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Structural Characterization of Poly(heterocycles) Formed Using Oxidative Methods

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STRUCTURAL CHARACTERIZATION OF POLY(HETEROCYCLES) FORMED USING OXIDATIVE METHODS

A Dissertation

Submitted to the Graduate Faculty of the Louisiana State University and Agricultural and Mechanical College in partial fulfillment of the requirements for the degree of Doctor of Philosophy in

The Department of Chemistry

by

Rebecca M. Brauch
B.S., Ohio University, 2002
December, 2006
Dedication

This dissertation is dedicated to my mom April and my dad Ken

I am so grateful to you for all the sacrifices you both so willingly made for me to receive the education that I have. It was never unnoticed or unappreciated. Without your love and support I would never have been able to achieve this.
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First and foremost I’d like to thank my parents. You have both been my biggest fans throughout these past years and were always there for me when I needed words of encouragement and support, no matter how many states separated us. I believe in myself because you both believed in me so much.

I also want to acknowledge my sister, Stephanie. Thank you for being such a source of wisdom and strength. I know that I’m the older one but sometimes I find myself looking up to you. And to my twin brother Eric, I couldn’t think of a person I’d rather be stuck with from day one. You both have been there for me through it all, thank you.

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Figure B.2 $^1$H-NMR of 8-mer of 3-hexylthiophene with Cl,Cl end groups (Fraction 17 from the RP-HPLC separation of P-3HT, monomer-to-oxidant ratio 1:12).

Figure B.3 $^1$H-NMR of 4-mer of 3-hexylthiophene with H,H end groups (Fraction 3 from the RP-HPLC separation of P-3HT, monomer-to-oxidant ratio 1:12).

Figure B.4 $^1$H-NMR of 4-mer of 3-hexylthiophene with Cl,Cl end groups (Fraction 6 from the RP-HPLC separation of P-3HT, monomer-to-oxidant ratio 1:12).
**List of Abbreviations**

<table>
<thead>
<tr>
<th>Abbreviation</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>(CH)$_x$</td>
<td>poly(acetylene)</td>
</tr>
<tr>
<td>Cl$^-$</td>
<td>chloride ion</td>
</tr>
<tr>
<td>DCM</td>
<td>dichloromethane</td>
</tr>
<tr>
<td>DBSA</td>
<td>dodecylbenzene sulfonic acid</td>
</tr>
<tr>
<td>DEHS</td>
<td>di(2-ethylhexyl) sulfosuccinate sodium salt</td>
</tr>
<tr>
<td>HCl</td>
<td>hydrochloric acid</td>
</tr>
<tr>
<td>FeCl$_3$</td>
<td>iron(III) chloride</td>
</tr>
<tr>
<td>KBr</td>
<td>potassium bromide</td>
</tr>
<tr>
<td>O$_2$</td>
<td>molecular oxygen</td>
</tr>
<tr>
<td>OH$^-$</td>
<td>hydroxide ion</td>
</tr>
<tr>
<td>P-3AT</td>
<td>poly(3-alkylthiophene)</td>
</tr>
<tr>
<td>P-3HT</td>
<td>poly(3-hexylthiophene)</td>
</tr>
<tr>
<td>DRI</td>
<td>differential refractive index</td>
</tr>
<tr>
<td>DSC</td>
<td>differential scanning calorimetry</td>
</tr>
<tr>
<td>GC-MS</td>
<td>gas chromatograph-mass spectrometer</td>
</tr>
<tr>
<td>GPC</td>
<td>gel-permeation chromatography</td>
</tr>
<tr>
<td>$^1$H-NMR</td>
<td>proton nuclear magnetic resonance</td>
</tr>
<tr>
<td>FT-IR</td>
<td>Fourier-transform infrared spectroscopy</td>
</tr>
<tr>
<td>MALDI-TOF MS</td>
<td>matrix-assisted laser desorption/ionization time-of-flight mass spectrometry</td>
</tr>
<tr>
<td>MALLS</td>
<td>multi-angle laser light scattering</td>
</tr>
<tr>
<td>RP-HPLC</td>
<td>reverse-phase high-performance liquid chromatography</td>
</tr>
</tbody>
</table>
UV  ultraviolet
XPS  X-ray photoelectron spectroscopy
\( \lambda_{\text{max}} \)  wavelength of maximum absorbance
cm  centimeter
C  coulombs
g  gram
M  molar
mol  mole
nm  nanometer
mL  milliliter
\( m/z \)  mass per charge
MW  molecular weight
MWD  molecular weight distribution
S  Siemens
V  volts
H-T  head-to-tail coupling
H-H  head-to-head coupling
T-T  tail-to-tail coupling
Abstract

This research focused on elucidation of structural information for conducting polymer systems using matrix-assisted laser desorption/ionization time-of-flight mass spectrometry (MALDI-TOF MS). The structure of conducting polymer systems has been found to directly influence their physical properties. Poly(pyrrole) and poly(thiophene) are two of the most widely studied conducting polymers due to their high electrical conductivity, stability in the doped state, low toxicity, and current/potential applications. The purpose of this research was to apply MALDI-TOF MS to heterocyclic conducting polymers, specifically those of pyrrole and thiophene, to investigate structural properties of these polymers, with the specific aim of determining end group and molecular weight dependence on polymerization conditions.

The common synthesis route of chemical oxidation was used for the production of poly(3-hexylthiophene) and it was demonstrated that solvent and monomer-to-oxidant ratio strongly influence the composition of the polymer, specifically halogen content and size. More specifically, it was demonstrated that the end groups of the polymer synthesized in nitromethane could be changed from hydrogen to chlorine by simply changing the monomer-to-oxidant ratio. This is important because studies on 3-hexylthiophene oligomers indicate that chlorine substituents do affect their optical properties. A red shift in the $\lambda_{\text{max}}$ was observed for thiophene oligomers with chlorine substituents versus pristine thiophene oligomers. A proposed mechanism was outlined to further describe the polymerization as well as chlorine substitution process in these polymers, during oxidative polymerization with FeCl$_3$.

For the first time, MALDI-TOF MS was successfully used to characterize soluble pyrrole polymers. The pyrrole polymers studied were much more structurally complicated than the thiophene polymers. One reason for this is that they are more susceptible to nucleophilic
substitution than the thiophene systems. Unlike the thiophene polymers, manipulation of the polymerization parameters did not lead to formation of pristine pyrrole polymer lacking chlorine and/or oxygen substitution, under the conditions used here. Also, it was observed from the MALDI-TOF MS analysis that hydrogen loss is a characteristic of these substituted pyrrole polymers, and it occurs regardless of the location of the side chain.
Chapter 1

Introduction and Background

1.1 Research Overview

Structural characterization of conducting polymers is important because the structure of conducting polymer systems has been found to directly influence the physical properties of the polymer.¹ The research presented in this dissertation focuses on elucidation of structural information on conducting polymer systems using matrix-assisted laser desorption/ionization mass spectrometry (MALDI-MS). The ultimate goal of the research is to evaluate changing chemical polymerization parameters to tailor the end groups and molecular weight of heterocyclic polymers. Specific aims of the research include determining the effect of solvent and monomer-to-oxidant ratio used during chemical polymerization on polymer end groups as well as polymer size.

Current research in the McCarley group targets the use of water-soluble, stimuli-responsive dendrimer systems as hosts for guest molecules.² In this system, the periphery/exterior of the host is functionalized with oligo(pyrrole) groups capable of undergoing electron-transfer-induced changes in structure that lead to geometric (steric) changes in the polymer.

![Figure 1.1 Schematic of stimuli-responsive dendrimer systems.](image-url)
dendrimer interior and exterior, thereby affecting the hosting capability of the system. The pyrrole functionality was added to the periphery of the dendrimer because oligo(pyrrole)s have been shown to undergo conformation changes when switched between their oxidized and reduced states. This is important because, upon oxidation, the cationic pyrrole groups should be in a planar, rigid state, which will lead to steric hindrance of guest molecules, trapping them in the core of the dendrimer system. Upon reduction, the pyrrole system will no longer be in a planar state, but will be in a less rigid, neutral state, resulting in a more flexible structure from which the trapped guest molecules can be released. Optimization of the hosting properties of these dendrimers requires knowledge of the host structure, and in particular the structure of the oligo(pyrroles).

The mechanism of oxidative polymerization of pyrroles is not fully understood, so in this simple substituted pyrrole polymers in solution were studied in order to find optimal polymerization/oligomerization conditions, by varying polymerization conditions such as solvent, monomer-to-oxidant ratio, and polymerization time. The structural properties of substituted pyrrole polymers were investigated using MALDI-MS to determine their repeat unit, molecular weight distributions and end-group structures. Because pyrrole polymerization is not fully understood, a model system, 3-hexylthiophene, which is a more studied system, was also investigated. The effect of varying chemical polymerization conditions of these systems was studied to determine their effect on the structure of the 3-hexylthiophene polymers.

Not only is structural characterization of heterocyclic polymers important for the monomer-capped dendrimer application, but it is also of great importance in the broader sense, in that the structure of conducting polymer systems directly influences the physical and chemical properties of the polymer. Two important structural characteristics of heterocyclic polymers are
molecular weight and end-group composition. Molecular weight (MW) and molecular weight distributions of polymers (MWD) are important because they can affect optical and electrochemical properties, as well as, physical properties of the polymer. Knowledge of end-group identity of polymers is significant because it too can affect the optical and electrochemical properties of the polymer. Knowledge of end-group identity also provides information on polymerization termination processes and end-group modification reactions. End-group modification of conducting polymers can lead to functionalized polymers and tailoring of polymers for specific applications leading to block copolymers, grafting of the polymer on to surfaces, attaching electro-active groups to polymers and use of these polymers systems in supramolecular assemblies.\textsuperscript{4, 5} Both end-group identity and molecular weight were the focus of the heterocyclic polymer characterizations done in the research presented here.

1.2 Background

1.2.1 A Historical Perspective on Conducting Polymers

Since the discovery of conducting and electro-active polymers in the 1970s\textsuperscript{6} researchers have continued to expand the diverse applications of these polymeric materials. Research in this field has centered on developments of more ordered and well-characterized materials, structure-property relationships, discovery and tuning of optical and electrical properties, and understanding of the processes in which electron transport occurs in these materials.\textsuperscript{7}

Conducting polymers are defined as polymers that contain unsaturated conjugated systems, in which the electrons are loosely bound. Doping, the addition or removal of electrons, of the polymers system allows electrons in the systems to move along the polymer chain. Electron acceptors and donors can increase the conductivity of polymers by creating charge-transfer complexes in the polymer backbone.
Studies of organic conducting polymers began with the simplest organic polymer poly(acetylene), (CH). Shirakawa et al. formed electrically conducting polymers of this material in the mid 1970s by doping acetylene polymers with halogens. This discovery earned him, as well as MacDiarmid and Heeger, the Nobel Prize in 2000, and opened the door to the field of conducting polymer systems. One of the main problems with poly(acetylene) is its poor environmental stability. Oxidation studies performed on poly(acetylene) show that after exposure to oxygen for short time intervals (10 min), the conductivity of the polymer decreases and can fall as low as that of an insulator.

Poly(pyrrole) and poly(thiophene) have been two of the most widely studied conducting polymers due to their high electrical conductivity, stability in the doped state, and low toxicity. They both have tremendous potential in the technological market, with applications in molecular electronic devices, chemically modified electrodes and sensors, and solid-state batteries. The major drawbacks with these two polymers are processability issues, due to the insolubility of the polymers formed by these compounds. The solubility issues have impeded structure analysis of thiophene and pyrrole polymers by conventional means. Because of this, major strides have been taken to overcome the solubility issues associated with poly(thiophenes) and poly(pyrroles), mainly by addition of side chains.

1.2.2 Mechanism of Heterocyclic Polymerization

Although the first pyrrole polymer was reported in the late 1970s, the mechanism of oxidative heterocyclic polymerization is still not fully understood. One of the reasons the mechanism of polymerization has yet to be conclusively determined is that small changes in experimental conditions can affect polymerization of the pyrroles. For example, the solvent in which the polymerization takes place affects the stability of pyrrole radical cations.
Polymerization may include oligomer-oligomer coupling, monomer-oligomer coupling, as well as coupling between radical cation-radical cation species and/or coupling between a radical cation-neutral species.

One proposed mechanism of pyrrole polymerization is shown in Figure 1.2. It was determined by Andrieux et al. by analysis of reaction kinetics that the first step in pyrrole polymerization is the coupling of a pyrrole cation radical with another cation radical to form a carbon-carbon bond. This has been generally accepted for the path to dimer formation. Guyard et al. investigated the oxidation of different substituted bipyroles using electrochemistry, flash photolysis and pulse radiolysis. These studies support the idea that polymerization of pyrrole occurs via the coupling of radical cations, and neutral pyrrole radicals do not play a role in the polymerization process. This is because the coupling process occurs before deprotonation does.

It has been generally accepted that the initial coupling occurs between two radical cations to form dimers, and then monomeric, dimeric and possibly oligomeric radical cations couple to
form heterocyclic polymers. However, a study done on the electrochemical polymerization of 3-methylthiophene in the presence of bithiophene and terthiophene does not support this polymerization mechanism.\textsuperscript{14} After addition of a small amount of bithiophene or terthiophene, the rate of electrochemical polymerization increases for the entire polymerization period. If the increase in the rate of polymerization is solely due to the oxidation and subsequent coupling of the bithiophene or terthiophene (both have lower oxidation potentials than 3-methylthiophene), the polymerization rate would decrease after the bithiophene and terthiophene were consumed. Also, the resulting polymer would be characteristic of poly(bithiophene) or poly(terthiophene) and not poly(3-methylthiophene). This was not observed.\textsuperscript{14} The electrochemical polymerization of 3-methylthiophene in the presence of bithiophene or terthiophene occurs at oxidation potentials lower than the oxidation potential of the 3-methylthiophene monomer, indicating that formation of the monomer radical cation is not necessary for polymerization to occur.

A new polymerization mechanism was proposed to explain these findings.\textsuperscript{14} When no bithiophene or terthiophene is present, the rate determining step in the polymerization is the formation of the monomer radical cation, which attacks neutral monomers via electrophilic aromatic substitution followed by oxidation and then deprotonation. The dimer formed is then oxidized and attacks another neutral thiophene monomer, forming a trimer, and then the trimer is oxidized and again attacks a neutral monomer and this continues resulting in the creation of polymer (shown in Figure 1.3). The slowest step in the polymerization is the initial dimer formation. When bithiophene or terthiophene is added, this first step is not needed, which increases the rate of polymerization. This also explains why polymerization proceeds at oxidation potentials that are lower than the oxidation potential of the 3-methylthiophene.
monomer. Oxidation of the bithiophene or terthiophene occurs at a lower potential and their radical cations attack neutral monomers resulting in polymer formation. Similar studies on the electrochemical polymerization of pyrrole where a small amount of 2,2’-bipyrrrole increased the rate of polymerization of pyrrole pointed to similar conclusions.\textsuperscript{15}

Polymerization of pyrrole dimers as the starting material, rather than monomers, produces polymers that have more structural defects than polymers made from polymerization of the monomer.\textsuperscript{11} Polymerization of trimers leads to polymer containing an even larger number of defects, and the polymerization stops after a few coupling steps. This supports the claim that monomer-oligomer coupling occurs rather than oligomer-oligomer coupling. Molecular modeling studies show that in all solvents, quaterpyrrole and sexipyrrole formation is slower for coupling of two radical cation oligomers than the coupling of a monomer radical cation with oligomer. Such studies also demonstrate that oligo-pyrrole dications may couple with neutral pyrrole units instead of coupling with another radical cation.\textsuperscript{11}

Some studies have focused on the polymerization mechanism of poly(pyrrole) and poly(thiophenes) synthesized chemically with iron(III) chloride, FeCl\textsubscript{3}, as the oxidant.\textsuperscript{16, 17} It was

![Figure 1.3 Mechanism of radical cation-neutral coupling for oxidative polymerization of pyrrole monomers. Adapted from Reference 14.](image-url)
initially thought that solid FeCl₃ is needed during the polymerization for polymer to form.¹⁶ This is because no polymerization occurred when FeCl₃ was completely dissolved in the polymerization solvent chloroform. It has since been shown that polymerization does occur if solid FeCl₃ is not present and FeCl₃ is completely dissolved. It was demonstrated by Oliga et al. that polymer was formed when thiophene monomers were polymerized in acetonitrile, in which the FeCl₃ was completely dissolved.¹⁸ Therefore, despite earlier claims, a solid FeCl₃ surface is not necessary for polymerization.

The polymerization solvent used during the chemical oxidative synthesis of pyrrole with FeCl₃ plays an important role in the synthesis and properties of the resulting polymer. Myers et al. studied the effect of the reaction medium on the resulting pyrrole polymers.¹⁷ Again it was demonstrated that the polymerization of pyrrole is not directly related to the solubility of FeCl₃. Polymer was formed in solvents in which FeCl₃ was completely soluble (nitromethane) and in solvents in which FeCl₃ was completely insoluble (hexane). It was noticed that no polymer formation occurred in solvents that are strong Lewis acid donors toward FeCl₃ such as dimethylsulfoxide and pyridine. It was proposed by Myer et al. that a pyrrole-FeCl₃ intermediate is formed during polymerization.¹⁷ The yield of polymer relies on the amount of FeCl₃-solvent interactions in comparison with the FeCl₃-pyrrole interactions. Reaction exotherms were used to monitor the interactions of FeCl₃ and pyrrole in different solvents. The dissolution of FeCl₃ in solvent results in an exotherm associated with the FeCl₃-solvent complex formation. A very strong exotherm was observed for the dimethylsulfoxide and pyridine solvents upon addition of FeCl₃. Typically a second exotherm is observed upon addition of pyrrole to the FeCl₃ solution. This exotherm is thought to result from the interaction of pyrrole and FeCl₃. No second exotherm and no polymer formation were observed upon addition of pyrrole to FeCl₃ dimethylsulfoxide.
and pyridine solutions. This is probably because the solvent-FeCl₃ complexes are very stable and the FeCl₃ is highly solvated, making it unlikely for the FeCl₃ to form a complex with the pyrrole monomer. This suggests that solvent-FeCl₃ interactions relative to pyrrole-FeCl₃ interactions may have a substantial impact on the formation of polymer made chemically using FeCl₃ as the oxidant.

It has also been demonstrated that polymerization of 3-octylthiophene while HCl gas was continuously infused into the container gave low polymer yields.¹⁶ This is explained by the complexation of the gas with the FeCl₃ resulting in FeCl₄⁻ which is not active. Polymerization of thiophenes and pyrroles with FeCl₃ results in the production of HCl, resulting from the Cl⁻ ions originating from the FeCl₃ and protons that are result of the deprotonation of the oligomers during polymerization. Because HCl is evolved during polymerization and it consumes some of the FeCl₃, an excess of FeCl₃ is required.

1.2.3 Mechanism of Conductivity in Heterocyclic Polymers

The conformation of pyrrole and thiophene units changes upon oxidation and reduction of the oligomers.⁷ Oxidation of the pyrrole/thiophene oligomer causes a polaron (radical cation or anion, the former in this case) to be formed. Further oxidation of the oligomer causes a bipolaron (dication) to be formed. Polarons and bipolarons are the charge carriers on the polymer backbone in these systems. The charge delocalizes on the pyrrole/thiophene oligomers to form a pyrrole/thiophene oligomer structure that has units in the quinodal state.⁷ As demonstrated by Figure 1.4, pyrrole units that are polarons are in a cationic state, forming a planar, rigid structure in which the pyrrole units are connected by double bonds. Upon reduction, the dendrimer structure becomes less rigid and less planar because the pyrrole units are connected by single bonds. Charge movement in these systems not only occurs along the polymer chain but also by
chain hopping from polymer chain to polymer chain.\textsuperscript{19, 20} This interchain transport is facilitated by $\pi$-dimers and $\pi$-stacking of poly(thiophene) and poly(pyrrole).\textsuperscript{21-23}

**1.2.4 Pyrrole Polymer Systems-Insoluble Films and Powders**

Pyrrole polymer was first synthesized by Diaz et al. electrochemically to form a strong, durable film with room temperature conductivities ranging from $10-100\ \Omega^{-1}\ cm^{-1}$.\textsuperscript{10} Since then, pyrrole polymers have been polymerized using electrochemical methods and chemical oxidative methods that employ metal halides. These synthesis routes have typically yielded insoluble polymers. Because of this, pyrrole polymers have not been as extensively characterized as thiophene polymers, and it has been difficult to characterize these polymers using standard analytical techniques. Most of the characterization work associated with pyrrole polymers has been done on pyrrole polymer films or powders. The main techniques that have been used to characterize these polymers are Fourier-transform infrared spectroscopy (FT-IR), X-ray photoelectron spectroscopy (XPS), and conductivity measurements.

Some of the FT-IR studies have focused on determining if addition of oxygen to pyrrole polymers occurs. Elemental analysis of pyrrole polymers usually shows oxygen that has added to the polymer.\textsuperscript{24} It has been demonstrated that pristine poly(pyrrole) is not air-stable and is susceptible to oxygen addition.\textsuperscript{25, 26} To investigate the reaction of pristine poly(pyrrole) with
oxygen, FT-IR studies have been done on pristine poly(pyrrole) compared to poly(pyrrole) exposed to water and oxygen.\textsuperscript{24, 26, 27} Street et al. were the first to report IR spectra for pristine poly(pyrrole).\textsuperscript{27} Comparison of the IR spectrum of the pristine pyrrole polymer to that of the polymer exposed to oxygen led to the conclusion that oxygen is capable of oxidizing the neutral film, and a polymer cation is formed similar to that present in electrochemically oxidized pyrroles. Lei et al. investigated the chemical interactions between molecular oxygen (O\textsubscript{2}) and poly(pyrrole), and it was determined that exposure of poly(pyrrole) to O\textsubscript{2} does not result in the addition of hydroxyl or carbonyl moieties to the pyrrole polymer.\textsuperscript{25} FT-IR analysis of poly(pyrrole) exposed to oxygen for 30 min did not show any evidence of these chemical functionalities. Prolonged exposure of poly(pyrrole) films to oxygen did however lead to the deprotonation of the nitrogen on the pyrrole ring, evidenced by the N-H stretching mode (3400 cm\textsuperscript{-1}) becoming weaker as the exposure time to O\textsubscript{2} increased.

It has been shown that electrochemical and chemical oxidative degradation of poly(pyrrole) can occur. The result is hydroxylation of the pyrrole unit which can lead to tautomerization and formation of a carbonyl group as shown in Figure 1.5.\textsuperscript{28, 29} This has been attributed to the presence of water or OH\textsuperscript{-} ions in the polymerization solutions.\textsuperscript{24} Ghosh et al. used infrared and Raman spectroscopy to study the oxidative degradation of pyrrole.\textsuperscript{28} They determined that the rate of over-oxidation is higher at higher potentials, and at higher pHs. Excess oxygen substitution on the pyrrole polymer causes problems in that the highly oxygenated material is less conjugated and electrochemically inactive,\textsuperscript{30} and oxygen addition to the alpha carbons can cause polymerization to be terminated, if the oxygen inhibits the carbon-carbon bond formation in the polymerization process. Highly oxygenated products are known to
give an insoluble black powder, some times referred to as “pyrrole black”, which is a term also used to described high-molecular-weight or cross-linked insoluble pyrrole polymer.\textsuperscript{31}

It has also been shown that poly(pyrrrole) undergoes chlorination in the presence of chloride ions (Cl\textsuperscript{–}).\textsuperscript{28, 32} This is attributed to nucleophilic attack of Cl\textsuperscript{–}, similar to that of OH\textsuperscript{–} on pyrrole polymer.\textsuperscript{28} Chloride can result from the electrolyte in the electrochemical synthesis\textsuperscript{28} or from FeCl\textsubscript{3} when it is used as the oxidant in the chemical synthesis.\textsuperscript{31, 33} Elemental analysis of poly(pyrrrole) synthesized with FeCl\textsubscript{3} (monomer-to-oxidant ratio 1:1) showed a chloride content of 8.7%.\textsuperscript{31} XPS studies of poly(pyrrrole) synthesized by FeCl\textsubscript{3} showed that chlorine in poly(pyrrrole) complexes exists in three chemical states.\textsuperscript{33} These are attributed to ionic chlorine (Cl\textsuperscript{–} counterion), covalent chlorine (attached to poly(pyrrrole) backbone), and possibly chloride ions that are still present in an FeCl\textsubscript{3} impurity. It was indicated that the portion of covalent chlorine increases with increasing FeCl\textsubscript{3} to monomer ratio and can account for 12-47% of the total chlorine present in the polymer sample. From this it can be concluded that the 8.7% chlorine content of chemically synthesized poly(pyrrrole) can not solely be attributed to chlorine that is covalently attached to the pyrrole polymer, with some of the chlorine resulting from chloride ions and residual FeCl\textsubscript{3}.

\textbf{Figure 1.5} Schematic of possible nucleophilic addition of water to cationic oligopyrrole.
Changing the conditions used to synthesize pyrrole polymers causes changes in the resulting structural characteristics of the polymer, which leads to changes in the properties of the polymers. Lei et al. systematically studied how changing the initial monomer and oxidant (FeCl₃) concentrations affected the chain, the conjugation lengths, as well as the concentration of chemical defect sites of the pyrrole polymers, and how the conductivity of the polymers were affected by these changes. In the study by Lei, the oxidant used was Fe³⁺, and the Fe³⁺ to pyrrole ratio was kept at 50:1 (in water), although the concentration of Fe³⁺ was varied from 2.0 M to 0.06 M and the pyrrole concentration was varied from 0.040 M to 0.0013 M. This study showed that the yield of poly(pyrrole), based on solid poly(pyrrole) formed, decreased as the reactant concentration was decreased. The explanation given for this was that soluble polymer was formed at the lower reactant concentrations, which was not collected by filtration and therefore was not measured as polymer product. The presence of soluble polymer indicates that polymer with shorter chain lengths is formed at lower reactant concentrations (slower polymerization rates).

As stated earlier, oxidized pyrrole polymer chains react with water, and it has been suggested a carbonyl group on the polymer backbone may be formed. FT-IR analysis of the poly(pyrrole) shows that the intensity of the carbonyl band (1705 cm⁻¹) increases as the concentration of the monomer and oxidant decreased. The concentration of the carbonyl defects in the polymer is greater in polymer made with lower reactant concentrations. The FT-IR data and UV-visible absorption data show that as the concentration of reactants increases, the conjugation length in the polymer increases, which is not surprising because the chain length also increases and the concentration of carbonyl defects decreases. The conductivities were measured for the polymers made with the different concentrations of reactants, and an increase in
conductivity was observed as the concentration of the reactants was increased. This is not surprising and correlates with the increase in chain length and conjugation length.

It has also been demonstrated that there is a correlation between synthesis temperature and number of structural defects and conductivity of the resulting poly(pyrrole). XPS studies indicate that some deprotonated imine-like nitrogens are present in the polymer samples. This is considered a defect site because it can interrupt the conjugation of the polymer. Polymer synthesized at lower temperatures has less of this defect, which leads to an increase in conductivity of those polymers. IR analysis show that polymers formed at lower temperatures do not have the absorption band attributed to a carbonyl, while polymer formed at higher temperatures have a weak carbonyl absorption band. The presence of the carbonyl groups also contributes to a decrease in conjugation of the pyrrole polymers made at higher temperatures, which causes them to have lower conductivities. This work demonstrates that the polymerization conditions, such as the concentration of reactants and the reaction temperature, affect the structure and resulting properties of pyrrole polymers.

1.2.5 Soluble Pyrrole Polymers

Efforts have been made to form soluble pyrrole polymers to improve the processability of the polymers. One way in which unsubstituted pyrrole polymers have been made soluble is by incorporating dopants that enhance the solubility. It is thought that this class of dopant makes the polymer molecules more soluble as a result of the dopant residing between pyrrole polymer chains and thereby reducing intermolecular interactions between poly(pyrrole) chains. Pyrrole polymer soluble in organic solvents was made using ammonium persulfate as the oxidizing agent and dodecylbenzene sulfonic acid (DBSA) as the dopant. The molar doping level was 22-25%, similar to the doping level of the poly(pyrrole) prepared electrochemically using the
same dopant. The absorption spectra of the resulting pyrrole polymer in DBSA/chloroform was similar to that of oxidized pyrrole made electrochemically, and therefore the electronic structure of the pyrrole polymers made electrochemically and chemically were thought to be very similar. Light scattering measurements were done on the poly(pyrrole)-DBSA in chloroform. For polymer that had a DBSA-polymer ratio of 2:1, the hydrodynamic radius of the polymer was 27 nm. As additional DSBA (added to DSBA-(poly)pyrrole to make it more soluble) was added to the polymer solution the hydrodynamic radius increased to about 45 nm and then leveled off. No change was observed in the electronic absorption spectra as additional DBSA was added. It was concluded that when additional DBSA molecules were added, they formed micelle like structures with the existing PPy-DBSA.

Another dopant that has been shown to increase the solubility of poly(pyrrole) in organic solvents and alcohol is di(2-ethylhexyl) sulfosuccinate sodium salt (DEHS). Polymer made when this dopant was present has ~2-5 % wt/vol solubility in weakly polar solvents and ~6-9% wt/vol solubility in polar solvents. GPC studies have been done on soluble pyrrole polymer doped with DEHS, and it was found that polymer synthesized for 12 h using ammonium persulfate as the oxidizing agent had an average of 159 pyrrole units and polymer synthesized for 20 h had an average of 303 pyrrole units (determined from GPC using polystyrene standards). Conductivities for (poly)pyrrole-DEHS thin films ranged from 8.2 x 10^{-3} to 3 S cm^{-1} depending on the solvent from which the films were cast. Poly(pyrrole)-DEHS conductivities were higher in films cast from more polar solvents and it is thought that pyrrole polymers adopt an expanded coil conformation in these solvents, which increases the mobility of the electron on the polymer chain. X-ray diffraction studies showed that the poly(pyrrole)-
DEHS polymers films were more crystalline for polymers cast from the more polar solvents, which is consistent with them having a more expanded conformation.\textsuperscript{36}

Another way in which pyrrole polymers have been made soluble is by adding alkyl or alkylsulfonate chains to the monomers.\textsuperscript{41-45} Poly(alkylpyrroles) that were synthesized electrochemically have room temperature solubilities between 3.5 g dm\textsuperscript{-3} and 681 g dm\textsuperscript{-3} in dichloromethane, depending on the polymerization solvent and electrolyte used.\textsuperscript{45} Electrochemical studies have been performed on substituted pyrroles to compare substituent effects on the electrochemical properties of pyrrole.\textsuperscript{46} Substitution at the \(N\)-position of the pyrrole ring with withdrawing groups results in stabilization of the pyrrole monomer and oligopyrroles. This stabilization increases the oxidation potential of the \(N\)-substituted pyrroles, which protects the oligopyrroles from air degradation via oxidation.\textsuperscript{46} Electrochemical studies have also been performed on 3-alkylpyrroles with different chain lengths. These studies suggest that 3-alkylpyrroles monomers have a lower oxidation potential than unsubstituted pyrrole monomers and that the electrical conductivity of poly(3-alkylpyrrole)s decreases with an increase in side chain length.\textsuperscript{47} A substantial decrease in electrical conductivity is only observed with monomer that has an alkyl chain that has beyond 12 carbons.\textsuperscript{48} This is a result of the charge transport in the polymers being influenced by the large bulky side chain.\textsuperscript{47, 48}

\(N\)-alkylpyrroles have been polymerized via chemical oxidation with FeCl\textsubscript{3} in nitromethane.\textsuperscript{42} Poly\((N\)-(2-hydroxyethyl)pyrrole) was found to be insoluble, but poly\((2-(N\textsuperscript{-}pyrrolyl)ethylacetate)\) and poly\((2-(N\textsuperscript{-}pyrrolyl)ethyl stearate)\) were partially soluble in THF, chloroform, nitromethane and acetone. \textsuperscript{1}H-NMR analysis of the soluble polymers led to the observation of very broad signals, and integration of the peaks gave values that were less than
expected for the aromatic protons. This may be due to aggregation of the polymers. The soluble polymers had relatively low conductivities of $10^{-7}–10^{-5}$ S cm$^{-1}$ when cast as films.

Poly(3-alkylpyrrole) has been synthesized electrochemically in acetonitrile with 0.02 M of monomer and 0.06 M of tertbutylammonium perchlorate electrolyte by applying a total current density of 30 C cm$^{-2}$. Polymer films in the reduced state were partially soluble in organic solvents. Solutions of the polymer were not stable and degraded when they were exposed to air, forming a black precipitate. GPC analysis (calibrated with polystyrene standards) indicated polymer was formed with molar masses ranging from 5000 to 10000 g/mol. The conductivity of the 3-alkylpyrrole polymers compressed into dense pellets ranged from 0.03 to 10 S cm$^{-1}$, depending on the length of the alkyl chain. The conductivity of the polymer decreased slightly with an increase in the length of the alkyl substituent.

Poly(3-alkylsulfonate pyrrole) has been synthesized electrochemically in acetonitrile. No electrolyte was added because the monomer itself acts as a “conduction salt”. The resulting polymers were slightly soluble in water (0.1 to 0.5 g L$^{-1}$) and are considered “self-doping” because the attached sulfonate groups act as counterions for the charged polymer. The solubility of the polymer increased with the length of the side chain. $^1$H-NMR analysis of the polymer showed broad signals in the aliphatic region and low signal in the aromatic region. The reported conductivities of the polymer films/pellets ranged from $10^{-5}$ to 0.5 S cm$^{-1}$ and X-ray analysis of the films showed they were amorphous.

The added difficulties of working with pyrroles because of solubility issues, as well as stability issues when the polymer is exposed to air, have led to these polymers not having been characterized or utilized nearly as much as thiophene polymers even though they have lower oxidation potentials and higher electrical conductivities. One of the main aims of this work was
to synthesize and characterize soluble substituted pyrrole polymers. For the first time, mass spectrometry was used to characterize N-alkylpyrrole polymers as well as 3-substituted pyrrole polymers. Structural analysis using MALDI-TOF MS, as well as other analytical techniques, will provide more insight into the structures of these polymer materials and show how synthesis conditions can be manipulated so as to obtain poly(pyrrole)s with superior properties.

1.2.6 Thiophene Polymer Systems – Electrochemical and Chemical Synthesis

Thiophene monomers consist of a heterocyclic ring similar to that of the pyrroles, except the heteroatom in the ring is sulfur instead of nitrogen. Initially, there were many solubility and processability issues with thiophene polymers, until the introduction of an alkyl side chain into the monomer. In 1985, poly(3-alkylthiophene), P-3AT, was successfully polymerized by Elsenbaumer and coworkers, and it was found to yield polymer soluble in common organic solvents, when the alkyl chain substituent was a butyl group or larger.\textsuperscript{49-51} The first soluble P-3ATs were synthesized chemically using Kumada cross-coupling, which consisted of iodinating the alkylthiophene monomers to form 2,5-diiodothiophenes, and then polymerizing them using a nickel-catalyzed Grignard coupling route.\textsuperscript{50} The polymers had an average molecular weight of 3000-8000 determined by vapor-phase osmometry. IR and NMR analyses indicated that random coupling occurred at the 2,5 positions of the thiophene rings. Since this initial report, different methods have been reported in the literature for forming P-3ATs with the three main polymerization methods being electrochemical polymerization,\textsuperscript{52, 53} chemical oxidation using iron(III) chloride,\textsuperscript{52, 54} and Grignard coupling methods.\textsuperscript{19, 55-58}

The electrochemical polymerization of P-3ATs generally consists of forming polymers films on an electrode surface (platinum or indium/tin oxide) from solutions containing monomer and electrolyte. Specific reaction conditions used by Leclerc et al. and Hotta et al.
electrochemically form P-3ATs consisted of using 0.1 – 0.2 M of monomer and 0.02 M of electrolyte while applying a constant current density of 2 mA cm\(^{-2}\) at 5 °C at the electrode surface for varying times (40 s for thin films, 6 h for large solid polymer).\(^{52, 53}\) Elemental analyses of the P-3ATs obtained by this method show chemical compositions consistent with theoretical values.\(^{52, 53}\) Molecular-weight analyses using GPC (calibrated with polystyrene standards) showed that as the polymerization time increased (2-6 h), the number average molecular weights of the P-3ATs increased from 12,000 to 80,000, and the polydispersity decreased from 10.9 to 4.5.\(^{52}\)

Chemical oxidative polymerization is the most utilized, and considered the simplest synthesis method for P-3ATs. The first chemical polymerization of P-3AT was reported in 1986 by Sugimoto et al.\(^{54}\) Leclerc et al. chemically polymerized 3-alkylthiophenes using iron(III) chloride (FeCl\(_3\)) as the oxidant with a procedure similar to that of Sugimoto et al.\(^{52}\) The polymerization was done by dissolving the alkylthiophene monomer in dry chloroform (0.003 mol in 20 mL of chloroform) and adding it dropwise to a suspension of solid FeCl\(_3\) in dry chloroform. The reaction was stirred under argon, at room temperature, for 24 h, and the polymer product was washed with methanol and acetone. Polymer formed using this method was shown by GPC analysis (using polystyrene standards for calibration) to have molecular weight averages from 37,800 to 55,100 and polydispersities around 5.0.\(^{52}\)

Structural comparisons were done by Leclerc et al. of P-3ATs formed electrochemically and chemically using FeCl\(_3\).\(^{52}\) Because the 3-alkylthiophene monomers are unsymmetrical, coupling of the monomers can occur in one of four ways, head-to-head, head-to-tail, tail-to-tail, or tail-to-head (shown in Figure 1.6). \(^1\)H-NMR analysis was done on the polymers to determine the percent of head-to-tail coupling of the monomer units. Head-to-tail coupling (H-T) is the
most favorable, because with the other three couplings, steric interactions between the alkyl chains cause defects in the planarity of the polymer backbone which leads to a decrease in the conjugation of the polymer.\textsuperscript{19} The H-T content is determined by \textsuperscript{1}H-NMR by comparison of the peak area ratios of the aryl methylene, where there are two resonances at 2.56 and 2.80 ppm, with the latter assigned to head-to-tail coupling.\textsuperscript{52, 59} The H-T content was determined to be \(~60-70\)% for P-3AT synthesized electrochemically and \(~80\)% for P-3AT synthesized chemically.\textsuperscript{52} The \textsuperscript{13}C-NMR analysis also showed a larger number of defects for polymer made electrochemically compared to that made chemically. These defects were attributed to possible 2,4'-couplings and/or the formation of branched polymers. Comparison of X-ray diffractograms of the polymers showed that chemically prepared P-3AT had a higher degree of crystallinity than that formed electrochemically. Optical studies on the polymers showed that they have a wavelength of maximum absorbance ($\lambda_{\text{max}}$) at 440 nm in chloroform. Thin films of chemically formed P-3AT had a lower band gap with a $\lambda_{\text{max}}$ of 505 to 510 nm, while the electrochemically formed P-3AT had a $\lambda_{\text{max}}$ between 450 and 480 nm. Conductivity measurements showed that chemically formed polymer also had a higher conductivity (25-30 S cm\textsuperscript{-1}) than that of

\begin{figure}[h]
\centering
\includegraphics[width=\textwidth]{possible_couplings.png}
\caption{Possible couplings of 3-alkylthiophene monomers, including head-to-tail (H-T), tail-to-tail (T-T), head-to-head (H-H), and tail-to-head (T-H).}
\end{figure}
electrochemically prepared thiophenes (1-10 S cm\(^{-1}\)). From these studies it was concluded that electrochemically formed P-3ATs have a more irregular structure than polymer formed using chemical oxidative methods.

1.2.7 Thiophene Polymer Systems – Regioregular Methods

More recently, work has been carried out on the chemical polymerization methods of P-3ATs that involves controlled coupling of the 3-substituted thiophene monomers. These methods are known as the McCullough method,\(^{19, 60}\) the Rieke method,\(^{55-57}\) and the GRIM method.\(^{58}\) These polymerization methods involve Kumada cross-coupling reactions using organomagnesium or zinc, which is specifically located on the 5-position on activated thiophene intermediates, and catalytic amounts of Ni(dppp)Cl\(_2\).\(^{19, 55-58, 60}\) These polymerization methods have been developed to regiochemically control the coupling of monomers and form structurally homogeneous poly(3-hexylthiophene)s. Polymers formed with these methods have been shown by \(^1\)H-NMR to possess exclusively H-T (98%) couplings.\(^{19, 57, 58}\)

The effect of structural regularity on the polymers was investigated by McCullough by examining model dimers, trimers and tetraters of alkylthiophenes by molecular mechanics.\(^{19}\) These studies showed that head-to-head couplings in the model compounds caused twisting of the thiophenes rings out of coplanarity, while head-to-tail couplings in the model compounds led to greater coplanarity along the rings and greater \(\pi\) overlap, resulting in lower band gaps. Comparisons of solution and solid-state UV-visible studies of P-3ATs made with FeCl\(_3\) and with the McCullough method showed improved properties for the polymer with a homogenous structure made with the McCullough method.\(^{19}\) The shift to a lower energy \(\lambda_{\text{max}}\) is 6 nm in solution and 24 nm in the solid state for poly(3-hexylthiophene) made with the McCullough method compared to poly(3-hexylthiophene) made with FeCl\(_3\).\(^{19}\) These results confirm that
coupling of the monomers of P-3ATs directly affects the optical and electrical properties of the resulting polymer.

### 1.2.8 Structure–Property Relationships in Poly(3-hexylthiophene)

It has also been shown that the substitutions on the polymer as end groups or on the backbone can affect the properties of the polymer. Qi et al. electrochemically substituted poly(thiophene) with nucleophiles, such as Cl\(^-\), Br\(^-\) and methanol, to determine the mechanism of nucleophilic addition and to study the effects of these substituents on the properties of the polymer.\(^{32}\) Electrochemically oxidizing electrode supported films of poly(thiophene) in the presence of Cl\(^-\) results in an irreversible anodic electrochemical wave, and it was concluded that the polymer has become inactive electrochemically.\(^ {32}\) The polymer can be re-oxidized at potentials higher than the normal peak potential of 0.6 V so as to yield reactivated polymer. The presence of the inactive intermediate provides support for the proposed mechanism for the halogenation of thiophene polymers shown in Scheme 1.3, where B is electrochemically inactive and nonconductive because it is poorly conjugated.\(^ {32, 61}\) Reactivation of the polymer is the result of hydrogen loss which restores conjugation to the polymer system. This reactivation has been done electrochemically and by applying a dehydrogenation

![Figure 1.7 Proposed mechanism of nucleophilic chlorine addition to P-3HT. Adapted from Reference 32.](image)
reagent.\textsuperscript{62} Poly(3-methylthiophene) begins to deactivate at a lower potential than poly(thiophene), because it is more easily oxidized. This demonstrates that nucleophilic addition to the polymer is more dependant on the oxidation state than the applied potential. This adds further support to the halogenation scheme, because it depicts chlorine addition occurring to oxidized polymer that is cationic.\textsuperscript{32} Upon addition of chlorine to thiophene polymers a slight shift to a higher oxidation potential is observed, which is attributed to the electron-withdrawing effect of the chlorine substituent.\textsuperscript{32} Upon over-oxidation, thiophene polymers have also been shown to undergo bromination in the presence of bromide. The number of sites that undergo nucleophilic substitution is dependant on the potential, the degree of oxidation of the polymer, and on the nucleophile.\textsuperscript{32}

The effect of different end-substitutions on the optical and electrochemical properties of small thiophene oligomers was investigated by Garcia et al.\textsuperscript{63} An effect opposite to that observed by Qi et al. was observed with methoxy, bromo, and nitro substituents on dimer, trimer, and tetramer thiophenes, in that the substituents that stabilized the radical cations lowered the ionization potential of the oligomer. These substituents also caused red shifts in the $\lambda_{\text{max}}$ compared to unsubstituted oligomers. A “fading” of the end substituent effect on the oxidation potential and $\lambda_{\text{max}}$ was observed; that is, the shifts observed in $\lambda_{\text{max}}$ as a result of the substituent identity were smaller as the oligomer length increased. The shifts in the ionization potential and the absorbance spectra of the polymers were attributed to electron donating effects of the substituents.

The molecular weight of thiophene polymers can also affect their optical and electrical properties.\textsuperscript{20, 64-67} Studies done on alkylthiophene oligomers, ranging from 3-mers to 11-mers, showed that the $\lambda_{\text{max}}$ in the absorbance spectra was red shifted with increasing length of the
oligomers. It was also shown that the conductivity of the oligomers increased with oligomer length. These observations are not surprising, because the conjugation length should be longer in larger oligomers. As expected, this is also true for larger thiophene polymers. Studies done on thiophene polymers with average molecular weights ranging from 3,000-21,000 have shown that the effective conjugation length of the polymer increases with an increase in the molecular weight, which causes red shifts in the wavelength of maximum absorbance. This effect is more pronounced in the absorption spectra of the P-3AT in the solid state compared to solution. It was also shown that polymers with higher average molecular weight have lower oxidation potentials. Studies done by Osawa et al. on P-3HT formed electrochemically showed that the electrical conductivities of the polymer films increased as the average molecular weight increased for polymers with average molecular weights below 25,000. As the average molecular weight increased above 25,000 there was not a prominent observable increase in the electrical conductivity. Molecular weight dependent shifts of the P-3HT oxidation potential and $\lambda_{\text{max}}$ were also more pronounced for smaller molecular weight polymer (< 25,000).

The conductivity of P-3ATs is dependant upon intrachain charge transport, which is the charge transport along the polymer chain, and also by interchain transport, which is charge hopping from one polymer chain to another. Because of this, the macroscopic structure and crystallinity of poly(3-hexylthiophene) has an impact on the electronic properties of the polymer. Differential scanning calorimetry (DSC) measurements on solution-crystallized poly(3-hexylthiophene) samples with average molecular weights ranging from 3,000 to 37,000 exhibits an increase in crystallinity with an increase in molecular weight. It has been observed the charge mobility in P-3HT films increases with molecular weight and this is most likely due to
higher molecular weight polymer being more crystalline, which allows for an increase in the effective conjugation length.

1.2.9 Applications of Poly(3-hexylthiophene)

Substituted thiophenes polymers are currently being used in sensor applications. These polymers are ideal for this application because they exhibit thermochromism, ionchromism, photochromism and biochromism.\textsuperscript{68} Significant color changes are observed when different stimuli cause disordering of the polymer chains, which leads to twisting of the polymer backbone. Disordering of the polymer can be caused by thermal disruption of the side groups,\textsuperscript{69-71} interactions of ions with side chains,\textsuperscript{69, 72, 73} photo-induced reactions of the side chains,\textsuperscript{74} and binding of the side chains with chemical or biochemical species.\textsuperscript{75} Also, control of the absorption properties of substituted thiophene polymers allows for tuning of their luminescence properties and has lead to the development of these polymers being used in other applications such as electrochromic devices\textsuperscript{76} and light emitting diodes.\textsuperscript{77-79}

Another specific application of thiophene polymers is in the area of organic field-effect transistors.\textsuperscript{64, 80-82} The solubility and processability of these polymers along with their electronic properties make these polymers very promising for this application. It has been shown that the structure, specifically the molecular weight and nanostructure, of the alkylthiophene polymers, directly affects the field-effect mobility of the polymers in thin-film field effect transistor devices.\textsuperscript{64, 80}

It is obvious that the structure and molecular weight of substituted thiophenes polymers directly affects the optical and electrical properties of the polymer. Because substituted thiophene polymers are being used in a wide range of applications and the performance of these polymers is mainly based on their electronic and optical properties, it is vital no matter what
polymerization method is used, to evaluate and optimize the structure and molecular weight of thiophene polymers for specific applications. One of the main aims of the work presented here was an in-depth study of how changing the oxidative chemical polymerization conditions of poly(3-hexylthiophene) affects the structure and molecular weight of the polymer and to further investigate the effect of structural differences on the optical properties of P-3HT. This work focuses on oxidative chemical polymerization of thiophenes using FeCl₃, although it has been shown that polymer formed with this method has a less regular structure than polymer made using the McCullough, Rieke and GRIM methods.¹⁹, ⁵⁷, ⁵⁸ Despite this drawback, the FeCl₃ method is the most utilized polymerization method due to its simplicity compared to the regio-regular polymerization methods. It has been shown that polymer made using the regio-regular polymerization methods may contain a large amount of bromine which is suspected to be present in the form of end groups.⁴, ⁵ Removal of these end groups requires post-polymerization treatment.⁴, ⁵, ⁸³ Herein, the common synthesis route of chemical oxidation is used for P-3HT and it is demonstrated that polymerization conditions, such as solvent and monomer-to-oxidant ratio, strongly influence the composition of the polymer end groups. More importantly, the methodology described here does not require any additional or post-polymerization modification steps. This is specifically important for applications where post-polymerization and complicated oligomerization is not an option, as is this case with the monomer capped dendrimer systems.

1.3 MALDI-MS Analysis of Synthetic Polymers

1.3.1 Background and History

Mass spectrometry has become a powerful analytical tool in the evaluation of synthetic polymers in that it can provide data with molecular weight information, structural information, repeat unit sequence, as well as information on polymer additives and impurities.⁸⁴ The
development of soft ionization techniques, specifically MALDI in 1988, expanded the mass range considerably over which polymers can be analyzed by mass spectrometry, by overcoming the issues of low volatility or thermal liability of high-molecular-weight polymers. MALDI-MS has become a more utilized mass spectrometry technique for characterization of polymers versus electrospray ionization mass spectrometry (ESI-MS), due to the added complication of multiple charging in ESI as well as the stringent solvent conditions.

MALDI-MS analysis of synthetic polymers was first reported in 1992 by three different groups. Hillenkamp et al. reported the successful MALDI-MS analysis of several poly(ethylene glycol), poly(propylene glycol), poly(methyl methacrylate), and poly(styrene) samples that had various molecular weights up to 70,000 Da. MALDI coupled to a Fourier-transform mass analyzer was used to evaluate poly(ethylene glycol); masses up to 10,000 Da were observed and the resolution was sufficient to resolve oligomers. Danis et. al reported the analysis of water soluble polymers, poly(acrylic acid) and poly(styrene sulfonic acid), by MALDI-TOF MS. For low-molecular-weight polymers, the peaks were sufficiently resolved to observe the mass of the monomer and the mass of the end group.

Since these initial studies, MALDI-MS has been used for evaluation of conducting polymer systems in which repeat unit, end group, and molecular weight analysis has led to a greater understanding of the structure of these polymers. The use of MALDI-MS to characterize conducting polymers was first reported by Visy and co-workers in which MALDI-MS was used to determine the degree of polymerization in electrochemically synthesized oligomers made of terthiophene derivatives containing aromatic substituents. Since then, MALDI-MS techniques have been utilized to characterize polyaniline, polyacetylene and polyene block co-polymers, poly(p-phenylene)s and poly(alkylthiophene)s.
1.3.2 MALDI-MS of Poly(alkylthiophene) Systems

MALDI-MS has been utilized to characterize poly(alkylthiophenes) synthesized via different routes. Lui et al. characterized poly(3-alkylthiophene) polymers made via three different methods, namely, the GRIM method, the Rieke method and the McCullough method, to determine molecular weight, molecular weight distributions, end-group structures and end-group modifications utilizing MALDI-MS.\cite{83} End-group analyses of P-3HT synthesized via the McCullough method showed that the polymer contained three end-group types: polymers terminated by hydrogen atoms at both ends (H-H), polymers terminated by a bromine atom on one end and hydrogen atom on the other end (Br-H), and polymers terminated by bromine on both ends (Br-Br). End-group analysis of P-3HT purchased from Aldrich (presumably made via the Rieke method) had polymer that contained H-H end groups, as well as H-Br end groups, while polymer made via the GRIM method had polymer with H-Br end groups, as well as polymer with one hydrogen and one methyl end group (H-CH₃). MALDI-MS was also utilized to monitor chemical modifications used to alter end groups of poly(alkylthiophenes) made via these routes.\cite{4, 5, 83}

Structural investigation of P-3HT made via chemical oxidation with iron(III) chloride using MALDI-MS was done by McCarley et al.\cite{91} The data contained peak series indicating polymer with two, three and four chlorine additions, with no peak series present for polymer with the expected end groups of hydrogen. The source of the chlorine atoms present in the P-3HT was investigated, with possible sources being the chlorinated polymerization solvent (chloroform) or the oxidant (FeCl₃). The possibility of the chlorine atoms in the P-3HT resulting from the oxidant FeCl₃ was tested by synthesis of P-3HT using a different oxidant, iron(III) bromide. Polymer synthesized with this oxidant contained two major ion series in the MALDI-
MS data, one resulting from polymer with two bromine additions and one from polymer with three bromine additions. No ions were detected from P-3HT with chlorine substituents. Based on this data, it was concluded that the chlorine addition to P-3HT polymer was a result of the oxidant and not a result of the chlorinated solvent.

1.3.3 End-Group Specific Discrimination in MALDI-MS

Liu et al. explored the possibility of end-group fragmentation during the MALDI process of P-3HTs which could cause inaccurate end-group determinations. To determine if this was occurring, the end-group signal intensity as a function of the laser power was investigated. In the lower molecular weight P-3HT samples, a correlation was found between the laser power and the ratio of the H-H:H-Br peaks. As the laser power increased, the ratio of the H-H to the H-Br peaks increased, possibly because bromine end-group fragmentation was occurring during the laser desorption/ionization process. This fragmentation would contribute to the H-H signal intensities. Negative-ion MALDI-MS was investigated to determine if any bromine anions were formed, and no such peak was detected, although it is possible that bromine radicals were produced instead of the anions. With higher molecular weight P-ATs, the laser energy did not have any effect on the relative peak signal intensities for polymer with different end groups.

The ionization efficiency of polymer blends based on the nature of their end groups was investigated using Nylon 6, Ny6, and poly(butylenterephalate), PBT, terminated with different end groups. Analysis of equimolar blends of Ny6 (end groups are COOH) and hydroxyl-terminated PBT shows an imbalance between the two components, with the signal for the hydroxyl terminated PBT being very low in comparison with the signal from the Ny6, even though the average molar mass and polydispersity of each component was similar. This shows that the ionization efficiency for the Ny6 is much higher than that of the hydroxyl-terminated
PBT. In the MALDI-MS analysis of an equimolar blend of Ph-Ny6-COOH and HOOC-PBT-COOH, the peak series belonging to the PBT is much more intense and almost has the same intensity as the peaks resulting from the Ny6. This clearly indicates that ionization/desorption efficiency is very different for PBT terminated with hydroxyl vs. carboxyl end groups. Further investigations were done on equimolar mixtures of PBT terminated with hydroxyl and carboxyl groups, and at lower masses ($m/z \leq 2,000$), the signals for the PBT terminated with carboxyl groups were dominant. At higher mass ranges, the signal for the hydroxyl-terminated PBT was more intense such that the signal for the PBT with hydroxyl and carboxyl end groups was nearly equal, indicating that the end groups ionization/desorption efficiency is more of an issue at lower molecular weights where the concentration of end groups is higher relative to monomer units.

Guttman et al. performed an interlaboratory comparison of the MALDI-MS analysis of mixtures of polystyrene with different end groups. Mixtures of polystyrene samples were made with hydrogen-terminated polystyrene (PS-H) and a 2-hydroxy-ethyl-terminated polystyrene (PS-OH) that had different mass ratios between 95:5 and 10:90 PS-OH/PS-H. The mixtures were sent to 14 different laboratories for MALDI-MS analysis. Surprisingly, there was no effect of the end group on determining proper mass distributions or fractions for each polymer in the mixture. The comparison did show that the laboratory as well as instrument manufacturer had a significant influence on the quantitative analysis of the polymer mixtures, while the matrix and the instrument mode (linear or reflectron) did not. Some of the main issues in the quantitative analysis of the polymer mixtures were poor mass calibration, poor data analysis techniques and inadequate optimization of instrumental parameters. Since end-group assignments were made herein based on MALDI-TOF MS analyses of P-3HTs, the possible issue of end-group specific discrimination with these specific polymers was addressed.
1.4 References


Chapter 2

Materials and Methods

2.1 Experimental

2.1.1 Chemicals

All solvents used were chromatographic grade or better and used as received, unless otherwise mentioned. \( n \)-Hexylamine (Aldrich, 99%, St. Louis, MO), \( n \)-heptylamine (Aldrich, 99%), 2,5-dimethoxytetrahydrofuran (Aldrich, 98%), iron(III) chloride (Aldrich, 99.99%), 3-\( n \)-hexylthiophene (Aldrich, 99%), dithranol (Bruker Daltonics, Bremen, Germany) and 2,2’;5’,2”-terthiophene (Aldrich, 99%) were all used without further purification.

2.1.2 Synthetic Methods

- Synthesis of \( N \)-alkylpyrrole monomer\(^1\)

The \( N \)-heptylpyrrole and \( N \)-hexylpyrrole monomers were synthesized using the Clauson ring-closure reaction.\(^1\) A purged three-neck round bottom flask (RBF) with a thermometer and stir bar was used for this reaction. To the RBF, a 225 mL degassed acetic acid solution (10% v/v) was added. To this 66.2 mmol of alkyl amine was added. The reaction was placed in a water bath, and the water bath was heated to 45 °C. To the reaction mixture, 66.2 mmol of 2,5-dimethoxytetrahydrofuran was added. The reaction mixture was left to stir for 2 h at 45 °C. After 2 h it was allowed to come to room temperature (~1 h), and the solution was washed three times with degassed dichloromethane (DCM). The DCM layers were kept and washed with 2.0 M hydrochloric acid (3x 200 mL). The DCM extract was rotary evaporated at room temperature, and then the remaining residue was placed under high vacuum overnight. GC-MS and \(^1\)H-NMR were used to analyze the pyrrole monomer products for purity. The chromatographic traces showed the presence of pure product for the \( N \)-hexyl pyrrole monomer.
1H-NMR assignments for the N-hexyl monomer (300 MHz, CDCl3): \( \delta \) 6.59 (t, 2H, Py-2,5-H), 6.04 (t, 2H, Py-3,4-H), 3.81 (t, 2H, -CH2-Py), 1.70 (m, 2H, CH2-CH2-Py), 1.27 (m, 6H, (CH2)3-CH2-CH2-Py), 0.87 (t, 2H, CH3-(CH2)3-CH2-CH2-Py). The GC-MS trace indicated pure product for the N-heptyl monomer. 1H-NMR assignments for the N-heptyl monomer (300 MHz, CDCl3): \( \delta \) 6.54 (t, 2H, Py-2,5-H), 6.07 (t, 2H, Py-3,4-H), 3.73 (t, 2H, -CH2-Py), 1.69 (m, 2H, CH2-CH2-Py), 1.29 (m, 8H, (CH2)4-CH2-CH2-Py), 0.87 (t, 2H, CH3-(CH2)4-CH2-CH2-Py).

- **Source of 3-n-hexylthiophene monomer, 3-(3,6,9-trioxadecanyl) pyrrole monomer and 3-hexylpyrrole monomer**

The 3-n-hexylthiophene monomer was purchased from Sigma-Aldrich (99%). The 3-(3,6,9-trioxadecanyl)pyrrole monomer was synthesized by group member Amy Morara. The 3-hexylpyrrole monomer was synthesized by Dr. Alfonso Dávila according to a procedure in the literature.

- **Initial chemical oxidative polymerization of substituted pyrrole monomers**

The polymerization procedure was modified from one found in the literature for the oxidative polymerization of pyrroles with iron(III) chloride. A RBF with a stir bar was used for the polymerization. The monomer (0.83 mmol) was dissolved in 12.5 mL of nitromethane. The monomer solution was added to the RBF and then purged for ~ 5 min. Iron(III) chloride (2.13 mmol) was dissolved in 12.5 mL of nitromethane; the resulting solution was added to the monomer solution, and it was allowed to stir for 5 min. The reaction was quenched with 150 mL of methanol (MeOH), and then was allowed to stir for 2 h, after which the solution was filtered. Insoluble polymer (a black dusty solid) was rinsed with ~100 mL chloroform (CHCl3). The chloroform was added to the nitromethane layer, and the CHCl3/CH3NO2 solution was washed three times with ~500 mL of 2.0 M hydrochloric acid, to remove residual iron(III) chloride. The resulting CHCl3/CH3NO2 solution was rotary evaporated at room temperature to remove the
solvent, and any residual solvent was completely removed by high vacuum overnight at room temperature.

- **Modified chemical oxidative polymerization for 3-hexylthiophene and \(N\)-heptylpyrrole studies**

  To determine how changing the polymerization procedure affected the molecular weight and end-group identity of the resulting polymer, the polymerization for the 3-hexylthiophene and some of the \(N\)-heptylpyrrole studies was modified slightly from the polymerization procedure initially used for the pyrroles described in the previous paragraph. The monomer-to-oxidant molar ratio was varied from 1:2.5 to 1:12, the polymerization solvent was varied from nitromethane to chloroform, and polymerization time was varied from 10 min to 24 h. For these studies, the monomer solution was added to the iron(III) chloride solution; this was done so that no iron(III) chloride would be lost during transfer because the iron chloride solution was more concentrated, and adding the iron(III) chloride solution to the monomer solution resulted in some insoluble iron(III) chloride being lost during transfer. All washing and solvent removal procedures were kept the same.

2.2 **End-Group Analysis**

End-group analysis of the polymers was performed using matrix-assisted laser desorption/ionization time-of-flight mass spectrometry (MALDI-TOF MS). MALDI is known as a “soft” ionization technique for mass spectrometry because a variety of large analyte molecules have been shown to stay intact and experience less fragmentation in comparison to outcomes obtained from other ionization techniques.\(^5\)

Figure 2.1 contains the diagram of a typical MALDI-TOF MS instrument with an ion reflector (reflectron).\(^6\) In a typical MALDI-TOF MS experiment, a dilute solution of sample is mixed with a more concentrated matrix solution, and placed on the MALDI target. The
MALDI-TOF MS target is placed in the instrument under vacuum, and a pulsed, focused laser beam is directed through lenses and mirrors onto the spot containing the sample/matrix mixture. The laser pulse causes vaporization of the matrix and desorption of the sample into the gas phase, resulting in the analyte molecules being entrained in a gas-phase plume. The analyte is ionized in the plume via gas-phase reactions. By applying a voltage at the entrance to the flight tube, the ions are accelerated to a constant kinetic energy into the field-free region (flight tube) of the mass spectrometer. In this region, ions are separated based on velocity differences in that higher mass ions travel more slowly than lighter ions. A schematic of the field-free region can be seen in Figure 2.2. Analytes, depending on their mass-to-charge ratio, have specific velocities in the flight tube and therefore transverse the length of the flight tube for different amounts of time.

Equation 2.1

\[ t = \frac{L}{\nu} = L \left( \frac{m}{2eV} \right)^{1/2} \]

This is demonstrated by Equation 2.1, in which \( t \) is the time needed for the ion to traverse the flight tube, \( L \) is the length of the flight tube, \( \nu \) is the velocity of the analyte ion, \( m \) is the mass of
the ion, \( z \) is the charge of the ion, and \( V \) is the accelerating potential.\(^7\) The instrument is calibrated with standards of known mass and charge, to determine flight time relative to mass.

![Diagram of the field-free region of a time-of-flight mass spectrometer](image)

**Figure 2.2** Diagram of the field-free region of a time-of-flight mass spectrometer. Adapted from Reference 7.

After ions travel through the flight tube they are either detected at the linear detector or they enter the reflectron. The reflectron contains a series of electrical lenses that have increasing repelling potential. Once ions have traveled through the first field region they are slowed down in the reflectron region until they come to rest, and then they are re-accelerated into a second field-free region and subsequently detected at the reflector detector (reflectron). Use of the reflector increases resolution. Mass resolution is typically less than 500 in typical linear TOF instruments.\(^7\) Although resolution is lower in linear mode, ion transmission is higher due to the shorter flight time and absence of the reflectron region, and this mode is used for high mass analyte ions in which ion signals are generally low.

Resolution in a time-of-flight mass spectrometer is limited, because ions in the accelerating region can be formed at different times (temporal issues), in different locations (spatial issues), ions can have opposite velocities and ions can be formed with different kinetic energies.\(^8\) The reflectron corrects for many of these issues in that iso-masses that have excess kinetic energy and are traveling down the flight tube faster/ahead of other iso-masses will
penetrate the reflectron region further, because the series of lenses in the reflectron region has an increasing repelling potential. These ions spend more time in the reflectron region, and this compensates for their shorter flight times, causing all iso-masses to arrive at the detector almost simultaneously. Temporal issues are also addressed by using very short ionization laser pulses and by prompt ejection of the ions from the accelerating region.

The laser energy applied to the sample target can also affect the mass resolution in MALDI-TOF MS spectra. It is commonly accepted that the best resolution is obtained slightly over the “threshold”, which is the laser energy necessary to obtain meaningful signal. As the laser power is raised by approximately 20% above the threshold, ions can still be observed, although the signal-to-noise ratio is worse.

To date, the mechanism of ion formation in MALDI-MS has not been fully delineated. The three types of ion formation pathways in MALDI-MS analyses are: proton transfer, ionization by attachment of metal cations (cationization), and electron transfer. Cationization is the major ion formation process in the MALDI analysis of most synthetic polymers. However, it has been shown that electroactive compounds which have low ionization energies can form radical molecular cations as a result of electron-transfer reactions between the matrix and the analyte. Electron-transfer has also been shown to be the major ion formation pathway during the MALDI-TOF MS analysis of electro-active polymers. This differs from proteins and peptides in which proton transfer is the most common way analytes are ionized.

MALDI-TOF MS can be used to identify polymer repeat units, as well as end groups. Repeat-unit mass can easily be calculated from a MALDI-TOF MS spectrum by taking the mass of a peak and subtracting the mass of the peak prior to it in the series of peaks. End-group mass can be determined from MALDI data by use of the following equations.
**Equation 2.2**\[ M_{\text{end}} = M_{\text{peak}} - M_{\text{cat}} - nM_{\text{re}} \]

**Equation 2.3**\[ M_{\text{end}} = M_{\text{peak}} - M_{\text{elec}} - nM_{\text{re}} \]

where \( M_{\text{end}} \) is the mass of the end group, \( M_{\text{peak}} \) is the mass of the selected peak, \( M_{\text{cat}} \) is the mass of the cation, \( M_{\text{elec}} \) is the mass of an electron and \( nM_{\text{re}} \) is \( n \) (number of repeat units) times the mass of the repeat unit.\(^{15}\) **Equation 2.2** is used for samples that are ionized by protonation or cationization, while **equation 2.3** is used for samples that undergo electron-transfer reactions.\(^{15}\)

MALDI-TOF MS can be employed to determine molecular weights of polymer samples. Average molecular weights are calculated using the following equations for the number-average molecular weight, \( M_N \), and the weight-average molecular weight, \( M_W \)\(^{15}\)

**Equation 2.4**\[ M_N = \frac{\sum M_i N_i}{\sum N_i} \]

**Equation 2.5**\[ M_W = \frac{\sum (M_i)^2 N_i}{\sum M_i N_i} \]

where \( M_i \) is the mass of an observed ion and \( N_i \) is the number of ions observed. The polydispersity, \( PD \), of a sample is calculated by:

**Equation 2.6**\[ PD = \frac{M_W}{M_N} \]

There has been much debate about the accuracy of MALDI-TOF MS average molecular weights in comparison to those obtained using other common techniques, such as gel-permeation (size-exclusion) chromatography. The issue for using MALDI-TOF MS to calculate average molecular weights of polymers is that discrimination-free experiments are needed, which is unrealistic for polymers with high polydispersities, because it is not feasible to get equal desorption/ionization as well as detection of ions over a very wide range of masses. Most studies
indicate that MALDI-TOF MS analysis underestimates the average molecular weight of polydisperse polymer samples due to underestimation of the amount of high-mass components, although it has been shown that discrimination can occur for low-mass polymers as well as high-mass polymers. Discrimination in the analysis of polydisperse polymer samples can result from sample preparation techniques as well as instrumental factors.\textsuperscript{10}

One issue that inhibits quantification of polydisperse polymers by MALDI-TOF MS is the formation of multimers, which is defined as the aggregation of two or more polymer distributions.\textsuperscript{16} Analysis of multi-component blends of poly(styrene) by Schriemer et al. has shown that a decrease in multimer formation occurs with an increase in matrix-to-analyte ratio, although there were still multimers present at the highest matrix-to-analyte ratio (8000). The presence of multimers can skew the average molecular weight calculations, as well as the observed molecular weight distributions in MALDI-TOF MS analysis, because multimers can lower the abundance of signal for principal polymer distributions. It was shown with these poly(styrene) samples that the higher molecular weight components were affected more by multimer formation than lower mass components, which decreased the calculated average molecular weights. Average molecular weight can also be skewed to higher-than-expected values by multimer formation if the polymer sample is very polydisperse and multimer formation overlaps the principal polymer signal.\textsuperscript{16}

Schriemer et al. investigated the mass dependence on matrix-to-analyte ratio used in the sample preparation of poly(styrene)s.\textsuperscript{16} At higher matrix-to-analyte ratios ($\geq 4000$), the average molecular weight was overestimated by MALDI-MS analysis, while at lower matrix-to-analyte ratios ($\leq 2000$), the average molecular weight was underestimated. From this it was concluded that the use of dilute analyte conditions favors desorption/ionization of higher-mass components
rather than lower-mass components, and that the optimal matrix-to-analyte ratio varies with polymer chain length. This makes it difficult to achieve uniform desorption/ionization of components of disperse polymer samples with only one MALDI sample preparation route.

An instrumental factor that influences the analysis of polymers with a high polydispersity is the optimal applied laser energy, which is thought to differ for high- and low-molecular-weight polymer of the same structure. Typically in MALDI-TOF MS experiments, the laser energy is set at slightly above the threshold for ionization to obtain optimal desorption/ionization of the sample, but for disperse mixtures there is no defined threshold.\textsuperscript{17} It has been demonstrated with polydisperse poly(styrene) mixtures that at low laser energies, only the low-molecular-weight polymer distribution is observed, and at high laser energies, the low-molecular-weight polymer distribution is shifted to lower observed masses and is broader.\textsuperscript{17} The shift and broadening are explained by fragmentation of the low-molecular-weight species resulting from high laser energy which was needed to obtain desorption/ionization of the high-molecular-weight polymer, making it observable in the obtained spectrum. It was shown that average molecular weight values of poly(methylmethacrylate) (PMMA) mixtures changed depending on the laser energy used. This was supported by studies done by Sakurada et al. on equimolar mixtures of 20-, 35-, and 50-mers of monodisperse PMMA, when the laser energy was increased the intensity of higher molecular weight ion signals increased, and there was a decrease in lower molecular weight ion signals.\textsuperscript{18} However, studies done on poly(styrene) samples with narrow polydispersities which were blended together to mimic polydisperse poly(styrene) samples showed ion signal intensities had no such laser energy dependence.\textsuperscript{16}

Wetzel et al. analyzed four polymers, poly(styrene) (PS), poly(ethylene glycol) (PEG), poly(methyl methacrylate) (PMMA), and poly(tetrahydrofuran) (PTHF), to determine the effect
of laser energy and matrix on polymers with different thermal stabilities. The order of the relative thermal stabilities for the polymers from highest to lowest is: PS, PEG, PMMA, and PTHF. Matrices were used that require different laser energies for ablation, with the softer matrices being all-trans-retinoic acid (RA) and dithranol, which require less energy than the harder matrix, 2,5-dihydroxybenzoic acid (DHB). The polymers had lower average molecular weights when analyzed with DHB versus RA, and this effect was the greatest for the polymers with lower thermal stability, PTHF and PMMA. More intense fragment peaks were observed for PEG and PTHF, and fragmentation was observed for PMMA when DHB was used as the matrix. But, little if any fragmentation was observed for these polymers when RA or dithranol was used as the matrix. Fragmentation influences the entire molecular mass distribution and cause shifts in the calculated average molecular weights. Also, the average molecule weight of PEG in dithranol increased as the laser energy increased, showing that higher laser energy is needed to ionize/desorb higher masses of this polymer. In addition, PEG was analyzed in DHB and dithranol at the same laser energies with very different results, indicating that although the molecular mass distribution is affected by the laser energy, the overall effect is a combined effect of the matrix and the laser energy. The influence of the laser energy on the molecular weight distribution and average molecular weight of the polymers was dependant on the matrix used as well as the thermal stability of the polymer. This means that sample preparation, as well as polymer type, affect the extent of changes in laser energy on resulting polymer ion signals.

Another instrumental factor that is an issue with the MALDI-MS analysis of polymer mixtures is saturation of the detector with matrix or small-molecular-weight oligomer ions. This has been demonstrated by McEwen et al. who analyzed a polydisperse PMMA (17K) sample and at approximately a m/z of 20,000 the ion signal was reduced into the background noise. It
was shown that the higher molecular weight PMMA polymer (above 20,000 u) could be ionized and observed by MALDI-TOF MS after a mass gate was applied so only a narrow mass range of polymer could reach the detector. This experiment demonstrated that although MALDI produces ions over the entire mass distribution, saturation of the detector with low mass ions can inhibit the detection of higher mass ions.

MALDI-MS molecular weight analysis is usually accurate for samples with a PD $\leq 1.2$ or less in which the mass range is small and therefore mass discrimination is not as much of an issue.\textsuperscript{5, 10} Using GPC or LC to fractionate polydisperse polymer to obtain samples with lower polydispersities for MALDI-TOF MS analysis has been done and more accurate molecular weight calculations have been obtained using these two techniques together.\textsuperscript{5, 10}

2.3 Molecular Weight Studies

Molecular weight studies of the polymers were done using gel-permeation chromatography, a type of size-exclusion chromatography, and a refractive index detector coupled to a multi-angle laser light scattering detector. The basic principle behind combining these two detectors with size-exclusion chromatography is that the refractive index detector serves as a polymer concentration detector, while the light scattering detector signal is proportional to concentration and molecular weight of polymer. Use of these detectors together allows for determining average molecular weights of polymers without having to calibrate the refractive index detector with polymer standards.

Gel-permeation chromatography is a technique used to physically separate macromolecules based on size. The columns used for the separation are packed with silica or polymer particles that contain uniform pores in which solute and solvent molecules can freely diffuse in and out of. The average time that molecules reside in the pores, and therefore on the
stationary phase, depends on the molecular size and the shape of the molecules. The residence
time in the pores increases as molecular size decreases, meaning larger molecules elute first
while smaller molecules elute later.

GPC coupled to only a differential refractive index (DRI) detector is traditionally
calibrated with standards of known molar mass, and the times required for an unknown sample to
elute is converted to a molecular weight based on the calibration. The problem with this method
is that appropriate standards (i.e. standards with the same conformation as the analyte) must be
used to calibrate the detector. This technique has been shown to give inaccurate molecular
weights if the polymer sample does not have the same shape as the standard. It has been shown
that GPC data overestimates the molecular weight of heterocyclic polymers, which tend to have
a rigid rod-like structure in solution.\textsuperscript{21} This is because GPC instrument measurements are
normally reported with respect to poly(styrene) standards, which are more sphere-like in
structure and have different hydrodynamic volumes than rod-shaped analytes of equivalent
molecular weight. The difference in structure and shape cause calibration curves constructed
using poly(styrene) to give higher molecular weights for heterocyclic polymers. Because of this
issue, the GPC-DRI was also coupled to the multi-angle laser light scattering (MALLS) detector.
MALLS allows molecular weights to be determined based on light scattering measurements and
concentrations and independent from standards.

MALLS is a form of classical (static) light scattering and is a well known technique to
characterize the size of macromolecules. In this technique a laser is directed onto a cell that
contains a solution of the analyte. The basic principle behind this technique is that by measuring
the scattered light, termed the Rayleigh ratio, which is the scattered light intensity in excess of
scattered light from the solvent, the molecular weight of the analyte can be determined if the
concentration as well as the optical constant is known. The differential refractive index detector thus serves as the concentration detector and the optical constant of the polymer sample can be calculated as long as the $dn/dc$, which is differential refractive index increment, is known for the sample.

The equation\textsuperscript{22, 23} that defines the basic relationship between molar mass and light scattering is:

\textbf{Equation 2.7} \quad \frac{R_\theta}{Kc} = M_w P(\theta) - 2A_2 M^2 P^2(\theta)c + ...

\textbf{Equation 2.8} \quad K = \frac{4\pi^2 n^2_0}{NA\lambda^4} \left(\frac{dn}{dc}\right)^2

where $R_\theta$ is the Rayleigh ratio, $K$ is the optical constant (defined in Equation 2.8, $n_0$ is the solvent refractive index, $N_A$ is Avogadro’s number and $\lambda$ is the vacuum wavelength of incident light), $c$ is the concentration of the scattering species, $M_w$ is the molecular weight, $P(\theta)$ is the form factor for the scattering function and $A_2$ is the second virial coefficient which is a thermodynamic term indicative of the solute-solvent interactions. Because the GPC fractions are diluted by axial dispersion, it is assumed that the concentration is very low and therefore the second and higher virial coefficient terms have been ignored under the assumption that they are negligible.\textsuperscript{22}

The form factor or scattering function relates the angular variation in scattering intensity to mean square radius of the analyte. The scattering function can be simplified into the following equation\textsuperscript{24} under the assumption that the scattering angle is low or the mean square radius is small compared to the wavelength of incident light.\textsuperscript{22}

\textbf{Equation 2.9} \quad P(\theta) = 1 - \left(\frac{16\pi^2}{3\lambda^2}\right)\left\langle r_{rms}^2 \right\rangle^2 \sin^2\left(\frac{\theta}{2}\right)
where $\lambda$ is the wavelength of the incident beam, $\theta$ is the angle between the incident light and the scattered light and $r_{rms}$ is the root-mean-square radius. From this function, light scattering measurements can also be used to determine the $r_{rms}$ of macromolecules.

Light scattering measurements are made at many different angles so that the Rayleigh ratio can be calculated at many different angles and then extrapolated at an angle of zero at which the combination of equation 2.7 and 2.9 can be simplified to:

\begin{equation}
\frac{R_\theta}{Kc} = M_w
\end{equation}

Different fitting methods can be used to extrapolate the scattering intensity at an angle of zero, which is nearly impossible to accurately measure directly. Once the scattering intensity at an angle of zero is known, the molecular weight can be calculated, as long as the concentration and optical constant are known.

2.4 Analysis

2.4.1 MALDI-TOF MS

MALDI-TOF MS analysis was performed with a Bruker ProFLEX III MALDI-TOF Mass Spectrometer that has a 337 nm nitrogen laser with a 3 ns pulse width, and microchannel plate detectors. Dithranol or terthiophene was used as the matrix. Use of anthracene as a matrix was also investigated, but better signal-to-noise ratios were obtained with dithranol and terthiophene; therefore, those two matrices were used in the MALDI-MS experiments. The matrices, as well as the samples, were dissolved in chloroform or dichloromethane. Saturated solutions of matrix were prepared and mixed with the sample prior to spotting on the plate. The matrix-sample mixtures were spotted in 1 µL aliquots on the MALDI-MS target and allowed to air dry. The mass spectrometer was calibrated with internal standards for mass measurements. The internal standards used for these experiments were oligo(ferrocenyldimethylsilanes), namely
Fc[Si(CH₃)₂Fc]₃H, Fc[Si(CH₃)₂Fc]₅H and Fc[Si(CH₃)₂Fc]₇H obtained from Professor Ian Manners at the University of Toronto. The internal standards were dissolved in the same solvents as the polymer samples and mixed with the polymer and matrix solutions prior to spotting on the target plate.

The Bruker Xmass software was used to calculate isotope patterns of pyrrole and thiophenenes oligomers with different end groups. Average molecular weights were calculated from the MALDI-TOF MS data using equation 2.4 and 2.5 and the signal abundances were used as \( N_i \) and the \( m/z \) values were used as \( M_i \).

2.4.2 Gel-Permeation Chromatography (GPC) Analysis with Multi-Angle Laser Light Scattering (MALLS) and Differential Refractive Index (DRI) Detection

Gel-permeation chromatography was done using two Phenogel columns from Phenomenex, the first with a linear bed configuration that had pore sizes ranging from 50Å to 10⁻⁶Å, and the second column that had pore sizes of 10⁻⁵ Å. The particle size in both columns was 10µm, and the columns were connected to an Agilent 1100 isocratic pump. The light scattering detector used was a Wyatt Dawn Heleos from Wyatt Technologies Corporation (Santa Barbara, California) with a 658 nm, 50mW GaAs linearly polarized laser and a K5 cell. The light scattering detector was connected to a Wyatt Optilab rEX differential refractive index detector. The solvent used was tetrahydrofuran and degassed by helium sparging or by using an on-line vacuum degasser. The flow rate of the solvent was 1.0 mL min⁻¹, and the injection volume of the samples was 0.1 mL. The data was collected and processed using Astra V software from Wyatt Technologies Corporation.

2.4.3 Measurement of \( dn/dc \)

The specific refractive index increment, \( dn/dc \), of the thiophene polymers was measured using a Brice-Phoenix differential refractometer with multiple filters. The \( dn/dc \) was measured at
three different wavelengths, 514.5 nm, 589 nm and 632.8 nm and at a temperature of 25°C. It was also measured using a Wyatt Optilab Rex differential refractive index detector, at a wavelength of 658 nm and temperature of 25°C. The $dn/dc$ of the $N$-heptylpyrrole polymer was measured only using a Wyatt Optilab Rex differential refractive index detector. The measurement was made at a wavelength of 658 nm and temperature of 25°C.

### 2.4.4 Reverse-Phase High-Performance Liquid Chromatography (RP-HPLC) Analysis

High-performance liquid chromatography (HPLC) was used to separate individual oligomers in the polymer samples. The instrument used was a Hewlett Packard 1090 Series 2 Liquid Chromatography system with a diode-array detector (270 nm - 600nm) and a deuterium lamp radiation source. The column used was a Spherisorb end-capped reverse phase C-18 with a particle size of 5 µm, a pore size of 80 Å, and 4.6 x 250 mm dimensions. Mobile phase solvents were purged continuously with nitrogen. All chromatographic bands were collected manually as fractions for MALDI-TOF MS analysis. A method was modified from the literature for the separation of P-3HT. A binary gradient was used and started initially at 50% THF/water and then was ramped for 95 min to 90% THF/water, 10 min to 100% THF and held for 5 min. The flow rate of the solvent was 1.0 mL min$^{-1}$, and the injection volume of the samples was 20 µL.

### 2.4.5 Ultraviolet-Visible Absorption Spectroscopy Analysis

Optical studies using ultraviolet-visible adsorption spectroscopy analysis of the polymers and monomers were performed using a Varian Cary 50 ultraviolet-visible spectrophotometer. Samples were analyzed using a quartz rectangular cell with a path length of 10 mm and a using a scan rate of 600 nm min$^{-1}$.  

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2.4.6 Fourier-Transform Infrared Spectroscopy Analysis (FT-IR)

Structural analysis of the polymers and monomers was done using Fourier-transform infrared spectroscopy with a Thermo Nicolet Nexus 670 Spectrometer. Polymer samples were dissolved in chloroform, spotted on KBr salt plates, and then allowed to air dry yielding a thin polymer film on the salt plate.

2.4.7 Nuclear Magnetic Resonance (NMR) Analysis

$^1$H-NMR analysis was done on either a Bruker ARX-300 MHz or a Bruker DMX-400 MHz spectrometer. All samples were dissolved in deuterated solvents purchased from Aldrich.

2.4.8 Gas Chromatography-Mass Spectrometry Analysis (GC-MS)

GC-MS analysis was done using a Hewlett Packard Series II 5890 GC with a Hewlett Packard 5971 A Mass-Selective Quadrupole detector or a Varian CP-3800 GC with a Saturn 2200 ion trap MS instrument, with EI. Both instruments contained DB-5 J&W columns (5% phenyl, 95% dimethyl polysiloxane), that were 30 meters in length and had a film thickness of 0.25 µm and an inner diameter of 0.25 mm. The method (DB-5) that was utilized employed an initial column temperature of 40 °C with 2 min hold time, a 20 °C min$^{-1}$ ramp for 14 min, and a 280 °C final temperature hold for 24 min. The total run time was 40 min.

2.4.9 Elemental Analysis

The pyrrole polymers were sent to MHW labs (Phoenix, AZ) for carbon, hydrogen and nitrogen content analysis. All pyrrole polymer elemental analyses were run in duplicates. The thiophene polymers were sent to Huffman Laboratories Inc. (Golden, CO) for carbon, hydrogen, sulfur, and chlorine content analysis. All thiophene elemental analyses were done in duplicate except for the sulfur due to insufficient sample.
2.5 References


Chapter 3

Studies on Substituted Pyrrole Polymers

3.1 Introduction

One of the main goals of the research presented in this dissertation is characterization of soluble pyrrole polymers, and to gain insight into the optimal chemical polymerization conditions for the pyrrole monomers on the dendrimer periphery. Substituted pyrrole monomers, whose structures closely resemble the pyrrole units attached to the dendrimer periphery, were polymerized to yield organic solvent soluble polymer as to allow structural characterization. One of the main structural characteristics of interest is the identity of the end groups of the pyrrole polymers, because this may provide information on polymerization termination processes. This is specifically important for the oligo(pyrrole) units on the dendrimer systems, because if after just a few of the monomers are oligomerized, an unwanted end group is added that inhibits any further oligomerization, the hosting capabilities of the dendrimer system could be affected. Initial studies focused on the synthesis of soluble polymer and its structural characterization using primarily MALDI-TOF MS, and also $^1$H-NMR, UV-visible and FT-IR spectroscopies. The substituted pyrrole polymers were synthesized as described in section 2.1.2, using nitromethane as the polymerization solvent, a monomer-to-iron(III) chloride ratio of 1:2.5, and a polymerization time of 5 minutes.

3.2 Polymer End-Group Studies

Structural characterization of the poly(substituted-pyrrole) materials was done using MALDI-TOF MS, specifically for the analysis of the repeat unit and end groups. The polymers and matrix were dissolved in dichloromethane and then spotted on the MALDI plate, where they were allowed to air dry prior to analysis. Several MALDI matrices were evaluated, specifically
terthiophene, dithranol and anthracene. Similar results were obtained with the terthiophene, 
dithranol and anthracene matrices, but the dithranol was preferred because it gave the highest 
quality poly(alkylpyrrole) spectra (highest signal-to-noise ratio).

3.2.1 Evaluation of Poly(N-hexylpyrrole)

Poly(N-hexylpyrrole) was synthesized as explained in section 2.1.2. The polymerization 
was performed in nitromethane, with a monomer-to-FeCl₃ ratio of 1:2.5, and using 
polymerization time of 5 min. The mass spectrum of poly(N-hexylpyrrole) is displayed in Figure 
3.1. The major series of ion peaks present in the polymer is \((149_n + 2)^+\), which corresponds to the 
repeat unit of the N-hexylpyrrole \((C_{10}H_{15}N, 149 \text{ u})\) and two hydrogen end groups. Specific end-

Figure 3.1 MALDI mass spectrum of poly(N-hexylpyrrole) and inset with the expanded 
8-mer region of spectrum with colored peaks representing calculated isotope patterns of the 
8-mer with different end groups.
group composition was determined by comparison of the observed and calculated isotopic abundances of oligomers with different compositions. The calculated isotope patterns were plotted using the Bruker Xmass software. For the isotopic abundance calculations, it was assumed that the ions formed in the MALDI-TOF MS analysis of this polymer are molecular radical cations, \( M^+ \), rather than protonated molecules, \([M + H]^+\). This assumption was made based on literature studies of other electro-active polymers for which electron transfer reactions are the major ion formation pathway.\(^1\), \(^2\) End-group analysis of this polymer shows that in addition to hydrogen end groups, some of the polymer also has chlorine and oxygen substituents. This is not surprising because it has been demonstrated that oxygenation and chlorination of pyrrole polymers occurs when \( \text{OH}^- \) and \( \text{Cl}^- \) nucleophiles are present during polymerization.\(^3\), \(^4\) The \( \text{OH}^- \) nucleophiles are most likely a result of a small amount of water being present in the polymerization solvent, because it has been shown that an impurity of water in the solvent as small as .2% by volume can result in oxygenation of pyrrole polymers.\(^3\) Previous work has suggested that the \( \text{Cl}^- \) nucleophiles result from the oxidant \( \text{FeCl}_3 \).\(^5\), \(^6\)

By comparing the observed and calculated isotopic abundances for the poly(\(N\)-hexylpyrrole), it is obvious that the calculated isotope pattern does not match the experimental data, which was unexpected. Although the calculated and experimental isotope patterns are similar, the experimental data have additional peaks at lower units that are not observed in the calculated isotope patterns. Because the instrument was calibrated with internal standards, this is not the result of a calibration issue. Due to the fact that pyrrole polymers have previously not been characterized using MALDI-TOF MS and an unusual isotope pattern was observed for the poly(\(N\)-hexylpyrrole), a polymer with a longer alkyl chain on the pyrrole units, poly(\(N\)-heptyl pyrrole), was examined to ensure that the observed peaks belonged to that of a
polymer. It is unlikely, but possible, that some sort of side product was formed during the polymerization reaction that has a similar repeat unit as poly(N-hexylpyrrole). The peaks observed are not the result of some sort of impurity in the matrix, because the same peaks and isotope patterns were observed for the polymer when anthracene and terthiophene were used as the matrix.

3.2.2 Evaluation of Poly(N-heptylpyrrole)

Poly(N-heptylpyrrole) was prepared in the same way as the poly(N-hexylpyrrole) polymer, with a monomer-to-FeCl₃ ratio of 1:2.5, and using a polymerization time of 5 min. Sample preparation with dithranol as the matrix gave the highest quality MALDI spectra. As can be seen from Figure 3.2, the major series of ion peaks present in the N-heptylpyrrole polymer is

![MALDI mass spectrum](image)

**Figure 3.2** MALDI mass spectrum of poly(N-heptylpyrrole) and inset with the expanded 8-mer region of spectrum with colored peaks representing calculated isotope patterns of the 8-mer with different end groups.
(163_n + 2)_+\), which corresponds to the repeat unit of the \(N\)-heptyl pyrrole (C_{11}H_{17}N, 163 u) and two H end groups. End-group analysis of the poly(\(N\)-heptylpyrrole) showed very similar results to that of the poly(\(N\)-hexylpyrrole), with the most abundant end groups being H; O and Cl end groups were also present. As was observed for the poly(\(N\)-hexylpyrrole), the calculated isotope pattern for the poly(\(N\)-heptylpyrrole) is similar but does not match the experimental data. Again, the experimental data have additional peaks at lower mass values that are not observed in the calculated isotope patterns. A 3-substituted pyrrole compound was polymerized and examined by MALDI-MS to determine whether the various end groups and unusual isotopic pattern observed with the \(N\)-alkylsubstituted pyrrole compounds are characteristic of \(N\)-alkylated pyrroles or substituted pyrrole polymers in general.

### 3.2.3 Evaluation of Poly(3-(3,6,9-trioxadecanyl) pyrrole)

3-(3,6,9-trioxadecanyl) pyrrole was obtained from another study\(^7\). This pyrrole monomer was investigated on the end of the dendrimer systems because the addition of the ethylene oxide chain increases dendrimer solubility in aqueous media\(^7\). The same polymerization method that was used for the \(N\)-alkylpyrroles was used for this pyrrole. It should be noted that during the wash cycles with 2.0 M HCl, it is possible that some of the polymer was retained in the aqueous phase because this pyrrole polymer is more water soluble than the poly(\(N\)-alkylpyrrole)s. The aqueous phases in the extractions were light purple in color (characteristic of poly(pyrrole)) rather than the bright yellow color (characteristic of FeCl_3) that was observed in the aqueous washes of the \(N\)-alkylpyrrole. Only the soluble polymer in the organic phase was characterized.

The sample preparation for the MALDI-MS analysis of poly(3-(3,6,9-trioxadecanyl) pyrrole) was the same as that of the poly(\(N\)-alkylpyrroles). Along with the matrixes used in the prior analysis (terthiophene, dithranol and anthracene), a more polar matrix, 4-hydroxy-\(\alpha\)-
cyanocinnamic acid, was also investigated. Similar data were obtained for the different matrices, but the 4-hydroxy-α-cyanocinnamic acid was preferred because it gave the highest signal-to-noise ratios in the MALDI-TOF MS data for this polymer. As can be seen from Figure 3.3, the major series of ion peaks present in the poly(3-(3,6,9-trioxadecanyl) pyrrole) is $(211_n + 2)^+$. This corresponds to the repeat unit of the pyrrole ($C_{11}H_{17}O_3N$, 211 u) with two H end groups. End-group analysis showed results similar to that of the poly($N$-alkylpyrrole)s, with H end groups being the most abundant; O and Cl end groups are also present. Investigations of isotopic distribution showed that the isotopic patterns of the observed polymer are comparable to that of

![Figure 3.3 MALDI mass spectrum of poly(3-(3,6,9-trioxadecanyl)pyrrole) and inset with the expanded 7-mer region of spectrum with colored peaks representing calculated isotope patterns of the 7-mer with different end groups.](image)
the poly(N-alkylpyrrole)s, thus providing evidence that the MALDI-MS of 3-substituted pyrrole polymers also results in the observation of an unusual isotope pattern. Because the polymers were all synthesized using the same polymerization procedure, and the polymerization was done in an atypical solvent, nitromethane (chloroform has been widely used), it was thought that the “unusual” isotope pattern could be a result of the polymerization procedure.

From the MALDI-MS characterization of these substituted pyrrole polymers made chemically using FeCl₃ as the oxidant, an unusual isotope pattern that is similar to the calculated isotope patterns, but contains peaks at lower mass units (-1, -2, -3 and -4 mass units), is observed for all pyrrole polymers investigated. It can be concluded that the pyrrole polymers have hydrogen end groups, as well as polymer with chlorine and oxygen additions.

3.3 Pyrrole Coupling Studies – ¹H-NMR Analysis of Polymers

Evaluation of the MALDI-TOF MS data led to the conclusion, that some of the polymers possessed H,H end groups with no substitution of hydrogens on the polymer backbone. Because the “unusual” isotope pattern was observed and because the pyrrole coupling is of interest, ¹H-NMR was explored to possibly examine coupling in the poly(pyrrole)s. The pyrrole monomers could couple in the alpha and/or beta regions of the polymer, as demonstrated in Figure 3.4. If coupling is occurring in the alpha and beta positions on the pyrrole monomer,

![Figure 3.4 Possible coupling of pyrrole units: A.) alpha-alpha coupling, B.) beta-beta coupling, and C.) alpha-beta coupling.](image_url)

66
resulting polymer could be branched instead of linear. GC-MS was run on all samples prior to $^1$H-NMR to make sure no residual monomer was left in the polymer solutions; none was observed.

The $^1$H-NMR data for the poly($N$-hexylpyrrole) did not show any signal for the alpha (2,5) and beta (3,4) protons on the pyrrole, which was unexpected because the MALDI-MS data showed signal for polymer with H,H end groups (Figure 3.5). Signal broadening was also observed for proton signals in the up-field region (1-2 ppm). No $^1$H-NMR assignments for the poly($N$-hexylpyrrole) were made because the origin of each signal was ambiguous. Similar data

**Figure 3.5** $^1$H-NMR of $N$-hexyl pyrrole: A.) monomer, B.) polymer, and C.) polymer with 2 drops concentrated dithiothreitol, DTT, solution added.
were observed for the poly(N-heptylpyrrole). The $^1$H-NMR data for poly(3-(3,6,9-trioxadecanyl)pyrrole) contained signal for protons on the ethylene oxide chain, but no signal was observed for the protons on the methylene attached to the pyrrole or the aromatic protons (Figure 3.6). Similar results have been observed in the literature for pyrrole polymers, in that very broad signal or no signal was observed for the aromatic protons.$^8,^9$

A possible reason that no signal was observed for the $\alpha$ (2,5) and $\beta$ (3,4) protons is that the polymer was still in a doped state, and the charge (electron) was delocalized on the polymer.

Figure 3.6 $^1$H-NMR of 3-(3,6,9-trioxadecanyl)pyrrole: A.) monomer, B.) polymer, and C.) polymer with two drops of concentrated DTT solution added.
backbone, causing the polymer to be paramagnetic. To test this theory, the reducing agent dithiothreitol, DTT, was added to the NMR samples to reduce any oxidized (doped) polymer. DTT is a suitable reducing agent for oxidized pyrrole polymers. A saturated solution of DTT in CDCl₃ was prepared, and two drops of the solution were added to the polymer solutions in the NMR tubes. As shown in Figures 3.5 and 3.6, the DTT had no effect on the ¹H-NMR data except that signals were seen from the protons in DTT itself.

Another possible reason that no signal was observed for the alpha (2,5) and beta (3,4) protons is that the polymer may have still contained some residual, paramagnetic Fe³⁺. After examination of the ¹H-NMR data for poly(3-(3,6,9-trioxadecanyl)pyrrole), Figure 3.6, specifically in the 3 to 4 ppm region, the sharp and resolved peaks for the protons on the ethylene oxide chain indicate that it is unlikely that a paramagnetic species is present in the polymer.

Another possible reason that signals were not observed for the aromatic protons on the pyrrole polymer is because of aggregation of the polymer. Aggregation of the polymer would cause broadening of the signals in the ¹H-NMR because of an increase in the T2 relaxation time of the protons, which increases the width of the peaks. There are a greater number of protons on the pyrrole side chains compared to the pyrrole ring, especially considering that two protons are lost every time two pyrrole units couple and a proton is lost if a substituent adds to the pyrrole ring. It is possible that these polymers are not coupling in the alpha positions on the pyrrole ring exclusively, with some coupling occurring in the beta position. The MALDI-TOF MS data indicates that there are some chlorine and oxygen additions to the pyrrole rings on the polymer chains. The different possible couplings and the addition of substituents on the pyrrole rings could lead to multiple chemical shifts of the protons on the pyrrole rings. The limited number of aromatic protons and broadening of the aromatic proton signals because of different couplings,
substituent addition and/or aggregation, could lead to signal intensities that are so broad and so small compared to those on the polymer side chain that they are not observed in the $^1$H-NMR of the polymer sample.

### 3.4 Optical Properties Studies

To further characterize the polymers, and because the $^1$H-NMR spectra exhibited unobservable and unassignable protons, UV-visible spectroscopy studies of the polymers and monomers were performed in chloroform to determine the shift in absorbance of the polymers relative to the monomers. Red-shifts in absorbance are expected for polymers relative to monomers because of an increase in conjugation and electron delocalization in pyrrole polymers systems.

![Figure 3.7 UV-visible spectra of N-hexylpyrrole and poly(N-hexylpyrrole) in CHCl$_3$](image)

**Figure 3.7** UV-visible spectra of $N$-hexylpyrrole and poly($N$-hexylpyrrole) in CHCl$_3$
The UV-visible spectra of chloroform solutions of \(N\)-hexylpyrrole and poly(\(N\)-hexylpyrrole) are shown in Figure 3.7. All three substituted pyrrole monomers (\(N\)-hexylpyrrole, \(N\)-heptylpyrrole, and 3-(3,6,9-trioxadecanyl)pyrrole), had similar UV-visible spectra with one absorption band having a maximum absorbance at 241 nm. The UV-visible spectra of the polymers were different from that of the monomers in that the \(N\)-alkylpyrrole polymers showed a broad band of absorbance in the region of 230-400 nm.

![Figure 3.7](image.png)

**Figure 3.7** UV-visible spectra of \(N\)-hexylpyrrole, \(N\)-heptylpyrrole, and 3-(3,6,9-trioxadecanyl)pyrrole in CHCl₃.

The UV-visible spectra of 3-(3,6,9-trioxadecanyl)pyrrole monomer and polymer are shown in Figure 3.8. The UV-visible spectrum of poly(3-(3,6,9-trioxadecanyl)pyrrole) has a broad absorbance in the range of 350 and 575 nm and an increasing absorption band at and beyond 650 nm. The optical spectrum of the polymer clearly indicates that it is partially oxidized. The reducing agent, DTT, which was used in the \(^1\)H-NMR studies, was added to the

![Figure 3.8](image.png)

**Figure 3.8** UV-visible spectra of 3-(3,6,9-trioxadecanyl)pyrrole and poly(3-(3,6,9-trioxadecanyl)pyrrole) in CHCl₃.
polymer sample in the cuvette. The decrease in absorption at and beyond 650 nm of the polymer with DTT compared to that without it shows that the polymer was reduced by the DTT. This indicates that if the polymers were oxidized during the $^1$H-NMR studies, DTT would indeed be a suitable reducing agent. The optical spectra of the three pyrrole polymers indicates that poly(3-(3,6,9-trioxadecanyl)pyrrole) has lower oxidation potential than the two $N$-alkylpyrrole polymers, due to its observed oxidation by air.

### 3.5 Elemental Analysis

The carbon (C), hydrogen (H), and nitrogen (N) elemental analysis data for all three of the pyrrole polymers is shown in Table 3.1. By looking at the column 100–(C+H+N) in the table, it is obvious that all polymers have some other element present than C, H, and N, because these values should be zero. The MALDI-MS data suggest that the other elements are most likely O and/or Cl additions. The poly(3-(3,6,9-trioxadecanyl)pyrrole) obviously has oxygen in the ethylene oxide chain, which accounts for a portion of the additional percentages in the 100–(C+H+N) of the table. However, the theoretical oxygen content is less than the calculated elemental percentages, indicating that this polymer has an additional amount of substituent additions. The C:N ratio was examined to see if any degradation of the pyrrole ring occurred.

<table>
<thead>
<tr>
<th>Sample:</th>
<th>%C</th>
<th>%H</th>
<th>% N</th>
<th>100–</th>
<th>C:N ratio</th>
</tr>
</thead>
<tbody>
<tr>
<td>Poly($N$-hexylpyrrole)</td>
<td>73.12 +/- 0.30</td>
<td>8.85 +/- 0.32</td>
<td>8.29 +/- 0.01</td>
<td>9.76 +/- 0.62</td>
<td>8.83 +/- 0.04</td>
</tr>
<tr>
<td><em>theoretical</em></td>
<td>79.41</td>
<td>11.33</td>
<td>9.26</td>
<td>0</td>
<td>8.58</td>
</tr>
<tr>
<td>Poly($N$-heptylpyrrole)</td>
<td>76.49 +/- 1.15</td>
<td>9.64 +/- 0.35</td>
<td>7.90 +/- 0.18</td>
<td>5.97 +/- 1.68</td>
<td>9.69 +/- 0.07</td>
</tr>
<tr>
<td><em>theoretical</em></td>
<td>79.94</td>
<td>11.59</td>
<td>8.47</td>
<td>0</td>
<td>9.44</td>
</tr>
<tr>
<td>Poly(3-(3,6,9-trioxadecanyl)pyrrole)</td>
<td>55.73 +/- 0.31</td>
<td>7.36 +/- 0.23</td>
<td>7.54 +/- 0.02</td>
<td>29.38 +/- 0.57</td>
<td>7.39 +/- 0.01</td>
</tr>
<tr>
<td><em>theoretical</em></td>
<td>61.95</td>
<td>8.98</td>
<td>6.57</td>
<td>0-22.51</td>
<td>9.43</td>
</tr>
</tbody>
</table>
during polymerization. As seen from the table, the C:N ratio for the poly(N-alkylpyrrole)s was roughly consistent with the expected ratio. The C:N ratio of the poly(3-(3,6,9-trioxadecanyl)pyrrole) was lower than expected, which suggests that some of the pyrrole rings or ethylene oxide chains are degraded during polymerization.

3.6 Structural Properties Studies

From the elemental analysis data and MALDI-TOF MS data, it can be concluded that there were substitutions on the pyrrole polymers other than hydrogen, most probably chlorine and/or oxygen. FT-IR analysis of the monomers and polymers was done to determine if oxygen substitution was occurring on the pyrrole rings, and if so, to try and determine if the functionalities are hydroxyl or carbonyl. The presence of carbonyl functionalities have been shown to decrease the conjugation length of the polymer, and they are considered a defect.\textsuperscript{11}

The IR data for poly(N-hexylpyrrole) and poly(3-(3,6,9-trioxadecanyl)pyrrole) is shown in Figure 3.9 and 3.10. Data for poly(N-heptylpyrrole), not shown, was similar to that of poly(N-hexylpyrrole). The absorption at wavenumbers values above 1600 cm\textsuperscript{-1} indicates that the pyrrole polymers are oxidized, because others have shown that a highly oxidized pyrrole polymers exhibit strong absorption over the 4000 cm\textsuperscript{-1} to 1600 cm\textsuperscript{-1} range, which results from absorption of a free-charge carrier on the poly(pyrrole).\textsuperscript{12} In the data here, the absorption event is not strong enough to completely obscure the C-H vibrations on the alkyl chain. No bands are observed in the 3500 to 3700 cm\textsuperscript{-1} region, which indicates that there are no hydroxyl substituents on the pyrrole polymers. Previously Lei et al. observed in their FT-IR investigations of poly(pyrrole) films in the undoped and doped forms that the doped form led to an increases in absorption above 1600 cm\textsuperscript{-1}, which is similar to the data presented here; however in the undoped form they observed a peak that was clearly visible at 3558 cm\textsuperscript{-1} due to the
The band at 1706 cm\(^{-1}\) can be attributed to a carbonyl which indicates that some of the pyrrole polymer has been oxygenated. Examination of the IR data of the pyrrole monomers

Figure 3.9 FT-IR spectra of \(N\)-hexyl pyrrole monomer and polymer thin films on a KBr plate.

presence of O-H. The N-H band is not visible in the IR spectrum of poly(3-(3,6,9-trioxadecanyl)pyrrole), and it is assumed that this band is also masked by the strong absorption from the free charge carrier in the blue region. It is unclear why the \(N\)-alkylpyrrole polymers exhibit IR data indicative of oxidized polymers, since they should not be susceptible to air oxidation, as observed with the UV-vis experiments. It may be possible that the thin films of these polymers oxidize easier than the polymers in solution.
indicates some of the monomers have been oxygenated because an IR absorption band at 1706 cm\(^{-1}\) is present. The \(^1\)H-NMR of the pyrrole monomers does not show any evidence of oxygenation, which means that very small amount of the pyrrole monomers are oxygentaed. This is supported by the fact that the carbonyl functionality is known to have a very high IR extinction coefficient.\(^{12}\) From this it can be concluded that oxygen susbstituents in the carbonyl form are present on the pyrroles in their polymeric forms and in a small amount in their monomeric forms.

\[\begin{array}{ll}
3365 & \text{v N-H} \\
2950-2920 & \text{v_S CH}_2 \text{ alkane chain} \\
1706 & \text{v C=O} \\
1456 & \text{v C=C aromatic} \\
1086 & \text{\(\delta\) C-H aromatic, in plane} \\
796 & \text{\(\omega\) C-H aromatic, out of plane} \\
722 & \text{\(\omega\) C-H aromatic out of plane}
\end{array}\]

**Figure 3.10** FT-IR spectra of 3-(3,6,9-trioxadecany1)pyrrole monomer and polymer thin films on a KBr plate.

Absorption bands are observed for C-H aromatic deformations in the pyrrole polymers. These bands are located in the 800-700 cm\(^{-1}\) (out-of-plane) and the 1000-1100 cm\(^{-1}\) (in-plane)
regions of the spectra. The presence of these bands indicates that although no aromatic protons were observed in the \(^1\text{H}-\text{NMR}\), hydrogens are present on the pyrrole polymer backbone.

3.7 Unusual Isotope Pattern Investigation in MALDI-TOF MS Data of Substituted Pyrrole Polymers

Due to the unusual isotope pattern being observed in the MALDI-TOF MS data of the substituted pyrrole polymers, the literature was consulted for previous mass spectrometry analysis of compounds containing pyrrole units. Previous studies were found in the literature of hydrogen loss being observed in EI spectra of \(N\)-alkylpyrroles\(^{13, 14}\) and FAB spectra of alkylated porphyrins\(^{15}\). It has been reported that the EI spectra of \(N\)-alkylpyrroles have intense M–1 ion peaks which result from H atom loss on the carbon adjacent to the nitrogen, as shown in Figure 3.11.\(^ {13, 14}\) FAB-MS studies on porphyrins with alkyl chains have also led to the observation of ions that are related to single and/or multiple hydrogen atom losses. The abundance of the signal for these ions increases as the number of alkyl chains increases in the porphyrin macrocycles. Unalkylated porphyrins do not demonstrate signals for ions associated with hydrogen atom loss. It has also been shown that unconjugated pyrrole oligomers, ranging from 2-mers to 12-mers, (structure shown in Figure 3.12) exhibit MALDI data indicative of single or multiple hydrogen losses with the

**Figure 3.11** Reported route of hydrogen loss in EI spectra of \(N\)-alkylated pyrroles.

**Figure 3.12** Structure of unconjugated pyrrole oligomers for which hydrogen loss was observed in the MALDI-TOF MS data.
M–1 ion peaks usually being observed. The larger oligomers show more hydrogen loss than smaller oligomers, with the MALDI-MS data for the 12-mer having an M–4 ion peak. For the FAB-MS studies of the alkylated porphyrins and the MALDI-MS analysis of the unconjugated pyrrole oligomers, the hydrogen loss could be similar to what was reported in Figure 3.11, because both systems have alkyl chains attached to the nitrogen.

Hydrogen loss similar to that shown in Figure 3.11 may occur in the N-alkylpyrrole polymers studied here, which could explain the unusual isotope pattern observed in the MALDI-TOF MS data. However this does not explain why a similar isotope pattern, also indicative of hydrogen loss, is observed in the MALDI-TOF MS of the poly(3-(3,6,9-trioxadecanyl) pyrrole). To investigate this further a 3-hexylpyrrole polymer was analyzed to determine if hydrogen loss also occurred with a pyrrole that had an alkyl side chain in the 3-position. 3-hexylpyrrole was polymerized using a monomer-to-oxidant ratio of 1:2.5, in nitromethane, using a polymerization time of 20 min. The mass spectrum of poly(3-hexylpyrrole) is displayed in Figure 3.13. The major series of ion peaks present in the polymer is \((149n+2)^+\), which corresponds to the repeat unit of the 3-hexylpyrrole \((C_{10}H_{15}N, 149 \text{ u})\) and two hydrogen end groups. Examination of the experimental isotope pattern compared to the calculated isotope pattern indicates that hydrogen loss is observed with this polymer. From this it can be concluded that hydrogen loss is observed in the MALDI-TOF MS analysis of alkylated pyrrole polymers, regardless of the location of the alkyl substituent. End-group analysis of poly(3-hexylpyrrole) indicates that polymer is formed with chlorine as well as oxygen end groups. The expanded 7-mer region in Figure 3.13 has a very intense signal for the 7-mer with one chlorine end group and no signal observed for the 7-mer with oxygen end groups. It should be noted that although chlorine additions are observed on other oligomers in the sample, the intensity is not as high, with the most intense signal
Figure 3.13 MALDI mass spectrum of poly(3-hexylpyrrole) and inset with expanded 6-mer and 7-mer region of spectrum with colored peaks representing calculated isotope patterns of the 6-mer and 7-mer with different end groups.

generally being that of oligomers with two hydrogen end groups, as seen in the expanded 6-mer region. The 6-mer region also indicates some oxygen addition to the polymers has occurred.

3.8 Effect of Polymerization Conditions on the Structure of Poly(N-heptylpyrrole)

Poly(N-heptylpyrrole) was synthesized using different monomer-to-oxidant ratios to determine if a trend similar to that observed with poly(3-hexylthiophene) would be observed. It
was of interest to determine if the end groups of the pyrrole polymer could be modified by simply changing the monomer-to-oxidant ratio used in the polymerization procedure, as was observed with the thiophenes. \(N\)-heptylpyrrole was polymerized using a monomer-to-oxidant ratio of 1:8, in nitromethane, for a polymerization time of 10 min, to determine if the pyrrole polymer made with this monomer-to-oxidant ratio would possess predominantly chlorine end groups. The polymerization time was increased to 10 min because it was determined that poly(\(N\)-heptylpyrrole) made with this polymerization time was still soluble and slightly higher signal intensities were observed in the MALDI-TOF MS data. From the comparison of the spectra from the polymerization of poly(\(N\)-heptylpyrrole) made with the polymerization times of 5 and 10 min (not shown) the polymerization time did not have an effect on the end groups of the polymer. As can be seen from Figure 3.14, poly(\(N\)-heptylpyrrole) made with a monomer-to-oxidant ratio of 1:8 has at least two chlorine additions, with some oligomers having four chlorine additions. This demonstrates that by decreasing the monomer-to-oxidant ratio the number of chlorine substituents on the poly(\(N\)-heptylpyrrole) can be increased.

It is of interest to form pyrrole oligomers with no oxygen or chlorine substituents because it is thought that these substituents could possibly interfere with oligomerization of the pyrrole units on the dendrimer periphery. Poly(3-hexylthiophene) made with a monomer-to-oxidant ratio of 1:2.5, in nitromethane had no chlorine or oxygen substituents. Poly(pyrrole) is more susceptible to chlorine and oxygen addition, as demonstrated in the MALDI-TOF-MS data of pyrrole polymers made with a monomer-to-oxidant ratio of 1:2.5 in nitromethane, in which chlorine and oxygen additions are observed. Poly(\(N\)-heptylpyrrole) was synthesized with a monomer-to-oxidant ratio of 1:1 to determine whether polymer made using less oxidant will have fewer chlorine and oxygen substituents. As can be seen from Figure 3.14 polymer was
formed when a monomer-to-oxidant ratio of 1:1 was used, but the polymer still contains chlorine and oxygen substituents, similar to poly(N-heptylpyrrole) made with a monomer-to-oxidant ratio of 1:2.5 (Figure 3.2). This demonstrates that with the pyrrole polymers, unlike the thiophenes polymers, increasing the monomer-to-oxidant ratio does not result in the formation of polymer with predominantly hydrogen end groups. The pyrrole polymers are more susceptible to

3.14 MALDI-TOF MS data for poly(N-heptylpyrrole) formed in nitromethane using different monomer-to-oxidant ratios for 10 min. In the expanded region of the spectra on the right isotope calculations for various end group compositions are shown in color.
nucleophilic attack than the thiophenes, most likely as a result of their lower oxidation potential.\textsuperscript{17}

It is also interesting to note that when a monomer-to-oxidant ratio of 1:1 is used, poly(\(N\)-heptylpyrrole) is formed. It has been previously reported that excess FeCl\(_3\) is needed when it is used as an oxidant for polymerization. This is because HCl gas is evolved during polymerization, which consumes some of the FeCl\(_3\) to form an FeCl\(_4^-\) complex. Formation of polymer with a monomer-to-oxidant ratio of 1:1 demonstrates that excess FeCl\(_3\) is not needed during the polymerization of substituted pyrroles in nitromethane. However, the polymer yield (Table 3.2) is lower for polymer made with a monomer-to-oxidant ratio of 1:1 compared to polymer made with monomer-to-oxidant ratios of 1:2.5 and 1:8.

3.9 Molecular Weight Analysis of Poly(\(N\)-heptylpyrrole)

Molecular weight analysis of poly(\(N\)-heptylpyrrole) was achieved using GPC-MALLS-DRI. The differential refractive index increment of poly(\(N\)-heptylpyrrole) was determined using a Wyatt Optilab Rex differential refractive index detector, the same detector that was used for the molecular weight analysis. A \(dn/dc\) value of 0.1738 was determined for poly(\(N\)-heptylpyrrole), made with a monomer-to-oxidant ratio of 1:2.5, at a wavelength of 658 nm. It was assumed that all poly(\(N\)-heptylpyrrole) samples had the same \(dn/dc\) values regardless of the monomer-to-oxidant ratios used for polymerization.

GPC analysis was done on the three poly(\(N\)-heptylpyrrole) materials made with different monomer-to-oxidant ratios. The refractive index and light scattering traces for the poly(\(N\)-heptylpyrrole) made with a monomer-to-oxidant ratio of 1:2.5 is in Figure 3.15. It is interesting to note that peak tailing was observed in the light scattering traces, which could indicate that the polymers are interacting with the columns. It especially interesting to note that
the second peak observed in the light scattering trace corresponds to a large negative peak in the refractive index trace. This most likely is due to two species being present in the sample that have completely different $dn/dc$ values, with the second species having a $dn/dc$ value smaller than the solvent. All poly(N-heptylpyrrole) samples had similar refractive index and light scattering chromatographic traces. The presence of a negative peak in the refractive index trace made it difficult to process the data, and no molecular weight determinations could be made using the negative refractive index data. The average molecular weights for the poly(N-heptylpyrrole) samples were made using the data points obtained before the negative refractive index data points. Because of this, the average molecular weights in Table 3.2 are not

Figure 3.15 Refractive index (blue) and light scattering traces (black) for poly(N-heptylpyrrole) made with a monomer-to-oxidant ratio of 1:2.5, in nitromethane, for 10 min.
Table 3.2 Molecular weight determinations for poly(\(N\)-heptylpyrrole) made with different monomer-to-oxidant ratios, in nitromethane with a polymerization time of 1h.

<table>
<thead>
<tr>
<th>Monomer-to-oxidant ratio</th>
<th>Polymer yield (%)</th>
<th>(M_n) (\pm 5000)</th>
<th>(M_w) (\pm 5700)</th>
<th>PD</th>
</tr>
</thead>
<tbody>
<tr>
<td>1:1</td>
<td>53.27</td>
<td>184,200</td>
<td>224,100</td>
<td>1.21 ± 0.01</td>
</tr>
<tr>
<td>1:2.5</td>
<td>82.24</td>
<td>198,700 ± 9900</td>
<td>221,700 ± 5100</td>
<td>1.12 ± 0.03</td>
</tr>
<tr>
<td>1:8</td>
<td>78.23</td>
<td>423,100 ± 7200</td>
<td>470,800 ± 5800</td>
<td>1.09 ± 0.01</td>
</tr>
</tbody>
</table>

representative of the entire polymer samples. It is surprising that the average molecular weights determined for these polymer samples are ~180,000 or higher, because the polymerization time for their formation was only 10 min. It is possible that the apparent high molecular weights are a result of polymer aggregates in solution.

The molar mass vs. elution volume plot for poly(\(N\)-heptylpyrrole) made with a monomer-to-oxidant ratio of 1:2.5, in Figure 3.16, indicates that the GPC method used was not successful in the size separation of the polymer samples. If the polymer samples were separated based solely on size on size, as the elution volume increased the molar mass would have decreased. This was not observed at earlier elution volumes, as the elution volume increased the molar mass also increased. A similar molar mass vs. elution volume plot was obtained for the sample made with a monomer-to-oxidant ratio of 1:1. The sample made with a monomer-to-oxidant ratio of 1:8 had a molar mass vs. elution volume trend similar to that expected for size separation of polymers. For the most part, as the elution volume increased, the molar mass of the polymer decreased. It is unclear why a different behavior was observed for the poly(\(N\)-heptylpyrrole)s made with a monomer-to-oxidant ratio of 1:1 and 1:2.5. It is also unclear what other species is present in the polymer samples. One possibility is that the polymer sample has highly aggregated polymer, which is responsible for the high average molecular weight values, and unaggregated polymer, with a different \(dn/dc\) value, which is responsible for the negative response observed in
the RI trace. It would be unusual for these two systems to have such different $dn/dc$ values. Other columns and solvent systems should be investigated to obtain a better separation of the poly($N$-heptylpyrrole) polymers.

**Figure 3.16** Plot of the molar mass vs. elution volume determined by GPC-MALLS-DRI for poly($N$-heptylpyrrole) made with a monomer-to-oxidant ratio of 1:2.5, in nitromethane, for 10 min.

### 3.10 Conclusions

The work in this chapter demonstrated that soluble pyrrole polymers were formed using chemical oxidative polymerization methods with iron(III) chloride as the oxidant. The first reported MALDI-TOF MS studies of the substituted pyrrole polymers indicate that the most abundant end groups are hydrogen, with other end groups being oxygen and possibly chlorine. FT-IR analysis of the monomers and polymers showed that both had oxygen substituents present in the carbonyl form. Elemental analysis data indicated that some additional elements beside
hydrogen, carbon and nitrogen are present in the polymer samples, which can be attributed to end groups such as oxygen and chlorine. The unusual isotope pattern observed in the MALDI-TOF MS data for pyrrole oligomers was observed for pyrrole systems with alkyl chains on the nitrogen as well as on the 3-position of the pyrrole ring. Therefore hydrogen atom loss is observed in the MALDI-TOF MS of alkylated pyrrole polymers regardless of the location of the alkyl substituent. Coupling studies using $^1$H-NMR were inconclusive because no signal was observed for the protons of the pyrrole ring.

3.11 References


Chapter 4

Investigations of a Model System – Poly(3-hexylthiophene)

4.1 Introduction

An unusual isotope pattern was observed in the MALDI-TOF MS data of the pyrrole polymers, described in Chapter 3, and it was thought that this mass spectral observation possibly resulted from the polymerization conditions. Because of this, 3-hexylthiophene was polymerized using the same conditions that were used to polymerize the pyrrole monomers. Poly(3-hexylthiophene), P-3HT, is considered a model system because poly(3-alkylthiophene)s have been studied more extensively in the literature than pyrrole polymers. In fact, there are very few studies on the characterization of soluble pyrrole polymers, from a structural point of view.1, 2 Pyrrole polymers have not been previously characterized using mass spectrometry, while thiophene polymers have.3-6 No unusual isotope patterns were reported previously in the mass spectrometry analysis of thiophene polymers; however they were not synthesized using the route described here.

P-3HT was initially made using the same chemical oxidative polymerization conditions as the substituted pyrroles, as described in Section 2.1. Investigations were done to determine if the structures of the polymer, i.e., end groups and molecular weight, could be varied by changing simple chemical polymerization parameters such as monomer-to-oxidant ratio, solvent, and polymerization time. Changes in structure based on the polymerization procedure were interpreted to help ascertain the mechanism of polymerization as well as chlorine addition to these polymers.

The effect of the various end groups on the polymer optical properties was investigated. The effect of end group substituents on the polymer properties is important, because the
polymerization pathway used here, as well as other commonly used polymerization pathways result in halogen (Br or Cl) end groups on the polymers.\(^3\text{-}^5\)

### 4.2 Structural Characterization of Poly(3-hexylthiophene) Using MALDI-TOF MS

#### 4.2.1 Initial Characterization of Poly(3-hexylthiophene)

3-hexylthiophene monomer was polymerized using the same chemical oxidative polymerization procedure that was used for the substituted-pyrrole polymers, as described in Section 2.1.2, using nitromethane as the solvent and a monomer-to-iron(III) chloride ratio of 1:2.5. The reaction time was increased to 1 h because thiophene monomers are known to have higher oxidation potentials than pyrrole monomers (1.6 in comparison to 0.8 V/SCE), making their reaction rates slower with a given oxidant.\(^7\) Terthiophene was used as the matrix for the MALDI-TOF MS analyses.

The MALDI-TOF MS analysis reveals one major peak series, with masses of \((166_n + 2)^+\), which corresponds to the repeat unit \((C_{10}H_{16}S, 166 \text{ u})\) with two H end groups, as can be seen in Figure 4.1. End-group analysis of the thiophene polymer demonstrated the presence of oligomers with predominantly H end groups. Examination of the calculated and observed isotopic abundance patterns indicates that with this thiophene polymer, radical molecular cations, \(M^{+}\), formed, as expected. Early studies by Hillenkamp on photoionization and photochemical reactions in MALDI postulated that photochemical reactions occurring during desorption/ionization could result in the observed ions being molecular radical cations.\(^8\) This was based on the UV-laser desorption ionization analysis of some small organic molecules, such as 1,4-dihydroxybenzene, for which the only signal observed in the mass spectra of these compounds was that of the radical cation.\(^8\) Since this initial report by Hillenkamp, electron transfer ion formation, resulting in molecular radical cations, has been observed in the MALDI-
Figure 4.1 MALDI-TOF mass spectrum of poly(3-hexylthiophene) made with a monomer-to-oxidant ratio of 1:2.5 in nitromethane for 1 h. Inset shows the expanded 6-mer region of the spectrum with colored peaks being calculated isotope patterns of the 6-mer with different end groups.
MS analysis of electro-active compounds such as bisphenol and ferrocene and in electro-active polymers that have relatively low ionization energies, such as poly(thiophene)\textsuperscript{s}.\textsuperscript{3, 9, 10}

No unusual isotope patterns were observed for the P-3HT, and there is good agreement (position and relative intensities) between that of the calculated isotope patterns for P-3HT and the observed isotope pattern of the polymer. This led to the conclusion that the unusual isotope pattern observed in the MALDI-TOF MS data of the substituted pyrrole polymers was a characteristic of the pyrrole polymers, and probably not directly related to the polymerization conditions.

The abundance of polymer with H end groups, as noted in Figure 4.1, was of interest because it has been shown previously that chlorine, as well as oxygen, substituents can affect the polymer properties by decreasing their effective conjugation and/or increasing their oxidation potential.\textsuperscript{11, 12} Previous work on the end-group analysis of P-3HT synthesized with FeCl\textsubscript{3} indicated the formation of polymers with chlorine end groups as well as possible chlorine substitutions on the polymer backbone.\textsuperscript{3} The previous work used a chlorinated polymerization solvent, chloroform; however the chlorine additions were thought to result from the oxidant, FeCl\textsubscript{3}, rather than the solvent because when FeBr\textsubscript{3} was used as the oxidant, polymer with bromine additions, rather than chlorine additions, was observed.\textsuperscript{3}

\textbf{4.2.2 Effect of Polymerization Solvent on Poly(3-hexylthiophene) End Groups}

To determine if the solvent used during the chemical polymerization of P-3HT affected the end groups of the resulting polymer, the polymerization was performed using chloroform as the solvent. All other polymerization conditions were kept the same, i.e., the monomer-to-oxidant ratio used was 1:2.5 and the polymerization time was 1 h.
The P-3HT formed in chloroform has a mass spectrum with a different mass distribution than that typically observed for polymers, as can be seen in Figure 4.2. The mass spectral data for P-3HT formed in chloroform shows an abundance of signal for some oligomers \(n = 6,7,11,12,16,17\), whereas signal for other oligomers is not observed \(n = 8,9,13,14\). It is interesting to note that a similar pattern is observed in the mass spectrum of P-3HT synthesized in nitromethane, in that the abundance values of the \(n = 6, n = 7\) and \(n = 11\) oligomers are much higher than those of the \(n = 8, n = 9\) and \(n = 10\) oligomers. From this, one of two things can be

![Figure 4.2](image-url)
concluded. Either in the chemical polymerization of P-3HT with FeCl₃, formation of the 6-mer, 7-mer, 11-mer and 12-mer is favored over the formation of the 8-mer, 9-mer and 10-mer or in the MALDI-MS analysis the desorption/ionization of the 6-mer, 7-mer, 11-mer and 12-mer is favored over the desorption/ionization of the 8-mer, 9-mer and 10-mer.

It is clear when comparing the MALDI spectra for P-3HT made in chloroform to that in nitromethane, signal is observed for larger polymers in the sample made with nitromethane, Figure 4.2. One issue to be considered when comparing polymerizations in different solvents is the solubility of FeCl₃ in the various solvents. The amount of FeCl₃ used in these polymerizations (0.825 mmoles) was completely soluble in the volume of nitromethane (12.5 mL) but only slightly soluble in an equal volume of chloroform. It can be concluded that the presence of solid FeCl₃, is the reason there was a broader distribution of oligomers observed in nitromethane. This is understandable because the monomer, 3-hexylthiophene, is only able to react with accessible FeCl₃ (Fe³⁺) on the surface of the solid clusters. Therefore the amount of Fe³⁺ available to react with the thiophene monomers in the chloroform solution is less than that in nitromethane, causing smaller oligomers and polymer to be formed in the reaction.

End-group analysis of poly(3-hexylthiophene) formed using FeCl₃ in chloroform indicates that polymer end groups include hydrogen, as well as chlorine, as can be seen from the spectral data in Figure 4.2. The presence of chlorine end groups, when chloroform was used as the solvent, versus the presence of predominantly hydrogen end groups, when nitromethane was used as the polymerization solvent, demonstrates that the polymerization solvent can affect the end groups of P-3HT polymerized using chemical methods.
4.2.3 Effect of Monomer-to-Oxidant Ratio on the Poly(3-hexylthiophene) End Groups

Based on the initial characterization of poly(3-hexylthiophene), it was also of interest to determine how the monomer-to-oxidant ratio used during the chemical polymerization of 3-hexylthiophene affected the end groups of the resulting polymer. Monomer-to-oxidant ratios were varied from 1:2.5 to 1:12 for the polymerization of the 3-hexylthiophene in nitromethane at a polymerization time of 1 h to evaluate if chlorine substitutions on the polymer would take place at higher oxidant concentrations. In addition, it was thought that this would ascertain whether the chlorine substituents on the polymer formed in chloroform are a direct result of the solvent.

Figure 4.3 MALDI-TOF MS data for poly(3-hexylthiophene) formed in nitromethane, for 1 h, using different monomer-to-oxidant ratios. Expanded regions of the spectra (right) include the data (black) and the theoretical isotope calculations (color) for various end-group compositions.
As seen in Figure 4.3, when the amount of oxidant relative to the monomer is increased, the apparent amount of chlorine end groups present in the polymer increases, assuming that the ionization efficiencies for the H and Cl materials are the same. As previously described, the mass spectral data for poly(3-hexylthiophene) synthesized with a monomer-to-oxidant ratio of 1:2.5 (Figure 4.2) exhibits signal for polymer with predominantly hydrogen end groups. The mass spectrum indicates that with a monomer-to-oxidant ratio of 1:4, a majority of the polymer is chlorine free, although some oligomers contain one chlorine addition, presumably as an end group. Polymer made using a monomer-to-oxidant ratio of 1:8 has predominantly one or two chlorine additions, again presumably end groups, and polymer made with a monomer-to-oxidant ratio of 1:12 has predominantly two or more chlorine additions. Because these reactions were carried out in nitromethane, the only source of chlorine was the oxidant. As the amount of FeCl₃ used in the polymerization reaction of P-3HT is increased, the amount of chlorine added to P-3HT is also increased. From this result it can be concluded that chlorine end groups on P-3HT, prepared using FeCl₃, originate from the FeCl₃.

4.2.4 Effect of Polymerization Time on Poly(3-hexylthiophene) End Groups

Another polymerization parameter that was evaluated was the polymerization time, to determine if it would have an effect on the polymer end groups. Polymerizations of 1 h and 24 h were performed using a monomer-to-oxidant ratio of 1:2.5, in nitromethane and chloroform. For polymerization of 3-hexylthiophene in nitromethane, the MALDI-TOF MS data indicated that the polymerization time did not affect the polymer end groups (Figure 4.1 and 4.4). The P-3HT formed in nitromethane using the two different polymerization times both have predominantly hydrogen end groups. From comparison of the MALDI-TOF MS spectra of the polymers formed at the two polymerization times (Figure 4.1 and 4.4), it appears that the polymers formed at
different times have similar molecular weights. However, it is possible that higher molecular weight materials exist in the samples but the MALDI-TOF MS is blind to them because of preferential ionization of smaller oligomers and/or saturation of the detector with smaller oligomers. Because of this, no conclusions have been made about the average molecular weights of the polymers made with different polymerization times based on the MALDI-TOF MS data. Further investigations were done to determine the average molecular weights of the polymers using GPC-MALLS-DRI and these studies are described in section 4.5. For the 24 h polymerization of 3-hexylthiophene in chloroform, the identity of the end groups of the polymer were similar to those observed for the polymer made for 1 h; however, there were additional signals present in the MALDI-TOF MS data that were unidentifiable (data not shown). The data indicates that polymers made in chloroform for 1 h and 24 h have similar molecular weights. Further molecular weight investigations were done on these polymers using GPC-MALLS-DRI.

Figure 4.4 MALDI-TOF MS data for poly(3-hexylthiophene) formed in nitromethane, with a monomer-to-oxidant ratio of 1:2.5, with a polymerization time of 24 h. The expanded region of the spectrum (right) contains the observed data (black) and theoretical calculations (colors) for various end-group compositions.
The conclusions about the presence of certain P-3HT end groups in the sample based on the MALDI-TOF MS analysis rely on the assumption that there is no preferential ionization occurring during the MALDI-TOF MS analysis for polymers with different end groups. If end-group specific discrimination occurs during the MALDI-TOF MS desorption/ionization process, the end-group analysis based on MALDI-TOF-MS data will be inaccurate. It is possible that polymer with hydrogen end groups ionizes preferentially, making the actual amount of polymer with chlorine end groups under-represented in the MALDI-TOF MS data. Further studies, discussed in sections 4.3 and 4.4 below, were carried out on the P-3HT made with different monomer-to-oxidant ratios to determine if the conclusions made about the end groups of the polymer samples based on the MALDI-TOF MS analysis are correct.

4.3 Elemental Analysis of Poly(3-hexylthiophene)

Based on the MALDI-TOF MS data, P-3HT made with more oxidant should have higher chlorine content than those made with less oxidant. Elemental analyses were done to determine the amount of carbon, hydrogen, sulfur and chlorine in each of the polymer samples made in nitromethane, for 1 h, with different monomer-to-oxidant ratios. As can be seen in Table 4.1, when the amount of oxidant used during the polymerization increases, the amount of chlorine in the poly(3-hexylthiophene) samples increases, which agrees with the hypothesis. The unexpected result was that there was a small amount of chlorine present in the sample made with a monomer-to-oxidant ratio of 1:2.5, which does not agree with the mass spectral data (polymer had only hydrogen end groups). In order to elucidate this point, some simple calculations were performed. A 90-mer (molecular weight 14,942 amu – similar to average molecular weight of the polymers determined by GPC-MALLS-DRI discussed in Section 4.5) of P-3HT would have 0.5% chlorine content if it had two chlorine end groups, and 0.2% chlorine content if it had one
Table 4.1 Elemental analysis of poly(3-hexylthiophene) samples made with different monomer-to-oxidant ratios in nitromethane with a polymerization time of 1 h.

<table>
<thead>
<tr>
<th>Monomer:oxidant ratio</th>
<th>%C</th>
<th>%H</th>
<th>%S</th>
<th>%Cl</th>
</tr>
</thead>
<tbody>
<tr>
<td>1:2.5</td>
<td>72.03±.14</td>
<td>8.66±.04</td>
<td>18.52</td>
<td>0.11±.01</td>
</tr>
<tr>
<td>1:4</td>
<td>72.21±.09</td>
<td>8.61±0</td>
<td>18.43</td>
<td>0.18±0</td>
</tr>
<tr>
<td>1:8</td>
<td>70.87±.21</td>
<td>8.45±.07</td>
<td>18.28</td>
<td>1.26±.04</td>
</tr>
<tr>
<td>1:12</td>
<td>68.77±.33</td>
<td>7.97±.04</td>
<td>19.02±04</td>
<td>5.15±18</td>
</tr>
</tbody>
</table>

chlorine end group. The P-3HT sample made with a monomer-to-oxidant ratio of 1:2.5 only had 0.1% chlorine content, so based on the previously mentioned calculation, the P-3HT samples have approximately one chlorine present for every two polymer chains. However, no chlorine additions were observed in the MALDI-TOF MS analysis of this polymer. It is my hypothesis that the chlorine content obtained by the elemental analysis results from residual FeCl₃ in the sample. The other possibility is that preferential ionization occurs during MALDI-TOF MS analysis and the Cl–material is unobservable using that technique.

4.4 Chromatographic Separation of Poly(3-hexylthiophene) Oligomers

To further investigate the accuracy of the end-group assignments made based on the MALDI-TOF MS data and determine if polymer with chlorine end groups is present in the sample made with a monomer-to-oxidant ratio of 1:2.5, separation of small molecular-weight oligomers and oligomers with different end groups was achieved using RP-HPLC coupled to a diode-array detector. The polymer samples were separated first using a simple solvent fractionation method. It has been shown that only the small molecular weight fraction ($M_n = 1962$) of P-3HT is soluble in acetone. This can be seen by inspection of the MALDI-TOF mass spectrum of the acetone fraction of P-3HT (made with a monomer-to-oxidant ratio of 1:2.5, in nitromethane, 1 h) shown in Figure 4.5. The acetone fraction was removed from each P-3HT sample and used for the RP-HPLC analysis. A method was slightly modified from the
Figure 4.5 MALDI-TOF MS data of different solvent fractions of P-3HT (monomer-to-oxidant ratio of 1:2.5, nitromethane, 1 h).

literature\(^{13}\) for the RP-HPLC separation of 3-hexylthiophene oligomers (described in section 2.4.4).

The chromatogram for the separation of poly(3-hexylthiophene) made with a monomer-to-oxidant ratio of 1:2.5 (detector wavelength of 400 nm), is shown in Figure 4.6, upper frame. Each numbered chromatographic band (1-13) was collected as a fraction for MALDI-TOF MS analysis. The MALDI-TOF MS data for fractions 1, 2, 4 and 12 are shown in Figure 4.6, lower frames, and the MALDI-TOF MS data for the other fractions can be found in Appendix A.
**Figure 4.6** Chromatogram for the RP-HPLC separation of poly(3-hexylthiophene) made with a monomer-to-oxidant ratio of 1:2.5, with MALDI-TOF MS data included for some of the chromatographic bands. The matrix used was terthiophene.
Fractions 1, 2, and 3 all exhibited MALDI-TOF MS data indicative of a 6-mer of 3-hexylthiophene, with two hydrogen end groups, although they are separated into three chromatographic bands. Similarly, fractions 4, 5, and 6 have MALDI-TOF MS data indicative of a 7-mer of 3-hexylthiophene with two hydrogen end groups. One of two things could be occurring, the first is that each band observed is the 6-mer or the 7-mer of the 3-hexylthiophene with different end groups. Because the chromatographic bands are not completely resolved, there could be an overlap of the bands in the collected fractions, and the 6-mer or the 7-mer with hydrogen end groups is solely observed in the MALDI-TOF MS data because of the possible issue of preferential ionization of oligomers with hydrogen end groups. The other possibility is that chromatographic bands 1–3 or 4–6 result from the separation of different isomers of the 6-mer or 7-mer of 3-hexylthiophene, respectively, with two hydrogen end groups. The regio-coupling of the monomers is not controlled during the synthesis of the P-3HT. Possible coupling of the unsymmetrical monomers could lead to head-to-head (H-H), head-to-tail (H-T), tail-to-tail (T-T) and tail-to-head (T-H) couplings as illustrated in Figure 1.6. The orientation of the side chain on the terminating thiophene rings (it could either be on the periphery of the oligomer or on the interior as can be seen from Figure 4.7) was shown to have an effect on the RP-HPLC retention time of similar 3-hexylthiophene oligomers by Vonk et al. In their studies the isomer with the lowest retention volume was thought to be the isomer with both side chains

![Figure 4.7](image-url)  
**Figure 4.7** Two possible isomers of the P-3HT oligomers, with terminating thiophenes having alkyl chains on the periphery or on the interior.
oriented inwards (H-H) and the highest retention volume was thought to result from the isomer with both side chains oriented outwards (T-T), with the isomers having one side chain oriented inwards and one oriented outwards (H-T) eluting in-between the other isomers. It should be noted that the model compounds they investigated only had one side chain for every three thiophenes rings instead of one on every ring, and the length of the alkyl side chains, dodecyl, is longer than the hexyl chains investigated here.

The poly(3-hexylthiophene) sample made with a monomer-to-oxidant ratio of 1:12 (in nitromethane, 1 h), that contained polymer chains with predominantly chlorine end groups based on the MALDI-TOF MS data, was also separated, and each numbered chromatographic band was collected for MALDI-TOF MS analysis. The chromatogram for the separation is shown in Figure 4.8, along with the MALDI-TOF MS data for fractions 4, 8, 17 and 20. The MALDI-TOF MS data for the other fractions can be found in Appendix A. As can be seen from the chromatogram and MS analysis of the fractions, 3-hexylthiophene oligomers with different end groups can be separated using this RP-HPLC method. It was also observed that different fractions in this separation, such as fractions 15 and 16, had similar MALDI-TOF spectra even though they were collected as different chromatographic bands.

To determine if end-group based discrimination was occurring during the ionization/desorption process in the MALDI-TOF MS analysis, a simple experiment was done with oligomers of 3-hexylthiophene with different end groups. From the RP-HPLC separations of poly(3-hexylthiophene), a relatively pure fraction was obtained of the 8-mer oligomer with H-H end groups (separation of P-3HT, monomer-to-oxidant ratio 1:2.5, fraction 7), the 8-mer with H-Cl end groups (separation of P-3HT, monomer-to-oxidant ratio 1:12, fraction 15), and the 8-mer with Cl-Cl end groups (separation of P-3HT, monomer-to-oxidant ratio 1:12, fraction 17).
Figure 4.8 RP-HPLC separation of poly(3-hexylthiophene) made with a monomer-to-oxidant ratio of 1:12 in nitromethane, with MALDI-TOF MS data of select chromatographic bands. The matrix used was terthiophene.
The resulting MALDI-TOF mass spectrum of solutions of equal concentration for each fraction is shown in Figure 4.9. As can be seen from the figure, signal is observed for each oligomer with the varying end groups, and all three oligomers have similar signal peak areas (± .08% based on three separate analyses). From this it can be concluded that no end-group specific discrimination and/or preferential ionization is occurring during the MALDI-TOF MS analysis for polymers with different end groups, as it is expected that larger molecular weight polymer would behave similarly to the 8-mers investigated here. The conclusions on the P-3HT end groups based on the MALDI-TOF MS analysis, described in section 4.2 are accurate. Preferential desorption/ionization of oligomers with hydrogen end groups compared to those with chlorine end groups does not occur, and therefore the signal observed in the MALDI-TOF MS is indicative of the contents of the polymer samples without bias. It can be concluded that the

Figure 4.9 MALDI-TOF MS spectrum of the mixture of HPLC fractions of the 8-mer of poly(3-hexylthiophene) with different end groups. The matrix was terthiophene.
different chromatographic bands that have similar MALDI-TOF MS data in the RP-HPLC separation are isomers with different couplings of the thiophenes units (H-T, H-H, T-T, and T-H).

Initially, the acetone fractions of the two P-3HT samples (made with a monomer-to-oxidant ratio of 1:2.5 and 1:12, in nitromethane, with a polymerization time of 1 h) were separated with the RP-HPLC because the goal of the separation was to collect fractions of the small molecular weight oligomers with different end groups for characterization. It was of interest to determine if higher molecular weight oligomers could also be separated with RP-HPLC, and so the separation was done on the unfractionated P-3HT samples. As can be seen

![RP-HPLC chromatogram of unfractionated P-3HT](image)

**Figure 4.10** RP-HPLC chromatogram of unfractionated P-3HT (made with a monomer-to-oxidant ratio of 1:2.5, in nitromethane, with a polymerization time of 1 h). Inset is expanded 84–100 min. range of chromatogram.
from Figure 4.10, separation of unfractionated P-3HT made with a monomer-to-oxidant ratio of 1:2.5 results in the separation, most probably, of individual oligomers beyond the 14-mer, the highest individual oligomer obtained from the separation of the acetone fraction of that material. Separation of the unfractionated P-3HT made with a monomer-to-oxidant ratio of 1:12, did not appear to result in an improved separation or in the separation of any additional oligomers (not shown). Both chromatograms for the unfractionated materials have a large broad peak at 100 min, which is most likely the elution of unresolved larger oligomers and polymer. More research needs to be done on the optimization of the separation of P-3HT to collect larger individual oligomers, perhaps using GPC or HPLC preparative columns first to obtain fractions with smaller molecular weight ranges.

4.5 Molecular Weight Analysis of Poly(3-hexylthiophene)

4.5.1. Measurement of \(dn/dc\) for Poly(3-hexylthiophene)

Before the average molecular weights of the P-3HT samples could be determined using the refractive index detector and the light scattering detector, the differential refractive index increment, \(dn/dc\), was determined. The \(dn/dc\) of P-3HT was determined using a Brice-Pheonix differential refractometer at multiple wavelengths (514.5, 589, and 632.8 nm). The \(dn/dc\) did vary depending on wavelength, as expected. It is well known that the \(dn/dc\) value decreases with an increase in the wavelength of light.\(^\text{15}\) For P-3HT (sample made with a monomer-to-oxidant ratio of 1:2.5, in nitromethane, with a polymerization time of 1h) the \(dn/dc\) was 0.394 ± 0.051 at 514.5 nm, 0.184 ± 0.010 at 589 nm, and 0.167 ± 0.007 at 632.8 nm. In addition, the \(dn/dc\) value was also determined using a Wyatt Optilab Rex differential refractive index detector which had a laser wavelength of 658 nm, because the GPC-MALLS-DRI analyses were carried out using this detector. A \(dn/dc\) value of 0.183 ± 0.005 was obtained from this instrument, and this value was
used for the molecular weight calculations. The $dn/dc$ value determined for the P-3HT sample made with a monomer-to-oxidant ratio of 1:2.5, in nitromethane, with a polymerization time of 1h, was used for all the P-3HTs made with the different polymerization conditions. It was assumed that the $dn/dc$ value did not change for P-3HTs made with different polymerization conditions, although this may not be the case. Two factors that can be responsible for $dn/dc$ variations are large changes in molar mass and changes in the chemical compositions of polymers, i.e. end groups.\textsuperscript{16} It has been demonstrated that variations in $dn/dc$ values are observed for cellulose with substantial alkyl or ester substituents or when branching occurs in the compounds.\textsuperscript{16}

### 4.5.2 Molecular Weight Measurements of P-3HT

The molecular weights of P-3HTs made with different monomer-to-oxidant ratios, in various solvents, and with different polymerization times, were determined using gel-permeation chromatography coupled to a differential refractive index detector, as well as a multi-angle laser light scattering detector. This was done to establish if the various polymerization conditions affected the molecular weight of the resulting polymers. As was expected, increasing the polymerization time from 1 h to 24 h causes the average molecular weight of the polymer to increase for P-3HT made in both chloroform and in nitromethane (Table 4.2). This makes sense because at longer polymerization times the thiophene monomers or oligomers are exposed to the oxidant for longer. Because of this, the number of thiophene monomers and oligomers that are oxidized will increase, and the coupling of these oxidized species will also increase, resulting in larger polymer.

Comparing the polymerizations of P-3HT made with the same monomer-to-oxidant ratios in chloroform and nitromethane, the polymer made in nitromethane has a higher molecular
weight than that formed in chloroform. This is true for the polymer made at a polymerization time of 1 h, as well as for a polymerization time of 24 h. These results are consistent with the MALDI-TOF MS data, in Figure 4.2, in which larger oligomers were observed in the mass spectrum of P-3HT made in nitromethane. This is again understandable when considering the solubility of the oxidant, FeCl₃, in the different solvents. Because FeCl₃ is not as soluble in chloroform as it is nitromethane, and there is solid FeCl₃ present in the reaction in chloroform, the monomer and oligomers have access only to the FeCl₃ on the surface of the solid. This results in a decrease of the amount of oxidant available to oxidize the neutral monomers/oligomers, and therefore the molecular weight of the P-3HT formed and the polymer yield, is decreased when chloroform is used. This may also affect the PD which is higher for the P-3HT made in chloroform than polymer formed in nitromethane.

Comparison of the average molecular weight of polymers made in nitromethane indicates that there is no direct trend between the monomer-to-oxidant ratio used and the average molecular weight of the resulting polymer, but the PD does seem to directly correlate with the monomer-to-oxidant ratio used. It was hypothesized that one of two trends would be observed

### Table 4.2 Molecular weights determined using GPC-MALLS-DRI and polymer yields for P-3HT made with different monomer-to-oxidant ratios, in different solvents and for different polymerization times.

<table>
<thead>
<tr>
<th>Monomer-to-oxidant ratio</th>
<th>Solvent</th>
<th>Time (h)</th>
<th>Yield (%)</th>
<th>$M_n$</th>
<th>$M_w$</th>
<th>PD</th>
</tr>
</thead>
<tbody>
<tr>
<td>1:2.5</td>
<td>nitromethane</td>
<td>1</td>
<td>66.9</td>
<td>9,400 ± 300</td>
<td>17,200± 300</td>
<td>1.82 ± .03</td>
</tr>
<tr>
<td>1:4</td>
<td>nitromethane</td>
<td>1</td>
<td>88.9</td>
<td>5,700 ± 200</td>
<td>13,500 ± 300</td>
<td>2.34 ± .05</td>
</tr>
<tr>
<td>1:8</td>
<td>nitromethane</td>
<td>1</td>
<td>117.1</td>
<td>7,800 ± 100</td>
<td>20,700 ± 300</td>
<td>2.67 ± .08</td>
</tr>
<tr>
<td>1:12</td>
<td>nitromethane</td>
<td>1</td>
<td>116.5</td>
<td>5,200 ± 100</td>
<td>13,700 ± 100</td>
<td>2.65 ± .03</td>
</tr>
<tr>
<td>1:2.5</td>
<td>chloroform</td>
<td>24</td>
<td>11.1</td>
<td>3,400 ± 300</td>
<td>14,000 ± 600</td>
<td>4.13 ± .27</td>
</tr>
<tr>
<td>1:2.5</td>
<td>chloroform</td>
<td>24</td>
<td>16.7</td>
<td>9,840 ± 200</td>
<td>29,600 ± 1500</td>
<td>3.01 ± .09</td>
</tr>
<tr>
<td>1:2.5</td>
<td>nitromethane</td>
<td>24</td>
<td>44.8</td>
<td>18,500 ± 500</td>
<td>38,300 ± 800</td>
<td>2.07 ± .03</td>
</tr>
</tbody>
</table>
with respect to the monomer-to-oxidant ratio used and the resulting average molecular weight of the polymer. The first being that as the amount of oxidant used for the polymerization increased, the molecular weight of the polymer would increase. This is because the neutral monomers/oligomers would be more likely to be oxidized by the FeCl₃ since the concentration of FeCl₃ in solution was greater. The other hypothesis is that when the amount of oxidant used in the reaction is increased, the molecular weight of the polymer will decrease. This is because as the amount of FeCl₃ used in the reaction increases, the amount of chlorine additions, presumably end groups, increases. If the chlorine additions are indeed end groups, after addition of chlorine to the alpha position on the terminal thiophenes, the polymerization will be terminated (assuming that polymerization only occurs at the alpha (2,5) positions on the thiophene rings). This will decrease the average molecular weight of polymer formed. Neither of these two hypotheses are supported by the data. No direct correlation was observed between the monomer-to-oxidant ratio used during the polymerization of P-3HT and the resulting molecular weight of the polymer. It is interesting to note however that as the amount of oxidant in the reaction was increased, the PD of the polymer increased as well as the polymer yield. Polymer yields of over a 100% were obtained for P-3HT.

![Figure 4.11 Plot of elution volume vs. molar mass (black) and LS (blue solid) and DRI (blue dashed) chromatograms of the unfractionated P-3HT (1:2.5, nitromethane, 1h).](image)
made with monomer-to-oxidant ratios of 1:8 and 1:12 because of chlorine addition to the polymer.

When examining the molecular weight data plots of the molar mass vs. the elution volume for the polymer formed in nitromethane, a deviation was observed from the expected linear plot. During a typical gel-permeation chromatography experiment, the analytes are separated based solely on size, and no interactions occur between the column and the analyte. If this is the case, a linear plot is observed for the molar mass vs. the elution volume; as the elution volume increases, the molar mass decreases. A deviation from the linear trend was observed for P-3HT made in nitromethane, as seen in portions of Figure 4.11. At some points on the plot (~20.5 to 22.0 min), the molecular weight increases with increasing elution volume. GPC-MALLS-RI was done on the acetone solvent fraction of the P-3HT (1:2.5,
nitromethane, 1h) and on the residual sample after the acetone fraction was removed. As can be seen from the molar mass plots in Figure 4.12, the P-3HT in the acetone fraction is responsible for the portion of the molar mass plot that is non-linear.

To determine if the molar mass does actually increase at some of the longer elution volumes, fractions were collected from the GPC eluent of the P-3HT acetone extract, for MALDI-TOF MS analysis. The fractions were collected every 20 sec starting at time an elution time of 21 min. Because of the delay from the detector to the collection vial is 1 min, the first fraction collected, as be seen in Figure 4.13, is the eluent at a time of 20 min in the chromatogram. The MALDI-TOF spectrum for each collected GPC fraction is in Appendix A and average molecular weights

**Table 4.3** Average molecular weights for GPC fractions collected from acetone extract of P-3HT (made with a monomer-to-oxidant ratio of 1:2.5, in nitromethane, using a polymerization time of 1 h) calculated from the MALDI-TOF MS data.

<table>
<thead>
<tr>
<th>Acetone GPC Fractions</th>
<th>$M_n$</th>
<th>$M_w$</th>
<th>PD</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fraction 1</td>
<td>1687</td>
<td>2089</td>
<td>1.24</td>
</tr>
<tr>
<td>Fraction 2</td>
<td>1749</td>
<td>2158</td>
<td>1.23</td>
</tr>
<tr>
<td>Fraction 3</td>
<td>1990</td>
<td>2211</td>
<td>1.11</td>
</tr>
<tr>
<td>Fraction 4</td>
<td>2020</td>
<td>2123</td>
<td>1.05</td>
</tr>
<tr>
<td>Fraction 5</td>
<td>1810</td>
<td>1900</td>
<td>1.05</td>
</tr>
<tr>
<td>Fraction 6</td>
<td>1285</td>
<td>1417</td>
<td>1.10</td>
</tr>
<tr>
<td>Fraction 7</td>
<td>1152</td>
<td>1227</td>
<td>1.06</td>
</tr>
</tbody>
</table>
determined from the MS data of each fraction are included in Table 4.3. The average molecular weights calculated from the MALDI spectra are lower than would be expected from the molar mass plot used from the GPC-MALLS-DRI data. This may be because the $dn/dc$ value used is not accurate for the small-molecular-weight portion of the sample. It is interesting to note that the calculated average molecular weights from the MALDI spectra of the fractions does increase for the first three fractions, and then they decrease for the rest of the fractions. However it does not follow the trend depicted by the plot of molar mass vs. elution volume based on the LS and DRI molar mass determinations, because fraction 6 should have a higher molecular weight than fractions 4 and 5. The calculated molecular weights from the MALDI-TOF MS data and the LS-DRI both indicate that at some point the molecular weight increases with elution volume. This is most likely a result of some interaction between the polymers and the GPC columns.

A possible explanation for the observed behavior in Figures 4.11, 4.12, 4.13 and Table 4.3 is the formation of aggregates that interact with the GPC columns and therefore elute later causing an increase in molecular weight at 20-22 min. To determine if aggregation was occurring over time for the P-3HTs studied here, average molecular weights were

Table 4.4 Molecular weight data determined by GPC-MALLS-DRI for P-3HT dissolved in THF (~3.0 mg/mL) measured over a seven day period.

<table>
<thead>
<tr>
<th></th>
<th>$M_n$</th>
<th>$M_w$</th>
<th>PD</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>P-3HT</strong></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Day 1</td>
<td>9,200</td>
<td>17,000</td>
<td>1.84</td>
</tr>
<tr>
<td>Day 2</td>
<td>8,800</td>
<td>16,500</td>
<td>1.88</td>
</tr>
<tr>
<td>Day 3</td>
<td>8,300</td>
<td>16,200</td>
<td>1.95</td>
</tr>
<tr>
<td>Day 7</td>
<td>7,300</td>
<td>15,200</td>
<td>2.07</td>
</tr>
<tr>
<td><strong>Acetone Fraction</strong></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Day 1</td>
<td>4,400</td>
<td>4,900</td>
<td>1.11</td>
</tr>
<tr>
<td>Day 2</td>
<td>5,300</td>
<td>5,900</td>
<td>1.11</td>
</tr>
<tr>
<td>Day 3</td>
<td>4,500</td>
<td>5,100</td>
<td>1.14</td>
</tr>
<tr>
<td>Day 7</td>
<td>4,200</td>
<td>4,700</td>
<td>1.13</td>
</tr>
<tr>
<td><strong>Acetone Fraction Removed</strong></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Day 1</td>
<td>12,300</td>
<td>21,200</td>
<td>1.73</td>
</tr>
<tr>
<td>Day 2</td>
<td>11,500</td>
<td>20,000</td>
<td>1.75</td>
</tr>
<tr>
<td>Day 3</td>
<td>11,500</td>
<td>19,900</td>
<td>1.73</td>
</tr>
<tr>
<td>Day 7</td>
<td>11,200</td>
<td>19,400</td>
<td>1.73</td>
</tr>
</tbody>
</table>
determined for solutions of P-3HT over a period of seven days for the unfractionated P-3HT (1:2.5, nitromethane, 1 h), as well as an acetone extract, and the remaining sample after the acetone fraction was removed. Molecular weight determinations were made immediately after dissolving the polymer samples in THF (day 1), the following two days (day 2 and 3), and six days later (day 7). The samples were stored in darkness between measurements because it has been shown that P-3HT can degrade in non-aqueous solutions containing molecular oxygen, via chain scission upon exposure to light.\textsuperscript{17} As can be seen from Table 4.4, aggregation of P-3HT over time was not observed, at least not in an amount substantial enough to increase the molecular weight. In general the molecular weight of the P-3HTs actually decreased slightly over the seven-day period. This is most likely due to a small amount of photo-degradation even though the samples were kept in amber vials.

4.6 Conclusions and Mechanistic Implications Based on MALDI-TOF MS and Molecular Weight Data

It has been concluded from structural investigations of P-3HT formed using FeCl\textsubscript{3} as the oxidant that P-3HT is formed with hydrogen and/or chlorine end groups. The proposed mechanism for the polymerization and chlorine substitution is in Figure 4.14. The coupling of the monomers was depicted to occur between two radical cations although it is also possible that couplings occur via electrophilic attack of the radical cation on the neutral monomers, as explained in Section 1.2.2.\textsuperscript{18}

The MALDI-TOF results indicate that more chlorine end groups are observed in the polymer made in chloroform versus nitromethane. This is understandable when considering the active iron chloride species in the different solvents. In chloroform, FeCl\textsubscript{3} has a very low solubility, so most of the redox activity occurs at the surface of solid FeCl\textsubscript{3}. Upon oxidation of the monomer, FeCl\textsubscript{3} leads to FeCl\textsubscript{2} and Cl\textsuperscript{-}.\textsuperscript{19} Because Cl\textsuperscript{-} ions are formed in the near vicinity of
the monomer/oligomer radical cations, these monomers/oligomers are susceptible to chlorine addition via radical or nucleophilic substitution. In nitromethane, FeCl$_3$ dissociates as shown in the following chemical equations.$^7,20,21$

**Equation 4.1** \[ 2\text{FeCl}_3 \rightarrow \text{FeCl}_4^- + \text{FeCl}_2^+ \]  
**Equation 4.2** \[ 2\text{FeCl}_3 \rightarrow \text{Fe}_2\text{Cl}_5^+ + \text{Cl}^- \]

The redox active species in nitromethane is FeCl$_2^+$ or Fe$_2$Cl$_5^+$ which is reduced to FeCl$_2$ or Fe$_2$Cl$_5$ upon oxidation of the monomer and no chlorine ions are formed. Based on this, it is clear why more chlorine additions to the polymer occur when chloroform is used as the polymerization solvent.

**Figure 4.14** Proposed mechanism for the polymerization and chlorine substitution of heterocyclic compounds.
This does not explain why the amount of chlorine substituents on P-3HT increase as the amount of oxidant used in the polymerization is increased. It has been reported that dimeric FeCl₃ dissociates to form not only FeCl₂⁺ and FeCl₄⁻ in nitromethane but also possibly Fe₂Cl₅⁺ and Cl⁻.²⁰ As the amount of FeCl₃ in the polymerization is increased the amount of Cl⁻ in the polymerization reaction is increased, resulting in an increase in the probability that it will add to the polymer chain via radical or nucleophilic addition.

When considering the proposed mechanism for polymerization and chlorine addition to P-3HT (Figure 4.14), it also is understandable why more chlorine additions occur when the amount of oxidant is increased. As outlined in the mechanism, when chlorine adds to the polymer via the radical route or the nucleophile route, an additional equivalent of the oxidant is required. Obviously as the amount of oxidant is increased there is more oxidant available to facilitate chlorine addition to the polymer.

It is interesting to note from the average molecular weight data obtained from GPC-MALLS-DRI that the amount of oxidant used during the polymerization does not affect the resulting average molecular weight of the polymer. It was initially thought that chlorine addition to the thiophene units would terminate the polymerization, as depicted in the termination box in Figure 4.14. This was based on the assumption that chlorine substituents on the polymer chains were indeed end groups, i.e. located on the alpha position of the terminal thiophene unit. This was also based on the assumption that polymerization only occurred at the alpha (2,5) positions on the thiophenes. If this were the case, and chlorine addition caused polymerization termination, polymer with more chlorine substituents would generally have a smaller average molecular weight. Because this was not observed, it can be concluded that chlorine addition occurs on the polymer backbone rather than on the alpha position of the terminal thiophene units and/or
coupling occurs in the beta position (3,4) as well as the alpha position of the thiophene units. If the latter is the case, polymerization would be terminated by chlorine addition only if the polymer chain was fully chlorinated on the alpha and beta carbons on the thiophene polymers.

4.7 Optical Analysis of P-3HT

The individual small-molecular-weight P-3HT oligomers that were obtained using RP-HPLC were studied using UV-visible spectroscopy, to determine how chlorine substituents affected the optical properties of the thiophene oligomers. In Table 4.5 and 4.6 the oligomer assignments based on the MALDI-TOF MS data are given, as well as the wavelength of maximum absorbance ($\lambda_{\text{max}}$) observed in the UV-visible spectra, for each fraction collected from the RP-HPLC separation of P-3HT made with a monomer-to-oxidant ratio of 1:2.5 and 1:12.

From these studies it is apparent that as the length of the oligomer increases, the $\lambda_{\text{max}}$ is red-

<table>
<thead>
<tr>
<th>HPLC Fraction 1:2.5</th>
<th>Assignment</th>
<th>$\lambda_{\text{max}}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>6-mer H,H</td>
<td>374 nm</td>
</tr>
<tr>
<td>2</td>
<td>6-mer H,H</td>
<td>371 nm</td>
</tr>
<tr>
<td>3</td>
<td>6-mer H,H</td>
<td>371 nm</td>
</tr>
<tr>
<td>4</td>
<td>7-mer H,H</td>
<td>368 nm</td>
</tr>
<tr>
<td>5</td>
<td>7-mer H,H</td>
<td>379 nm</td>
</tr>
<tr>
<td>6</td>
<td>7-mer H,H</td>
<td>379 nm</td>
</tr>
<tr>
<td>7</td>
<td>8-mer H,H</td>
<td>382 nm</td>
</tr>
<tr>
<td>8</td>
<td>9-mer H, H</td>
<td>not discernable</td>
</tr>
<tr>
<td></td>
<td>8-mer H,Cl</td>
<td></td>
</tr>
<tr>
<td>9</td>
<td>10-mer H,H</td>
<td>392 nm</td>
</tr>
<tr>
<td>10</td>
<td>11-mer H,H</td>
<td>394 nm</td>
</tr>
<tr>
<td>11</td>
<td>12-mer H,H</td>
<td>400 nm</td>
</tr>
<tr>
<td>12</td>
<td>13-mer H,H</td>
<td>404 nm</td>
</tr>
<tr>
<td>13</td>
<td>14-mer H,H</td>
<td>292 nm, 412 nm (2 bands)</td>
</tr>
</tbody>
</table>
shifted, which is expected because conjugation is increased in larger oligomers. As stated earlier, the extent of conjugation in conducting polymers directly affects the energy transitions from the \(\pi-\pi^*\) orbitals, with the energy gap being smaller for more conjugated systems.\(^{22}\)

Table 4.6 Identification and UV-vis characterization of HPLC fractions from the separation (see Figure 4.8 for chromatogram) of P-3HT (made with a monomer-to-oxidant ratio of 1:12, nitromethane, 1h).

<table>
<thead>
<tr>
<th>HPLC Fraction 1:12</th>
<th>Assignment</th>
<th>(\lambda_{\text{max}})</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>4-mer H,H</td>
<td>334 nm</td>
</tr>
<tr>
<td>2</td>
<td>4-mer H,H</td>
<td>348 nm</td>
</tr>
<tr>
<td>3</td>
<td>4-mer H,H</td>
<td>343 nm</td>
</tr>
<tr>
<td>4</td>
<td>4-mer H,Cl</td>
<td>355 nm</td>
</tr>
<tr>
<td>5</td>
<td>4-mer H,Cl</td>
<td>348 nm</td>
</tr>
<tr>
<td>6</td>
<td>4-mer Cl,Cl</td>
<td>371 nm</td>
</tr>
<tr>
<td>7</td>
<td>4-mer Cl,Cl; 5-mer H,Cl</td>
<td>349 nm</td>
</tr>
<tr>
<td>8</td>
<td>4-mer Cl,Cl</td>
<td>371 nm</td>
</tr>
<tr>
<td>9</td>
<td>4-mer Cl,Cl</td>
<td>383 nm</td>
</tr>
<tr>
<td>10</td>
<td>6-mer H,H; 5-mer Cl,Cl</td>
<td>372 nm</td>
</tr>
<tr>
<td>11</td>
<td>5-mer Cl,Cl; 6-mer H,H</td>
<td>366 nm</td>
</tr>
<tr>
<td>12</td>
<td>5-mer Cl,Cl; 6-mer H,H</td>
<td>373 nm</td>
</tr>
<tr>
<td>13</td>
<td>6-mer H,Cl</td>
<td>(not discernable)</td>
</tr>
<tr>
<td>14</td>
<td>unidentifiable</td>
<td>-----</td>
</tr>
<tr>
<td>15</td>
<td>8-mer H,Cl</td>
<td>385 nm</td>
</tr>
<tr>
<td>16</td>
<td>8-mer H,Cl</td>
<td>386 nm</td>
</tr>
<tr>
<td>17</td>
<td>8-mer Cl,Cl</td>
<td>397 nm</td>
</tr>
<tr>
<td>18</td>
<td>8-mer Cl,Cl</td>
<td>392 nm</td>
</tr>
<tr>
<td>19</td>
<td>9-mer Cl, Cl</td>
<td>394 nm</td>
</tr>
<tr>
<td>20</td>
<td>9-mer Cl, Cl</td>
<td>378 nm</td>
</tr>
<tr>
<td>21</td>
<td>Mix</td>
<td>377 nm</td>
</tr>
<tr>
<td>22</td>
<td>Mix</td>
<td>397 nm</td>
</tr>
<tr>
<td>23</td>
<td>12-mer Cl,Cl; 13-mer Cl,Cl</td>
<td>(not discernable)</td>
</tr>
</tbody>
</table>
It is interesting to compare $\lambda_{\text{max}}$ for different fractions that have the same oligomer assignments, as it has been concluded that these fractions are isomers of one another. Because the 3-hexylthiophene monomers are unsymmetrical, possible coupling of the thiophene units include head-to-head, head-to-tail, tail-to-tail and tail-to head, as explained in section 1.3.6 and illustrated in Figure 1.6. The coupling of the monomers has been shown to effect the conjugation of the polymer chain, and therefore the $\lambda_{\text{max}}$ of the resulting polymers in solution and cast into thin films. Molecular mechanics have shown that head-to-head couplings results in twisting of the thiophene rings out of coplanarity, due to steric interactions of the alkyl chains, which leads to a decrease in the effective conjugation length. If head-to-head couplings are indeed present in some of the thiophene oligomers collected, it would be expected that they would have a blue shift in $\lambda_{\text{max}}$ compared to oligomeric isomers with more regular head-to-tail couplings. These shifts in absorbance are observed for some of the oligomeric isomers, in Table 4.5 and 4.6. A shift in absorbance of 11 nm is observed between different isomers of the 7-mer with H,H end groups (Table 4.5: fraction 4, $\lambda_{\text{max}} = 368$ nm; fraction 5 and fraction 6, $\lambda_{\text{max}} = 379$ nm). It is interesting that a shift in absorbance of this magnitude is observed for isomeric oligomers. Presumably the oligomers with the higher energy $\lambda_{\text{max}}$ have more head-to-head couplings than their isomers that have lower energy $\lambda_{\text{max}}$. Similarly, a shift in absorbance of 12 nm is observed for isomers of the 4-mer with Cl,Cl end groups (371 nm to 383 nm) and a shift as great as 16 nm is observed for isomers of the 9-mer with Cl,Cl end groups (378 nm to 394 nm).

A question that arises when comparing oligomeric isomers with chlorine substituents is whether the location of the chlorine substituent, as well as the coupling of the monomers, affects the $\lambda_{\text{max}}$. In the discussion of polymer end groups in previous sections, it has been assumed that the chlorine additions occur as end groups on the polymer (at the alpha carbons on the terminal
thiophene units), because that has been thought to be the most reactive site on the thiophene rings. Therefore it is the most probable location for nucleophilic addition of chlorine to occur. However, in the data presented here, there is no evidence that the location of the chlorine substituents is on the end group of the thiophene oligomers/polymers rather than the polymer backbone.

Other notable observations are the differences in $\lambda_{\text{max}}$ of oligomers with chlorine additions versus that for those which have no chlorine additions. This comparison was done for the P-3HT 4-mer and 8-mer, which had pure fractions available for each oligomer with H-H, Cl-H and Cl-Cl assignments, and is shown in Table 4.7. It should be noted that if more than one fraction had a particular assignment the $\lambda_{\text{max}}$ values were averaged for that assignment. As can be seen from the table, one chlorine addition results in a red shift in $\lambda_{\text{max}}$ and two chlorine additions result in an even larger red shift in $\lambda_{\text{max}}$. The effect of the chlorine is greater on the energy levels of the smaller oligomer, the 4-mer, compared to the 8-mer, and as a result, greater $\lambda_{\text{max}}$ shifts are observed. The red shift in the $\lambda_{\text{max}}$ upon the addition of chlorine could be attributed to an increase in conjugation of the polymer, due to the resonance from the halogen. If this is the case, one would expect the oxidation potential of the halogenated oligomer to decrease because the resulting oxidized oligomer would be more stable than the unhalogenated oligomer, due to the increase in conjugation and increase in the delocalization of the electrons. This disagrees with what was observed electrochemically by Qi et al. who reported that upon halogenation of thiophene polymers there was a slight increase in the oxidation potential, which they attributed to

<table>
<thead>
<tr>
<th>Oligomer</th>
<th>H,H</th>
<th>H, Cl ($\Delta \lambda_{\text{max}}$)</th>
<th>Cl,Cl ($\Delta \lambda_{\text{max}}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>4-mer</td>
<td>342 nm</td>
<td>358 nm (16 nm)</td>
<td>377 nm (35 nm)</td>
</tr>
<tr>
<td>8-mer</td>
<td>382 nm</td>
<td>386 nm (4 nm)</td>
<td>395 nm (15 nm)</td>
</tr>
</tbody>
</table>

Table 4.7 Values for $\lambda_{\text{max}}$ for the 4-mer and 8-mer of P-3HT with different end groups in chloroform.
the electron withdrawing effects of chlorine.\textsuperscript{12} It should be noted that because the coupling of the monomers is not known for the oligomers described here, some of the shifts in absorbance attributed to chlorine addition could also be the result of favorable (head-to-tail) and unfavorable (head-to-head) couplings.

To further investigate the effects of chlorine substituents on P-3HTs the optical properties of the unfractionated polymers made with varying monomer-to-oxidant ratios were studied using UV-visible spectroscopy. The UV-visible data for the polymers made with different monomer-to-oxidant ratios (different chlorine contents) is shown in Figure 4.15. The P-3HT made with a monomer-to-oxidant ratio of 1:12, which has been shown to have the most chlorine substituents (section 4.2.3 and 4.3), has the highest energy $\lambda_{\text{max}}$. Because the $\lambda_{\text{max}}$ of the polymer made with a monomer-to-oxidant ratio of 1:8, which has also been shown to have chlorine substituents, has the lowest energy $\lambda_{\text{max}}$, it can be presumed that no correlation of $\lambda_{\text{max}}$ and the number of chlorine substituents in the unfractionated polymer samples can be observed. This may be because the number of chlorine substituents is relatively small compared to the size of the polymers in the unfractionated

\textbf{Figure 4.15} UV-visible spectra of P-3HTs made with different monomer-to-oxidant ratios.
solution, which is not the case for the oligomers described earlier. The shifts in \( \lambda_{\text{max}} \) are more likely attributed to the differences in average molecular weight of the unfractionated polymer samples.

### 4.8 Conclusions

In conclusion, it has been demonstrated that end-group composition of P-3HTs can be determined by varying the polymerization conditions in the chemical oxidative polymerization of 3-hexylthiophene. P-3HT can be made with various amounts of chlorine by simply modifying monomer-to-oxidant ratio, and/or the solvent used during polymerization. The issue of end-group specific discrimination occurring during end-group analysis of P-3HT using MALDI-TOF MS was addressed and it was determined no such discrimination was occurring with P-3HT and the end groups studied here. The molecular weight of P-3HTs is affected by the solvent and the polymerization time but no correlation was observed for the monomer-to-oxidant ratio used and the average molecular weight of the resulting polymer. Optical studies revealed that the not only the monomer coupling, but also the presence of halogen substituents can substantially affect the optical properties of 3-HT oligomers. The findings presented in this chapter are important because tailoring of polymer structure, and thus polymer properties, to suit a given application is readily achieved with the simple approach described here.

### 4.9 References


Chapter 5
Conclusions and Future Work

5.1 Summary of Conclusions

The purpose of this research was to apply MALDI-TOF MS to heterocyclic conducting polymers, specifically those of pyrrole and thiophene, in hopes of enhancing the understanding of structural properties of these polymers, with the specific aim of determining end group and molecular weight dependence on polymerization conditions. Further investigations were done to determine how the end groups affected the optical properties of thiophene oligomers. This research has demonstrated that use of a simple and common chemical oxidative polymerization procedure leads to the modification of the structure of the resulting polymers by changing the polymerization parameters.

Soluble N-alkylpyrrole polymers were synthesized, and for the first time, successfully characterized using MALDI-TOF MS. With an initial set of polymerization conditions (monomer-to-oxidant ratio 1:2.5, nitromethane solvent, polymerization time of 5 min), polymer was formed with hydrogen, as well as oxygen and chlorine end groups. Increasing the amount of oxidant used in the polymerization resulted in the formation of polymer with at least two or more chlorine additions. Under the conditions used, completely pristine pyrrole polymer samples lacking any chlorine and/or oxygen substituents were never formed.

Unexpectedly, hydrogen atom loss was observed in the mass spectra of the poly(N-alkylpyrrole)s. Because of this observation, polymers were also synthesized from pyrrole monomers possessing alkyl substituents in the 3-position of the pyrrole ring. The mass spectra of these polymers also indicated that hydrogen atom loss occurred. From these observations, it was concluded that single and multiple hydrogen loss is observed in the mass spectra of pyrrole
polymers regardless of the location of the alkyl side chain, and this is a characteristic of these systems.

Poly(3-hexylthiophene) was synthesized using various polymerization conditions to determine their effect on the end groups and/or the molecular weight of the resulting polymers. The solvent, as well as the monomer-to-oxidant ratio, used during polymerization were found to have an effect on the structure of the polymer, while the polymerization time did not. Polymerization of P-3HT in chloroform versus nitromethane, using the same monomer-to-oxidant ratio and polymerization time, demonstrated that P-3HT formed in chloroform has more chlorine substituents than P-3HT made in nitromethane. It was also demonstrated that by increasing the amount of oxidant used during the polymerization in nitromethane the amount of chlorine substituents increased. The polymerization time did not have an effect on the polymer composition, however as expected, polymer made with longer polymerization times had higher average molecular weights.

The effect of chlorine substituents on the optical properties of small oligomers of 3-hexylthiophene was determined. It was found that chlorine additions to oligomers of 3-hexylthiophene cause a red-shift in UV-visible absorbance. This is attributed to the electron donating properties of the chlorine and the resonance structure of the oligomer resulting in an increase in effective conjugation length of the oligomer. This finding is very important because most common polymerization methods, such as the one used here, as well as Rieke, McCullough and GRIM methods, result in polymer with halogen substituents.
5.2 Future Work

5.2.1 Pyrrole Polymers

It has been determined in this work that hydrogen atom loss is observed in the MALDI-TOF mass spectra of substituted pyrrole polymers. Further investigations should be done to determine if hydrogen loss is occurring from the alkyl side groups attached to the pyrrole units or if it is a result of hydrogen loss from the pyrrole backbone. One avenue to determine this is polymerization of a pyrrole monomer that has a deuterated alkyl side chain.

Some studies could be done to determine if hydrogen loss is occurring during the MALDI-TOF MS analysis. Different MALDI matrices could be investigated to determine if more or less hydrogen loss occurs based on the ionization potentials of the matrix used for analysis. Another straightforward experiment to investigate if hydrogen loss occurs in the TOF field free region would be to compare MALDI-TOF MS data collected in linear mode and reflectron mode, to determine if more hydrogen loss is observed for the polymers that have longer flight paths (detected in reflectron mode).

Because the $^1$H-NMR data, as well as GPC measurements, indicate aggregation may be occurring with the pyrrole polymers in solution, dynamic light scattering studies could be employed on these polymers to determine if, and if so to what extent, aggregation occurs for these polymers in organic solvents. Studies done on the pyrrole polymers at different temperatures could help determine if intermolecular interactions are occurring between polymer chains. Studies done at different temperatures could help ascertain if aggregation only becomes an issue at higher concentrations of the pyrrole polymers in solution. If aggregation is an issue, the samples could be heated during $^1$H-NMR analysis to break up any aggregated polymer so as to allow for recovery of better spectra.
The GPC analysis of the pyrrole polymers contained two light scattering peaks one which had a corresponding apparent negative refractive index peak. From these observations it was concluded that the pyrrole polymer sample consisted of two components that had very different \(dn/dc\) values. It would be interesting to collect the chromatographic bands possessing the two different refractive index values, positive and negative, in separate fractions and characterize them using MALDI-TOF MS, as well as possibly other spectroscopic techniques to determine what the two components in the pyrrole polymer samples are.

As previously stated, the chemical polymerization procedure herein utilized the commonly used oxidizing agent, FeCl\(_3\). Other oxidizing agents such as iron(III) nitrate and sodium persulfate could be investigated to determine if they are suitable oxidants for polymer formation and to determine the structure of the polymers formed using these oxidants.

### 5.2.2 Thiophene Polymers

Further studies should be performed on the collected oligomer fractions to obtain more detailed information on the electronic properties of oligomers with different numbers of repeat units as well as different end groups. \(^1\)H-NMR studies should be done on the oligomer fractions to determine the percent of regio-regular (H-T) and irregular couplings (T-T, H-H) in the oligomers fractions, because as previously stated, this has an effect on oligomer optical and electrochemical properties. Preliminary NMR data obtained from the analysis of four of the oligomer samples on the 700MHz NMR is included in Appendix B. Because of the limited amount of sample, more investigations are being done to correctly identify the peaks and determine the \% H-T coupling. Electrochemical studies could be done to determine the electronic properties of the oligomers, specifically their oxidation and reduction potentials. This, coupled with the optical data already obtained, will give an understanding of the energy band...
levels (HOMO and LUMO) for the thiophene oligomers and how they differ for oligomers with different compositions.\textsuperscript{2} Conductivity measurements on the oligomers with different end groups would ascertain the effect of the substituents on the electrical properties of these oligomers.

Development of an HPLC methodology that would allow for better separation of higher molecular weight oligomers (20-30 mers) would be very beneficial. This could possibly be done by pre-fractionation of the samples either by solvent extraction or by GPC to remove the smaller molecular weight oligomers to obtain polymer with a small molecular weight range for separation by HPLC. It would also be more efficient to develop a methodology to separate these oligomers on an LC system that is coupled directly to a mass spectrometer. In addition, the optical and electrochemical properties of the larger oligomers could be studied to determine if the effect of the halogen substituent on these oligomer properties lessened and if so at what oligomer lengths. It would also be interesting to collect fractions of higher molecular weight polymers with narrow mass ranges from the GPC for UV analysis to determine at what polymer sizes the molecular weight of the polymer no longer affects the $\lambda_{\text{max}}$.

To investigate the mechanism of polymerization further and to determine why larger molecular weight polymer is not formed when the amount of oxidant used in the polymerization is increased, the amount of unreacted monomer could be quantified using GC-MS. It would be interesting to determine if unreacted monomer remains after the polymerization is quenched and if so if the amount of unreacted monomer changes with the amount of oxidant used in the polymerization.

A similar system, poly(phenylene oxide) made by oxidative coupling, has been shown to have a polycondensation step-wise growth polymerization mechanism.\textsuperscript{3} The degree of polymerization is low for most of the reaction and increases sharply near the end of the reaction.\textsuperscript{3}
This means that polymer growth is occurring not only from coupling of the monomers but also by coupling of the growing polymer chains with one another. To investigate if a similar polymerization mechanism is occurring for the pyrrole and thiophenes polymer systems, the polymerization intermediates can be characterized by taking aliquots of the reaction out of the reaction mixture at various time intervals. By monitoring the reaction products over time, the degree of polymerization at different reaction time intervals can be determined.

Polymerization may reach an equilibrium where higher molecular weight polymer is not produced and chain transfer is a possible polymerization termination process. More monomer could be added to the reaction at later times and if the polymerization reaction is reversible the addition of monomer could cause the polymer molecular weight to drop. These experiments could also be done at low temperature where the rate of the reaction may be slower. It would also be interesting to determine if the polymerization temperature has an affect the structure of the resulting polymer. It has been reported that when the reaction temperature is decreased, the regio-regularity (head-to-tail content) of the polymer can be increased from ~70-80% to as high as 91%. This is very important because regio-regular polymer has been shown to have superior properties compared to polymer that has an irregular structure.

5.3 References


(3) Endres, G. F.; Kwiatek, J. Polymerization by Oxidative Coupling. III. Mechanistic Type in the Copper-Amine Catalyzed Polymerization of 2,6-dimethylphenol. Journal of Polymer Science. 1962, 58, 593-609.


Appendix A: Supplemental MALDI-TOF MS Data

A.1 MALDI-TOF MS Data from HPLC Chromatograms from Separation of P-3HT (polymerized with a monomer-to-oxidant ratio of 1:2.5, in nitromethane, for 1 h).

Figure A.1.1 HPLC fraction #1 from the separation of P-3HT (polymerized with a monomer-to-oxidant ratio of 1:2.5, in nitromethane, for 1 h).

Figure A.1.2 HPLC fraction #2 from the separation of P-3HT (polymerized with a monomer-to-oxidant ratio of 1:2.5, in nitromethane, for 1 h).
Figure A.1.3 HPLC fraction #3 from the separation of P-3HT (polymerized with a monomer-to-oxidant ratio of 1:2.5, in nitromethane, for 1 h).

Figure A.1.4 HPLC fraction #4 from the separation of P-3HT (polymerized with a monomer-to-oxidant ratio of 1:2.5, in nitromethane, for 1 h).
Figure A.1.5 HPLC fraction #5 from the separation of P-3HT (polymerized with a monomer-to-oxidant ratio of 1:2.5, in nitromethane, for 1 h).

Figure A.1.6 HPLC fraction #6 from the separation of P-3HT (polymerized with a monomer-to-oxidant ratio of 1:2.5, in nitromethane, for 1 h).
Figure A.1.7 HPLC fraction #7 from the separation of P-3HT (polymerized with a monomer-to-oxidant ratio of 1:2.5, in nitromethane, for 1 h).

Figure A.1.8 HPLC fraction #8 from the separation of P-3HT (polymerized with a monomer-to-oxidant ratio of 1:2.5, in nitromethane, for 1 h).
Figure A.1.9 HPLC fraction #9 from the separation of P-3HT (polymerized with a monomer-to-oxidant ratio of 1:12, in nitromethane, for 1 h).

Figure A.1.10 HPLC fraction #10 from the separation of P-3HT (polymerized with a monomer-to-oxidant ratio of 1:12, in nitromethane, for 1 h).
**Figure A.1.11** HPLC fraction #11 from the separation of P-3HT (polymerized with a monomer-to-oxidant ratio of 1:2.5, in nitromethane, for 1 h).

**Figure A.1.12** HPLC fraction #12 from the separation of P-3HT (polymerized with a monomer-to-oxidant ratio of 1:2.5, in nitromethane, for 1 h).
Figure A.1.13 HPLC fraction #13 from the separation of P-3HT (polymerized with a monomer-to-oxidant ratio of 1:2.5, in nitromethane, for 1 h).
A.2 MALDI-TOF MS Data from HPLC Chromatograms from Separation of P-3HT (polymerized with a monomer-to-oxidant ratio of 1:12, in nitromethane, for 1 h)

![Figure A.2.1](image1)

**Figure A.2.1** HPLC fraction #1 from the separation of P-3HT (polymerized with a monomer-to-oxidant ratio of 1:12, in nitromethane, for 1 h).

![Figure A.2.2](image2)

**Figure A.2.2** HPLC fraction #2 from the separation of P-3HT (polymerized with a monomer-to-oxidant ratio of 1:12, in nitromethane, for 1 h).
Figure A.2.3 HPLC fraction #3 from the separation of P-3HT (polymerized with a monomer-to-oxidant ratio of 1:12, in nitromethane, for 1 h).

\[ n=4 \] (667.11)

Figure A.2.4 HPLC fraction #4 from the separation of P-3HT (polymerized with a monomer-to-oxidant ratio of 1:12, in nitromethane, for 1 h).

\[ n=4+\text{Cl} \] (701.22)
Figure A.2.5 HPLC fraction #5 from the separation of P-3HT (polymerized with a monomer-to-oxidant ratio of 1:12, in nitromethane, for 1 h).

Figure A.2.6 HPLC fraction #6 from the separation of P-3HT (polymerized with a monomer-to-oxidant ratio of 1:12, in nitromethane, for 1 h).
Figure A.2.7 HPLC fraction #7 from the separation of P-3HT (polymerized with a monomer-to-oxidant ratio of 1:12, in nitromethane, for 1 h).

Figure A.2.8 HPLC fraction #8 from the separation of P-3HT (polymerized with a monomer-to-oxidant ratio of 1:12, in nitromethane, for 1 h).
**Figure A.2.9** HPLC fraction #9 from the separation of P-3HT (polymerized with a monomer-to-oxidant ratio of 1:12, in nitromethane, for 1 h).

\[ n = 4 + 2\text{Cl} \]

\[ (734.03) \]

**Figure A.2.10** HPLC fraction #10 from the separation of P-3HT (polymerized with a monomer-to-oxidant ratio of 1:12, in nitromethane, for 1 h).

\[ n = 6 \]

\[ (998.49) \]

\[ n = 5 + 2\text{Cl} \]

\[ (900.28) \]
Figure A.2.11 HPLC fraction #11 from the separation of P-3HT (polymerized with a monomer-to-oxidant ratio of 1:12, in nitromethane, for 1 h).

$n=5+2\text{Cl}$  
$(900.44)$ 

$n=6$  
$(998.54)$

$? \quad (1112.30)$

Figure A.2.12 HPLC fraction #12 from the separation of P-3HT (polymerized with a monomer-to-oxidant ratio of 1:12, in nitromethane, for 1 h).

$n=6+\text{Cl}$  
$(1032.95)$

$n=6$  
$(999.02)$

$n=5+2\text{Cl}$  
$(900.81)$
Figure A.2.13 HPLC fraction #13 from the separation of P-3HT (polymerized with a monomer-to-oxidant ratio of 1:12, in nitromethane, for 1 h).

Figure A.2.14 HPLC fraction #14 from the separation of P-3HT (polymerized with a monomer-to-oxidant ratio of 1:12, in nitromethane, for 1 h).
Figure A.2.15 HPLC fraction #15 from the separation of P-3HT (polymerized with a monomer-to-oxidant ratio of 1:12, in nitromethane, for 1 h).

Figure A.2.16 HPLC fraction #16 from the separation of P-3HT (polymerized with a monomer-to-oxidant ratio of 1:12, in nitromethane, for 1 h).
Figure A.2.17 HPLC fraction #17 from the separation of P-3HT (polymerized with a monomer-to-oxidant ratio of 1:12, in nitromethane, for 1 h).

Figure A.2.18 HPLC fraction #18 from the separation of P-3HT (polymerized with a monomer-to-oxidant ratio of 1:12, in nitromethane, for 1 h).
Figure A.2.19 HPLC fraction #19 from the separation of P-3HT (polymerized with a monomer-to-oxidant ratio of 1:12, in nitromethane, for 1 h)

Figure A.2.20 HPLC fraction #20 from the separation of P-3HT (polymerized with a monomer-to-oxidant ratio of 1:12, in nitromethane, for 1 h)
Figure A.2.21 HPLC fraction #21 from the separation of P-3HT (polymerized with a monomer-to-oxidant ratio of 1:12, in nitromethane, for 1 h)

Figure A.2.22 HPLC fraction #22 from the separation of P-3HT (polymerized with a monomer-to-oxidant ratio of 1:12, in nitromethane, for 1 h)
Figure A.2.23 HPLC fraction #23 from the separation of P-3HT (polymerized with a monomer-to-oxidant ratio of 1:12, in nitromethane, for 1 h).
A.3 MALDI-TOF MS Data from GPC Fractions of the Acetone Extract of P-3HT

Figure A.3.1 MALDI-TOF mass spectrum of GPC fraction #1 from acetone extract of P-3HT.

Figure A.3.2 MALDI-TOF mass spectrum of GPC fraction #2 from acetone extract of P-3HT.
Figure A.3.3 MALDI-TOF mass spectrum of GPC fraction #3 from acetone extract of P-3HT.

Figure A.3.4 MALDI-TOF mass spectrum of GPC fraction #4 from acetone extract of P-3HT.
Figure A.3.5 MALDI-TOF mass spectrum of GPC fraction #5 from acetone extract of P-3HT.

Figure A.3.6 MALDI-TOF mass spectrum of GPC fraction #6 from acetone extract of P-3HT.
**Figure A.3.7** MALDI-TOF mass spectrum of GPC fraction #7 from acetone extract of P-3HT.
Appendix B: Supplemental $^1$H-NMR Data

Figure B.1 $^1$H-NMR of 8-mer of 3-hexylthiophene with H,H end groups (Fraction 7 from the RP-HPLC separation of P-3HT, monomer-to-oxidant ratio 1:2.5).

Figure B.2 $^1$H-NMR of 8-mer of 3-hexylthiophene with Cl,Cl end groups (Fraction 17 from the RP-HPLC separation of P-3HT, monomer-to-oxidant ratio 1:12).
Figure B.3 $^1$H-NMR of 4-mer of 3-hexylthiophene with H,H end groups (Fraction 3 from the RP-HPLC separation of P-3HT, monomer-to-oxidant ratio 1:12).

Figure B.4 $^1$H-NMR of 4-mer of 3-hexylthiophene with Cl,Cl end groups (Fraction 6 from the RP-HPLC separation of P-3HT, monomer-to-oxidant ratio 1:12).
Vita

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