the plane of incidence. As an experimental control we monitored the SHG output from an isotropic film of malachite green (MG) prepared by spin-casting onto a similar substrate (Figure 73). MG is an organic dye that has a known, large second harmonic response. Deposition of the multilayer films for the external reflection SHG studies was accomplished by standard dipping procedures onto microscope slides, as described previously.

Figure 71: A schematic of the x-y-z rotation stage used to control the movement of the film (left) and the relationship between the orientation of the film and the azimuthal rotation angle, $\phi$ (right).
Figure 72: The angles defining the orientation of the molecule with respect to the laboratory frame of reference associated with the deposited molecular film.

Figure 73: The structure of Malachite Green.
4.1.2 Results and Discussion

Optical SHG is a powerful method to probe molecules adsorbed at an interface, and it can be used to determine the orientation distribution of a surface layer of molecules. LB films of PTHPUDT are anisotropic and are expected to possess $C_{1v}$ symmetry. Under these conditions, the polarization dependence of the sample can be related to the ten non-zero tensor elements of $\hat{\chi}^{(2)}_s$ by (70).\textsuperscript{116} A more detailed derivation is shown in Appendix III and Appendix IV.\textsuperscript{117}
\[ s_{on} - s_{out} \]
\[ \hat{X}_{eff}^{(2)} = -\hat{X}_{acc}^{(2)}(\sin^2 \phi)L_y(2\omega)L_y^2(\omega) - 2\hat{X}_{acc}^{(2)}(\cos^2 \phi)(\sin \phi)L_y(2\omega)L_y^2(\omega) \]
\[ - 2\hat{X}_{acc}^{(2)}(\cos \phi)(\sin \phi)L_y(2\omega)L_y^2(\omega). \]

\[ P_{on} - s_{out} \]
\[ \hat{X}_{eff}^{(2)} = -\hat{X}_{acc}^{(2)}(\cos \phi)(\sin \phi)L_y(2\omega)L_y^2(\omega) \cos \theta(2\omega) \]
\[ + 2\hat{X}_{acc}^{(2)}(\sin \phi)(\cos \phi)L_y(2\omega)L_y^2(\omega) \cos \theta(2\omega) \]
\[ - 2\hat{X}_{acc}^{(2)}(\sin \phi)(\cos \phi)L_y(2\omega)L_y^2(\omega) \cos \theta(2\omega) \]
\[ + \hat{X}_{acc}^{(2)}(\sin \phi)L_y(2\omega)L_y^2(\omega) \sin \theta(2\omega) \]
\[ + \hat{X}_{acc}^{(2)}(\cos \phi)L_y(2\omega)L_y^2(\omega) \sin \theta(2\omega). \]

\[ P_{on} - P_{out} \]
\[ \hat{X}_{eff}^{(2)} = \hat{X}_{acc}^{(2)}(\cos \phi)L_y(2\omega)L_y^2(\omega) \cos \theta(2\omega) \cos^2 \theta(\omega) \]
\[ + 2\hat{X}_{acc}^{(2)}(\sin \phi)(\cos \phi)L_y(2\omega)L_y^2(\omega) \cos \theta(2\omega) \cos^2 \theta(\omega) \]
\[ + \hat{X}_{acc}^{(2)}(\sin \phi)(\cos \phi)L_y(2\omega)L_y^2(\omega) \cos \theta(2\omega) \cos^2 \theta(\omega) \]
\[ + \hat{X}_{acc}^{(2)}(\sin \phi)L_y(2\omega)L_y^2(\omega) \sin \theta(2\omega) \cos \theta(\omega) \cos^2 \theta(\omega) \]
\[ + 2\hat{X}_{acc}^{(2)}(\sin \phi)(\cos \phi)L_y(2\omega)L_y^2(\omega)[- \cos \theta(2\omega) \cos \theta(\omega) \sin \theta(\omega)] \]
\[ + \hat{X}_{acc}^{(2)}(\sin \phi)L_y(2\omega)L_y^2(\omega) \sin \theta(2\omega) \cos \theta(\omega) \sin \theta(\omega) \]
\[ + 2\hat{X}_{acc}^{(2)}(\sin \phi)(\cos \phi)L_y(2\omega)L_y^2(\omega)[- \cos \theta(2\omega) \cos \theta(\omega) \sin \theta(\omega)] \]
\[ + \hat{X}_{acc}^{(2)}(\sin \phi)L_y(2\omega)L_y^2(\omega) \sin \theta(2\omega) \cos \theta(\omega) \sin \theta(\omega) \]
\[ + \hat{X}_{acc}^{(2)}(\cos \phi)L_y(2\omega)L_y^2(\omega) \sin \theta(2\omega) \sin \theta(\omega). \]

The constants \( L_y(\omega) \) in (70) are the Fresnel factors at the corresponding frequencies. The calculation of these constants has been outlined for a variety of different experimental geometries, including that of external reflection, the geometry employed for these SH studies. The azimuthal angle \( \phi \) is the angle...
between the plane of incidence and the angle of the $C_{1v}$ axis (Figure 97). By rotating $\phi$ under various polarization conditions, one can extract the individual tensor elements of $\tilde{\chi}^{(2)}$. Once obtained, these values of the macroscopic surface nonlinear susceptibility tensor can be related to the elements of the molecular nonlinear polarizability tensor ($\tilde{\beta}_{ijk}$) to obtain the molecular orientation distribution function. The direction cosines required to evaluate the distribution function can be obtained from the Euler transformation connecting the molecular ($x'y'z'$) and laboratory (xyz) reference frames (Appendix II).

Figure 74 shows the polarized SHG signals from a 100-layer LB film of PTHPUDT and their corresponding best fits to the experimental data assuming the functional dependence described in (70). In this experiment, the SH intensity was monitored as a function of the azimuthal orientation angle of the sample for different input and detected output polarization geometries. Also shown in Figure 74 are the data and best fit curves for an isotropic film of MG. As expected for an isotropic film, the SH data from MG is isotropic in $\phi$. SHG with $s_{in}-s_{out}$ and $\rho_{in}-s_{out}$ geometries is symmetry forbidden in an isotropic film and therefore, generated no detectable signal. It is clear from Figure 74, that SHG from the 100-layer polymer LB film is indeed anisotropic. This is supported by the clear anisotropic nature of the signal as well as the non-zero signal level obtained in the $s_{in}-s_{out}$ geometry. The best fits were determined by a nonlinear least-squares fitting algorithm (Appendix VI) that permitted the extraction of the individual nonvanishing components of the $\tilde{\chi}^{(2)}$ tensor.
Figure 74: Polarized SH intensity vs $\phi$ for an LB film with 100-layers of PTHPUDT deposited onto one monolayer of ferric stearate on a hydrophilic glass slide. The input-output polarization combinations are: $p_{in}-p_{out}$ (top left), $s_{in}-p_{out}$ (top right), $s_{in}-s_{out}$ (bottom left), $p_{in}-s_{out}$ (bottom right). The points represent the collected data. The solid lines represent a nonlinear least-squares best fit to the data. The open diamonds represent data for an isotropic malachite green film SC onto a glass slide. The dipping direction corresponds to 90°.
The $s_{in}$-$s_{out}$ SH signal was fit first to obtain the best fit values of the three elements describing its functional dependence as described in (70). These elements were then held fixed for the fitting of the $p_{in}$-$s_{out}$ curves and so on until all polarization curves had been fitted in succession. The elements of $\chi^{(2)}$ so determined are presented in Table 6 and are used to extract an averaged orientation angle.

**Table 6: Relative susceptibility components.**

<table>
<thead>
<tr>
<th>Relative susceptibility components extracted from the fits to the 200-layer LB film SH data</th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>$\chi_{zzz}$</td>
<td>-0.01</td>
</tr>
<tr>
<td>$\chi_{zzs}$</td>
<td>-3.92</td>
</tr>
<tr>
<td>$\chi_{syy}$</td>
<td>0.15</td>
</tr>
<tr>
<td>$\chi_{sss}$</td>
<td>1.31</td>
</tr>
<tr>
<td>$\chi_{zzz}$</td>
<td>11.29</td>
</tr>
<tr>
<td>$\chi_{yyz}$</td>
<td>1.40</td>
</tr>
<tr>
<td>$\chi_{yyz}$</td>
<td>2.40</td>
</tr>
<tr>
<td>$\chi_{xyz}$</td>
<td>-2.42</td>
</tr>
<tr>
<td>$\chi_{xxz}$</td>
<td>-2.40</td>
</tr>
<tr>
<td>$\chi_{zzz}$</td>
<td>-14.00</td>
</tr>
</tbody>
</table>

As (46) indicates, a complete description of the orientation distribution function also depends on which components of the nonlinear polarizability tensor contribute to the total molecular polarizability. This calculation can be simplified for many molecules by assuming that only one element of the polarizability tensor contributes significantly to the molecular nonlinear response in the UV-visible spectral region. $\hat{P}$ is a tensor that is formed by the direct product of the vectors $r_{ng}$ (transition dipole matrix element between the excited state ($n$) and
the ground state \((g)\) along the molecular \(x'\) axis) and \(\Delta r_n\) (the difference in permanent dipole moment between \(n\) and \(g\)).\(^{67}\) In the case of PTs, the optical properties are governed primarily by the \(\pi\)-electrons in the thiophene backbone and display only one dominant low-energy excited electronic state. The corresponding transition dipole for the \(S_1 \leftrightarrow S_0\) transition is polarized along the \(z'\)-molecular axis and is responsible for the strong absorption of PTs in the vicinity of 400 nm.

Unsubstituted PT is centrosymmetric and one expects no second-order nonlinear response from it unless its polarization is distorted. Substituents added to the PT chain may break this centre of symmetry; however, one expects, at most, a weak second-order nonlinear response. RR PTHPUDT is non-centrosymmetric because of the net orientation of the pendant chain, but, as noted, SH signals from PTHPUDT films are very small. The second-order response likely results from the highly-ordered and anisotropic alignment of molecules in the film, in conjunction with the low energy \(z'\)-polarized transition in near two-photon resonance with our fundamental frequency. Since \(r_{ng}\) and \(\Delta r_n\) are collinear for the case of PTHPUDT, we make the reasonable assumption that only the \(\beta_{zz}\) term contributes significantly to the observed nonlinear response.

Evaluating the product of direction cosines implied by (46), one can derive a relationship describing the averaged orientation within the film.\(^{74}\) Equation (71) describes \(D\), a molecular orientation parameter (\(D = \cos^2 \theta\)), expressed in terms of the experimentally determined susceptibility components:
\[ D = \frac{\hat{\chi}_{zzz}}{\hat{\chi}_{zzz} + \hat{\chi}_{zxx} + \hat{\chi}_{zyy}} \]  

(71)

where \( \theta \) is the angle between the surface normal and the molecular \( z' \) axis (Figure 72).

The agreement between the experimental and fit data is good. However, small differences between the fit and data are apparent in Figure 74 (the \( s_{in}-p_{out} \) curve.) In an attempt to improve the fit for this curve, all of the parameters associated with it were allowed to vary. The fit improved slightly, however, the parameters required for this yielded fits of slightly lower quality for the \( p_{in}-p_{out} \) and the \( p_{in}-s_{out} \) curves. The angle obtained using these parameters was similar to that obtained by our original fitting procedure and was used to provide a measure of the uncertainty in the averaged orientation angle extracted from the fits.

Under these circumstances, (71) dictates that the angle \( \theta \) between the surface normal and the molecular \( z' \) axis is \( -90^\circ \pm 5^\circ \). This is consistent with an orientation in which the thiophene backbone lies parallel to the surface. This orientation correlates well with the experimental observations on the LB films.

It should be noted that in this analysis, we have ignored some aspects of the local field effects. In particular, while we have compelling evidence for film birefringence, we have not formally incorporated this \textit{in-plane} birefringence into our fitting algorithm. While the importance of accounting for the effects of birefringence in SHG analyses in uniaxial systems has been recognized\textsuperscript{120}, the effects of \textit{in-plane} birefringence have not been appropriately addressed.
Knowledge of the interfacial optical constants is critical for relating the macroscopic SHG polarization measurements to the $\chi^{(2)}$ tensor elements describing the nonlinear optical response of the interface. Even subtle differences in the assumed optical constants for the nonlinear optically active interfacial layer can produce substantial changes in the calculated $\chi^{(2)}$ tensor elements describing the surface, and correspondingly, in the interpretation of surface structure.\textsuperscript{121} One approach to evaluate the linear interfacial optical constants is simply to assign the interfacial refractive index to be identical to that of one of the two media at the interface.\textsuperscript{74, 118, 122, 123} However, it is not clear which of the two media should be selected and why one should be preferred over the other. Others have employed models in which the refractive index is intermediary between the two bulk interfacial media.\textsuperscript{124-127} The results obtained using these intermediary approaches appear to be quantitatively reliable. In this regard there are two possible limiting cases.

When the film thickness is far less than the wavelength of light, the effective refractive index for the interfacial layer becomes the average of the two media sandwiching the interface. When the film thickness is on the order of the wavelength of light, as it is in the case of our samples, the effective refractive index for the interfacial layer is the average refractive index within the multilayer film, which we have measured with ellipsometry. Thus, expressions similar to those currently used widely to interpret polarization phenomena in SHG surface measurements are recovered.\textsuperscript{120} Therefore, our analysis is sufficient to capture
the nature of the anisotropy in the film and provide a reasonable estimate of the averaged polymer orientation within the film.

The spectra in Figure 74 can be fit with our model if the polymer index of refraction is taken to be the index of refraction along either a) the x-direction, b) the y-direction, or c) the *in-plane* average at the fundamental and SH wavelengths obtained from the ellipsometry experiments. For case a), where the index of refraction is approximately that of the overall film, the spectra is fit equally as well. For cases b) and c), where the index of refraction is smaller than the average, the angle $\theta$ falls within the range of 55° - 60°. However, this orientation is inconsistent with our other experimental evidence. Thus, our model is flexible enough to allow quality fits over a large range of possible film indices of refraction. However, the model used to analyze this fit either breaks down or is inconsistent with our other experimental evidence at small refractive indices. Our data can be fit well with this simple model and suggests that the thiophene backbone of the polymer lies parallel to the surface with its pendant alkyl groups oriented normal to the surface, consistent with the order of the films previously observed from the LB trough experiments.

### 4.1.3 Conclusions

The polarization dependence of the surface second harmonic response can be used to extract the elements of the second-order nonlinear susceptibility tensor $\chi^{(2)}$ and, therefore, used to obtain orientation information. It is clear from Figure 74 that SHG from the 100-layer LB film is indeed anisotropic. The
experimental data were fit assuming a functional dependence as described in (69) using a nonlinear least-squares fitting algorithm which permitted the extraction of the individual nonvanishing components of the $\chi^{(2)}$ tensor. This fitting program assumes that the optical properties are governed primarily by the $\pi$-electrons in the thiophene backbone, that the transition dipole in the polymer is polarized along the $z'$-molecular axis and that it is responsible for the strong absorption of PTs in the vicinity of 400 nm, and that only the $\beta_{zzz}$ hyperpolarizability term contributes significantly to the observed nonlinear response. We also have not formally incorporated any in-plane birefringence into our fitting algorithm. Even with these assumptions, the experimentally determined susceptibility components when incorporated into (70) dictate that the angle $\theta$ between the surface normal and the molecular $z'$ axis is $\sim 90^\circ \pm 5^\circ$, consistent with an orientation in which the thiophene backbone lies parallel to the surface. This orientation correlates well with the thickness and order of the films we have previously measured. Our simplified analysis sufficiently captures the nature of the anisotropy in the film and provides a reasonable estimate of the averaged polymer orientation within the film.

4.2 Z-scan Technique

The z-scan technique is a simple and sensitive method that can be used to measure both the size and magnitude of the nonlinear index of refraction ($\gamma$) and the nonlinear absorption coefficient ($B$) of a material. As described in
Section 2.2.10, the z-scan method is based upon the $\chi^{(3)}$-related self-lensing (focusing or defocusing) effects that occur when a sample is subjected to high peak intensity light as it is moved through the focus of a laser beam.

4.2.1 Experimental Setup

The third-order nonlinear optical measurements described in this thesis were carried out using the z-scan technique. The experimental setup is shown schematically in Figure 75. For these measurements, the light source was the regeneratively amplified output of a mode-locked titanium:sapphire oscillator. This system is capable of producing 100 fs pulses with energy of 1 mJ, at a repetition rate of 1 KHz and nominal wavelength of 800 nm. Since pulses of such high peak intensity can lead to optical damage of the films under investigation, only a fraction (typically < 1 mW) of the available laser power was employed during these studies. The peak powers and power densities used in these experiments were comparable to those typically employed in z-scan studies. The beam had a Gaussian spatial profile and was focused by a 100 mm- focal length lens. The LB film under investigation was placed in a region far from the waist of the focused beam and moved in the direction of the propagation of light (-z to +z) through the focus (Figure 34). The transmittance of the film was measured with and without a finite aperture in the far field as a function of sample position z. The intensity of the far field laser beam was collected with a photodiode after passing through a 50 mm collection lens. The
LB films of PTHPUVT were deposited onto 0.4 mm-thick glass microscope slides using the LB techniques described previously.

**Figure 75:** Schematic of the Z-scan experimental setup.
4.2.2 Results and Discussion

Prior to measuring the nonlinear refractive index and absorption coefficients of PTHPUDT LB films, our z-scan apparatus was tested and optimized by examining ideal standard samples. First, the effect of aperture size on transmittance was examined by varying the size of the far field aperture while keeping the incident power on a bare 1-mm-thick glass microscope slide constant at 2.5 mW. We observed that with a fully open aperture ($S_a = 1$), the measured transmittance was independent of sample position. However, when the aperture was partially closed, a characteristic dispersion lineshape, symmetric z-scan profile resulted. The closed aperture z-scan traces show a pre-focal valley followed by a post-focal peak, indicative of a positive refractive nonlinearity ($\gamma$ or $\tilde{\varepsilon}^{(3)} > 0$). Figure 76 shows the raw data for a variety of aperture sizes and the best fit line to the data according to (65). The effective peak-to-valley transmittance, $\Delta T_{p-v}$ was found to increase with $S_a$ in accordance with (59):

$$T = 1 + \frac{2(-\rho x^2 + 2x - 3\rho)}{(x^2 + 9)(x^2 + 1)} \Delta Z$$  \hspace{1cm} (65)

$$\Delta T_{p-v} \approx 0.406(1 - S_a)^{0.25} |\Delta Z| \text{ for } |\Delta Z| \leq \pi$$  \hspace{1cm} (59)
Figure 76: Measured z-scan traces of a 1-mm-thick glass microscope slide with a fixed input intensity of 2.5 mW and aperture sizes ($S_a$) of 0.05 (red x's), 0.65 (blue triangles), 0.84 (green +'s), 0.98 (orange squares), and 1 (black circles). The lines represent best fits to the data according to (65). The peak-to-valley normalized transmittance, $\Delta T_{p-v}$, was found to increase in accord with (59).

The dependence of $\Delta T_{p-v}$ on beam irradiance was also investigated by fixing the aperture size ($S_a = 0.4$) and obtaining z-scan traces at various incident powers. For these studies, both closed and open aperture scans were performed on a bare 0.4 mm-thick glass microscope slide. The open aperture trace in Figure 77 shows no response, indicating that at the intensities employed,
there were no observable nonlinear absorption or saturation effects. A series of closed aperture scans were obtained at different incident beam intensities. The resulting z-scan traces were fitted to (65) and the magnitude of $\Delta T_{p-w}$ was found to depend linearly on the incident power (inset in Figure 77). As described previously, fitting (65) in the absence of nonlinear absorption effects, allows one to extract the radius of the beam at the beam waist ($\omega_0$). In this way best-fit curves to the data obtained for the 0.4-mm-thick glass slide gave a beam radius of $13 \pm 1 \mu m$. Following the analysis procedure described earlier, we found the 0.4-mm-thick glass slide to have $\chi^{(3)} = 3.1 \times 10^{-11}$ esu $\pm 6.2 \times 10^{-12}$ esu. The corresponding value of the nonlinear index ($\gamma$) is close to some of the smallest reported values found in solid media, at only $2.8 \times 10^{-18}$ m$^2$/W$^{131}$ It should be noted that the 0.4-mm-thick glass microscope slides examined here were subsequently employed as the substrates for deposition of the PTHPUDT LB films. At the considerably lower laser powers employed for examination of the LB films, both the closed and open aperture z-scan traces of the substrates showed no response.
Figure 77: Measured z-scan trace of a 0.4-mm-thick glass microscope slide with a fixed aperture size ($S_a = 0.4$) and an incident intensity of 1.1 mW. Closed aperture scan (red circles), open aperture scan (blue circles) and their best fits (solid lines) as described in the text. The dependence of $\Delta T_{p-v}$ on the incident power is shown in the inset.

Figure 78 shows the closed and open aperture z-scan traces from a 200-layer PTHPUDT LB film obtained at an incident laser power of 0.17 mW. The closed aperture trace of the polymer film shows a pre-focal transmittance maximum (peak) followed by a post-focal transmittance minimum (valley), indicative of a negative refractive nonlinearity ($\gamma$ or $\chi^{(3)} < 0$). As shown in the inset of Figure 78, the magnitude of $\Delta T_{p-v}$ of the polymer thin film is also linearly dependent on the incident laser power up to a power level of ~0.20 mW (see
below). Analysis of the peak-to-valley transmittance data obtained for the polymer film gives \( \chi^{(3)}_R = -1.2 \times 10^{-8} \) esu \( \pm 2.4 \times 10^{-10} \) esu, approximately two orders of magnitude larger than that of the bare substrate, with opposite sign. Open aperture z-scan traces obtained at these incident powers showed the presence of a small feature at \( z = 0 \) with an increase in normalized transmittance, indicating the presence of saturable absorption effects at this wavelength. This observation is consistent with the strong linear absorption band of PTHPUDT in the vicinity of 400-500 nm, in approximate two-photon resonance with the 800 nm incident wavelength used for these studies. As described, fitting the open aperture trace to (63) and (64) gives \( \chi^{(3)}_J = -3.5 \times 10^{-11} \) esu \( \pm 7 \times 10^{-12} \) esu.
Figure 78: Measured z-scan trace of a 200-layer PTHPUDT film at an incident power of 0.17 mW with a fixed aperture size of $S_a = 0.4$. Closed scan (red circles), open scan (blue circles), and their best fits (solid lines). The dependence of $\Delta T_{p-v}$ on the incident intensity is shown in the inset. Prolonged exposure with greater than $\sim 0.20$ mW results in a $\Delta T_{p-v}$ that is independent of incident power.

At incident laser powers in excess of 0.2 mW, the behaviour of the z-scan traces display markedly different characteristics. The observed behavior was intensity and exposure-time dependent and consistent with an irreversible, nonlinear phenomenon. Repeated z-scan measurements of the same sample spot with the same incident intensity resulted in consistent changes in the peak-to-valley transmittance profile. Sequential z-scans obtained under identical conditions witnessed a growth in peak-to-valley transmittance and the onset of increased asymmetry with each z-scan. Prolonged exposure of the films to these
intensity levels ultimately led to saturation of the z-scan traces, after which no further changes were observed. Representative changes of this type (in this case initiated with an incident power of 0.23 mW) are illustrated in Figure 79. The nonlinear dependence of these effects on incident intensity was confirmed by various exposure experiments. It appeared that the changes in the z-scan profiles were correlated with the length of time spent in the focal region. Long exposure times at sample positions far from the focal region led to no evolution in the z-scan profiles, whereas even very short exposures in the high-intensity focal region led to rapid evolution and saturation of the effects.
Figure 79: Repeated z-scan traces of the 200-layer PTHPUDT film obtained at constant incident power of 0.23 mW and aperture size $S_a = 0.4$. First scan (red squares), second scan (blue diamonds), third scan (green triangles), fourth scan (orange circles), and fifth scan (black dashes). The lines between data points are to guide the eye. The inset shows the growth of the peak and shoulder in the open aperture scans (see the text). First scan (red squares), third scan (green triangles), and fifth scan (black dashes). Other scans are omitted for clarity. Closed aperture followed by open aperture scans were obtained alternately.

After saturation, the signature z-scan pre-focal peak and post-focal valley remain, however, the z-scan profiles show a large degree of asymmetry. This asymmetry is observed in both the closed and open aperture scans and appears as a shoulder to the main pre-focal peak. The position of this shoulder is the same in both the open and closed scans. Following the onset of these intensity dependent effects, the magnitude of $\Delta T_{p-r}$ was found to be independent of the incident power (see inset of Figure 78). Indeed, even when the incident power
was decreased by orders of magnitude, the z-scan profile and the magnitude of
the peak-to-valley transmittance remained unchanged. These observations
suggest that following this level of irradiation, the observed z-scan traces are no
longer attributable to the $\chi^{(3)}$-based self-lensing effects described earlier.
Rather, they are likely the result of nonlinear photoinduced effects within the
polymer film.

To examine more closely the effects of the laser beam on the polymer
films at both low and high powers, we analyzed a large area spot following
exposure under conditions of comparable peak power to those found at the beam
focus. Even under low peak power conditions, well below those required to
observe any nonlinear response from the film, exposure of the pristine
pink/purple polymer film resulted in a colour change to yellow. Subsequent
analysis of the photoexposed film showed that its wavelength of maximum
absorption shifted from 550 nm to 406 nm upon irradiation. Thus, it appears that
our earlier analysis of the z-scan measurements of the polymer film was more
accurately a reflection of a photoconverted polymer film and that at the intensities
required to observe any self-lensing effects from the pristine polymer,
photoconversion of the pristine PTHPUDT film has already occurred.

To determine whether photoconversion may have occurred in the LB films
during the SHG experiments, the irradiance of the beam was calculated and
compared to that found under the lowest peak power conditions used in the z-
scan experiments. The irradiance for the SHG experiment was 20 x smaller than
that found at the focus during the z-scan experiments. It should also be noted
that in the SHG experiments the sample position was fixed far from the focus, as opposed to the z-scan experiments where the sample was made to pass through the focus. In addition, no colour change or sample damage was observed after exposure to the laser in the SHG experiments.

The same experiment was repeated with an 80-layer LB film exposed at comparable peak intensities to those found at the z-scan focus with a 0.23 mW laser beam (i.e. those in the high power regime employed to obtain Figure 79). Surface profile measurements of the photoexposed region indicated that material had been removed from where the beam was incident on the film. This hole (Figure 80) was found to be over 50 nm in depth on a film whose thickness was 120 nm ± 5 nm. Local heating of the film at the focus, due to two-photon absorption (2PA) may result in the melting of the polymer, causing subsequent resolidification away from the beam spot. This may lead to the formation of the areas of higher elevation (50 - 60 nm wide) surrounding the perimeter of the beam spot, as is clearly visible in Figure 80. Other spots that had been exposed for either a longer period of time, or with a more intense beam, showed near total removal of the film.
Figure 80: Surface profilometer scan of the photoirradiated region of an 80-layer PTHPUDT LB film showing the region of film removal. The incident power was 0.23 mW and corresponds to the same incident power as that used to obtain Figure 79.

Previous work performed on thin copper-doped silica films has shown that it is possible to obtain data that closely resembles typical results for z-scan measurements, but which actually arise from linear optical effects caused by sample removal. These studies have shown that ablation of material from a thin film can result in a lensing effect similar to that of a diverging lens, which can produce a z-scan signal similar to a material with a negative refractive index. The removal of material effectively results in a local aperture in the sample, the Fourier components of which can give rise to dispersion-type line shapes in the
far field. This phenomenon would explain why following prolonged exposure to intensities greater than \( -0.20 \) mW, either increasing or decreasing the incident intensity still results in traces that show the usual z-scan peak-valley shape for a material with a negative refractive index, but with no change in the magnitude of the transmittance. It is interesting to note that while these linear aperture effects due to sample removal would be expected to give rise to symmetric z-scan traces (i.e. Fourier components appearing on both sides of the beam focus), the traces obtained following prolonged exposure consistently and reproducibly show substantial asymmetry. It is possible that the observed asymmetry results from an imperfect, non-Gaussian beam profile or beam astigmatism effects. Nevertheless, under the prolonged exposure conditions employed here, there is clear evidence of sample removal.

Our results indicate a substantial interaction of the PTHPUDT thin films with the incident probe radiation. Previous work on the solid state photochemistry of PT and other CPs has shown that polymer films can undergo simultaneous irreversible photobleaching, cross-linking, and chain scission when irradiated in air with UV or visible light. Indeed, the photochemically induced insolubilization of these systems has been exploited in order to pattern them via photolithographic techniques for device applications. In the case of P3ATs, the mechanism of cross-linking was found to proceed via classical photooxidation pathways, involving free radical chain reactions initiated by photolysis of residual iron impurities. Photobleaching appears to be the result of photosensitization and reaction with singlet oxygen. Photobleaching in P3ATs including P3HT is
observed to result in a loss of \( \pi \)-conjugation, a blue-shift in the absorption spectrum of the polymer and a decrease in its optical density, attributed to disruption and shortening of the \( \pi \)-conjugated segments.\(^6\) Our results regarding the colour change and shift in absorption maximum from 550 nm to 406 nm upon exposure of PTHPUDT films are consistent with these observations.

Fourier transform infrared spectroscopy (FTIR) measurements were also used to compare the pristine pink/purple PTHPUDT film with the resulting photoirradiated (yellow) product Figure 81. Upon irradiation, the intensity of the bands at 2934 and 2856 cm\(^{-1}\), attributed to the aliphatic CH's of PTHPUDT's long alkyl chains, decreased with exposure time. Simultaneously, a broad signal attributed to \((-\text{OH})\) functionalities at \(~3400\text{ cm}^{-1}\), as well as a peak at 1735 cm\(^{-1}\) attributed to C=O stretching, appear. These observations are consistent with the spectral changes observed following exposure of P3ATs to UV or visible light in air.\(^{133}\) In this previous report, the appearance of the carbonyl stretch is accompanied by the growth of bands at 1610 cm\(^{-1}\) (C=C stretch) and an intense band at 1045 cm\(^{-1}\), thought to arise from C=S\(^+\)-O\(^-\) residues that result from the 1,4 Diels-Alder addition of photosensitized singlet oxygen to thienyl groups in the main polymer chain. Interestingly, our observations on the photoexposure of PTHPUDT films in air show the growth of the carbonyl feature and that attributed to the C=C stretch; however, we observe no growth of an intense band in the vicinity of 1045 cm\(^{-1}\). This notable difference may be attributed to different photochemical pathways available in PTHPUDT or to the unique and highly-ordered structure of the PTHPUDT LB films.\(^{37}\) Nevertheless, our observations
regarding the electronic spectral shifts and changes in the FTIR spectra of the irradiated PTHPUDT films, provide strong evidence for their photochemical transformation.

![FTIR spectra of 100-layer PTHPUDT LB films (blue trace) and the photoirradiated product (red trace). The traces have been offset for clarity.](image)

**Figure 81:** FTIR spectra of 100-layer PTHPUDT LB films (blue trace) and the photoirradiated product (red trace). The traces have been offset for clarity.

Our z-scan measurements indicate that at the intensities required to observe any self-lensing effects from the pristine polymer, photoconversion of the PTHPUDT film is prevalent. Analysis of the resulting z-scan traces yielded values of $\chi^{(3)} = -1.2 \times 10^{-9}$ esu and $\chi^{(3)}_{i} = -3.5 \times 10^{-11}$ esu. These values appear to be consistent with many previous determinations of the third-order nonlinear susceptibilities of PT-based systems which range typically from $10^{-8} - 10^{-12}$ esu, depending upon the particular polymer studied, the experimental method
employed as well as the particular conditions (e.g. resonant or nonresonant) of the experiment. It is worth noting that in at least one example, application of the z-scan technique with a HeNe laser yielded extraordinary values of \( \hat{\chi}_R^{(3)} = -9 \times 10^{-4} \) esu and \( \hat{\chi}_I^{(3)} = -2 \times 10^{-4} \) esu, leading the authors to infer that the origin of the exceptionally high values were thermal, leading to subsequent structural changes in the polymer.\(^{22}\)

The results of our experiments clearly have bearing on past attempts to determine the third-order nonlinear optical response of PT-based systems. While our results pertain specifically to PTHPUDT, the observation of photoinduced chemical changes, and their similarity to those observed in the broader class of PT-based polymers, leads one to question whether the previously reported values of the third-order nonlinear susceptibilities reflect properties of the polymers in question, or their photochemical products. In addition, the observation of linear optical effects due to sample removal and hole burning that appear similar to those expected from nonlinear z-scan measurements, may explain the exceptionally large \( \hat{\chi}^{(3)} \) values mentioned above. The independence of the peak-to-valley transmittance on incident power that results from the formation of holes in the sample could lead one to infer erroneously large nonlinear responses at very small input intensities.

Although at high incident powers, it appears that thermal effects may well lead to the formation of holes and, therefore, erroneous values of \( \hat{\chi}^{(3)} \). By contrast, at low incident powers, the origin of the nonlinear optical response from these films remains unclear and may result from both electronic and thermal...
effects. The work by Kamada *et al.* suggest that cumulative thermal effects can occur even for the low-duty cycle systems (100 fs pulses at repetition rates of 1 kHz), that we have employed in these studies. These thermal effects can occur in cases where the repetition rate is faster than the time required for the film to relax back to its equilibrium temperature, and thus depend on the degree of absorption, the heat capacity, and the thermal conductivity characteristics of the materials in question. Kamada *et al.* examined the time evolution of the thermal-lens signal that was induced by two-photon absorption of the excitation pulse of PMMA in a variety of solvents. The heat dissipation was modelled using literature values for the specific heat, density, and thermal conductivity of the samples. The relaxation time of the accumulated thermal effects was found to be tens of milliseconds by time resolved thermal lens experiments and simulations. An accurate modeling of these effects is precluded by a lack of specific information regarding the appropriate material characteristics of PTHPUDT (or its photoconverted product); however, calculations based on the thermodynamic and thermo-optical parameters of other classes of polymer films (poly(methyl methacrylate) (PMMA Figure 82), for example) lead us to believe that accumulated thermal effects may contribute, at least in part, to the z-scan effects observed here. Also, given that the powers required to observe a nonlinear response from these films are smaller, but on the order of the powers that have been shown to induce sample removal, it is reasonable to consider that the origin of the measured nonlinear optical response in these films may have a substantial thermal contribution.
These studies lead to the obvious suggestion that future nonlinear optical experiments carried out in order to determine the nonlinear response of PT and other similar systems be conducted in inert environments where photo-bleaching, cross-linking, and chain scission are found to be considerably reduced in the absence of oxygen.\textsuperscript{133}

### 4.2.3 Conclusions

The z-scan technique was employed to measure the third-order nonlinear optical response from high-quality LB films of the RR polymer PTHPUDT. The results of the z-scan data indicated values for $\tilde{\chi}^{(3)}_R$ and $\tilde{\chi}^{(3)}_I$ similar to those previously reported in the literature. The incident power required to observe a nonlinear response from this material was found to be sufficiently large to result in photoinduced changes in the polymer film. These photoinduced changes were characterized by a blue-shift in the interband ($\pi - \pi^*$) transition in the UV-vis absorption spectrum, indicating a significant loss in the degree of $\pi$-conjugation,
and changes in the FTIR spectrum, including those attributed to the formation of a carbonyl group, the emergence of a broad -OH band, and a decrease in intensity of the aliphatic CH bands. These changes were consistent with the onset of photooxidation, photobleaching, and chain scission processes in PT-based systems.

Examination of the irradiated portion of the film indicated the removal or partial removal of the polymer with prolonged exposure at powers greater than ~0.20 mW. The resulting linear optical effects appear to behave similarly to the nonlinear effects expected in the z-scan technique, except that we are able to observe the onset of significant levels of asymmetry in the z-scan profiles. In addition, following the onset of these effects, the peak-to-valley transmittance is found to remain independent of incident intensity.

Our results provide strong evidence for the interaction of the PT-based PTHPUDT thin films with the incident probe radiation. Although our observations pertain specifically to PTHPUDT, it is reasonable to expect that our results may extend to the broader class of PT-based materials generally and thus call into question whether the nonlinear optical susceptibility values currently being reported in the literature result from pristine polymers or from their photoconverted products.
CHAPTER 5: CHARACTERIZATION OF HEAT-TREATED FILMS

There is an extensive literature concerning the synthesis and photophysical characterization of poly(3-alkylthiophenes) (P3ATs).\textsuperscript{135-140} One particularly interesting property of P3ATs is their response to temperature. The ability of a substance to change colour because of a change in temperature is known as thermochromism. It has been previously observed that some films of P3ATs undergo a continuous colour change with increasing temperature.\textsuperscript{36} This phenomenon has been attributed to the twisting of the thiophene chain with a concomitant decrease in the conjugation length. It is generally accepted that, at low temperatures, adjacent thienyl units adopt a trans-planar conformation which favours a longer conjugation length and a red-shifted absorption maximum. At elevated temperatures, the trans-planar conformation of the side chains is less stable and a trans-to-gauche conversion can occur with an increase in disorder of the side chains. This conversion forces the thiophene rings along the main chain to twist with respect to each other, resulting in a coiled chain with shorter conjugation lengths and a corresponding blue-shift of the absorption maximum.

In addition to changes in the optical properties of P3ATs with temperature, the properties of polymers differ depending on what solvent the material interacts with.\textsuperscript{141} Solvents can be used to alter the morphology of thin films. Solvent vapour annealing (SVA) is a common and versatile technique used to increase
the crystalline character of a material. In SVA, a film is exposed to an atmosphere saturated with the vapour of a solvent in which the molecules are soluble. The solvent molecules adsorb on the substrate, partially dissolving the deposited layer leading to self-healing and ultimately to the evolution of thermodynamically stable crystalline morphologies. A less dramatic response to solvent involves changes in their optical properties, such as their UV–vis absorption and fluorescence emission maxima.

Chapter 3 was concerned with the different structure/property relationships between LB and spin-cast films. An unresolved issue is how the different architectures present in films of varying deposition methods should affect the optical and physical properties. Upon heat-treatment, LB films exhibit vastly different solubility and solvatochromic behaviour than spin-cast films. In what follows, we describe the thermal response and solvatochromic studies of PTHPUDT LB and SC films.

5.1 Experimental

LB films were prepared as described in Section 3.1.2.1, while SC films were formed as explained in Section 3.1.2.2. Heat-treatment and variable temperature FT-IR spectra of LB and spin-cast films on a CaF₂ disk were recorded using a ABB FTLA 2000 series spectrometer at a resolution of 4 cm⁻¹ coupled to a portable heater (Specac), temperature controller, and sample holder. Samples were heated at a rate of 5 °C/minute and held for 20 minutes at
a given temperature under vacuum or under a constant flow of \( \text{N}_2 \) prior to recording a spectrum. Solvatochromic experiments involved immersion of the heat-treated films under solvent or exposure to solvent vapour. Transmission electron microscopy (TEM) experiments were performed with an FEI Tecnai STEM 200 keV Field Emission STEM with a Lorentz lens and bi-prism, high angular annular dark field (HAADF) image filtering, energy dispersive (X-Ray) spectroscopy (EDS), and a CCD detector. TEM studies were carried out on multilayer films deposited onto carbon-coated copper grids.

5.2 Thermochromism

The temperature dependent absorption spectra of LB films of PTHPUDT are examined, where \( \lambda_{\text{max}} \) is measured as the temperature is varied. Figure 83 shows the temperature dependence of the electronic absorption spectrum of an LB film of PTHPUDT. At room temperature, the absorption maximum is \( \sim 560 \) nm. Two other features are present, including a smaller peak centred at 520 nm and a shoulder at 605 nm. Heating the film to 60 °C causes the peak at 520 nm to become the new absorption maximum, and the intensity of the band at 560 nm to decrease. Further heating to 140°C causes a new band to emerge at 445 nm and grow in magnitude as the temperature increases to 150 °C. An isosbestic point (the wavelength at which two or more chemical species have the same absorptivity) is seen at 465 nm. Further heating causes a small decrease in the size of the peak at 445 nm along with a blue-shift to 430 nm.
In Figure 83, there is a decrease in the magnitude of the peaks at 597 nm, 555 nm, and 524 nm upon heating, such that at 60 °C the peak at 524 nm becomes the most intense peak. The intensity of a vibronic transition is proportional to the square of the overlap integral between the vibrational wavefunctions of the two states that are involved in the transition (Section 2.2.1). A possible explanation for why the peak at 524 nm becomes the most intense at higher temperatures may be that, at elevated temperatures, there is a better overlap integral from the wavefunction of a higher vibrational level of the ground electronic state ($v''+2$) than is the case for lower vibrational levels ($v''+1$, $v''$) of the ground electronic state, with the wavefunction of a vibrational level of the excited electronic state. This could be possible since increasing the temperature
of the LB films, results in a greater population distribution in the higher vibrational levels of the ground electronic state than at lower temperatures, in accord with the Boltzmann distribution. This also agrees with the assignment of the peaks in the LB film absorption profile corresponding to vibrational fine structure in Section 3.6.

A convenient way to illustrate a material's thermochromic is to plot the $\lambda_{\text{max}}$ against the temperature (Figure 84). Upon heating the LB film under a constant flow of N₂, the $\lambda_{\text{max}}$ exhibits a step-wise blue-shift as the temperature is increased. The first noteworthy shift is observed at 60°C when the $\lambda_{\text{max}}$ shifts from ~560 nm to 520 nm. Recall that, by observing the film between crossed polarizers, we find the film to exhibit uniform optical retardation of constant magnitude when cooled to -180°C followed by heating to 30°C. However, when heated to 50°C under a constant flow of N₂ gas, only a dark field of view was observed as the film was rotated. This has been previously attributed to a loss of in-plane anisotropy in the LB film.$^{34}$
Figure 84: Irreversible thermochromism for an LB film of PTHPUDT during the heating cycle (red squares) and cooling cycle (blue squares). The inset shows the second heating cycle (black squares) and cooling cycle (green squares).

The second dramatic change in the spectrum of the LB film coincides with the blue-shift observed at 110 °C when the $\lambda_{\text{max}}$ shifts from ~515 nm to 450 nm. Previous studies of regioregular P3ATs have shown distinct differential scanning calorimetry (DSC) transitions at temperatures that coincide with changes in the $\lambda_{\text{max}}$. For example, poly(3-dodecylthiophene) (P3DT) exhibits two DSC transitions at 69 °C and 147 °C. Those DSC transitions have been interpreted to result from side chain melting, and melting of the main chain crystallites, respectively. The transition at 147 °C correlates well with the temperature at which a dramatic change in its $\lambda_{\text{max}}$ occurs. Because of the similar structures of
P3DT and PTHPUDT and similarities in their thermochromic spectra, the shift observed at 110 °C could result from melting of the main chain.

The DSC transition at 69 °C for P3DT was not accompanied by distinct changes in its thermochromic spectrum. Transitions observed in the thermochromic spectrum result from changes in the $\lambda_{\text{max}}$, which result from changes in the electronic structure of the thiophene main chain upon heating. Thus, the side chains in P3DT do not significantly affect the main chain. In contrast, the LB film of PTHPUDT shows two dramatic changes in the thermochromism spectrum at 60 °C and 110 °C. In the particular architecture present in the LB film, the side chains must have a larger impact on the main chain in order to affect the $\lambda_{\text{max}}$ to this degree.

The thermochromism data shows three distinct plateaus upon heating. The thermochromism data on each of the first two plateaus appears to be reversible. Specifically, heating and cooling cycles between room temperature and 50 °C show no changes in the $\lambda_{\text{max}}$. The same is true if the temperature is cycled between 70 °C and 90 °C.

Upon cooling, the film does not reversibly red-shift to the starting $\lambda_{\text{max}}$ of ~560 nm. Instead, a red-shift occurs from 450 nm to 520 nm. When the heating and cooling cycle from room temperature to 240 °C is repeated, the $\lambda_{\text{max}}$ changes from ~520 nm to 450 nm upon heating, and from 450 nm to ~520 nm upon cooling, in a reversible manner.

The thermochromic behavior of a PTHPUDT SC film is shown in Figure 85. This film undergoes reversible thermochromism in that there is a continuous
blue-shift with heating, and a continuous red-shift upon cooling. Only one sharp thermochromic shift is detected in the heating cycle at 130 °C, where the $\lambda_{\text{max}}$ shifts from ~515 nm to 430 nm. As suggested previously, this shift may result from melting of the main chain. The fact that only the melting of the main chain is observed in the thermochromism spectrum indicates that the alkyl chain has little or no effect on the main chain. Upon cooling, the film reversibly red-shifts to the starting $\lambda_{\text{max}}$ of 520 nm. This behaviour is consistent with previous studies of SC films of P3ATs and stands in contrast to what was observed for the first heating and cooling cycle for the LB film (Figure 84), and is consistent with the argument of dramatically different film architecture between pristine LB and SC films. However, the second heating and cooling cycle for the LB film looks similar to the heating and cooling cycle of the SC film in that only one transition is observed, consistent with the first step-wise transition in the first heating cycle of the LB film leading to the irreversible isotropization of the chain orientation.\textsuperscript{34}
Figure 85: Reversible thermochromism for a SC film of PTHPUDT during the heating cycle (red squares) and cooling cycle (blue squares).

5.3 X-ray Diffraction

The results of our X-ray analysis of a 100-layer LB film of PTHPUDT were described in Section 3.10, and its XRD pattern is shown in Figure 86. The observed three peaks at 2.95°, 5.87°, and 8.97° were assigned to the first-, second-, and third-order peaks of the repeat interlayer d-spacing normal to the surface of the substrate. Heat-treatment refers to heating a sample and then maintaining an elevated temperature followed by subsequent cooling. Heat-treatment is used to relieve internal stresses and to allow structures which are kinetically trapped to achieve more thermodynamically stable conformations. Heating the LB film at 50 °C under vacuum for 20 minutes removes the second- and third-order diffraction peaks.
Figure 86: X-ray diffraction pattern from a 100-layer PTHPUDT LB film before heating (blue trace); room temperature diffraction pattern after heating at 50 °C for 20 minutes under vacuum (red trace). The inset shows a magnified image of the (002) and (003) peaks in the film before heating.

The results of our X-ray analysis of an equivalent thickness SC film of PTHPUDT were described in Section 3.10, and its XRD pattern is shown in Figure 87. The three peaks at 2.81°, 5.81°, and 8.65° represent a d-spacing normal to the surface of the substrate. In contrast to LB films of PTHPUDT, a thermally annealed SC film of equivalent thickness showed a fifth-order diffraction peak, as well as a peak at 23° due to π-stacking (Figure 87). It is worth noting that much thicker, thermally annealed SC films have shown up to sixth-order diffraction peaks, as well as peaks at 19.5° and 23° resulting from chain crystallization and π-stacking, respectively.36
Figure 87: X-ray diffraction pattern from a SC film of PTHPUDT before heating (blue trace); room temperature diffraction pattern after heating at 50 °C for 20 minutes under vacuum (red trace). *Much thicker, heat-treated SC films have shown a peak at 23° resulting from $\pi$-stacking.

The temperature dependence of the lattice spacing and the crystallite size were investigated by analyzing the XRD patterns of both the LB and SC films after the films had been heat-treated and allowed to cool to room temperature (Table 7). The crystallite size was calculated using the Scherrer equation:

$$t = \frac{0.9\lambda}{B_{FWHM} \cos \theta}$$  \hspace{1cm} (72)

where $t$ is the crystallite size, $\lambda$ is the wavelength of the X-rays, $B_{FWHM}$ is the full width at half maximum (FWHM) of the peak in radians and $\theta$ is the angle at which the peak appears. It is recognized that the calculated crystallite sizes are only one-dimensional values that indicate the size of a coherently diffracting...
domain, and are only used to examine trends in changes in the size of the lattice dimension.\textsuperscript{145}

Table 7: The peak indexing of the XRD patterns and the crystallite sizes as determined by the Scherrer equation. The error in the crystallite size includes uncertainties in the peak position, peak shape, the \(d\) spacings, peak intensity, the FWHM and the peak symmetry caused by the step size and scanning speed of the instrument.\textsuperscript{146}

<table>
<thead>
<tr>
<th></th>
<th>(100) 2(^\circ) d spacing (Å)</th>
<th>crystallite size (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>LB film at 25 °C</td>
<td>2.93</td>
<td>30.2</td>
</tr>
<tr>
<td>LB film annealed at 50 °C</td>
<td>2.93</td>
<td>30.2</td>
</tr>
<tr>
<td>LB film annealed at 240 °C</td>
<td>3.05</td>
<td>29.0</td>
</tr>
<tr>
<td>SC film at 25 °C</td>
<td>2.81</td>
<td>31.4</td>
</tr>
<tr>
<td>SC film annealed at 240 °C</td>
<td>2.97</td>
<td>29.7</td>
</tr>
</tbody>
</table>

Heating the LB film past its first step-wise blue-shift in its thermochromism spectrum (60 °C) (Figure 84) results in no change in the interlayer spacing, nor the crystallite size, which remains roughly constant within the experimental uncertainty. A decrease in both the \(d\) spacing and crystallite size is observed after the LB film has been heated to 240 °C. Assuming a lattice spacing of \(\sim 30\) Å per PTHPUDT bilayer, the 18 nm – 22 nm crystallite size at 25 °C and 50 °C implies that the 6 or 7 diffracting planes from which the X-rays coherently scatter, decreases to \(\sim 2\) after heat-treatment. This implies a substantial decrease in long-range order. This is consistent with the decrease in the number of peaks observed following heat-treatment and with major structural changes within the LB film. For the case of the SC film, the \(d\) spacing decreases slightly upon heating, while the number of diffracting planes remains more or less unaffected. This behaviour is very different from that of the LB film and is consistent with
previous heat-treatment studies used to refine the film structure and relieve internal stresses.

5.4 Solvatochromism

Freshly prepared LB films of PTHPUDT were heat-treated under N\textsubscript{2} or vacuum at 220 °C for 20 minutes and then allowed to cool to room temperature over several hours, following the removal of the heat source. The absorption spectra of the films were recorded after cooling and the \( \lambda_{\text{max}} \) was found to be 520 nm. In order to examine the solubility of the film following the heating and cooling cycle, the film was rinsed with CHCl\textsubscript{3}, and the solvent was allowed to evaporate. The \( \lambda_{\text{max}} \) of the film changed to 500 nm and the absorbance decreased modestly. This indicated that the small amount of polymer which had remained soluble after the heating and cooling cycle must have dissolved in the organic solvent. The film that remained on the substrate was insoluble in common organic solvents and was blue-shifted with respect to the original polymer (Figure 88).
In contrast to the LB film, SC films subjected to the same heat-treatment remain soluble and dissolve when rinsed with an organic solvent such as CHCl₃. Thus, heat-treatment of the LB film renders its physical properties (solubility) substantially altered, whereas similar treatment of SC films does not appear to perturb their properties significantly.

One possible explanation for the difference in solubilities observed between the LB and SC films is that at elevated temperatures the LB film underwent thermal chemistry (Figure 89). At elevated temperatures the tetrahydropyranyloxy (OTHP) substituent in PTHPUDT films is known to undergo thermolytic cleavage with the elimination of dihydropyran, which vapourizes at 90 °C, so that at elevated temperatures it is released from the film. The resulting
polymer is rendered insoluble in organic solvents (deprotected). SC films of PTHPUDT are stable up to 275 °C and only above this temperature do they experience the elimination of dihydropyran. The deprotection temperature was easily identifiable via a colour change from pink/purple to yellow and also from the Thermal Gravimetric Analysis (TGA) spectra (Figure 90) where a 25 % mass loss consistent with the loss of THP was observed.

\[
\text{Figure 89: The deprotection reaction of PTHPUDT and the resulting deprotected polymer.}
\]
Figure 90: The Thermal Gravimetric Analysis (TGA) spectra of 7 mg of PTHPUDT showing a 25 % mass loss at 275 °C (red trace), as well as the derivative of the scan (blue trace).

The SC film remains soluble in organic solvents as long as the heating temperature remains below 275 °C. After this temperature is reached, the film undergoes the deprotection reaction shown in Figure 89. The deprotected polymer is insoluble in organic solvents. The behaviour of the SC films is consistent with these observations. Since heat-treatment involved temperatures of only ~220°C, the loss of THP and the resulting solubility changes would not be expected until temperatures of 275°C were reached. Exposure of the SC films to solvent resulted in film dissolution.

To address the possibility of the LB film having undergone thermal chemistry, we obtained a temperature-dependent IR spectra under a constant flow of N₂ for an LB film deposited on a CaF₂ disk (Figure 91) and a SC film. The
films did not show any chemical signatures of the loss of the OTHP functionality below 275 °C. Only after this temperature had been exceeded did the signature peaks of deprotection appear, such as a broad peak at ~3400 cm⁻¹ resulting from the formation of a hydroxyl group, and the complete loss of the OTHP peaks at 1130, 1120, and 1040 cm⁻¹. Like the SC film, the LB film also became insoluble in common organic solvents. The deprotected LB film showed little or no solvatochromic effects (Figure 92). On the basis of this behaviour, we conclude that the difference in the solubility between the LB and SC films is not due to a thermal deprotection reaction. Rather, differences in the solubility result from differences in the film architectures and that heat-treatment of the LB film alters the morphology of the LB film sufficiently to change its solubility dramatically.
Figure 91: IR spectra of a pristine LB film of PTHPUHT (blue trace) and after heat-treatment at 275°C (deprotected film is shown in red). The traces have been offset for clarity.

The solvatochromism of the heat-treated LB and SC films was investigated by measuring $\lambda_{\text{max}}$ upon exposure of the films to solvent vapour or upon immersion under a layer of solvent (Figure 92). After which, the film was removed from the solvent, and the solvent was allowed to evaporate from the film. The $\lambda_{\text{max}}$ of the evaporated films was recorded and it was discovered that the solvatochromic behaviour of the LB films was reversible. This procedure was repeated for a number of different solvents of various polarities. A list of the solvents and their relative polarities\textsuperscript{148} is shown in Table 8. The result was a clear linear dependence of the $\lambda_{\text{max}}$ on the relative polarity of the solvent. The film was observed to change colour from red/orange to yellow when submerged under nonpolar solvents but remained red under the more polar solvents.
Figure 92: The dependence of the $\lambda_{\text{max}}$ on the relative polarity of the solvent for the heat-treated LB film (red squares) and of a deprotected LB film (blue squares).
Table 8: The relative polarity of the solvents using the $E^N_T$ solvent polarity scale\textsuperscript{148} in the solvatochromic experiments as well as the $\lambda_{\text{max}}$ of the films when immersed under solvent.

<table>
<thead>
<tr>
<th>Solvent</th>
<th>Relative polarity</th>
<th>$\lambda_{\text{max}}$ (nm) of the annealed LB film</th>
<th>$\lambda_{\text{max}}$ (nm) of the deprotected LB film</th>
</tr>
</thead>
<tbody>
<tr>
<td>water</td>
<td>1</td>
<td>498</td>
<td>449</td>
</tr>
<tr>
<td>methanol</td>
<td>0.762</td>
<td>501</td>
<td>458</td>
</tr>
<tr>
<td>ethanol</td>
<td>0.654</td>
<td>497</td>
<td></td>
</tr>
<tr>
<td>2-propanol</td>
<td>0.546</td>
<td>481</td>
<td></td>
</tr>
<tr>
<td>acetonitrile</td>
<td>0.460</td>
<td>479</td>
<td>447</td>
</tr>
<tr>
<td>acetone</td>
<td>0.355</td>
<td>476</td>
<td></td>
</tr>
<tr>
<td>dichloromethane</td>
<td>0.309</td>
<td>463</td>
<td></td>
</tr>
<tr>
<td>chloroform</td>
<td>0.259</td>
<td>460</td>
<td></td>
</tr>
<tr>
<td>ethyl acetate</td>
<td>0.228</td>
<td>465</td>
<td>443</td>
</tr>
<tr>
<td>diethyl ether</td>
<td>0.117</td>
<td>461</td>
<td></td>
</tr>
<tr>
<td>benzene</td>
<td>0.111</td>
<td>454</td>
<td></td>
</tr>
<tr>
<td>toluene</td>
<td>0.099</td>
<td>454</td>
<td></td>
</tr>
<tr>
<td>carbon disulphide</td>
<td>0.065</td>
<td>457</td>
<td></td>
</tr>
<tr>
<td>carbon tetrachloride</td>
<td>0.052</td>
<td>450</td>
<td>455</td>
</tr>
<tr>
<td>cyclohexane</td>
<td>0.006</td>
<td>452</td>
<td>444</td>
</tr>
</tbody>
</table>

In UV-vis spectroscopy, it is well known that the solvent in which the absorbing species is dissolved has an effect on the spectrum of the species. Typical electronic absorption bands resulting from $\pi-\pi^*$ transitions are shifted to longer wavelengths (red-shifted) with increasing solvent polarity. This is caused by attractive polarization forces between the solvent and the absorber, which lower the energy levels of both the excited and ground electronic states. Since this effect is greater for the excited state, the energy difference between the excited and unexcited states is slightly reduced, resulting in a small red-shift.\textsuperscript{149}

LB films of PTHPUDT are soluble until they are heated past the second major blue-shift in the absorption spectra (Figure 78). After this temperature has been reached, the films are rendered insoluble. The reversible solvatochromic
wavelength dependence on the polarity of the solvent exhibited in the UV-vis absorption spectra implies the existence of pores in the LB film, into which the solvent molecules can readily penetrate and escape. The more red-shifted $\lambda_{\text{max}}$ with polar solvents suggests attractive polarization forces between the solvent and the absorber. Upon immersion in nonpolar solvents, the nonpolar solvent molecules can displace the polar solvent molecules from the pores. Without the attractive polarization forces between the solvent and the absorber, there is a larger $\pi - \pi^*$ band gap, and a corresponding blue-shifted $\lambda_{\text{max}}$.

Depending upon the processing conditions, distinct film morphologies can result in striking differences in properties. The different thermochromic, solubility, and solvatochromic behaviour of the LB and SC films can be attributed to the distinct film morphologies resulting from the two deposition methods. It is well recognized that P3ATs assume different structural conformations depending on the extent of rotational freedom about the interannular bond (the bond connecting two thiophene subunits). If the rotation is completely restricted, the polymer will adopt a rigid-rod configuration with adjacent thienyls being coplanar. Stacking of the polymer chains in this configuration leads to highly crystalline regions and the appearance of a $\pi$-stacking peak. Heat-treated SC films of PTHPUDT have been previously interpreted as being composed of domains of this type (Figure 85).36

The LB technique produces films with vastly different architectures than the spin-casting technique. The Y-type film structure of the LB film is due to the amphiphilic nature of the PTHPUDT polymer and can be rationalized in terms of
hydrophilic and hydrophobic interactions at the air-water interface. Surfactants at the air-water interface and when deposited on solid substrates are well known to form bilayers, cylinders, and micelles. Micelles have a spherical shape with the hydrophilic polar groups in contact with the surrounding solvent and the hydrophobic tails inhabiting the central core. In water, the hydrophobic effect is the driving force for micelle formation, even though assembling surfactant molecules together reduces their entropy. The entropic penalty of assembling the surfactant molecules is less than the entropic penalty of having the hydrophobic portion of surfactant molecules surrounded with polar water molecules. Micelles form when the concentration of surfactant is greater than the critical micelle concentration (CMC) and the temperature of the system is greater than the critical micelle temperature when amphiphilic materials are dissolved in an appropriate solvent. The formation of micelles in a solvent is an example of phase segregation in the solvent. One possible explanation of what may occur upon heat-treatment of the LB films of PTHPUDT is that the hydrophilic and hydrophobic segments in the bulk phase undergo microphase separation. Microphase separation can lead to the formation of microdomains which can possess spherical, cylindrical, and lamellar morphologies depending on the relative volume fractions of the hydrophilic and hydrophobic segments.

The freshly prepared LB film shows third-order diffraction peaks. However, heating the film past 60 °C causes the disappearance of the second- and third-order diffraction peaks. If microphase separation has occurred, the ordered architecture of the film would be disrupted and the higher-order peaks
may be expected to disappear. The number of diffracting planes from which the X-ray intensity coherently scatters would be reduced, giving a smaller crystallite size from the diffraction pattern.

Pristine and heat-treated LB and spin-cast films were examined via transmission electron microscopy (TEM) in order to examine their internal structure. The films were peeled from glass microscope slides and deposited onto carbon-coated copper grids and stained via 20-minute exposure to the vapour of 10 mg of RuCl₃ dissolved in 2 mL of NaClO₄. Figure 93 shows the TEM micrographs of the peeled LB films after exposure to the RuCl₃ solution. Small uniformly distributed roughly circular dark spots were observed after heat-treatment. These dark spots result from greater contrast, meaning that within these spots there must be less electron transmission. One possible explanation for the dark spots is the incorporation of ruthenium (IV) oxide into these areas of the film. The ruthenium oxide would be expected to attack the double bonds and stain the polythiophene segments. However, ruthenium (IV) oxide would also be expected to incorporate into the pristine LB film. Since the circular dark spots are only observed in the micrograph from the heat-treated film, it is more likely that the dark spots correspond to regions of nanoscale segregation that have occurred following heat-treatment.
Pristine and heat-treated spin-cast films were also examined via TEM (Figure 94). As in the case of the LB films, heat-treatment of the SC films to temperatures beyond the main-chain melting temperatures (150 °C) is expected to lead to microphase segregation. Figure 94 shows roughly circular dark spots after heat-treatment, consistent with microphase separation. While the heat-treated LB and spin-cast films both display signatures of microphase segregation, it is difficult to discern from the TEM micrographs whether the differences in the resulting morphologies between the two are sufficient to explain the dramatically different physical properties that follow heat-treatment. The more subtle differences in morphology (texture, domain size, porosity) between the heat-treated LB and SC films may be responsible for the large differences in solubility, thermochromic, and solvatochromic behaviour. Further
experiments will be required to elucidate the differences in structure and nature of the microphase segregation in these materials.

Figure 94: TEM micrograph of a pristine PTHPUDT spin-cast film of approximately the same thickness as the LB film (left) and a heat-treated PTHPUDT spin-cast film (right).

5.5 Conclusions

The highly-ordered PTHPUDT LB film structures show significantly different thermochromic and solvatochromic properties from spin-cast films of the same chemical composition. The thermochromic data of the LB film show two transitions corresponding to alkyl chain melting and main chain melting. No such alkyl chain transition is observed in the thermochromism spectrum of the SC film. This suggests different structural arrangements in the films. A decrease in both the crystallite size, and in the number of peaks is observed following heat-
treatment of the LB film, implying a decrease in long-range order. This is consistent with major structural changes within the LB film, which are absent in the SC film. The IR studies indicate that the chemical composition of the polymer does not change at the temperatures at which the films are heat-treated. The solvatochromic differences are therefore, not due to chemical differences between the LB and SC films, but must be due to the different structural environments in the different films. Thus, the vastly different physical and chemical behaviours observed between LB and SC films are attributed to their distinctive film morphologies. The LB films offer a unique opportunity to examine the thermal chemistry in highly-ordered environments and suggest a route for the construction of highly-ordered polymer films that have potentially useful solvatochromic properties for use in a sensor device.
CHAPTER 6: CONCLUSIONS AND FUTURE WORK

6.1 Conclusions

The structure/property relationships of PTHPUDT deposited as thin films onto various substrates have been examined via linear and nonlinear optical techniques and other characterization methods. The purpose of these studies was to resolve the connection between polymer conformation and physical property in well-ordered and highly structured environments as opposed to films fabricated through conventional casting methods, which are typically characterized by complex morphologies.

Because of its amphiphatic balance at the air-water interface, PTHPUDT is a model polymer system to investigate and compare the structure/property relationships of Langmuir-Blodgett and spin-cast films. Langmuir films of PTHPUDT exhibit an area per molecule consistent with the hydrophilic THP head group being anchored in the water subphase. The orientation of PTHPUDT at the air-water interface differs from that of other regioregular bithiophene-based amphiphilic PTs. The thiophene backbone of PTHPUDT lies parallel to the surface with its pendant alkyl groups oriented normal to the surface, while RR bithiophene-based amphiphilic PTs, which possess a hydrophilic and hydrophobic pendant group on each thiophene sub-unit, occupy an edge-on conformation of the thiophene chains with respect to the water surface. Multilayer films of PTHPUDT are readily transferred onto solid substrates via the
vertical dipping mechanism of the LB trough. The polymer deposits in a Y-type, head-to-head and tail-to-tail type of architecture. Upon close examination via optical microscopy, these films are found to be of high optical-quality and domains at least 1 mm² in size are observed. The domains are not separated via cracks, nor is there a distribution of sizes as observed in other RR P3AT systems. PTHPUDT LB films possess significant in-plane anisotropy as demonstrated by anisotropic optical absorption, emission, ellipsometry, and conductivity measurements, attributed to a change in conjugation length with orientation, where the alkyl chains from segments of polymers with greater conjugation lengths are preferentially oriented along the dipping direction compared to segments of polymers with shorter conjugation chains. The directions associated with the film birefringence are determined to be parallel/perpendicular to the LB dipping direction with the high index parallel to the dipping direction. The birefringence is found to be of a sizeable magnitude and constant across the film. SC films showed no evidence of any in-plane anisotropy. The LB deposition of PTHPUDT results in the formation of a semi-crystalline film with third-order X-ray diffraction peaks observed normal to the substrate. Heat-treatment leads to a reduction in the number of diffraction peaks for the LB film and an increase in the number of peaks for spin-cast films. This implies that different architectures are produced by the different deposition methods. A hexagonally packed lattice spacing arrangement is observed via molecular resolution atomic force microscopy of the PTHPUDT LB film. Microscopic domains (of minimum dimension 100 Å x 100 Å) are observed in a
20-layer LB film, dramatically larger than those found using XRD studies of a floating monolayer, ascribed to epitaxial deposition in the LB film, leading to well-defined order 20-layers from the surface of the substrate.

The polarization dependence of the surface second harmonic response can be used to extract the elements of the second-order nonlinear susceptibility tensor $\chi^{(2)}$, and, therefore, to obtain orientation information. The SHG from the 100-layer LB film is anisotropic. The SHG data provides an angle between the surface normal and the molecular $z'$ axis of $\sim 90^\circ \pm 5$, consistent with an orientation in which the thiophene backbone lies parallel to the surface of the substrate. This orientation compares well with the thickness obtained from AFM experiments and ordering of the films we have measured from the LB experiments. Our analysis sufficiently captures the nature of the anisotropy in the film and provides a reasonable estimate of the averaged polymer orientation within the film.

The highly-ordered architecture in the LB films appears to present an inherent barrier to charge transport. The LB technique allows for the formation of highly-ordered polymer films with a head-to-head and tail-to-tail layered structure with a narrow distribution of morphologies in contrast to films fabricated through conventional casting methods like spin- or drop-casting, which consist of a much broader and more complex range of morphologies. The semiconducting LB films become conducting upon doping with FeCl$_3$ or I$_2$. They exhibit anisotropic conductivity consistent with the deposition behaviour inferred from optical microscopy observations. The smaller conductivity of PTHPUDT with respect to
P3HT is due to the absence of $\pi - \pi$ transport mechanisms. Charge transport along the PTHPUDT alkyl chain is unlikely due to the large 3 nm bilayer repeat unit distance.

The z-scan technique is employed to measure the third-order nonlinear optical response from high-quality LB films of the RR polymer PTHPUDT. The incident power required to observe a nonlinear response from this material is found to be sufficiently large to result in photoinduced changes in the polymer film. These changes are consistent with the onset of photooxidation, photobleaching, and chain-scission processes in PT-based systems. The observed third-order nonlinear optical effects from the z-scan experiments indicate that PTHPUDT is in approximate two-photon resonance with the 800 nm incident wavelength we used to probe the films. Although our observations pertain specifically to PTHPUDT, it is reasonable to expect that our results may extend to the broader class of PT-based materials and suggest the possibility that $\chi^{(3)}$ values currently being reported in the literature may not actually be from a nonlinear response of the material but rather from the formation of “holes” as a result of burning or from a “photoconverted” product. One of the goals of making highly-ordered films was to determine whether there was any effect of order on the resulting $\chi^{(3)}$ properties. However, thermal effects may have masked any actual effect of order in our experiments.

The highly-ordered LB films showed significantly different thermochromic and solvatochromic properties from spin-cast films of the same chemical composition. The SC films exhibited reversible thermochromism and remained
soluble in organic solvents following heating and cooling cycles, whereas, the LB films are rendered insoluble after being similarly heated and cooled. Our data suggest that upon heat-treating the LB film, there is a decrease in both the crystallite size and in the number of peaks observed in X-ray diffraction, implying a decrease in long-range order, consistent with major structural changes within the LB film. This also indicates that the polymer in its LB-deposited architecture is kinetically stable. In contrast, heat-treatment of a SC film results in a film possessing a higher degree of crystallinity. The IR studies indicate that the chemical composition of the polymer does not change at the temperatures at which the films are heat-treated. The solvatochromic differences are, therefore not due to chemical differences between the LB and SC films, but must be due to the different structural environments in the different films. Thus, the different physical and chemical behaviour observed between LB and SC films are attributed to their distinctive film morphologies. This is a new method of making layered structures with a distinctive film morphology, whose physical and chemical behaviors are vastly different from either pristine Langmuir-Blodgett, spin-cast, or drop-cast films. These studies suggest a route for the construction of highly-ordered polymer films that have potentially useful solvatochromic properties for use in a sensor device.

The results of the work reported here provide a broad overview of the structure/property relationships of a highly-ordered polymer LB film from the microscopic to the macroscopic regime. Though PTHPUDT is a useful polymer for fundamental research on polymer systems, it would not be a practical material
for use in devices due to its limited luminescence and conductivity properties. However, taken as a model system, this work can provide insights into future experiments on thin polymer films with unique properties. The combination of low cost, and ease of LB film fabrication into possible device structures allows for the possibility to examine the detailed chemistry and structure/property relationships of the photoactive and electroactive layers in the devices, which have to date represented a major challenge.

6.2 Future Work

The performance of organic light-emitting diodes (OLEDs) is heavily dependent on the charge carrier mobility of the organic layers. Research efforts have demonstrated that charge transport mechanisms in thin films of these molecular compounds are intimately related to the degree of order, and that relatively high charge carrier mobilities may be achieved with well-organized assemblies. One experiment to consider is to measure the charge carrier mobility of PTHPUOT when it used as the light emitting layer in an OLED. A typical OLED consists of a hole injecting electrode (ITO anode), a hole transporting layer (TPD, for example), a light emitting layer, an electron transporting layer (Alq₃, for example), and an electron-injecting electrode (Al cathode) (Figure 95). Electrons and holes recombine in the light-emitting layer where an excited state is created that decays to the ground state by the emission of a photon.
The time of flight (TOF) technique is the most commonly used method to measure the mobility of charge carriers within organic materials used in OLED's. A pulsed laser beam can be used to illuminate the carrier generating layer. The generated charge carriers would then drift across the organic layer under the influence of an applied electric field across the organic layers between the two electrodes. The time taken by the charge carriers to move across the organic layer ($t$) can be determined by monitoring the

Figure 95: Schematic illustration of an OLED.
photocurrent passing through the organic layer. The carrier mobility ($\mu$) could be determined if the applied electric field ($E$) and the thickness of the layers ($D$) are known according to:  

$$\mu = \frac{D}{Et} \quad (73)$$  

The solvatochromic experiments on heat-treated LB films of PTHPUDT should be further investigated. It has been established that there is a clear linear dependence of the $\lambda_{\text{max}}$ on the relative polarity of the solvent (Section 5.4), and this solvatochromic behaviour is reversible. There is also an increase in the conductivity of the LB films upon doping with either FeCl$_3$ or I$_2$ (Section 3.12). In these redox reactions, the dopant acts as an oxidizing agent, removing an electron from the polymer. Thus, it may be possible to use powerful electron withdrawing solvents such as dimethyl sulphoxide (DMSO) to dope the films. If solvent vapour can penetrate into the film and cause a redox reaction to result, the semiconducting LB film will be transformed to a conducting film. The increase in conductivity can be monitored via the two- or four-point probe techniques. The resulting film would then behave as a sensor. If the solvent can then be removed from the film, the result is a reversible sensor. A series of solvents should be investigated from moderately to very strongly electron withdrawing to determine the magnitude of the conductivity change and, therefore, the efficacy of these materials for this type of device application.
APPENDIX I

The synthesis of PTHPUDT has been discussed in detail previously. PTHPUDT was synthesized from its corresponding brominated monomer (Figure 96) using the Grignard cross coupling reaction according to the general method described by McCullough et al.78

![Synthetic scheme for PTHPUDT.](image)

**Figure 96:** Synthetic scheme for PTHPUDT.

The following procedure was used by Dr. Jianfei Yu to synthesize PTHPUDT. To an ice-cooled solution of 35.17 g (140 mmol) 11-bromo-1-undecanol (1) and ~64 mL freshly distilled dihydropyran (700 mmol) in 380 mL dry dichloromethane was added 0.27 g (1.4 mmol) p-toluenesulphonic acid monohydrate under N₂. After stirring for 10 min at 0 °C followed by 1.5 hours at...
ambient temperature, the mixture was poured into 500 mL of ice-water and extracted 3 - 4 times with 100 mL dichloromethane each time. The organic phases were combined, washed with saturated NaHCO$_3$ solution twice, water 2 - 3 times and finally dried over anhydrous MgSO$_4$. Evaporation of the solvent and purification by chromatography on silica gel with dichloromethane gave 38.09 g of 11-Bromo-1-(2-tetrahydropyranloxy)undecane (2) with a yield of 81 %.

To a dry three-necked flask fitted with a condenser, anti-pressure funnel and stir bar was added 60 mL dry diethyl ether, 40 mL dry THF and 2.64 g (110 mmol) magnesium under N$_2$. The suspension was heated to reflux, and a crystal of I$_2$ was added, followed by a 2 - 3 mL solution of (2) (36.88 g, 110 mmol) in 40 mL dry diethyl ether and 20 mL dry THF. After the red colour of I$_2$ disappeared, the rest of the solution was added slowly. The mixture was refluxed until almost all of the magnesium disappeared (about 1.5 hours). Into a solution of 19.97 g (110 mmol) of 3-bromothiophene in the presence of 0.5 g Ni(dpdp)Cl$_2$ catalyst in 100 mL dry diethyl ether and 50 mL dry THF was added the prepared Grignard reagent at a rate sufficient to keep the reaction mixture refluxing without heating. After stirring and refluxing for 15 hours, the reaction was quenched by the addition of 300 mL ice-water and the mixture extracted 4 times with 100 mL aliquots of diethyl ether. The organic phases were combined, washed with water and dried over anhydrous MgSO$_4$. Evaporation of the solvent and purification by chromatography on a silica gel column using hexane yielded 19.98 g of 3-(11-(2-tetrahydropyranloxy)undecyl)thiophene (3) with a yield of 54 %.
Under subdued light, a solution of 9.97 g (56 mmol) NBS in 60 mL DMF was added slowly to a solution of 18.95 g (56 mmol) (3) in 120 mL DMF. After stirring for 3 hours at room temperature, the reaction mixture was poured into ice, and extracted 3 – 4 times with 50 mL aliquots of diethyl ether. The organic phases were combined, washed with water and dried over anhydrous MgSO₄. Evaporation of the solvent and further purification by chromatography on a silica gel column using hexane/ether (95/5 vol %) afforded 15.58 g of 2-Bromo-3-(11-(2-tetrahydropyranyloxy)undecyl)thiophene (4) with a yield of 67 %.

Into a dry round bottom 3-neck flask were added 15 mmol diisopropylamine and 60 mL freshly distilled THF. At room temperature, 15 mmol n-butyllithium was slowly added to the mixture via syringe. The mixture was cooled to -40 °C and stirred for 40 min. The mixture containing freshly prepared LDA was cooled to -78 °C, and 15 mmol brominated monomer (4) in 30 mL THF was slowly added. The reaction mixture was allowed to warm to -40 °C and stirred for 40 min. The mixture was cooled to -60 °C and 15 mmol magnesium bromide diethyletherate added. After stirring for 20 min at -60°C, the mixture was allowed to slowly warm to -5 °C, whereupon MgBr₂·Et₂O reacted. 0.5 ~1 % (by mass) of Ni(dppp)Cl₂ was added as a catalyst and the mixture was warmed to room temperature. After stirring for 8 – 18 hours, the reaction was quenched with MeOH. The polymer was purified by Soxhlet extraction using MeOH and hexane, consecutively. Extraction with CHCl₃ and evaporation of solvent afforded poly(3-(11-(2-tetrahydropyranyloxy)undecyl)thiophene) (5) with a yield of 42 %.
This polymer is regioregular (RR), possessing a minimum 95% head-to-tail coupling, as determined by NMR spectroscopy. The weight average molecular weight is 22,100 Daltons with a polydispersity index \( PDI = \frac{M_w}{M_n} \) of 1.56.
APPENDIX II

Molecular Orientation Distribution Function and Euler Transformation

The elements of the surface susceptibility ($\hat{\chi}^{(12)}_{s}$) are related to the elements of the molecular hyperpolarizabilities ($\hat{\beta}_{ijk}$) as follows:\textsuperscript{166}

$$\hat{\chi}_{ijk} = N_{s} \sum_{ijk} <l_{i}l_{j}l_{k}> \hat{\beta}_{ijk}$$  \hspace{1cm} (74)

where $N_{s}$ is the number of adsorbate molecules on the surface, $l_{i}$ are the direction cosines between the macroscopic ($IJK$) and the molecular ($ijk$) Cartesian axes and the brackets denote an average taken over all adsorbate orientations. The molecular and surface reference frames as well as the definition of the molecular orientation angles are shown in Figure 97. The orientation distribution function depends on the three Euler angles $\theta$, $\delta$ and $\xi$ which define the orientation of the molecular coordinate frame with respect to the surface coordinate frame.
Figure 97: The molecular $x'y'z'$ molecular coordinate system and the angles defining the orientation of the molecule with respect to the laboratory frame of reference associated with the deposited molecular film.

The direction cosines required to evaluate the molecular distribution function can be obtained through the Euler transformation from the molecular $(x'y'z')$ coordinate frame to the laboratory $(xyz)$ coordinate frame. This transformation can be described by three successive counterclockwise rotations:  

1) a rotation from the $x'y'z'$ coordinate frame to the $x''y''z''$ coordinate frame via rotation of $\delta$ about the molecular $z'$ axis:

$$
\begin{bmatrix}
  x'' \\
y'' \\
z''
\end{bmatrix} =
\begin{bmatrix}
  \cos\delta & \sin\delta & 0 \\
  -\sin\delta & \cos\delta & 0 \\
  0 & 0 & 1
\end{bmatrix}
\begin{bmatrix}
  x' \\
y' \\
z'
\end{bmatrix}
$$

(75)

2) a rotation from the $x''y''z''$ coordinate frame to the $x'''y'''z'''$ coordinate frame via rotation of $\theta$ about the $y''$ axis:

...
\[
\begin{bmatrix}
  x''' \\
y'''
  z'''
\end{bmatrix} = \begin{bmatrix}
  \cos \theta & 0 & -\sin \theta \\
  0 & 1 & 0 \\
  \sin \theta & 0 & \cos \theta
\end{bmatrix} \begin{bmatrix}
  x'' \\
y''
  z''
\end{bmatrix}
\] (76)

3) A rotation from the \(x''y''z''\) coordinate frame to the laboratory \(xyz\) coordinate frame via rotation of \(\phi\) about the \(z''\) axis:

\[
\begin{bmatrix}
  x \\
y \\
z
\end{bmatrix} = \begin{bmatrix}
  \cos \phi & \sin \phi & 0 \\
  -\sin \phi & \cos \phi & 0 \\
  0 & 0 & 1
\end{bmatrix} \begin{bmatrix}
  x''' \\
y'''
  z'''
\end{bmatrix}
\] (77)

The Euler transformation of the \(x'y'z'\) molecular frame to the \(xyz\) laboratory frame can be described by the following matrix:

\[
\begin{bmatrix}
  x \\
y \\
z
\end{bmatrix} = \begin{bmatrix}
  \cos \phi \cos \delta - \sin \phi \sin \phi \cos \delta & \cos \phi \cos \theta \sin \delta + \sin \phi \cos \delta & -\cos \phi \sin \theta \\
  -\sin \phi \cos \delta - \cos \phi \sin \delta & \sin \phi \cos \theta \sin \delta + \cos \phi \cos \delta & \sin \phi \sin \theta \\
  \sin \theta \cos \delta & \sin \theta \sin \delta & \cos \theta
\end{bmatrix} \begin{bmatrix}
  x' \\
y'
  z'
\end{bmatrix}
\] (78)

\[
\begin{bmatrix}
  x \\
y \\
z
\end{bmatrix} = \begin{bmatrix}
  \cos \phi \cos \theta \cos \delta - \sin \phi \sin \phi \sin \delta & \cos \phi \cos \theta \sin \delta + \sin \phi \cos \delta & -\cos \phi \sin \theta \\
  -\sin \phi \cos \theta \cos \delta - \cos \phi \sin \delta & \sin \phi \cos \theta \sin \delta + \cos \phi \cos \delta & \sin \phi \sin \theta \\
  \sin \theta \cos \delta & \sin \theta \sin \delta & \cos \theta
\end{bmatrix} \begin{bmatrix}
  x' \\
y'
  z'
\end{bmatrix}
\] (79)

The elements of the matrix above represent the direction cosines \((l_{x''}, l_{y''}, l_{z''})\) in (70). Thus, \(l_{xx'} = \cos \phi \cos \theta \cos \delta - \sin \phi \sin \phi \sin \delta\) and \(x = l_{xx'} x' + l_{xy'} y' + l_{xz'} z'\). For an isotropic distribution in the \(xy\) plane, integrating over all \(\phi\) angles yields the following relationships which further simplify the orientation distribution function of the two remaining parameters, \(\theta\) and \(\delta\):

\[
\sin \phi \cos \phi = \langle \sin 2\phi \rangle = 0
\] (80)

\[
\cos^{2} \phi \sin^{2} \phi = \langle \cos 2\phi \rangle = 0
\] (81)
\[
\sin^2 2\phi = \frac{1}{2} \tag{82}
\]
\[
\cos^2 2\phi = \frac{1}{2} \tag{83}
\]

For example, if there is a non-zero second-order susceptibility component \( \chi_{zzz}^{(2)} \) and there are two dominant molecular nonlinear hyperpolarizability components \( \hat{\beta}_x x' x' \) and \( \hat{\beta}_y y' x' \), the relationship between them can be described using (74) with expressions for the direction cosines from the transformation matrix (79) and assuming that \( (ax + by) = a(x) + b(y) \):

\[
\hat{\chi}_{zzz} = \hat{\beta}_{x' x' z} \langle l_{zz} l_{xx} l_{zz} \rangle = \hat{\beta}_{x' x' z} \langle \cos \theta \sin^2 \theta \cos^2 \delta \rangle + \hat{\beta}_{y' y' z} \langle \sin^2 \theta \cos^2 \delta \cos \theta \rangle \tag{84}
\]

Similarly, each linearly independent \( \chi^{(2)} \) component can be expressed through a linear combination of dominant \( \hat{\beta} \) components and important relationships describing the molecular orientation can be described.
APPENDIX III

Symmetry of Nonlinear Susceptibilities

There is inherent symmetry in the microscopic expressions of nonlinear susceptibilities. Just as certain media have structural symmetry, so do the nonlinear susceptibility tensors. For that reason, some tensor elements are zero and others are related to each other, which significantly reduces the total number of independent elements. For example, let us consider the second-order nonlinear susceptibility tensor ($\tilde{\chi}^{(2)}$).

In each medium there are a group of symmetry operations $\{S\}$, under which the medium does not change and so $\tilde{\chi}^{(n)}$ remains unaffected. For example, rotation by an angle $\varphi$ about the z-axis, transforms a vector $\hat{e}$ with coordinates $(x,y,z)$ into a vector $\hat{e'}$ with coordinates $(x',y',z')$, which can be obtained by:

$$
\begin{bmatrix}
  x' \\
  y' \\
  z'
\end{bmatrix} =
\begin{bmatrix}
  \cos \varphi & \sin \varphi & 0 \\
  -\sin \varphi & \cos \varphi & 0 \\
  0 & 0 & 1
\end{bmatrix}
\begin{bmatrix}
  x \\
  y \\
  z
\end{bmatrix}
$$

(85)

(here, $x' = x \cos \varphi + y \sin \varphi$). Here the matrix represents the symmetry operator $S$.
\[
S = \begin{bmatrix}
\cos \varphi & \sin \varphi & 0 \\
-\sin \varphi & \cos \varphi & 0 \\
0 & 0 & 1 
\end{bmatrix}
\]  \hspace{1cm} (86)

\(S\) is a second rank, three dimensional tensor with elements \(S_{mn}\). Invariance of \(\chi^{(2)}\) under a symmetry operation is described by: \(^{165}\)

\[
(i \cdot S^\dagger) \cdot \chi^{(2)} : (S \cdot j)(S \cdot k) = \chi^{(2)}_{ijk} 
\]  \hspace{1cm} (87)

where \(i, j, k\) represent unit vectors in \(i, j\) and \(k\) directions and \(S^\dagger\) is an operator conjugated with the operator \(S[(S^\dagger_m) = (S_m)^*] \). For a medium with \(n\) symmetry operations, \(n\) such equations will exist. \(^{66}\)

A centrosymmetric medium is symmetric with respect to inversion, which can be described by the symmetry operator \(S\), such that:

\[
S = \begin{bmatrix}
-1 & 0 & 0 \\
0 & -1 & 0 \\
0 & 0 & -1 
\end{bmatrix} \quad \text{and} \quad S \cdot \hat{e} = -\hat{e}
\]  \hspace{1cm} (88)

For example, consider the element \(\hat{\chi}^{(2)}_{xyz}\). The polarization induced in the \(x\) direction by a combination of electric fields in the \(y\) and \(z\) directions can be written as: \(^{165}\)

\[
\hat{P}_x = \hat{\chi}^{(2)}_{xyz} \hat{e}_y \cdot \hat{e}_z
\]  \hspace{1cm} (89)

With \(S\) corresponding to the inversion operator, the unit vectors of the electric fields in the \(y\) and \(z\) directions are reversed: \(\hat{e}_y \cdot S = -\hat{e}_y\), and \(\hat{e}_z \cdot S = -\hat{e}_z\). The polarization component \(\hat{P}_x\) also changes sign with this symmetry operation.
\( \hat{p}_x \cdot S = -\hat{p}_x \). After inversion, the polarization in the x direction can be written as:

\[-\hat{p}_x = \hat{x}^{(2)}_{xyz} - \hat{e}_x \cdot \hat{e}_z \] which is simplified to \(-\hat{p}_x = \hat{x}^{(2)}_{xyz} \hat{e}_y \cdot \hat{e}_z\). Since \(\hat{p}_x = -\hat{p}_x\), it follows that \(\hat{x}^{(2)}_{xyz} = -\hat{x}^{(2)}_{xyz}\), and so \(\hat{x}^{(2)}_{xyz}\) must be zero. Thus, \(\hat{x}^{(2)}\) and all even-ordered susceptibilities must be zero in centrosymmetric media.

\(\hat{x}^{(2)}\) is a rank 3 tensor meaning it has \((3^3)\) 27 elements:

\[
\hat{x}^{(2)} = \begin{bmatrix}
\hat{x}^{(2)}_{xx} & \hat{x}^{(2)}_{xy} & \hat{x}^{(2)}_{xz} \\
\hat{x}^{(2)}_{yx} & \hat{x}^{(2)}_{yy} & \hat{x}^{(2)}_{yz} \\
\hat{x}^{(2)}_{zx} & \hat{x}^{(2)}_{zy} & \hat{x}^{(2)}_{zz}
\end{bmatrix}
\] (90)

which can be reduced substantially by symmetry considerations. The intrinsic permutation symmetry, expressed by \(\hat{x}^{(2)}_{ijk} = \hat{x}^{(2)}_{ikj}\) reduces the number of independent components from 27 to 18:

\[
\hat{x}^{(2)} = \begin{bmatrix}
\hat{x}^{(2)}_{xx} & \hat{x}^{(2)}_{xy} & \hat{x}^{(2)}_{xz} \\
\hat{x}^{(2)}_{yx} & \hat{x}^{(2)}_{yy} & \hat{x}^{(2)}_{yz} \\
\hat{x}^{(2)}_{zx} & \hat{x}^{(2)}_{zy} & \hat{x}^{(2)}_{zz}
\end{bmatrix}
\] (91)

In the case of a surface with a distribution of adsorbed species in the surface xy plane with symmetry described by the group \(C_{iv}\), the independent elements of the susceptibility tensor are reduced to ten linearly independent elements. As an example, consider the element \(\hat{x}^{(2)}_{yaz}\) and reflection through the xz mirror plane as a symmetry operation. \(S\) is then be represented by the matrix:
The polarization induced in the $y$ direction by a combination of electric fields in the $x$ and $z$ directions can be written as:\(^{165}\)

\[
\hat{p}_y = \hat{\chi}^{(2)}_{yxy} \hat{e}_x \cdot \hat{e}_z
\]

With $S$ corresponding to the $xz$ mirror plane reflection operator, the unit vectors of the electric fields in the $x$ and $z$ directions remain unchanged: $\hat{e}_x \cdot S = \hat{e}_x$, and $\hat{e}_z \cdot S = \hat{e}_z$. But the polarization component $\hat{p}_y$ induced by these electric fields changes sign with this symmetry operation: $\hat{p}_y \cdot S = -\hat{p}_y$. Since $\hat{p}_y = -\hat{p}_y$, it follows that $\hat{\chi}^{(2)}_{yxy} = -\hat{\chi}^{(2)}_{yxy}$, and $\hat{\chi}^{(2)}_{yxy}$ must be zero.

A similar symmetry argument proves that the element $\hat{\chi}^{(2)}_{yzy}$ does not vanish under this symmetry operation. In this case, $\hat{e}_y \cdot S = -\hat{e}_y$, but $\hat{p}_y$ does not change sign. Thus, the relationship $\hat{p}_y = \hat{\chi}^{(2)}_{yzy} \hat{e}_y \cdot \hat{e}_z$ becomes $\hat{p}_y = \hat{\chi}^{(2)}_{yzy} - \hat{e}_y \cdot -\hat{e}_y$ after the symmetry operation, which is identical to the relationship before the symmetry operation. Thus, the expression $\hat{p}_y = \hat{\chi}^{(2)}_{yzy} \hat{e}_y \cdot \hat{e}_y$ can only be satisfied with a nonzero $\hat{\chi}^{(2)}_{yzy}$ component. Each of the 10 independent elements of $\hat{\chi}^{(2)}$ with symmetry described by the group $C_{1v}$ have been considered in a similar fashion, and the results are summarized below:
\[ \hat{\chi}^{(2)}_{C1v}(xz \ plane) = \begin{bmatrix} \hat{x}_{xxx}^{(2)} & \hat{x}_{xyy}^{(2)} & \hat{x}_{xzz}^{(2)} & 0 & \hat{x}_{xx}^{(2)} & 0 \\ 0 & 0 & 0 & \hat{x}_{yy}^{(2)} & 0 & \hat{x}_{yy}^{(2)} \\ \hat{x}_{zxx}^{(2)} & \hat{x}_{zyy}^{(2)} & \hat{x}_{zzz}^{(2)} & 0 & \hat{x}_{zz}^{(2)} & 0 \end{bmatrix} \]
APPENDIX IV

Expressing Laboratory-Fixed Tensor Components ($\chi_{ijk}$) in Terms of Surface Fixed Components ($\chi_{iljk}$)

The relationships of the observed features with the orientations and the structures of the probed absorbates are best described through the Cartesian components of the tensor $\hat{\chi}$. The transformation of the molecule-fixed Cartesian components into the surface- or laboratory-fixed components is carried out through the $27 \times 27$ matrix elements, which are functions of the Euler angles defining the orientation of the molecule-fixed coordinate system with respect to the surface- or laboratory-fixed systems.

The tensor components associated with the observed features of SHG signals are the ones described in the laboratory-fixed axis system, $\hat{\chi}_{ijk} (i,j,k = X,Y,Z)$, while the characteristics of the interface are best described by the components taken along the interface-fixed (xyz) system, $\hat{\chi}_{iljk} (i,j,k = x,y,z)$.

For example, the equation relating the laboratory $\hat{\chi}_{yyy}$ with the surface $\hat{\chi}$ elements (for our $s_{in}-s_{out}$ polarization combination) is:\textsuperscript{117}
\[
\hat{\chi}_{YYY} = \hat{\chi}_{yy} \cos \phi + (\hat{\chi}_{xyy} - \hat{\chi}_{jyy} + \hat{\chi}_{jxx}) \frac{(\cos \phi - \cos 3\phi)}{4} \\
- \hat{\chi}_{xxx} \sin \phi + (\hat{\chi}_{xxx} - \hat{\chi}_{jxx} - \hat{\chi}_{jyy} + \hat{\chi}_{jxy}) \frac{(\sin \phi + \sin 3\phi)}{4}
\]

(95)

This equation can be simplified since the elements \( \hat{\chi}_{xx}, \hat{\chi}_{yy}, \hat{\chi}_{xy} \), \( \hat{\chi}_{j} \) are zero in materials with symmetry described by the group \( C_{1v} \). The equation is thus, reduced to:

\[
\hat{\chi}_{YYY} = -\hat{\chi}_{xxx} \sin \phi + (\hat{\chi}_{xxx} - \hat{\chi}_{jxx} - \hat{\chi}_{jyy} + \hat{\chi}_{jxy}) \frac{(\sin \phi + \sin 3\phi)}{4}
\]

(96)

while the intrinsic permutation symmetry allows the similar terms to be grouped:

\[
\hat{\chi}_{YYY} = -\hat{\chi}_{xxx} \sin \phi + (\hat{\chi}_{xxx} - 2\hat{\chi}_{jyy} + \hat{\chi}_{jxy}) \frac{(\sin \phi + \sin 3\phi)}{4}
\]

(97)

The term \( \frac{(\sin \phi + \sin 3\phi)}{4} \) is converted to \( \cos^2 \phi \sin \phi \) using the following trigonometry functions:

\[
\sin 3\phi = \sin(\phi + 2\phi) = \sin \phi \cos 2\phi + \cos \phi \sin 2\phi \\
\cos 2\phi = \cos^2 \phi - \sin^2 \phi \\
\sin 2\phi = 2 \sin \phi \cos \phi
\]

(98)

\[
\hat{\chi}_{YYY} = -\hat{\chi}_{xxx} \sin \phi + (\hat{\chi}_{xxx} - 2\hat{\chi}_{jyy} + \hat{\chi}_{jxy}) \cos^2 \phi \sin \phi
\]

(99)

and is simplified to:

\[
\hat{\chi}_{YYY} = -\hat{\chi}_{xxx} \sin^3 \phi - 2\hat{\chi}_{jyy} \cos^2 \phi \sin \phi - \hat{\chi}_{jxy} \cos^2 \phi \sin \phi
\]

(100)

If we consider the case where a thin film is sandwiched between two bulk media and an intense laser beam of frequency \( \omega \) is incident from media 1 at an
angle \( \theta_i \) with respect to the surface normal and the reflected SH output is
detected (Figure 33). The SH signal at frequency \( 2\omega \) is given by:74

\[
I_{2\omega} = \frac{32\pi^2 \omega^5 \sec^2 \theta_i(2\omega)}{c^3 [\varepsilon_i(2\omega)]^{0.5} \varepsilon_1(\omega)} |\tilde{\chi}_{\text{eff}}^{(2)}| I_{\omega}^2 T A
\]  

where \( I_{\omega} \) is the intensity of the incident beam, \( T \) is the laser pulse width, \( A \) is
the area of the laser spot on the surface, \( \varepsilon_i \) is the dielectric constant of medium
1, \( \theta_i(2\omega) \) is the SH reflection angle, and \( \tilde{\chi}_{\text{eff}}^{(2)} \) is the effective nonlinear
susceptibility. The effective nonlinear susceptibility has the form:74

\[
\tilde{\chi}_{\text{eff}}^{(2)} = [\hat{e}_{2\omega} \cdot L_{2\omega}] [\hat{e}_{\omega} \cdot L_{\omega}] [\hat{e}_{\omega} L_{\omega}]
\]  

where \( \hat{e}_{\omega} \) and \( \hat{e}_{2\omega} \) are the unit polarization vectors at the respective frequencies,
and \( L_{\omega} \) and \( L_{2\omega} \) are local field factor tensors at the incident field and at the
SH field. The local field factor tensors are also known as Fresnel coefficients, and
they are corrections to the incident laser fields and to the SH field generated at
the interface. These Fresnel factors take into account the reflection, refraction
and enhancement of fields due to the presence of the interface.

A detailed description of the Fresnel factors for the general case of a
polarization sheet sandwiched between two infinite bulk media has been
previously published.74 They are described below:
\[ L_{xx}(\omega) = \frac{2n_1(\omega) \cos \theta_2}{n_2(\omega) \cos \theta_1 + n_1(\omega) \cos \theta_2} \]  

\[ L_{yy}(\omega) = \frac{2n_1(\omega) \cos \theta_1}{n_1(\omega) \cos \theta_1 + n_2(\omega) \cos \theta_2} \]  

\[ L_{zz}(\omega) = \frac{2n_1^2(\omega)n_2(\omega) \cos \theta_1}{n_1^2(\omega)[n_2(\omega) \cos \theta_1 + n_1(\omega) \cos \theta_2]} \]

where \( n_1, n_2, n_m \) are the indices of refraction of media 1, 2, and the polarization sheet, respectively. Incorporating the Fresnel coefficients into (100) gives (106), which is the model to which our experimentally determined \( s_{in}-s_{out} \) polarization combination SHG data are fit:

\[ \tilde{\chi}_{eff}^{(2)} = -\tilde{\chi}_{xxx}^{(2)} \sin^{3} \phi L_{x}(2\omega) L_{y}(\omega) L_{z}(\omega) \]
\[ -2\tilde{\chi}_{yxy}^{(2)} \cos^{2} \phi \sin \phi L_{x}(2\omega) L_{y}(\omega) L_{z}(\omega) \]
\[ -\tilde{\chi}_{xyy}^{(2)} \cos^{2} \phi \sin \phi L_{x}(2\omega) L_{y}(\omega) L_{z}(\omega) \]  

The same method is used to fit the other three polarization combinations, and the results are summarized below:
$$\begin{align*}
\dot{S}_{in} - \dot{S}_{out} & = \dot{S}^{(2)}_{\text{ext}}(\sin^3 \phi)L_1(2\omega)L_1^2(\omega) - 2\dot{S}^{(2)}_{\text{ext}}(\cos^2 \phi)(\sin \phi)L_1(2\omega)L_1^2(\omega) - \dot{S}^{(1)}_{\text{ext}}(\cos^2 \phi)(\sin \phi)L_1(2\omega)L_1^2(\omega). \\
\dot{P}_{in} - \dot{P}_{out} & = -\dot{S}^{(1)}_{\text{ext}}(\cos^2 \phi)(\sin \phi)L_1(2\omega)L_1^2(\omega) \cos \theta_1(\omega) \\
& + 2\dot{S}^{(1)}_{\text{ext}}(\cos^2 \phi)(\sin \phi)L_1(2\omega)L_1^2(\omega) \cos^2 \theta_1(\omega) \\
& - \dot{S}^{(1)}_{\text{ext}}(\sin^3 \phi)L_1(2\omega)L_1^2(\omega) \cos^2 \theta_1(\omega) \\
& - 2(\dot{S}^{(2)}_{\text{ext}} - \dot{S}^{(1)}_{\text{ext}}) (\sin \phi)(\cos \phi)L_1(2\omega)L_1(\omega)L_1(\omega)[-\sin \theta_1(\omega) \cos \theta_1(\omega)] \\
& - \dot{S}^{(1)}_{\text{ext}}(\sin \phi)L_1(2\omega)L_1^2(\omega) \sin^2 \theta_1(\omega).
\end{align*}$$

$$\begin{align*}
\dot{S}_{in} - \dot{S}_{out} & = \dot{S}^{(2)}_{\text{ext}}(\cos^3 \phi)L_1(2\omega)L_1^2(\omega) \cos \theta_1(2\omega) \\
& + \dot{S}^{(2)}_{\text{ext}}(\sin^2 \phi)(\cos \phi)L_1(2\omega)L_1^2(\omega) \cos \theta_1(2\omega) \\
& - 2\dot{S}^{(2)}_{\text{ext}}(\sin^2 \phi)(\cos \phi)L_1(2\omega)L_1^2(\omega) \cos \theta_1(2\omega) \\
& + \dot{S}^{(2)}_{\text{ext}}(\sin^2 \phi)L_1(2\omega)L_1^2(\omega) \sin \theta_1(2\omega) \\
& + \dot{S}^{(1)}_{\text{ext}}(\cos^3 \phi)L_1(2\omega) L_1^2(\omega) \sin \theta_1(2\omega).
\end{align*}$$

$$\begin{align*}
\dot{P}_{in} - \dot{P}_{out} & = \dot{S}^{(2)}_{\text{ext}}(\cos^3 \phi)L_1(2\omega)L_1^2(\omega) \cos \theta_1(2\omega) \cos^2 \theta_1(\omega) \\
& + 2\dot{S}^{(2)}_{\text{ext}}(\sin^3 \phi)(\cos \phi)L_1(2\omega)L_1^2(\omega) \cos \theta_1(2\omega) \cos^2 \theta_1(\omega) \\
& + \dot{S}^{(2)}_{\text{ext}}(\sin^2 \phi)(\cos \phi)L_1(2\omega)L_1^2(\omega) \cos \theta_1(2\omega) \cos^2 \theta_1(\omega) \\
& + 2\dot{S}^{(2)}_{\text{ext}}(\sin^3 \phi)L_1(2\omega)L_1^2(\omega) \sin \theta_1(2\omega) \cos^2 \theta_1(\omega) \\
& + 2\dot{S}^{(2)}_{\text{ext}}(\cos^3 \phi)L_1(2\omega)L_1^2(\omega) \sin \theta_1(2\omega) \sin \theta_1(2\omega) \\
& + \dot{S}^{(2)}_{\text{ext}}(\cos \phi)L_1(2\omega)L_1^2(\omega) \cos \theta_1(2\omega) \sin^2 \theta_1(\omega) \\
& + \dot{S}^{(2)}_{\text{ext}}(\cos \phi)L_1(2\omega)L_1(\omega)L_1(\omega)[-\sin \theta_1(2\omega) \sin \theta_1(\omega) \cos \theta_1(\omega)] \\
& + \dot{S}^{(2)}_{\text{ext}}(\cos \phi)L_1(2\omega)L_1(\omega)L_1(\omega)[-\sin \theta_1(\omega) \sin \theta_1(\omega) \cos \theta_1(\omega)] \\
& + \dot{S}^{(2)}_{\text{ext}}(\cos \phi)L_1(2\omega)L_1^2(\omega) \sin \theta_1(2\omega) \sin^2 \theta_1(\omega).
\end{align*}$$

(107)
APPENDIX V

Ellipsometry Fitting Program

The ellipsometry data was fitted using the simple model as described in Section 3.9. The layers of the model are shown in Figure 98, and the variable parameters are indicated with the symbol F. The bottom layer consisted of a layer of voids. On top of this layer was a 0.2 mm-thick SiO₂ layer from the glass substrate. Above this was a biaxial polymer layer with three orthogonal indices of refraction. The total thickness of this polymer layer was assumed to be 225 nm; however, this value was allowed to vary in the fitting routine. Also shown in Figure 98 are the experimentally determined $I_1$ and $I_2$ curves as well as their fits using the double amorphous dispersion equation (Figure 99). The fit has a $T^2$ value of ~2. The fitted parameters along with their uncertainties are shown in Figure 100.
Figure 98: Details of the ellipsometry model used to describe the PTHPUDT LB film.
\[
\begin{align*}
n(E) &= \sqrt{E_0} + \sum_{n=1}^{2} \frac{B_0 \cdot E + C_0}{E^2 - B_n \cdot E + C_n}, \\
k(E) &= \begin{cases} \\
\sum_{n=1}^{2} \frac{A_n \cdot (E - E_g)^3}{E^2 - B_n \cdot E + C_n}, & E > E_g \\
0, & E \leq E_g
\end{cases}
\end{align*}
\]

where

\[
\begin{align*}
B_0 &= \frac{A_2}{Q_n} \left( -\frac{B_2^2}{2} + E_g \cdot B_2 - B_g^2 + C_n \right), \\
C_0 &= \frac{A_2}{Q_n} \left( (E_g^2 + C_n) \cdot \frac{B_2}{2} - 2 \cdot E_g \cdot C_n \right), \\
Q_n &= \frac{1}{2} \sqrt{4 \cdot C_n - B_2^2}
\end{align*}
\]

**Figure 99:** The double amorphous dispersion formula used to extract the fitted parameters.
\( T^2 \) minimization on Is,lc

\[
\text{Is} = \sin(2\psi) \times \sin(\Delta), \quad \text{lc} = \sin(2\psi) \times \cos(\Delta)
\]

\( T^2 = 2.017026 \)

Iterations Number = 39

**Parameters**

1) L2 Thickness [Å] = 2491.351 ± 231.057
2) DAx \( \varepsilon \infty \) = 0.5391467 ± 0.0763907
3) DAx Eg = -1.6541130 ± 0.2586212
4) DAx A1 = 0.1178637 ± 0.0700035
5) DAx B1 = 1.6114310 ± 0.3118441
6) DAx C1 = 8.5976490 ± 0.9300728
7) DAx A2 = 0.0652127 ± 0.0448122
8) DAx B2 = 2.3739630 ± 0.2750145
9) DAx C2 = 3.7105600 ± 0.3670254
10) DAy \( \varepsilon \infty \) = 0.7815737 ± 0.0549002
11) DAy Eg = -0.2799911 ± 0.3516964
12) DAy A1 = 0.0000789 ± 0.0000686
13) DAy B1 = 3.6733470 ± 0.0043573
14) DAy C1 = 2.8840940 ± 0.0043264
15) DAy A2 = 0.0197204 ± 0.0079535
16) DAy B2 = 4.1413710 ± 0.1038350
17) DAy C2 = 4.5363740 ± 0.2248548
18) DAz \( \varepsilon \infty \) = 0.8241920 ± 0.0288384
19) DAz Eg = -1.0875040 ± 0.1043529
20) DAz A1 = 0.0417071 ± 0.0064651
21) DAz B1 = 1.5023040 ± 0.1075164
22) DAz C1 = 1.7513490 ± 0.1087091
23) DAz A2 = 0.0005721 ± 0.0000976
24) DAz B2 = 4.7049830 ± 0.0319720
25) DAz C2 = 5.6107540 ± 0.0769555
26) AOI = 60.075 ± 0.011

**Initial data for fit**

Model File : 08june6.mdl
Fitting Choice : Default
Fitting Routine : Simple Fit
Experimental file: 2007.07.17\n\text{ov3b}07\text{Jul17.fresh film perp to dip dir.16h 34mm 22s.spe}

**Spectrum**

Range : 270.0000 - 1200.0000 nm
Increment : 5.0000 nm
Points Number: 187

**Figure 100:** The fitted parameters in the ellipsometry model.
APPENDIX VI

SHG Fitting Program

This appendix discusses the SHG fitting program used to fit the experimental SH data in Figure 74. The following table gives the SH signal responses from the LB film. A 9.9 \% attenuator was used to attenuate the input laser intensity in front of the LB film for the $p_{in}$-$p_{out}$ polarization combination. The measured power was 40 mW. A 21\% attenuator was used before the LB film for the $s_{in}$-$s_{out}$, $s_{in}$-$p_{out}$ and $p_{in}$-$s_{out}$ polarization combinations. The measured power was 85 mW. This means that the signal of the $p_{in}$-$p_{out}$ polarization combination is about four times larger than the other three input-output combinations.

Table 9: The SH response from the 200-layer LB film.

<table>
<thead>
<tr>
<th>LB Film Angle (deg)</th>
<th>Angle (rad)</th>
<th>$s_{in}$-$s_{out}$</th>
<th>$p_{in}$-$s_{out}$</th>
<th>$s_{in}$-$p_{out}$</th>
<th>$p_{in}$-$p_{out}$</th>
</tr>
</thead>
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<tr>
<td>0</td>
<td>0</td>
<td>0.11</td>
<td>0.05</td>
<td>0.54</td>
<td>0.93</td>
</tr>
<tr>
<td>10</td>
<td>0.17</td>
<td>0.14</td>
<td>0.13</td>
<td>0.34</td>
<td>0.84</td>
</tr>
<tr>
<td>20</td>
<td>0.35</td>
<td>0.28</td>
<td>0.32</td>
<td>0.29</td>
<td>0.69</td>
</tr>
<tr>
<td>30</td>
<td>0.52</td>
<td>0.41</td>
<td>0.54</td>
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<td>0.35</td>
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<td>0.11</td>
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<tr>
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<td>160</td>
<td>2.79</td>
<td>0.16</td>
<td>0.31</td>
<td>0.29</td>
<td>1.20</td>
</tr>
</tbody>
</table>
The raw SH data for the LB film is shown in Figure 101 (below). At the relative input light intensities used to obtain the SH response from the LB films, we cannot measure a response from the bare glass substrate.
Figure 101: Polarized SH intensity vs $\phi$ for an LB film with 100-layers of PTHPUDT deposited onto one monolayer of ferric stearate on a hydrophilic glass slide. The input-output polarization combinations are: $\rho_{in}$-$\rho_{out}$ (top left), $s_{in}$-$\rho_{out}$ (top right), $s_{in}$-$s_{out}$ (bottom left), $\rho_{in}$-$s_{out}$ (bottom right). The points represent the raw collected data. The solid lines represent a nonlinear least-squares best fit to the data. The open diamonds represent data for an isotropic malachite green film SC onto a glass slide. The dipping direction corresponds to $90^\circ$. 
**$s_{in}$-$s_{out}$ Polarization Combination**

The fitting program takes the square root of the SH response of the film and from this, subtracts the square root of the SH response of the background (BG). The result is then squared and is known as the $s_{in}$-$s_{out}$ BG subtracted data. Then a fit to the $s_{in}$-$s_{out}$ polarization combination data is obtained from (69) using only the three $\chi^{(2)}$ components in the $s_{in}$-$s_{out}$ polarization combination ($\chi^{(2)}_{xxx}$, $\chi^{(2)}_{yy}$, and $\chi^{(2)}_{xy}$). The error between the experimental data and the fit is calculated and squared. The square of the error is then summed for the column and is minimized (using the solver function in Microsoft Excel) allowing only the values of $\chi^{(2)}_{xxx}$, $\chi^{(2)}_{yy}$, and $\chi^{(2)}_{xy}$ to vary. Several initial guesses are made as to both the magnitude and sign of the susceptibility components to ensure that the absolute minima and not a local minima is reached.

**Table 10:** The BG subtracted SH response from the 200-layer LB film, the fit according to (70) and the minimized error.

<table>
<thead>
<tr>
<th>Angle (deg)</th>
<th>$s_{in}$-$s_{out}$ (experimental)</th>
<th>$s_{in}$-$s_{out}$ fit (equation 70)</th>
<th>$s_{in}$-$s_{out}$ error^2</th>
</tr>
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<tbody>
<tr>
<td>0</td>
<td>0.11</td>
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<td>0.01</td>
</tr>
<tr>
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<td>0.14</td>
<td>0.11</td>
<td>0.00</td>
</tr>
<tr>
<td>20</td>
<td>0.28</td>
<td>0.31</td>
<td>0.00</td>
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<td>0.41</td>
<td>0.50</td>
<td>0.00</td>
</tr>
<tr>
<td>40</td>
<td>0.55</td>
<td>0.58</td>
<td>0.00</td>
</tr>
<tr>
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<td>0.53</td>
<td>0.00</td>
</tr>
<tr>
<td>60</td>
<td>0.45</td>
<td>0.41</td>
<td>0.00</td>
</tr>
<tr>
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<td>0.33</td>
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<tr>
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<td>0.17</td>
<td>0.21</td>
<td>0.00</td>
</tr>
<tr>
<td>90</td>
<td>0.15</td>
<td>0.19</td>
<td>0.00</td>
</tr>
<tr>
<td>100</td>
<td>0.25</td>
<td>0.22</td>
<td>0.00</td>
</tr>
<tr>
<td>110</td>
<td>0.43</td>
<td>0.31</td>
<td>0.01</td>
</tr>
<tr>
<td>Angle (deg)</td>
<td>$s_{in} - s_{out}$ (experimental)</td>
<td>$s_{in} - s_{out}$ fit (equation 70)</td>
<td>$s_{in} - s_{out}$ error$^2$</td>
</tr>
<tr>
<td>------------</td>
<td>---------------------------------</td>
<td>---------------------------------</td>
<td>-------------------------</td>
</tr>
<tr>
<td>120</td>
<td>0.56</td>
<td>0.44</td>
<td>0.01</td>
</tr>
<tr>
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<td>0.50</td>
<td>0.55</td>
<td>0.00</td>
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<tr>
<td>140</td>
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<td>0.02</td>
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<td>0.46</td>
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<tr>
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</table>

The other parameters used in the fitting routine are Fresnel reflection coefficients, indices of refraction and the incident and reflected angles which have been incorporated as described by Shen et al.\textsuperscript{74} (Appendix IV).
Table 11: Other parameters used in the fitting routine.

<table>
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<tr>
<th>Fresnel coefficients</th>
<th>Indices of refraction</th>
<th>Angles</th>
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<td>$n_2(\omega)$</td>
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<tr>
<td>$L_{zz}(\omega)$</td>
<td>$n_1(2\omega)$</td>
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</tr>
<tr>
<td>$L_{xx}(2\omega)$</td>
<td>$n_2(2\omega)$</td>
<td>1.53</td>
</tr>
<tr>
<td>$L_{yy}(2\omega)$</td>
<td>$n_m(\omega)$</td>
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</tr>
<tr>
<td>$L_{zz}(2\omega)$</td>
<td>$n_m(2\omega)$</td>
<td>1.44</td>
</tr>
</tbody>
</table>

$p_{in}-s_{out}$, $s_{in}-p_{out}$ and $p_{in}-p_{out}$ Polarization Combinations

A similar procedure was used to determine the susceptibility components of the $p_{in}-s_{out}$ polarization combination ($\chi^{(2)}_{xx}$, $\chi^{(2)}_{yy}$ and $\chi^{(2)}_{zz}$) without allowing the previously established susceptibility components from the $s_{in}-s_{out}$ polarization combination to vary. Once the $p_{in}-s_{out}$ components were established, the $s_{in}-p_{out}$ components ($\chi^{(2)}_{xx}$ and $\chi^{(2)}_{yy}$) were determined followed by the $p_{in}-p_{out}$ components ($\chi^{(2)}_{xx}$ and $\chi^{(2)}_{zz}$).
Table 12: The relative susceptibility components obtained from the fitting routine.

<table>
<thead>
<tr>
<th>Relative susceptibility components extracted from the fits to the 200-layer LB film SH data</th>
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<tbody>
<tr>
<td>$\chi_{zzz}$</td>
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<td>$\chi_{xxx}$</td>
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<td>$\chi_{zzx}$</td>
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