Solvato-Controlled Doping of Poly(3-alkylthiophene)s and Other Conjugated Polymers Using Silver (I) Triflate

by

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B.Sc. Simon Fraser University, 1995

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Simon Fraser University

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ABSTRACT

This work is focused on the development of a new oxidation technique, solvato-controlled doping, which provides electrically conductive films from a single solution by simultaneously removing the solvent and stabilizing agent.

The reduction potential for silver(I) was found to shift to less positive values upon complexation with pyridine. This shift was sufficient to prevent silver(I)-induced oxidation of poly(3-hexylthiophene) (P3HT). Thus, the oxidant (silver triflate) and the polymer could be mixed in solution, and no chemical reaction was observed. The pyridine was later readily removed by evaporation. The resulting P3HT films had initial electrical conductivities of 2 S/cm and exhibited half-lifetimes that were 17 times greater than P3HT films oxidized by ferric chloride. Thick electrically conductive polymer films were readily produced, and they showed no sign of the cracking and peeling normally evident when similar films were oxidized by immersion into an oxidizing solution.

P3HT films were oxidized by silver triflate and ferric chloride. The silver-doped films exhibited open-circuit potentials that were lower than those of the ferric chloride doped films. The effect of the open-circuit potential on stability was investigated by electrochemically oxidizing polymer films (in the presence of the triflate anion) to a range of potentials and observing their resultant stability. Only a small dependence was observed. Other P3HT films were doped chemically and electrochemically with the triflate anion. Both techniques resulted in conductive films that were much less stable than the silver triflate doped films.
Transmission electron microscopy indicated the presence of 100 nm silver particles in the latter films. These particles are proposed as the source of the enhanced stability found in these conductive films.
DEDICATION

For my parents and family for all of their support and encouragement.

To Carmen.
ACKNOWLEDGMENTS

I would like to thank my senior supervisor, Dr. Steven Holdcroft, for the privilege and opportunity of studying under him, and for his guidance and patience throughout my studies.

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I am also grateful to Dr. Steven Holdcroft and to Simon Fraser University for the financial support and the abundance of analytical equipment available throughout this research project.
# TABLE OF CONTENTS

<table>
<thead>
<tr>
<th>Section</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>APPROVAL</td>
<td>ii</td>
</tr>
<tr>
<td>ABSTRACT</td>
<td>iii</td>
</tr>
<tr>
<td>DEDICATION</td>
<td>v</td>
</tr>
<tr>
<td>ACKNOWLEDGMENTS</td>
<td>vi</td>
</tr>
<tr>
<td>TABLE OF CONTENTS</td>
<td>vii</td>
</tr>
<tr>
<td>LIST OF ABBREVIATIONS AND SYMBOLS</td>
<td>x</td>
</tr>
<tr>
<td>LIST OF SCHEMES</td>
<td>xiii</td>
</tr>
<tr>
<td>LIST OF TABLES</td>
<td>xiii</td>
</tr>
<tr>
<td>LIST OF FIGURES</td>
<td>xiv</td>
</tr>
<tr>
<td>1. Introduction</td>
<td>1</td>
</tr>
<tr>
<td>1.1 Chemical Structure of Poly(3-alkylthiophene)s</td>
<td>4</td>
</tr>
<tr>
<td>1.2 Electrical Conductivity in Conjugated Polymers</td>
<td>9</td>
</tr>
<tr>
<td>1.3 Charge Carriers in Conducting Polymers</td>
<td>14</td>
</tr>
<tr>
<td>1.4 Electronic Structure of Polythiophene</td>
<td>17</td>
</tr>
<tr>
<td>1.5 Environmental Stability of Conducting Polymers</td>
<td>18</td>
</tr>
<tr>
<td>1.5.1 Factors Affecting Stability of the Doped State</td>
<td>19</td>
</tr>
<tr>
<td>1.6 Goals</td>
<td>23</td>
</tr>
<tr>
<td>2. Experimental</td>
<td>25</td>
</tr>
<tr>
<td>2.1 Chemicals</td>
<td>25</td>
</tr>
<tr>
<td>2.2 Synthesis</td>
<td>25</td>
</tr>
</tbody>
</table>
3. Results and Discussion .................................................................47
  3.1 Doping of P3HT by Silver Triflate ..................................................47
  3.2 Characterization of Doped P3HT Films .............................................50
    3.2.1 Transmission Electron Microscopy ..........................................50
  3.3 Solvato-Controlled Doping ..........................................................54
    3.3.1 The Physical Basis of Solvato-Controlled Doping .........................56
    3.3.2 Electrochemistry of Polymer Films ..........................................58
    3.3.3.1 Solvation of Polymer Films for Charge Injection .......................59
    3.3.3.2 Electrochemistry of P3HT Films and Silver(I) Species ..................61
  3.3.4 Dependence of Film Conductivity on Silver(I) Content .....................64
  3.3.5 Effect of Regioregularity on Solvato-Controlled Doping ...................65
  3.3.6 Solvato-Controlled Doping of Other Conjugated Polymers ................67
  3.4 Lifetime of Doped Films ..........................................................70
    3.4.1 In-situ Conductivity of P3HT ................................................73
    3.4.2 Doping Level at Various Applied Potentials ................................75
    3.4.3 Lifetimes of Electrochemically Doped P3HT Films .........................77
  4. Conclusions ...........................................................................81

References ................................................................................83
LIST OF ABBREVIATIONS AND SYMBOLS

HH  Head-to-head dyad configuration
HT  Head-to-tail dyad configuration
P3HT Poly(3-hexylthiophene)
P3DDT Poly(3-dodecylthiophene)
P3BuOT Poly(3-butoxythiophene)
P3MeOT Poly(3-methoxythiophene)
PANI Polyaniline
TT  Tail-to-tail dyad configuration
NMR Nuclear magnetic resonance
P3ATs Poly(3-alkylthiophene)s
CV  Cyclic voltammogram
ITO Tin-doped indium oxide
UV-vis Ultra-violet / visible absorption spectroscopy
TEM Transmission electron micrograph
TPA Trans-polyacetylene
α  Alpha position of the thiophene ring
β  Beta position of the thiophene ring
IR  Infra-red spectroscopy
3AT  3-alkylthiophene
SCE Saturated calomel electrode

x
<table>
<thead>
<tr>
<th>Symbol</th>
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</tr>
</thead>
<tbody>
<tr>
<td>PCrTh</td>
<td>Polythiophene with a crown ether subunit</td>
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<tr>
<td>$\sigma$</td>
<td>Conductivity (S/cm)</td>
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<tr>
<td>$n_i$</td>
<td>Number of free charge carriers per unit volume (cm$^3$)</td>
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<td>$\mu_i$</td>
<td>Charge carrier mobility (cm$^2$/V·s$^{-1}$)</td>
</tr>
<tr>
<td>$\varepsilon$</td>
<td>Electronic charge on each carrier</td>
</tr>
<tr>
<td>PT</td>
<td>Polythiophene</td>
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<tr>
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<td>Band gap energy (eV)</td>
</tr>
<tr>
<td>$t_{1/10}$</td>
<td>Time for conductivity to decrease by a factor of 10</td>
</tr>
<tr>
<td>$t_{1/2}$</td>
<td>Time for conductivity to decrease by a factor of 2</td>
</tr>
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<td>GPC</td>
<td>Gel permeation chromatography</td>
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<td>sym.</td>
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<td>asym.</td>
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<tr>
<td>$d$</td>
<td>Film thickness (cm)</td>
</tr>
<tr>
<td>$i$</td>
<td>Electric current (A)</td>
</tr>
<tr>
<td>$V$</td>
<td>Voltage (V)</td>
</tr>
<tr>
<td>$\rho$</td>
<td>Resistivity ($\Omega$·cm)</td>
</tr>
<tr>
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<td>Resistance ($\Omega$)</td>
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<tr>
<td>$\lambda_{max}$</td>
<td>Wavelength of maximum absorption (nm)</td>
</tr>
<tr>
<td>$K_f$</td>
<td>Complex formation constant (mol$^2$·L$^{-2}$)</td>
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</tr>
</tbody>
</table>

$\text{xi}$
<table>
<thead>
<tr>
<th>Symbol</th>
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</tr>
</thead>
<tbody>
<tr>
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<td>Transition metal cation</td>
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<td>$E_{\text{red}}$</td>
<td>Reduction potential (V)</td>
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<td>$L$</td>
<td>Coordination ligand</td>
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<td>$\Delta H_M$</td>
<td>Enthalpy of mixing</td>
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<td>$\Delta E$</td>
<td>Molar energy of vaporization</td>
</tr>
<tr>
<td>$\delta$</td>
<td>Solubility parameter (cal/cm$^3$)$^{1/2}$</td>
</tr>
<tr>
<td>$\text{vol.}$</td>
<td>Volume</td>
</tr>
</tbody>
</table>
LIST OF SCHEMES

Scheme 2.1: Preparation of ITO-coated glass slides for electrochemical doping of conjugated polymer films. ................................................................. 42

Scheme 3.1: The solvato-controlled doping process. ............................................. 58

LIST OF TABLES

Table 1.1: Charge carriers found in neutral and oxidatively doped TPA and PT. 16

Table 3.1: Selected ligands and their associated formation constants for complexation with silver(I). ................................................................. 47

Table 3.2: Solubility parameters for P3HT and some common solvents............. 60
LIST OF FIGURES

Figure 1.1: Chemical structures of common conjugated polymers. .........................2

Figure 1.2: Desirable ($\alpha-\alpha'$) and undesirable ($\alpha-\beta'$) monomer linkages resulting
from electrochemical oxidative polymerization of 3-alkylthiophenes. ......5

Figure 1.3: Possible coupling reactions in the oxidative polymerization of 3-
alkylthiophenes. .................................................................7

Figure 1.4: Configurational triads found in irregular P3ATs, and labeled as: Tail-
to-Tail, Head-to-Tail (TT-HT); Head-to-Tail, Head-to-Head (HT-HH);
Head-to-Head, Tail-to-Tail (HH-TT) and Head-to-Tail, Head-to-Tail (HT-
HT). $^1$H-NMR Chemical shifts ($\delta$, ppm) are reported for the aromatic
proton on the central ring. ............................................................8

Figure 1.5: Protonic doping of P3ATs where $X^-$ is an anion such as $SO_4^-$ or
$R-SO_3^-$. .................................................................................10

Figure 1.6: Reductive doping of polythiophene with a crown-ether sub-unit. ......11

Figure 1.7: Doping reaction between poly(3-alkylthiophene) and ferric chloride
leading to a bipolaron charge carrier..............................................14

Figure 1.8: a) Degenerate ground states of TPA, and b) Non-degenerate ground
states of polythiophene...............................................................15

Figure 1.9: Energy level description of conjugated polymers............................18

Figure 1.10: Alkyl substituted poly(ethylene dioxy thiophene). .........................21

Figure 2.1: $^1$H NMR spectrum of regioregular P3HT in CDCl$_3$. ......................32
Figure 2.2: Linear-sweep cyclic voltammograms (CV) of a P3HT film deposited on a dual-band platinum electrode with (K1) the first platinum electrode connected, (K2) the second electrode connected, and (K1+K2) with both electrodes connected. 38

Figure 2.3: Schematic of the experimental setup used to determine the in-situ conductivity of P3HT films on a platinum dual-band electrode. 39

Figure 2.4: Co-linear four-point probe used in conductivity measurements. 43

Figure 2.5: Parameters for resistance measurements in electrochemically doped P3AT films on an acid-etched ITO-coated glass slide. 44

Figure 3.1: Evolution of the UV-vis spectra for poly(3-dodecylthiophene) (98% HT) (1 mg/mL) in the presence of silver triflate (3.5 mM) over a period of 6 h. The solvent was toluene/heptane (volume ratio 1:1), and spectra were recorded 20 min apart. 48

Figure 3.2: Possible doping reactions between silver(I) and poly(3-hexylthiophene): (i) single electron transfer, and (ii) charge transfer complex formation. 50

Figure 3.3: TEM micrograph of 100 nm silver particle clusters in a thin P3HT film after doping by immersion in AgOTf. 51

Figure 3.4: Schematic of a P3HT film on glass covered by evaporated layers of NaCl and carbon. 53

Figure 3.5: TEM of a silver particle in a carbon film extracted from the surface of a silver triflate doped P3HT film. 53
Figure 3.6: Cyclic voltammograms of a) poly(3-hexylthiophene), b) 1 mM AgOTf in nitromethane, and c) 1mM AgOTf in nitromethane with 5 % (vol.) pyridine.

Figure 3.7: UV-vis spectra of a 1 mg/mL solution of P3DDT in a mixture of toluene/heptane/pyridine. a) pristine solution, and b) 6 hours after the addition of 3.5 mM AgOTf.Inset: UV-vis of a polymer film cast from this solution.

Figure 3.8: Plot of the conductivity of 98% HT P3DDT films vs. molar ratio of AgOTf:thienyl groups present in the films.

Figure 3.9: UV-vis spectra of (a) a neutral 80% HT P3HT film, (b) a 80% HT P3HT film treated with AgOTf, (c) a neutral 0% HT P3HT film, and (d) a 0% HT P3HT film treated with AgOTf.

Figure 3.10: Schematic representation of the standard reduction potential for Ag\(^+\) and oxidized P3HT with varying dyad content (100%HT, 80%HT, and 0%HT).

Figure 3.11: UV-vis absorption spectra showing the stabilizing effect of the addition of pyridine added to a n-methyl pyrrolidinone (NMP) solution of PANI and AgOTf. a) a pristine PANI solution, b) PANI solution containing 10 %(vol.) pyridine and 0.5 equivalents AgOTf, and c) PANI solution with 0.5 equivalents of AgOTf.

Figure 3.12: Radical cations in PANI responsible for the electronic absorptions at a) 430 and b) >800 nm.
Figure 3.13: UV-vis absorption spectra for (a) a CHCl₃ solution of P3BuOT with 25 mol% AgOTf and 10 vol% pyridine, and (b) a conductive film cast from this solution ................................................................. 70

Figure 3.14: Lifetime plots for 100 nm P3DDT films doped by a) AgOTf, b) FeCl₃ and c) ONOTf. ........................................................................................................ 72

Figure 3.15: The normalized drain current (representing in-situ conductivity) between two 80 μm thick, P3HT coated, platinum band electrodes separated by a 100 μm Mylar film, as a function of the applied potential in an acetonitrile solution containing 0.1 M lithium triflate. ................. 74

Figure 3.16: Evolution of UV-vis absorption spectrum of a 95% HT P3HT film doped at various potentials (vs. Ag/AgCl) in a 0.1 M LiOTf /CH₃CN solution. ........................................................................................................ 75

Figure 3.17: Absorbance due to the a) π→π* (556 nm), and b) bipolaron (840 nm) species in a regioregular P3HT film doped in 0.1 M LiOTf/CH₃CN at applied potentials ranging from 0.0 to +1.0 V (Ag/AgCl). ............... 76

Figure 3.18: Decay of the normalized conductivity in regioregular P3HT doped at +0.75 V (Ag/AgCl) with the triflate anion. ......................................................... 77

Figure 3.19: Half-lifetimes (of conductivity) for thick P3HT films electrochemically doped with LiOTf in acetonitrile to various applied potentials for a) short-term stability and b) long-term stability. ........................................ 79

xvii
1. **Introduction**

Conjugated polymers, such as polythiophene, polyaniline, and polypyrrole, (Figure 1.1) have been the focus of intense research for more than twenty years. Potential applications for conjugated polymers are widely varied and include electrochromic or smart windows, anti-static coatings, chemical sensors, batteries, electromagnetic shielding materials, artificial noses, polymer modified electrodes, electronic interconnects, and polymer based transistors.\(^1^2\) The potential of super-conductivity in these "ultimate poly(ene)s", and their optical properties, were some of the driving forces behind early investigations into the properties of these molecules.

Samples of pristine conjugated polymers, however, exhibited electrical conductivities of similar magnitude as the more conventional electrically insulating polymers like polyethylene, nylon, and poly(vinylchloride). In 1977, a shift in focus occurred when Chiang and co-workers discovered that oxidation of polynacetylene with Lewis acids, such as Br\(_2\), I\(_2\), or AsF\(_5\), resulted in an increase in electrical conductivity by twelve orders of magnitude.\(^3\) This discovery led to a renewed effort in the synthesis and characterization of many more conjugated polymers possessing both aromatic and heteroaromatic repeat units.\(^4^5\) Some of the more well-known conjugated polymers which have been rendered electrically conductive by oxidation techniques include trans-polyacetylene (TPA), polythiophene, poly(paraphenylene), poly(phenylenevinylene), polypyrrole and polyaniline. These chemical structures are shown in Figure 1.1.
The rigid planar backbones and strong interchain interactions in these well-known polymer systems allow close packing of the polymer chains; thus, the bulk polymers are rendered intractable, infusible, and in general non-processable. A lack of processability imparts severe limitations on the methods available for synthesis and characterization of high molecular weight conjugated polymers. Poor solubility, for example, renders many procedures such as NMR spectroscopy, film casting, and purification, much more difficult. The applications available to a conjugated polymer are therefore highly dependent on its degree of processability.

Several techniques have been developed which introduce processability into the neutral or insulating forms of conjugated polymers. The most common of
these is derivatization of the conjugated backbone with alkyl or ionic moieties. The source of enhanced processability in such polymers is the result of strong interactions between the pendant groups and solvent molecules. If the substituent groups are long enough, or interact strongly enough with the solvent, their displacement can result in a twisting of the conjugated backbone and a subsequent decrease in the attractive interchain forces.\(^6\)

Thiophene is a molecule with well-developed chemistry for introducing functional groups at specific locations. These molecules can often be polymerized to produce poly(thiophene)s derivatized with a variety of functional groups including aromatic, ionic, and alkyl substituents. This diversity allows poly(thiophene)s to be solubilized in numerous solvents ranging from chloroform to water. Alkyl-substituted poly(thiophene)s exhibit optical and electrical properties similar to those of the parent polymer,\(^7\) polythiophene, and are classified as poly(3-alkylthiophene)s (P3ATs). Synthesis of alkyl-derivatized polythiophene was first demonstrated by Elsenbaumer and co-workers in 1985. Solubility was introduced by derivatization of the 3 position of the thiophene monomer with alkyl chains of butyl and greater length.\(^7\)\(^-\)\(^9\) Functionalization by this single class of molecules (i.e. \(-\text{C}_n\text{H}_{2n+1}\)) results in polymers that are soluble in common organic solvents including chloroform, THF, xylene, toluene, methylene chloride, anisole, nitrobenzene, benzonitrile, and nitropropane.

These highly processable polymers are readily cast from solution or extruded from melts into films of controllable and reproducible thickness. Additionally, their high processability and solubility facilitates extensive
characterization of the chemical structure, optical, non-linear optical, and electrical properties of the neutral polymers.\textsuperscript{10,11} When the polythiophene backbone is functionalized by long alkyl chains (hexyl and greater), a regioregular substitution pattern results in polymers with high electrical conductivities which are comparable to those found in pristine polythiophene, although this is not always the case for irregularly functionalized polythiophene.

1.1 Chemical Structure of Poly(3-alkylthiophene)s

The chemical structure of P3ATs is of substantial interest since the conductive (or doped) state of this polymer, when exposed to the ambient atmosphere, can be made more stable than many other conducting polymers provided a suitable oxidant is chosen.\textsuperscript{7,12-15} High processability has facilitated characterization of P3ATs by UV-vis, IR, near-IR, ESR, and NMR techniques; thus allowing excellent characterization of the products from various polymerization reactions. Until recently, poly(thiophene)s were generally synthesized with either oxidative or nickel-catalyzed coupling techniques; however, loose control of the alkyl substitution pattern in the polymers is usually the result. One of the oxidative coupling techniques which has been used is direct electrochemical polymerization of the 3-alkylthiophene (3AT) monomer.\textsuperscript{16} Oxidation of these monomers at a platinum electrode, in the presence of a supporting electrolyte, results in durable films that adhere well to the electrode surface. The thickness of these films is easily controlled, and they are readily
switched between their conducting (doped) or insulating states by the application of an appropriate potential difference. Unfortunately, electrochemical preparation of P3AT is not practical for large-scale synthesis of the polymer. Additionally, it results in a significant number of $\alpha$-$\beta'$ linkages rather than the desired $\alpha$-$\alpha'$ type (Figure 1.2), and so the effective conjugation length is reduced.\textsuperscript{17}

\begin{figure}[h]
\centering
\includegraphics[width=0.8\textwidth]{figure1.2.png}
\caption{Desirable ($\alpha$-$\alpha'$) and undesirable ($\alpha$-$\beta'$) monomer linkages resulting from electrochemical oxidative polymerization of 3-alkylthiophenes.}
\end{figure}

Alternatively, the 3AT monomer may be oxidatively coupled in solution with a strong Lewis acid such as FeCl$_3$.\textsuperscript{18} The resulting polymer has a lower oxidation potential than the monomer, thus it is formed in the oxidized (insoluble) state, and contains charge-balancing FeCl$_4^-$ anions. The neutral and processable form of the polymer is obtained by washing with aqueous ammonia. After purification, characterization by NMR and IR spectroscopy shows that the number of $\alpha$-$\beta'$ linkages in the resulting polymer is insignificant.\textsuperscript{17} Grignard type cross-coupling polymerizations have also been demonstrated to be effective methods which introduce, almost exclusively, $\alpha$-$\alpha'$ linkages in P3ATs.\textsuperscript{7-9} In this
respect, nickel-catalyzed condensation polymerizations of 3-alkyl-2,5-diiodothiophene reagents have been reported by several authors.\textsuperscript{7,19} The products of these polymerization methods are known as regioirregular polymers since the alkyl substitution may be either at the 3- or 4-position on the thiophene ring. The lack of a strong directing force in the polymerization, and of symmetry in the 3-alkylthiophene monomers, are the accepted sources of the irregular substitution pattern.

When the unsymmetrical 3AT monomer undergoes polymerization using a strong Lewis acid, or the previous Grignard procedure, coupling most often occurs between the 2 and 5 positions on the aromatic rings (\(\alpha-\alpha'\)) and may proceed in a head-to-tail (HT), head-to-head (HH), or tail-to-tail (TT) manner as shown in Figure 1.3.\textsuperscript{20} The relative abundance of these dyads (or 'bithiophene' species) describes the regiochemistry of P3ATs, and it can be quantified via \(^1\text{H}\)-NMR spectroscopy by integration of the peaks corresponding to the methylene group \(\alpha\) to the thiophene ring (\(\delta = 2.56-2.79\) ppm, TMS). These coupling reactions are named for the orientation of the alkyl groups on adjacent thiophene rings; where 'head' denotes the aromatic carbon to which the alkyl chain is closest, and tail represents the carbon center furthest removed from the alkyl substituent.
Figure 1.3: Possible coupling reactions in the oxidative polymerization of 3-alkylthiophenes.

These coupling reactions result in the formation of four distinct triads ('terthiophene' repeat units) in the polymer chain (Figure 1.4) which can also be identified and quantified through integration of $^1$H signals in the aromatic region of the NMR spectrum ($\delta = 6.98-7.05$, relative to tetramethylsilane).\textsuperscript{21,22} Henceforth, a regioregular polymer will denote one consisting of purely HT-HT couplings (or HT dyads) although other definitions of a regioregular polymer are clearly possible (such one consisting of purely HH-TT couplings).
Figure 1.4: Configurational triads found in irregular P3ATs, and labeled as: Tail-to-Tail, Head-to-Tail (TT-HT); Head-to-Tail, Head-to-Head (HT-HH); Head-to-Head, Tail-to-Tail (HH-TT) and Head-to-Tail, Head-to-Tail (HT-HT). $^1$H-NMR Chemical shifts (δ, ppm) are reported for the aromatic proton on the central ring.

The degree of regioregularity was expected to have a large effect on the electrical and optical properties of films cast from solution, thus McCullough and co-workers developed a ‘one-pot’ reaction to synthesize poly(3-hexylthiophene) (P3HT), among other derivatized P3ATs, containing >98% HT dyads. It was found that increasing the content of HH and TT dyads resulted in increased steric repulsion which forced the aromatic rings into a more twisted conformation and reduced the inter-annular pi-orbital overlap (the effective conjugation length). This effect is evident in poly(3-octylthiophene) in which the absorption maximum in chloroform solution decreases from 460 to 426 nm, while in the solid state, an even larger decrease results (from 525 to 480 nm), when the head-to-tail content is reduced from 100% to 70%. Mao, Xu, and Holdcroft have shown similar trends in the UV-vis spectra for chloroform solutions and films of P3HT with the
HT dyad content ranging from 52% to 80%.\textsuperscript{25} When oxidized by nitrosonium tetrafluoroborate, the electrical conductivities of the P3HT films were found to increase from 0.0089 to 6.0 S/cm with increasing head-to-tail content. With the maximum head-to-tail content of ca. 98%, electrical conductivities of regioregular P3HT films have been reported to be as high as 150 S/cm.\textsuperscript{26} As a corollary to this effect, cyclic voltammetry on thin films of regioregular poly(3-dodecylthiophene) (P3DDT) shows two reversible peak oxidation potentials at $E_{pa} (1) = 0.8$ V and $E_{pa} (2) = 0.99$ V (vs. SCE). Polymer films of only 80% HT content showed only a small peak at $E_{pa} (1) = 0.8$ V with the most electrochemical activity at $E_{pa} (2) = 1.1$ V.\textsuperscript{26} It has been proposed that lower oxidation potentials in polymers, such as found in regioregular P3HT, enhances the environmental stability by decreasing the reactivity of the doped polymer relative to moisture and other nucleophiles.\textsuperscript{27-29}

From these studies, it is clear that the absence of undesirable couplings in regioregular P3ATs has enhanced their electrical conductivity and environmental stability. These are properties desirable for their use in technological applications requiring the conductive form of conjugated polymers.

1.2 Electrical Conductivity in Conjugated Polymers

Conjugated polymers may be rendered conductive (doped) in a variety of ways, some of which are specific to certain polymers. Since conjugated polymers are inherently insulators or, at best, weak semiconductors, most require a
second, separate doping step after the sample preparation (i.e. film casting, pellet pressing, etc.) to render the sample electrically conductive. This step generally consists of exposing the polymer sample to either a solution or vapor of the doping agent (such as FeCl₃ or I₂).³⁰ During this doping reaction, the polymer chains are rearranged to allow a more planar conformation between adjacent monomer units. Polyaniline is a special case since it can be both doped and rendered soluble in many solvents by the addition of a bulky strong acid such as camphor sulfonic acid.³¹,³² Other polymers, such as P3ATs, can be doped by strong acids, but this generally results in loss of solubility and processability. Additionally, acid doping of poly(thiophene)s results in protonation of aromatic carbon centers during which sp² carbon atoms are re-hybridized to sp³ centers (Figure 1.5). This decreases the effective conjugation length in the doped polymer, which in turn decreases the conductivity and affects the optical properties of the conducting film.³³,³⁴ This effect can be avoided by using other techniques (such as oxidation or reduction reactions) to dope the conjugated polymer films.

Figure 1.5: Protonic doping of P3ATs where X⁻ is an anion such as SO₄⁻ or R-SO₃⁻.
Conjugated polymers such as polythiophene may be rendered conductive by reduction with chemical reagents like sodium metal or by electrochemical techniques. The success of this approach is strongly affected by the nature of the charge-balancing cation and its effective solvated size. Poly(thiophene)s bearing a crown-ether sub-unit (PCrTh) have only recently been reductively doped and stabilized under dry-air conditions (though their stability under humid conditions is still lacking). This polymer and its accompanying reduction reaction are shown in Figure 1.6.

![Figure 1.6: Reductive doping of polythiophene with a crown-ether sub-unit.](image)

Unlike protonic or reductive doping, oxidative doping of conjugated polymers can be achieved between a variety of polymer structures and oxidizing agents. A small number of these possibilities includes those polymers previously shown in Figure 1.1. Hereafter, due to the prevalence of the technique, doping will generally refer to oxidization of the polymer backbone with coincident injection of charge-balancing anions.
Successful doping by a chemical agent requires the reduction potential of the oxidant to be more positive than the oxidation potential of the polymer. For poly(3-alkylthiophene)s these species include iodine, ferric chloride, gold chloride, and nitrosonium salts such as nitrosonium tosylate. The difference between the reduction and oxidation potentials of these chemicals dictates whether a reversible charge-transfer complex forms, as in the case of oxygen doping of poly(thiophene)s,\textsuperscript{37,38} or whether complete electron transfer occurs between the polymer and oxidant. This last case is by far the most common as, for example, found in ferric chloride doped P3HT where the dopant is reduced according to equation 1:

\[
2 \text{ e}^- + 2 \text{FeCl}_3 \rightarrow \text{FeCl}_4^- + 2 \text{FeCl}_2
\]  

(1)

In doping of P3HT with FeCl\textsubscript{3}, both the counter-ion (FeCl\textsubscript{4}\textsuperscript{-}) and the reaction by-products (FeCl\textsubscript{2}) remain in and may affect the chemistry of the doped polymer. This has been evidenced in the poor environmental stability of P3HT films doped by FeCl\textsubscript{3} in which the photolysis and photoreduction of the counter-ion FeCl\textsubscript{4}\textsuperscript{-} is followed by electron transfer to the charge carriers in the conducting polymer.\textsuperscript{37} This has the effect of decreasing the concentration of charge carriers in the doped film, and so the conductivity is reduced over time. Clearly, the stability of conducting polymer films may be affected by the chemistry of any products from the doping reaction.

Full electron-transfer reactions can be used to minimize the presence of reaction by-products by implementing reagents that form volatile reaction products. For example, nitrosonium triflate (ONOTf) can be used to dope P3HT
via a reaction where the nitrosonium cation (NO$^+$) is reduced according to equation 2:

$$e^- + \text{ONOTf} \rightarrow \text{NO}_2 + \text{OTf}^-$$

(2)

For the oxidation of P3HT with ONOTf, elemental analyses of doped films indicates the absence of nitrogen, and the lack of C-N stretches in the IR suggests there is negligible nitration of the polymer backbone. The nitrosonium cation is most likely ejected from the film as nitrous oxide. These salts, therefore, represent a class of dopant able to deliver anions to doped polymer films while lending careful control over the species present in the final product.

Electrochemical doping is another method capable of oxidizing polymer films and delivering anions, without the formation of ancillary reaction products. This is achieved by simply immersing the polymer film (on an appropriate substrate) into an electrolyte solution and applying a potential difference sufficient to oxidize the polymer film. This method allows analytical control over the potential applied to the film, whereas in the case of chemical agents, a continuum of potentials is not available. Also, the degree of oxidation can be quantitatively evaluated and controlled since the total charge passed is directly related to the number of anions injected into the polymer film.

In the field of conducting polymers, the terms 'doping' and, consequently, 'dopant' have significantly different meaning than traditionally recognized by solid-state physicists. Inorganic semiconductors possess rigid, covalently bound structures and charge carriers often exhibit high mobilities. High conductivities can therefore be attained in these materials at low dopant concentrations.
(0.1 ppb to 100 ppm). Dopants for this class of materials consist of electron deficient (or rich) species. Conversely, conjugated polymers such as poly(3-alkylthiophenes) (P3ATs) require doping levels on the order of 25 mole percent. Additionally, the dopant is not simply incorporated into the polymer structure; rather, it undergoes an oxidation-reduction (redox) reaction with the conducting polymer as charge carriers are generated in the conjugated polymer chain. A schematic of the doping reaction between P3AT and ferric chloride is shown in

\[
\text{RR}R + 4 \text{FeCl}_3 \rightarrow 2 \text{FeCl}_4^- + 2 \text{FeCl}_2
\]

**Figure 1.7.**

**Figure 1.7:** Doping reaction between poly(3-alkylthiophene) and ferric chloride leading to a bipolaron charge carrier.

### 1.3 Charge Carriers in Conducting Polymers

The direct result of removal of electrons from the \( \pi \)-cloud of a conjugated polymer is an increase in the number of charge carriers present in the polymer chain. The conductivity of a material, \( \sigma \) (S/cm), often follows the relationship:

\[
\sigma = \sum n_i \mu_i \varepsilon
\]  \hspace{1cm} (3)
where \( n \) is the number of charge carriers of type \( i \), \( \mu \) is the carrier mobility, and \( \varepsilon \) is the electronic charge. The type of carriers present in a conjugated polymer is dependent on the degeneracy of the ground state, and so conjugated polymers may be placed into two subclasses, i.e. those having, and those lacking degenerate ground states.

Trans-polyacetylene (TPA) is an example of a polymer having a degenerate ground state; that is, a rearrangement of chemical bonds results in a chemical structure which is indistinguishable in energy from its ancestor (Figure 1.8a). This characteristic of TPA allows for the existence of a soliton (Table 1.1) since the required rearrangement of chemical bonds results in polymer chains of equal energy on each side of the soliton.

\[
\begin{align*}
\text{a} & \quad \begin{array}{c}
\text{(a)} \\
\text{(b)}
\end{array}
\end{align*}
\]

\text{Figure 1.8: a) Degenerate ground states of TPA, and b) Non-degenerate ground states of polythiophene.}

Conversely, the rearranged form of polythiophene exhibits the quinonoid structure (Figure 1.8b) and is at higher energy than the aromatic form due to the increased inter-annular double bond character. As a result, polarons and bipolarons (and not solitons) are believed to be the only charge carriers permitted
in poly(thiophene)s. Furthermore, the separation between the charge and radical in a polaron (and the two charges in a bipolaron) is limited. This occurs since increasing the separation between these two species increases the quinonoid character of the polymer, and therefore, the energy stored in the polymer. Thus, the force of coulombic repulsion (between the charges in a bipolaron) is balanced by the increase in stored energy. A variety of charge carriers is possible in conjugated polymers: among the possibilities for neutral and oxidatively doped polymers are spin-containing, spinless, charged, and neutral species which are shown in Table 1.1.

Table 1.1: Charge carriers found in neutral and oxidatively doped TPA and PT.

<table>
<thead>
<tr>
<th>Species</th>
<th>trans-Polyacetylene</th>
<th>Polythiophene</th>
</tr>
</thead>
<tbody>
<tr>
<td>soliton</td>
<td><img src="image1" alt="Soliton" /></td>
<td>N/A</td>
</tr>
<tr>
<td>polaron</td>
<td><img src="image2" alt="Polaron" /></td>
<td><img src="image3" alt="Polaron" /></td>
</tr>
<tr>
<td>bipolaron</td>
<td><img src="image4" alt="Bipolaron" /></td>
<td><img src="image5" alt="Bipolaron" /></td>
</tr>
</tbody>
</table>

Electronic conduction in conjugated polymers is believed to result from migration of these charge carriers along the polymer chain, under an applied electrical field, by an electron hopping mechanism. An interchain transfer of
charge must also occur if the bulk polymer is to exhibit electrical conductivity. It is probably this factor which limits the electrical conductivity of regioregular P3ATs.\textsuperscript{37}

1.4 Electronic Structure of Polythiophene

The electronic structure of P3AT is altered by the presence of charge carriers and may be described in the following manner. In a conjugated carbon chain consisting of alternating single and double bonds (as found in TPA and P3AT), three of the four outer-shell electrons from each carbon atom occupy sp\textsubscript{3} hybridized orbitals. These three electrons are used to form sigma-type bonds within the main polymer chain and from the chain to the ancillary substituents. The remaining electron singly occupies a p\textsubscript{z} orbital which overlaps with adjacent p\textsubscript{z} orbitals to form the valence (\(\pi\)) and conduction (\(\pi^*\)) bands which are separated by an energy gap (E\textsubscript{g}). In a pristine sample of P3HT100, this energy gap may be estimated from the low-energy edge of the \(\pi\rightarrow\pi^*\) absorption in UV-vis spectra of solid films, and corresponds to ca. 675 nm or 1.8 eV.\textsuperscript{23} Upon single-electron oxidation of a polymer chain, a single polaron is formed, and the energy level description changes to include two more electronic states located between the valence and conduction bands (Figure 1.9). Further oxidation leads to the formation of more such states, and since theoretical calculations predict that adjacent polarons are unstable, they apparently coalesce into spinless dications (bipolarons) which are likely the dominant charge storage species in P3ATs with
hexyl or longer alkyl chains.$^{39-42}$ A high concentration of bipolarons leads to overlap of their energy levels and the formation of bipolaron bands. The presence of these doping-induced bands is evident from the new peaks generated in both the UV-vis (850 nm, 1.5 eV) and in the near infra-red spectra (1800-1900 nm, 0.65 - 0.7 eV). The energy gap of the polymer and energy of the bipolaronic species, among other factors, are characteristics of conjugated polymers thought to impact the stability of the conductive form.

![Energy level description of conjugated polymers](image)

**Figure 1.9:** Energy level description of conjugated polymers.

### 1.5 Environmental Stability of Conducting Polymers

Many of the potential applications of conjugated polymers will take advantage of the electrical conductivity of the doped state. Although doped poly(thiophene)s demonstrate better-than-average environmental stability, they have yet to reach levels suitable for large scale or widespread commercialization.
Several studies have been performed to determine which intrinsic and extrinsic factors influence the stability of conducting polymers. These are discussed in more detail in the following sections.

1.5.1 Factors Affecting Stability of the Doped State

In 1990, Wang and Rubner investigated the effect of environmental factors and structural properties on the lifetime of electrical conductivity in doped P3AT films. The authors observed the conductivity of doped films over time while reaction conditions were varied in such a way that the effects (on stability) of both intrinsic and extrinsic factors could be differentiated. Extrinsic factors examined included elevated temperatures and the environment (dry nitrogen, dry air, and humid air) while the intrinsic factors examined included the length of the alkyl substituent (methyl, butyl, hexyl, and octyl), nature of the dopant anion (PF$_6^-$, FeCl$_4^-$, and Fe(OTs)$_4^-$), and the polymerization method (electrochemical vs. chemical).

This and similar investigations indicate that the stability trends observed in P3ATs are affected differently by, and are dependent on, the regioregularity of the polymer. Wang and Rubner examined P3AT films of only 80% HT content which were oxidized by either nitrosonium hexafluoroborate or ferric chloride. It was demonstrated that a thermally activated dedoping process was present, and at a given temperature (40°C to 120°C), the stability was found to decrease as the alkyl side chain was lengthened from methyl to hexyl. In this case, the authors defined the stability of doped films as the time required for an order-of-
magnitude decrease in conductivity ($t_{1/10}$). Films of methyl, butyl, and hexyl-substituted polythiophene (30-50 μm) demonstrated $t_{1/10}$ values of 1300, 140, and 60 minutes, respectively. A similar trend was also observed in films doped by ferric chloride although the non-linear decay of conductivity discouraged quantitative treatment.

The nature of the counter ion is one of the strongest factors in determining the stability of doped polymer films. It has been postulated that those anions able to support a greater delocalization of negative charge appear to lend the greatest degree of stability to the system. Counter-ions which have most widely appeared in the literature include PF$_6^-$, OTs$^-$, FeCl$_4^-$, OTf$^-$, AuCl$_4^-$, and more recently bis(trifluoromethanesulfonimide) ([(CF$_3$SO$_2$)$_2$N]$^-$, TFSI).$^{13,43,44}$ In fact, it has been postulated that a polarizable counter-ion reduces the susceptibility of the positively charged bipolaronic charge carriers to nucleophilic attack by species such as water. This process is also known as reducing the degree of charge-pinning.

The oxidation potential of conjugated polymers has also been reported as having significant impact on the resistance of doped polymer films to chemical attack. Specifically, poly(thiophene)s that have been functionalized at the 3 and 4 positions with electron releasing alkoxy groups have been investigated.$^{45-47}$ Among this class of polymers, the best conductivities have been obtained with alkyl-substituted poly(ethylenedioxy thiophene)s, as shown in Figure 1.10.$^{12,48,49}$ The higher conductivity of this polymer is possible through the lower steric requirement of the substituents since i) they are 'tied-back' by the adjoining
ethylene group, and ii) the ether linkage has a smaller steric requirement than a methylene group. This permits adjacent thiophene rings to assume a more planar configuration.

![Figure 1.10: Alkyl substituted poly(ethylenedioxy thiophene).](image)

Reportedly, the low oxidation potential for this polymer increases its resistance towards chemical reduction. Unfortunately, there has been little to no quantitative evidence published regarding its stability relative to alkyl-substituted poly(thiophene)s. One class of polymers that has been quantitatively shown to possess greater resistance towards de-doping reactions are those with crown-ether sub-units (the chemical structure of which was previously shown in Figure 1.6). In these polymers, the strong affinity of the crown-ether sub-unit for alkali-metal counter-ions\(^{50,51}\) shifts the \(n\)-undoping potential from -2.0 to +0.2 V (\(vs.\ Ag/Ag^+\)) compared to normal P3ATs while the \(n\)-doping potential is unchanged from the potential of -2.2 V (\(vs.\ Ag/Ag^+\)) reported for the \(n\)-doping of polythiophene.\(^{52}\) This extremely large change in the de-doping potential represents a significant stabilization of the doped state that is also reflected in an increase in the lifetime of conductivity from minutes (for polythiophene) to several months for these \(n\)-doped films.
The environmental stability of doped poly(3-alkylthiophene) films also correlates with the hydrophobicity of the film surface. This is a logical result since any polymer film exposed to the atmosphere is also subject to the reducing power of water; therefore, a hydrophobic film would shield the internal electrophiles (polarons and bipolarons) from reduction by water. Experimentally, the water contact angles and the conductivity (over time) were measured for poly(3-octylthiophene) films doped with nitrosonium salts of tetrafluoroborate (BF₄⁻), triflate (CF₃SO₃⁻), and TFSI. The stability of conductivity and hydrophobicity of these films were found to be in the order: TFSI > CF₃SO₃⁻ > BF₄⁻.

In addition to the extrinsic effects, two other factors have been found to influence the stability of conductivity in doped P3ATs, these are the polymerization reaction and the doping technique. In regard to the effect of the coupling reaction, polymerization with FeCl₃ followed by doping with either PF₆⁻ or FeCl₄⁻ anions results in conducting polymers that are more stable than their electrochemically polymerized counterparts. Similarly, the method of anion injection into the polymer film has also been found to affect the stability. Doping of P3HT by chemical agents results in films that exhibit greater stability than those doped by electrochemical means, albeit the anion injected into the polymer is identical. Both of these results indicate that chemical, rather than electrochemical, methods of polymerization and doping maximize the stability of conductivity in conducting polymers.
1.6 Goals

Presently, many conjugated polymers have been made processable and soluble by the attachment of pendant groups. However, the majority of these polymers are only processable in their neutral, or insulating, form. Except for polyaniline, there has been little progress in rendering the conductive form of conjugated polymers soluble. Thus, a relatively complex process is required to obtain a conducting polymer film since the polymer must be cast from a solution or melt, dried, exposed to the oxidant, rinsed, and dried again. This project seeks to simplify this process with the following goals:

1) to develop the chemistry required to obtain a conductive polymer film from a single solution via a single casting step.

2) to characterize the resultant polymer films and to compare the film composition and the stability of its conductivity with films oxidized by conventional means.

3) to understand the source of any difference between films cast and doped by conventional methods and those doped by the single-step process.

This work also describes the methods and the results of, transmission electron microscopy (TEM); energy dispersive X-ray analysis (EDX); UV-vis spectroscopy; chemical and electrochemical doping techniques; and conductivity
lifetime experiments used in the investigation of the poly(3-alkylthiophene) and silver (I) trifluoromethanesulfonate system.
2. **Experimental**

2.1 **Chemicals**

n-Bromohexane, 3-bromothiophene, butyllithium, diisopropylamine, magnesium, magnesium bromoetherate, [1,3-bis(diphenylphosphino)propane] nickel(II) chloride, lithium trifluoromethanesulfonate, and silver triflate were used as received (Aldrich Chemical Co.). Ammonium peroxydisulfate, acetic acid and methanol (Anachemia Canada Inc.), bromine and anhydrous ferric chloride (BDH), hydrochloric acid and tetrabutylammonium perchlorate (Fisher Scientific), were also used as received. Aniline (BDH) was purified by vacuum distillation prior to use while pyridine and diethyl ether (Caledone Laboratories Ltd.) were distilled over potassium hydroxide and sodium, respectively. Acetonitrile and nitromethane (spectroscopic grades, BDH Chemicals) were stored over molecular sieves (3A, Fisher Scientific) and distilled prior to use. Xylene (Caledone) was used without further purification. Chloroform (BDH Chemicals) was distilled over calcium hydride (Fisher Scientific) and tetrahydrofuran (VWR Canlab) was distilled over sodium (Anachemia Canada Inc.).

2.2 **Synthesis**

2.2.1 **Preparation of 3-Hexylthiophene**

3-Hexylthiophene was synthesized from 3-bromothiophene and n-bromohexane using a Grignard coupling method reported by Tamao et al. Hexylbromide (16.51 g, 0.10 mol) was added to a suspension of magnesium
(2.4 g, 0.10 mol) in anhydrous diethyl ether (20 mL). Following reaction of the magnesium, 3-bromothiophene (13.0 g, 0.08 mol) and [1,3-bis(diphenylphosphino)propane]nickel(II) chloride (60 mg, Ni(dppp)Cl₂) were added slowly. The reaction mixture was stirred while heating for 15 hours and quenched by pouring into crushed ice. After dilution with HCl (2 N) the product was extracted with several aliquots of diethyl ether. The organic layers were combined, dried over MgSO₄, and concentrated. The colorless oil was purified by vacuum distillation. IR (neat): 3051 (ν aromatic C-H); 2956, 2927, 2856 (ν C-H); 1465 (ν C=C); 835 cm⁻¹ (C-H out-of-plane bend). ¹H NMR (CDCl₃ 400 MHz): δ = 7.17 (1H, dd, J₂,5 = 3 Hz, J₄,5 = 5 Hz, H₅), 6.98 (1H, dd, J₂,4 = 1 Hz, J₄,5 = 5 Hz, H₄), 6.94 (1H, dd, J₂,4 = 1 Hz, J₂,5 = 3 Hz, H₂), 2.63 (2H, t, J = 6 Hz, ring-CH₂-), 1.71 (2H, dd, J = 6 Hz, ring-CH₂-CH₂-), 1.51-1.36 (6H, m, -(CH₂)-CH₃), 0.99 (3H, t, J = 5 Hz, -CH₃).

### 2.2.2 Preparation of Regioirregular Poly(3-hexylthiophene)

Poly(3-hexylthiophene) was polymerized via an oxidative coupling reaction using ferric chloride and a procedure reported by Sugimoto et al.⁵⁴ 3-Hexylthiophene (1.71 g, 10.3 mmol) was dissolved in anhydrous chloroform (30 mL), and added drop-wise (1 drop/sec) to a stirred slurry of ferric chloride (6.72 g, 41.4 mmol) in anhydrous chloroform (20 mL). The vessel was fitted with a dry-nitrogen aerator and the reaction was allowed to proceed for 4 hours after which it was quenched by the addition of water. The reaction mixture was washed with
water and the resultant polymer was precipitated by pouring the solution into acidified methanol. After stirring for 24 hours, the polymer was collected by vacuum filtration. The polymer was washed successively with methanol and hexane in a Soxhlet extractor, and the soluble fraction was eluted with hot chloroform. The number average molecular weight and polydispersity were determined via gel permeation chromatography (GPC) and were found to be 24,500 g/mol and 2.8, respectively. IR (film on KBr disk): 3085 (ν aromatic C-H); 2956, 2930, 2852 (ν C-H); 1459 (ν C=C). ¹H NMR (CDCl₃, 400 MHz) δ = 7.05, 7.02, 6.99, 6.97 (1H, aromatic H); 2.79, 2.55 (2H, ring -CH₂-); 1.70, 1.61 (2H, ring-CH₂-CH₂-); 1.45-1.33 (6H, -(CH₂)₂-(CH₂)₃-); 0.90 (3H, -CH₃).

2.2.3 Preparation of 2-bromo-3-hexylthiophene

2-Bromo-3-hexylthiophene was prepared by brominating 3-hexylthiophene according to a procedure reported by Consiglio et al.⁵⁵ 3-Hexylthiophene (17.0 g, 0.12 mol) was added to acetic acid (125 mL) in a flask equipped with a nitrogen aerator, magnetic stirrer, and an ice bath. A solution of bromine (15.98 g, 0.1 mol) in acetic acid (40 mL) was added over 25 minutes and the reaction was stirred for another 30 minutes. The mixture was poured into ice water and the product was extracted with several aliquots of chloroform. The organic fractions were combined, washed with NaOH (2N) and water, dried over magnesium sulfate, and concentrated. The product, 2-bromo-3-hexylthiophene, was purified by vacuum distillation. NMR data were consistent with those reported in
literature.\textsuperscript{23} \textsuperscript{1}H NMR (CDCl\textsubscript{3}): 7.18 (d, $J = 5.5$ Hz, 1 H), 6.79 (d, $J = 5.5$ Hz, 1 H), 2.62 (t, $J = 7.5$ Hz, 2 H), 1.62-1.52 (m, 2H), 1.35-1.23 (m, 6H), 0.89 (t, $J = 5$ Hz, 3 H).

2.2.4 Preparation of Regioregular poly(3-hexylthiophene)

A Grignard cross-coupling reaction reported by McCullough \textit{et al.}\textsuperscript{23} was used in the polymerization of 2-bromo-3-hexylthiophene to produce a regioregular polymer. Diisopropylamine (1.18 g, 12 mmol) was added to 42 mL of anhydrous THF under a dry nitrogen blanket. Butyllithium (3.34 mL at 2.5 M, 8.36 mmol) in hexane was slowly added at room temperature. The mixture was cooled to -40°C in an acetone bath and stirred for 40 minutes. The mixture was then cooled to -78°C and 2-bromo-3-hexylthiophene (2.09 g, 8.36 mmol) was added drop-wise. The mixture was stirred for 40 minutes at -40°C and cooled to -60°C when magnesium bromoetherate, MgBr\textsubscript{2}•Et\textsubscript{2}O, (2.16 g, 8.36 mmol) was added. The mixture was stirred for 20 minutes at -60°C, slowly warmed to -40°C and stirred 15 minutes, then allowed to warm further to -5°C by which time all of the MgBr\textsubscript{2}•Et\textsubscript{2}O had reacted. A catalytic amount of Ni(dppp)Cl\textsubscript{2} (0.5 mol %) was added and the mixture was allowed to warm to room temperature overnight. The reaction was quenched and the polymer precipitated by pouring the mixture into methanol. The solid polymer was collected by filtration and washed with hot methanol in a Soxhlet extractor for 24 hours. The number average molecular weight and polydispersity, as determined by GPC, were 80,000 g/mol and 2.5,
respectively. Spectral data were consistent with those reported in literature.\textsuperscript{23,56} IR (film on NaCl): 3059 (\nu aromatic C-H); 2956, 2925, 2857 (\nu aliphatic C-H); 1511, 1451 (\nu ring); 1379 (methyl deformation); 819 (out-of-plane aromatic C-H); 721 (methyl rock). NMR (CDCl\textsubscript{3}, 400 MHz) \delta = 6.98 (s, 1H); 2.80 (t, 2H); 1.70 (t, 2H); 1.44 (m, 2H); 1.34 (m, 4H); 0.92 (t, 3H).

Regioregular (>98% HT) poly(3-dodecylthiophene) (P3DDT) and poly(3,3'-dihexyl-2,2'-bithiophene) (0% HT, P3HT) were supplied by Dr. M. Lebedev, and were synthesized using similar techniques.

\subsection{2.2.5 Preparation of Polyaniline}

Polyaniline was polymerized from aniline via an oxidative polymerization reaction adopted from Mattoso \textit{et al.}\textsuperscript{57} Initially, the author's method was used to obtain polyaniline of high-molecular weight. The authors report that this is possible by increasing the ionic strength of the solution through the addition of LiCl to the reaction mixture. Higher ionic strength environments enhance reaction rate between species of similar charge while decreasing the rate between those of opposite charge. Higher molecular weights result since the polymerization of aniline proceeds through the coupling of anilinium radical cations.\textsuperscript{58} The product from this reaction was only partially soluble. Thus, to obtain polymer films of reproducible and constant thickness, homogeneous polymer solutions of known concentration were required. Decreasing the molecular weight of a polymer often
enhances its solubility, therefore the reaction was repeated in the absence of LiCl.

Aniline was freshly distilled under vacuum and 5.0 mL (55 mmol) was added to 75 mL of 1 M HCl and cooled to 0°C. Ammonium peroxydisulfate, \((\text{NH}_4)_2\text{S}_2\text{O}_8\) (2.87 g, 12.6 mmol) was dissolved in 50 mL of 1 M HCl, cooled to 0°C, and added drop-wise to the stirring aniline solution. Upon reaction, the solution turned green-blue and a dark solid precipitated from solution. The reaction was allowed to proceed under a nitrogen blanket for 1.5 hours, after which the precipitate was collected on a Buchner funnel and washed with 1.0 M HCl until the filtrate was colorless (10 portions of 80 mL). The solid green polymer was then stirred in 1.0 L of 0.2 M NaOH for 72 hours and collected on a Buchner funnel. The polymer was dried under vacuum for 48 hours to provide a copper-colored polymer. Infrared data corresponds well to that reported in literature.\(^{59,60}\) IR (KBr pellet): 3456 (ν -NH-); 3252 (H-bonded -NH-); 2970 (ν C-H); 1590 (ν sym. quinonoid C₆ ring); 1505 (ν asym. benzoid C₆ ring); 1308 (ν aromatic C-N); 1152 (in-plane aromatic C-H); 956, 834 (out-of-plane aromatic C-H).

2.3 Instrumentation and Procedures

Molecular weights and molecular weight distributions for P3HT were determined by gel permeation chromatography (GPC) (Waters) using polystyrene as a standard and corrected for the difference in hydrodynamic
UV-visible spectra of polymer solutions and polymer films were recorded with a Cary 3E UV-Visible Spectrometer. Infrared spectra were recorded using a Bomem Michelson FTIR spectrometer. NMR spectra were recorded with a Bruker AMX400 spectrometer. Electrical conductivities were measured with a co-linear four-point probe technique, and are discussed in more detail in Section 2.5.

2.3.1 Measurement of Regioregularity

The regioregularity of a poly(3-hexylthiophene) sample was determined via $^1$H-NMR spectroscopy using methods outlined by Sato and Morii. The regiochemistry of a polythiophene sample can be described by the relative abundance of the 'bithiophene' (dyad) or 'terthiophene' (triad) moieties as described in Section 1.1. When using dyads to define the regiochemistry, $^1$H NMR signals in the aliphatic region at 2.79 and 2.56 ppm are integrated. These signals correspond to the protons on the methylene group α to the thiophene ring, and their integrals indicate the relative abundance of the head-to-tail (HT) and head-to-head (HH) dyads. Alternatively, the frequency of occurrence for each triad (HT-HT, HT-HH, TT-HT, or TT-HH) can be determined by integration of $^1$H signals in the aromatic region at 6.98, 7.00, 7.02, or 7.05, respectively. These signals arise from the differing chemical environments (as defined by each triad) for the single remaining proton on the thiophene ring. A NMR spectrum for a regioregular sample of P3HT is shown in Figure 2.1, the low intensity of the signals for the HT-HH, TT-HT, and TT-HH triads (in the aromatic region) lends
credence to the regioregularity of the polymer. Using the above procedures, the regioregularity of this polymer may be defined as having 96% HT or 97% HT-HT linkages.

![Figure 2.1: $^1$H NMR spectrum of regioregular P3HT in CDCl$_3$.](image)

2.3.2 Cyclic Voltammetry

A conventional three-electrode cell was fitted with a glassy carbon working electrode (0.07 cm$^2$), a platinum gauze counter electrode, and a saturated calomel reference electrode (SCE). The working electrode was polished with 1µm diamond paste, rinsed with distilled water, and dried before use. The electrochemical measurements were performed using a Pine Instrument Model RDE4 Bipotentiostat (equipped with an Allen X-Y Recorder) and were conducted in 0.1 M Bu$_4$N$^+$/ClO$_4^-$ solutions in nitromethane or acetonitrile by sweeping the applied potential at rates of 100 to 250 mV·s$^{-1}$. A single channel of a
bipotentiostat was used in the determination of the oxidation and reduction potentials of polymer films and dopant species through cyclic voltammetry experiments. Prior to measurements, electrolytes were deaerated by purging with nitrogen. Cyclic voltammograms of P3HT films were obtained by casting a toluene solution of P3HT onto a glassy carbon electrode and allowing them to dry for 1 hour at room temperature. Dichloromethane solutions of P3HT were also studied via cyclic voltammetry; in this case, 0.1 M Bu₄N⁺ClO₄⁻ was added to the polymer solutions as supporting electrolyte. Lastly, the reduction potentials of various dopants were determined via cyclic voltammetry by studying 1 mM solutions at room temperature.

2.3.3 Chemical Doping of P3ATs

2.3.3.1 Thin Polymer Films on ITO Substrates

Films of P3HT were spin-cast onto indium-tin-oxide coated glass slides from a 1:1 mixture of chloroform/xylenes. Reproducible film thicknesses were obtained by spreading 0.25 mL of a 5 mg/mL polymer solution onto a 2 cm² substrate, and rotating it at 1000 rpm for 30 seconds. Dryness was evident when the film changed from pale orange to deep red-violet. The resulting films were visually inspected for defects such as streaking and uneven optical density. After oven drying at 65°C for 30 min, the polymer-coated substrates were immersed in a 0.1 M nitromethane solution of ferric chloride or a diethyl ether solution of silver trifluoromethanesulfonate. Upon immersion into FeCl₃ solutions, the thin P3HT films changed from their red-violet color to pale clear blue; while immersion into
AgOTf solutions resulted in opaque, purple-black polymer films. After 5 minutes, the samples were removed, rinsed once with the appropriate dry solvent, and air-dried.

The effect of the regioregularity of the polymer on the extent of oxidative doping was determined by spin-casting CHCl₃ solutions of P3HT having 95%, 80%, and 0% HT content. The UV-vis spectra of these films were collected before and after immersion into a 0.1 M diethyl ether solution of AgOTf.

2.3.3.2 Thin Free-Standing Polymer Films

Free-standing thin films of P3HT were obtained from a 5 mg/mL chloroform solution of the polymer by slowly dropping the solution onto a quiescent surface of distilled water. The chloroform spread evenly across the surface and evaporation provided a thin (ca. 70 nm) free-floating film. The film was transferred to a substrate (either a copper grid for TEM studies, or a glass slide for thickness and UV-vis measurements) by lifting the substrate through the polymer film at an angle of ca. 30° to the surface. The sample was blotted with filter paper and oven dried at 65°C for 30 min before doping by immersion as previously mentioned in section 2.3.3.1.

2.3.3.3 Solvato-Controlled Doping of Conjugated Polymers

P3HT was dissolved (5 mg/mL) in a 1:1 solvent mixture consisting of xylenes and chloroform. A pyridine solution of silver triflate was prepared and
added to the polymer solution to obtain a solution consisting of 1:1:0.1 xylenes/chloroform/pyridine by volume. Silver trifluoromethanesulfonate was then added in the appropriate amount to provide one silver atom for 4 thiophene rings. After thorough mixing, the solutions were filtered through a 0.22 µm Millipore Millex GV disposable filter. Evaporation of the solvent, by either spin- or solvent-casting, followed by drying at 65°C, led to films of doped polymer.

The dependence of the conductivity on increasing silver(I) content was determined by introducing a weighed amount of silver triflate into a toluene/heptane/pyridine solution of 98% HT P3DDT. Since ambient temperatures were used for drying polymer films, the P3DDT/AgOTf ratio was retained in the doped polymer.

2.3.3.3.1 Effect of Silver(I) Content on Electrical Conductivity

Solutions were made which had a known concentration of P3HT in 1:1 toluene/heptane and AgOTf in pyridine. These were combined to provide solutions with molar ratios of polymer to silver(I) ranging from 0 to 1.25 while maintaining a final solvent composition of 1:1:0.1 toluene/heptane/pyridine (volume ratio).

Polymer films were spin-cast from these solutions and heated at 80°C to remove the solvent and the volatile pyridine ligand. XPS analysis indicated the absence of pyridine in the final film. The conductivity of the resultant films was measured with a co-linear four point probe (Section 2.3.5).
2.3.3.3.2 Effect of Regioregularity on Silver(I) Doping of P3HT

Poly(3-hexylthiophene) samples containing 100%, 80%, and 0% head-to-tail (HT) dyad content were dissolved in 1:1 toluene/heptane (to a concentration of 5 mg/mL) and spin-cast on glass slides. UV-vis absorption spectra were collected before and after immersion in a 0.1 M diethyl ether solution of silver triflate.

2.3.3.4 Electrochemical Potential of Chemically Doped Films

Films of Regioregular P3HT were spin cast from a 5 mg/mL 1:1 toluene/heptane solution onto tin-doped indium oxide coated glass slides. These samples were immersed for 60 seconds in a 0.1 M solution of the dopant (either AgOTf in diethyl ether, or FeCl₃ in nitromethane). Doping of the polymer film was evident from the immediate color change. The doped polymer film and a silver chloride coated silver wire reference electrode were immersed in a 0.1 M chloroform solution of tetrabutyl ammonium trifluoromethanesulfonate and the potential difference between them was measured with a FLUKE 8000A digital multimeter.

2.3.4 Electrochemical Doping of P3ATs

2.3.4.1 In-Situ Conductivity of P3HT

The potential region in which regioregular P3HT is conductive was determined using a procedure adopted from Schiavon et al. In this method, a two-band platinum electrode (constructed by Ms. E. Lai) was used to qualitatively
measure the conductivity of a thin film under an applied potential difference. The dual-band electrode consisted of two platinum strips (0.3 x 0.3 x 0.07 cm) to which electrical contact was made. These were used to 'sandwich' an electrically insulating 80 μm thick Mylar film. The assembly was encapsulated in a 4 mm glass tube and sealed with 5-minute epoxy. The exposed end of the dual-band electrode was ground with emery cloth, polished with diamond paste, and rinsed with distilled water and acetone. Three drops of a 5 mg/mL P3HT solution in CHCl₃ were then spread evenly over the surface. The amount of polymer deposited was sufficient to bridge both electrodes while the thickness was not determined since the absolute conductivity of the polymer film was not required. This working electrode was placed in a 0.1 M acetonitrile solution of lithium triflate (LiOTf) with an Ag/AgCl wire reference and a platinum-gauze counter electrode.

Electrical contact with the polymer film was confirmed by applying a potential to one of the platinum bands and sweeping it linearly from 0.0 to +1.0 V (vs. Ag/AgCl) at 100 mV/s. A plot of the current developed vs. the applied potential generated the cyclic voltammogram shown in Figure 2.2 (K1) and clearly shows both oxidation and re-reduction of the polymer film. This procedure was repeated for the other platinum band (K2), and a third time for the two bands connected in parallel (K1+K2). The area under the three cyclic voltammograms is roughly the same and, since the x-axis is directly proportional to time, the area between the curve and the x-axis represents the total charge passed. Consequently, in this case, both platinum bands are capable of completely
oxidizing the polymer film in the region between the two electrodes, otherwise a voltammogram with twice the area of that due to a single-band potential sweep would have resulted in curve 3. Consequently, there is sufficient contact to the polymer film so that the polymer in the region between the two bands is homogeneously oxidized to the potential applied by either band electrode.

Figure 2.2: Linear-sweep cyclic voltammograms (CV) of a P3HT film deposited on a dual-band platinum electrode with (K1) the first platinum electrode connected, (K2) the second electrode connected, and (K1+K2) with both electrodes connected.

The conductivity of the P3HT film was measured by connecting both bands to a bipotentiostat and using the same reference, counter electrode, and
electrolyte solution as in the previous step. A schematic of the experimental setup is shown in Figure 2.3.

![Schematic of the experimental setup](image)

**Figure 2.3:** Schematic of the experimental setup used to determine the in-situ conductivity of P3HT films on a platinum dual-band electrode.

The two platinum bands were set at the same potential (initially +1.0 V) and the polymer allowed to equilibrate. The potential of the first band electrode was then decreased by 20 mV. This potential difference created a current flow between the two platinum electrodes. After equilibration, the resulting current was measured via a voltage drop across a 150 Ω resistor connected in series to one of the platinum bands. The potential of the second band electrode was then decreased by 20 mV. These three steps were repeated so that the 'conductivity' of the P3HT film, or the magnitude of the resulting drain current, was monitored from +1.0 to +0.28 V at decrements of 50 mV. The applied potential was decreased from the upper to the lower limit as it has been reported that polymer
films equilibrate more quickly when traversing the potential window from the oxidized to the insulating state. This effect is likely due to the expanded morphology that the polymer must attain in order to imbibe the charge-balancing counter-ions into the oxidized form.

2.3.4.2 Substrate Preparation for Electrochemical Doping

In order to examine the stability of P3HT films oxidized at varying potentials, it was necessary to electrochemically oxidize a large number of polymer films. The previously mentioned dual-band electrode sufficed; however, the construction and cost of numerous such electrodes was prohibitive so that another procedure was necessary. It was desirable that the polymer films be homogeneously oxidized and that the substrate be transparent in the UV-vis region so that an estimate of film thickness and the level of doping could be determined. The substrate must therefore be flat and electrically conductive. However, measuring the electrical conductivity of the polymer film requires that a portion of the film is not in direct contact with the conducting substrate; otherwise conduction would occur through the less resistive substrate rather than through the polymer film. Tin-doped indium oxide (ITO) coated glass slides (Delta Technologies Ltd.) fulfilled the necessary criteria. In order to obtain an electrically insulating region on the substrate, the ITO surface was scratched with a diamond pencil. This approach, however, resulted in incomplete breakage of conductivity, and produced a rough trench with a visually high aspect ratio. A smooth profile (gradient) between the insulating and ITO-coated regions of the glass slide was
necessary to obtain a polymer film that was continuous over the entire surface. To achieve this, the ITO in the region of interest was removed by an acid-etching process in which the presence of an oxidizing agent has been reported to result in ITO features with well-defined and smooth edges.63

A pictorial representation of the process used to develop the desired ITO features is shown in Scheme 2.1. Glass slides of ITO were cut to 2 cm x 1 cm and masked lengthwise with a 0.7 mm wide band of vinyl tape. The masked substrate was then spin-coated with resist (manufacturer) at an initial speed of 1000 rpm for 30 seconds, and then ramped up to 5000 rpm for a 2 minute drying period. The substrate was dried further in an oven at 100°C for 20 minutes before the tape was removed.

The ITO layer was etched by a 20 minute immersion in a 6 M HCl bath containing 0.4 M FeCl₃. The substrate was removed, rinsed with water and acetone, and ultrasonically cleaned in a 1:1 mixture of acetone/ether for 5 minutes. Resistance measurements confirmed the presence of two intact ITO pads separated by an electrically insulating region. Electrical contacts were made to the ITO pads by affixing wires with Electrodog (Acheson Colloids Ltd.) and insulating the contacts with 5 minute epoxy. Thin polymer films were then deposited onto the substrate by spin coating the entire apparatus at 1000 rpm as previously described.
Scheme 2.1: Preparation of ITO-coated glass slides for electrochemical doping of conjugated polymer films.

2.3.4.3 Electrochemical Doping of P3HT

The polymer coated ITO substrate was used as the working electrode in a three electrode system and was immersed in a 0.1 M acetonitrile solution of lithium triflate (LiOTf). The reference and counter electrodes consisted of an Ag/AgCl wire and platinum gauze, respectively. An applied potential difference (between +0.60 and +1.0 V) resulted in oxidative doping of the polymer film; this was evident since the polymer film changed from red-violet to a pale clear blue. The sample was removed from the electrolyte solution, rinsed once with dry acetonitrile, and air-dried.

2.3.5 Conductivity Measurements

The conductivities of poly(3-alkylthiophene) films spin cast on glass slides were measured using a co-linear four-point probe technique. An EG&G Model 363 Potentiostat/Galvanostat and a FLUKE 8000A digital multimeter were used in the measurements. The four-point probe used was
custom built with four co-linear stainless steel probes, ground to a fine round point, and mounted in a plexi-glass holder at a spacing of 3 mm point-to-point (Figure 2.4). In this technique, the galvanostat is used to pass a controlled current through the polymer between the outer two probes (A and D) while the resulting potential drop (developed) across the film is measured with the two inner probes (B and C).

![Co-linear four-point probe used in conductivity measurements.](image)

When the spacing between adjacent probes is large compared to the radius of the probe (i.e. point contact), and the area of the polymer film is large compared to the spacing between the probes, the conductivity ($\sigma$) of the polymer film can be calculated via equation 3:

$$\sigma = 100 \frac{\ln(2)}{\pi d} \frac{i}{V}$$

where $\sigma$ is the conductivity in S/m, $d$ is the film thickness (cm), $i$ is the current (A) between probes A and D, and $V$ is the potential drop (V) between probes B and C. Film thicknesses below 100 nm were determined using the optical absorbance of the P3HT film (at $\lambda_{\text{max}}$) in conjunction with a calibration curve of
film thickness versus the optical absorbance. Film thicknesses greater than 100 nm were directly measured with an Alpha-Step 100 profilometer.

The co-linear four-point probe was unsuitable for measuring the conductivity of electrochemically doped polymer films since the underlying (conductive) ITO surface present in these samples is much more conductive than the doped polymer films; thus, the resistance of each film was measured directly with the digital multimeter and the conductivities (σ) were estimated according to equation 4:

\[ \sigma = \rho^{-1} = \frac{1}{R \cdot I/(w*d)} \]  

(4)

Where \( \rho \) represents the resistivity of the polymer (Ω·cm), \( R \) is the measured resistance (Ω), \( I \) is the length (cm), and \( (w*d) \) is the cross-sectional area (cm²) of the conductive pathway. These parameters are schematically shown in Figure 2.5.

![Figure 2.5](image_url)

**Figure 2.5:** Parameters for resistance measurements in electrochemically doped P3AT films on an acid-etched ITO-coated glass slide.
In hindsight, a more analytical method may have been to use a four-lead technique in these resistance measurements, to eliminate loading errors in the two-lead digital multimeter. However, in this case, the two-lead technique is likely sufficient as the resistances measured were between $40\Omega$ and $1\text{M}\Omega$ and the manufacturer reports an accuracy of $0.5\% + 2$ digits for measured resistances within this range.

2.3.6 Transmission Electron Microscopy

2.3.6.1 Direct Observation

Transmission electron microscopy (TEM) studies were performed on neutral and AgOTf doped polymer films that were formed as described in section 2.3.3. An Hitachi H-8000 Transmission Electron Microscope, operating at 200 kV, was used to image the bulk polymer film and to magnify any noticeable features. Qualitative elemental analysis of these features was achieved with the LINK QX2000 Thin Window Energy Dispersive X-ray Analyzer. X-ray emission spectra were collected over a period of 600 s, and the observed signals were well above the baseline noise.

2.3.6.2 Indirect Observation

The surfaces of AgOTf doped polymer films were also indirectly examined using the TEM. Polymer films were spin-cast and doped on glass substrate as previously described. These were covered with a layer of evaporated NaCl and subsequently a layer of carbon. The carbon impression of the film surface was
released by slow immersion of the sample edge into distilled water. The TEM sample grid was then lifted through the carbon extraction film, and dried before insertion into the electron microscope. Visual inspection and EDX analyses were performed on each sample as described in section 2.3.6.1.
3. **Results and Discussion**

3.1 **Doping of P3HT by Silver Triflate**

Silver(I) is known to form coordination complexes with many organic ligands which contain aromatic, heteroaromatic, and amine functional groups. A few of these coordinating ligands and their silver(I) formation constants are shown in Table 3.1. Clearly, these complexes vary greatly in their stability.

**Table 3.1:** Selected ligands and their associated formation constants for complexation with silver(I).

<table>
<thead>
<tr>
<th>Ligand</th>
<th>( K_f )</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>toluene</td>
<td>1.2</td>
<td>66</td>
</tr>
<tr>
<td>benzene</td>
<td>46</td>
<td>67</td>
</tr>
<tr>
<td>pyridine</td>
<td>120</td>
<td>68</td>
</tr>
<tr>
<td>dimethylamine</td>
<td>( 5.9 \times 10^5 )</td>
<td>69</td>
</tr>
</tbody>
</table>

Silver(I) can also be used to effect the single electron oxidation of many systems. Frequently, it is used in conjunction with another oxidizing agent such as in the silver(I) catalyzed oxidation of aspartic acid by cerium(IV).\(^{70}\) The versatility of silver(I), along with its ability to coordinate to numerous aromatic and heteroatom-containing ligands suggests that it may be effective in doping poly(3-alkylthiophenes). This process is proposed to proceed by either an oxidative or coordinative interaction.

Figure 3.1 shows the change in the UV-vis absorption spectra for a regioregular (98% head-to-tail) poly(3-dodecylthiophene) (P3DDT) solution in
toluene/heptane (volume ratio 1:1) upon addition of 3.5 mM silver triflate (AgOTf). Oxidative doping of the polymer solution is evident from the decrease in the $\pi \rightarrow \pi^*$ absorption at 440 nm and the subsequent growth of a broad absorption band at 844 nm. This latter electronic absorption in polystyrene has been attributed to the presence of bipolaronic charge carriers. Absorption spectra collected after 6 hours (in this example) have been omitted since further oxidation resulted in an insoluble product and precipitation of the polymer from solution. The isobestic point in this set of UV-vis spectra appears precise and illustrates that doped polymer chains contain two species that exist in equilibrium. These consist of neutral polymer segments and those thienyl units over which the charge carriers extend (bipolarons in this case).

Figure 3.1: Evolution of the UV-vis spectra for poly(3-dodecylthiophene) (98% HT) (1 mg/mL) in the presence of silver triflate (3.5 mM) over a period of 6 h. The solvent was toluene/heptane (volume ratio 1:1), and spectra were recorded 20 min apart.
Associated with these doping-induced changes in the UV-vis absorption spectra is an increase in conductivity from $<10^{-6}$ to 10 S/cm. This increase is of similar magnitude to conductivities observed in P3DDT films oxidized by the more conventional dopant FeCl$_3$ (2-10 S/cm).

Upon silver(I)-promoted oxidation, the UV-vis spectra of 80% head-to-tail poly(3-hexylthiophene) (P3HT) solutions exhibit similar changes as observed in the doping of 98% HT P3DDT solutions. Additionally, solutions of electrochemically polymerized P3HT (typically 65-80% HT) have been reported to exhibit similar behavior when oxidized by electrochemical techniques. Oxidative doping, (and the changes observed in the UV-vis spectra) is therefore general for P3ATs of varying head-to-tail content, and similar spectral changes are observed when either chemical or electrochemical methods are used.\textsuperscript{71}

Since silver(I) is so versatile, it was necessary to identify the nature of the reaction by which it effects the doping of poly(thiophene)s. Possible reaction pathways include (i) a single electron transfer reaction or (ii) by formation of a charge transfer complex, and are depicted in Figure 3.2. Reaction by the first mechanism should lead to metallic silver particles, whereas the second mechanism should not produce such entities. Transmission electron microscopy provided a visual examination of the product of the doping reaction.
Figure 3.2: Possible doping reactions between silver(I) and poly(3-hexylthiophene): (i) single electron transfer, and (ii) charge transfer complex formation.

3.2 Characterization of Doped P3HT Films

3.2.1 Transmission Electron Microscopy

Poly(3-hexylthiophene) was doped by silver triflate and examined via transmission electron microscopy (TEM). Figure 3.3 shows a TEM micrograph obtained from a 70 nm thick (95% head-to-tail) film doped by immersion in an ether solution of silver triflate. As is evident from the micrograph, these polymer films contain two distinguishable regions. The X-ray analyzer attachment, when used in conjunction with the TEM, was capable of differentiating between these two. EDX analysis indicated that the dark regions of the micrograph contained metallic silver, carbon, and sulfur. Visually, these regions were found to consist of 10 nm particles, which had aggregated to form the larger (100 nm) particles. EDX
analysis also indicated that the light (gray) regions of the micrograph contained carbon and sulfur, while no evidence was found for the presence of silver in this area. This region must therefore be the bulk conjugated polymer. From this sample, it is not clear whether the carbon and sulfur signals (observed in the particulate region) are due to polymer interspersed within the particle, or whether they are just background signals. Similar structural features were observed in polymer films which were cast and oxidized via solvato-controlled doping (as compared to those doped by immersion in the dopant solution).

**Figure 3.3:** TEM micrograph of 100 nm silver particle clusters in a thin P3HT film after doping by immersion in AgOTf.

It is known that a high-energy electron beam can be used to generate metallic silver particles by the reduction of a silver(I) salt. In a recent example of
this effect, a TEM was operated at 100 kV, and 6.4 A/cm², to achieve the reduction of silver(I) in a sample of soda-lime glass that had been partially ion-exchanged with AgNO₃. At this high current density, metallic silver particles precipitated within the 30 nm thick glass slide after only a few seconds of irradiation. The authors characterized the particles by high resolution electron microscopy (HREM) to determine lattice plane spacings, and it was concluded that the particles were metallic silver, of nearly spherical shape, mostly single crystalline, and they showed a narrow size distribution with a mean diameter of 4.2 nm.

The features of these recently reported silver particles are strikingly similar to those observed when poly(3-hexylthiophene) films (doped by silver triflate) were examined via the TEM. The determination of the pristine state of silver in doped P3HT films requires elimination of the direct interaction between the 200 kV electron beam and the silver-doped films. In order to prevent the destruction of a polymer-silver charge-transfer complex by the electron beam, TEM studies were performed on carbon films which had been extracted from the surface of an AgOTf-doped poly(3-hexylthiophene) film. Figure 3.4 shows a schematic of the sample and substrate with a silver particle penetrating through several of the layers. As shown in Figure 3.5, the micrographs obtained from these samples were similar to those observed in the immersion-doped polymer films.
Figure 3.4: Schematic of a P3HT film on glass covered by evaporated layers of NaCl and carbon.

Figure 3.5: TEM of a silver particle in a carbon film extracted from the surface of a silver triflate doped P3HT film.

Again, EDX analysis indicated that the particles lifted from the polymer surface contained silver; although, as expected, they occurred less frequently than observed in the polymer films directly examined by the TEM. EDX analysis of these samples found no evidence of sulfur (due to the polymer) in the area of
the bulk carbon, nor in the region occupied by the silver particles, and it was concluded that the carbon film had lifted cleanly from the surface of the polymer. Since the carbon film was removed from the surface of the doped polymer film before exposure to the 200 kV electron beam, the 100 nm silver particles must have been present in the polymer film before irradiation. Therefore, to produce metallic silver, the doping reaction between P3HT and AgOTf must be a full-electron transfer reaction, and is likely of the form denoted in Figure 3.2 (i). This reaction is rewritten below for clarity:

$$P + 2n \text{AgOTf} \rightarrow n P^{++} + 2n \text{OTf}^- + 2n \text{Ag(s)}$$

where $P$ and $P^{++}$ denote neutral polymer and bipolarons, respectively.

### 3.3 Solvato-Controlled Doping

As mentioned in the introduction, conjugated polymer films are generally oxidized via an additional step after film casting or sample preparation. Unfortunately, this technique poses several disadvantages since: i) immersion of thick polymer films (and subsequent doping) often results in swelling and cracking of the sample, ii) the doping level (ratio of dopant to monomer units) can not be predicted a priori, iii) the concentration of dopant through a thick sample may not be uniform when lightly doped samples are desired, iv) the solvent for the dopant solution, or the doping agent, itself, may be incompatible with other components on the substrate, and v) for solution doping, there is a large amount of wasted reagent since practical use exposes the dopant solutions to air and
moisture, resulting in quenching of the active species. Many of these factors would be ameliorated by a technique that provides both simultaneous film casting and polymer oxidation (doping). Additionally, it would be useful to control the conductivity of the product polymer by controlling the doping level, that is, by setting the ratio of injected anions to monomer units a priori. As will be shown, both of these goals have been achieved for several conjugated polymers by a new technique which is termed solvato-controlled doping.

A single-step casting and doping process requires incorporation of both the oxidizing agent, and the charge-balancing counter ions into the polymer solution. However, an effective oxidizing agent is a chemical species which has a reduction potential more positive than that of the polymer. Therefore, upon mixing of the oxidant with the polymer, the dissolved polymer chains become oxidized, they assume a more planar conformation (due to the enhanced inter-annular double bond character) (Figure 1.5), and they precipitate from solution. Clearly, the polymer and oxidant must be shielded from each other if an intimate mixture is to be obtained while keeping the polymer both neutral and soluble. We postulated that the oxidant could be shielded from the polymer by the presence of coordinating ligands. Silver(I) was chosen as the oxidant as we found it to be an effective oxidizing agent for P3HT films, and it is known to coordinate to numerous organic compounds. The counter-ion chosen was trifluoromethanesulfonate (or triflate) (CF$_3$SO$_3^-$, OTf$^-$) since the silver(I) salt was commercially available, and the anion has a low nucleophilicity.
3.3.1 The Physical Basis of Solvato-Controlled Doping

As shown previously in Table 3.1, formation constants for silver (I) coordination complexes span several orders of magnitude. The size of these constants depends, in large part, upon the nature and number of electron-donating groups within the ligand. Ethers, alcohols, thio-ethers, and amines are just a few of the many silver(I) coordinating ligands. One of the parameters which reflects the ability of ligands to act as electron donors is the donor number (D.N.) of the solvent.\textsuperscript{73} This parameter is defined as the negative of the enthalpy for the reaction ($\Delta H^\circ$) of the Lewis base with antimony pentachloride (a strong Lewis acid) in 1,2-dichloroethane. This reaction is shown below:

$$\text{SbCl}_5 + \text{B} : \rightarrow \text{Cl}_5\text{Sb-B} \quad \Delta H^\circ$$

Based on this scale, diethyl ether (with a D.N. of 19.2) forms the weaker complex while sulfur and nitrogen donors such as dimethylsulfoxide (D.N. = 29.8) and pyridine (D.N. = 33.1) are among the strongest.

The shielding effect of complexation of silver (I) by Lewis bases arises from an increase in the electron density at the metal center. This interaction stabilizes the cation and causes the oxidizing ability of the complexed metal cation to be less than that of the pristine metal (i.e. it shifts the reduction potential, $E_{\text{red}}$, to less positive values). The extent of this shift should depend on the stability of the complex formed, with the largest decrease in oxidizing ability coinciding with the most stable complex. It is precisely this effect which makes solvato-controlled doping possible. The ligand to be used in solvato-controlled
doping must therefore be chosen such that the metal complex is incapable of oxidizing the conjugated polymer, yet the complex formed must not be excessively strong so as to prevent later removal of the ligands.

If an oxidant (such as a transition metal cation, \(M^{x+}\)) meets the following criteria:

1) \(E_{\text{red}}\) of \(M^{x+}\) is more positive than \(E_{\text{red}}\) of the oxidized polymer.
2) \(M^{x+}\) forms coordination complexes.
3) Upon complexation of \(M^{x+}\) by some ligand \(L\), \(E_{\text{red}}\) of \(ML_n^{x+}\) is more negative than \(E_{\text{red}}\) of the oxidized polymer.
4) The coordinating ligands can be readily and reversibly removed from the metal-ligand complex.

then solvato-controlled doping is possible. That is, the prediction can be made that a solution comprising of the conjugated polymer and the complexed transition metal will be stable with respect to oxidation of the polymer; thus allowing the polymer to retain its neutral and soluble form. Upon subsequent casting and evaporation of both the solvent and coordinating ligands, the 'ligand-free' transition metal will be generated, and its reduction potential will be sufficient to oxidize the polymer film. This procedure is outlined in Scheme 3.1.
Appropriate polymers and dopants may be selected for the solvato-controlled doping process based on their electrochemical properties. The results of these investigations for silver(I), polythiophene, and the silver(I)-pyridine complex are described in the forthcoming sections.

3.3.2 Electrochemistry of Polymer Films

Since the goal of this research is to produce oxidized (conductive) polymer films from a solution of neutral polymer, and since this dictates that oxidation of the polymer occurs when the polymer is in the solid form (to keep the polymer solution processable), the electrochemistry of polymer films (rather than solutions) was investigated. The electrochemical properties pertinent to solvato-controlled doping are the oxidation and reduction potentials for the conjugated polymer and the oxidant. These parameters were determined by cyclic-voltammetric techniques which involve observing the current flow while ramping the potential applied to the analyte, this technique is described in detail in section 2.3.2.
Three basic requirements should be satisfied to effect electrochemical oxidation of a conjugated polymer film. Since the polymer film must be immersed into an electrolyte solution, the solvent for the electrolyte must be chosen so that the polymer remains insoluble yet the film is sufficiently swollen (or porous enough) to allow an influx of charge-balancing counter-ions upon oxidation of the film. Second, the applied potential difference must be sufficiently positive to oxidize (or partially oxidize) the polymer film. Third, the counter-ion should be non-nucleophilic and polarizable in order to avoid quenching of (and to stabilize) the positive charge carriers generated in the doped polymer chains.

3.3.3.1 Solvation of Polymer Films for Charge Injection

Solvation of a conjugated polymer is dependent on the interaction between the polymer and the solvent. This interaction is partially described by the enthalpy of mixing ($\Delta H_M$) for a polymer and a solvent, and it has been quantified by Hildebrand and Scott via equation 5:

$$\Delta H_M = V_M \left[ \left( \frac{\Delta E_1}{V_1} \right)^{X_1} - \left( \frac{\Delta E_2}{V_2} \right)^{X_2} \right] v_1 v_2$$

(5)

where $V_M$ is the total volume of the mixture, $\Delta E$ is the molar energy of vaporization (to a gas at zero pressure) for each component, $V_i$ represents the respective molar volumes, and $v_i$ is the volume fraction of each component. Thus, the quantity $\Delta E / V$ represents the energy of vaporization per cm$^3$, or the cohesive energy density for each species. The square root of this term is known
as the solubility parameter, \( \delta = (\Delta E / V)^{\frac{1}{2}} \). Although the solubility of a polymer in a given solvent is dependent on many other factors, such as temperature, molecular weight, and the degree of hydrogen bonding, it is common for a polymer to dissolve in a solvent having a solubility parameter within about one unit of its own. Values of \( \delta \) for neutral poly(3-hexylthiophene) and a variety of solvents are shown in Table 3.2.

**Table 3.2: Solubility parameters for P3HT and some common solvents.**

<table>
<thead>
<tr>
<th>Solvent</th>
<th>( \delta ) (cal/cm(^3))(^{\frac{1}{2}} )</th>
</tr>
</thead>
<tbody>
<tr>
<td>water</td>
<td>23.4</td>
</tr>
<tr>
<td>nitromethane</td>
<td>12.7</td>
</tr>
<tr>
<td>acetonitrile</td>
<td>11.9</td>
</tr>
<tr>
<td>chloroform</td>
<td>9.6</td>
</tr>
<tr>
<td>P3HT</td>
<td>9.3</td>
</tr>
<tr>
<td>xylenes</td>
<td>8.8</td>
</tr>
<tr>
<td>diethyl ether</td>
<td>7.4</td>
</tr>
</tbody>
</table>

Thus, the high value of \( \delta \) for water precludes its use as an electrolyte solvent for P3HT while nitromethane, acetonitrile, and diethyl ether represent favorable solvents for the swelling and subsequent doping of P3HT films, and will not result in dissolution of the polymer film. Chloroform and xylenes, on the other hand, possess solubility parameters in close proximity to that of the polymer and are observed to readily dissolve poly(3-hexylthiophene). Thus, electrochemical experiments on polymer films were conducted in nitromethane, acetonitrile, or diethyl ether.
3.3.3.2 Electrochemistry of P3HT Films and Silver(I) Species

Figure 3.6 displays a series of three cyclic voltammograms showing oxidation and reduction of: a) a regioregular P3HT film, b) 1 mM AgOTf, and c) 1 mM AgOTf with 5% (vol.) pyridine. These results were obtained in nitromethane with 0.1 M Bu4N+ClO4− as supporting electrolyte. Under these conditions, the onsets of oxidation of the polymer film and reduction of silver(I) are observed to occur at +0.45 V and +0.50 V, respectively.

Figure 3.6: Cyclic voltammograms of a) poly(3-hexylthiophene), b) 1 mM AgOTf in nitromethane, and c) 1 mM AgOTf in nitromethane with 5% (vol.) pyridine.
The spontaneity of the doping reaction is determined by first calculating the driving force ($\Delta E$) using equation 6:

$$\Delta E = E_{ox} - E_{red}$$

(6)

where $E_{ox}$ and $E_{red}$ are the half-cell potentials for the reduction of the oxidized species (silver (I)) and oxidation of the reduced species (the polymer), respectively. The spontaneity of the reaction is then predicted via the sign of the Gibbs free energy change ($\Delta G$) for the redox reaction:

$$\Delta G = -nF\Delta E$$

(7)

In equation 7, $n$ is the moles of electrons involved in the overall reaction; $F$ is Faraday’s constant, 96485 C mol$^{-1}$; and $\Delta E$ is the driving force calculated from equation 6. For the reaction between Ag(I) and P3HT, calculated values for $\Delta E$ (+0.05 V) and $\Delta G$ (-5 kJ/mol) indicate that the doping reaction is thermodynamically favorable.

The third cyclic voltammogram in Figure 3.6 demonstrates that the presence of 5 % (vol.) pyridine causes a shift in the onset of reduction for Ag(I) from +0.50 V to −0.1 V. The resulting $\Delta E$ (-0.50 V) and $\Delta G$ (+48 kJ/mol) indicate that oxidation of the polymer by the silver-pyridine complex is not thermodynamically favorable.

Indeed, these conclusions were reinforced for the case of a 1 mg/mL poly(3-dodecylthiophene) solution (and for poly(3-hexylthiophene)) when mixed with a solution which contained AgOTf and pyridine. The suppression of Ag(I)-induced doping induced by pyridine is demonstrated in Figure 3.7 which shows a
UV-vis spectrum of a toluene/heptane/pyridine (volume ratio 1:1:0.1) solution of P3DDT (a) before, and (b) 6 hours after mixing with a pyridine solution of AgOTf.

**Figure 3.7:** UV-vis spectra of a 1 mg/mL solution of P3DDT in a mixture of toluene/heptane/pyridine. a) pristine solution, and b) 6 hours after the addition of 3.5 mM AgOTf. **Inset:** UV-vis of a polymer film cast from this solution.

From comparison with Figure 3.1, it is apparent that the intensity of the $\pi \rightarrow \pi^*$ transition has not decreased, and neither has the bipolaron absorption (~800 nm) increased in intensity. Therefore, pyridine is very capable of suppressing the Ag(I) promoted oxidation of P3HT. Polymer solutions of this type were observed to remain neutral and soluble indefinitely with no change in their UV-vis spectra.

Also shown in Figure 3.7 (Inset) is a UV-vis spectrum of a P3DDT film cast from this solution containing both the polymer and the oxidant. In this spectrum,
the intensity of the $\pi \rightarrow \pi^*$ absorption at 450 nm has greatly decreased while a broad absorption centered at 800 nm has appeared. As previously stated, these features are indicative of oxidative doping for poly(thiophene)s. Further evidence of doping is found in the increased conductivities (1-10 S/cm) of such films compared to the pristine polymer. Therefore, it can be concluded that removal of the solvent and the pyridine from the system has released the silver(I), and that this oxidant has proceeded to oxidize the polymer film.

3.3.4 Dependence of Film Conductivity on Silver(I) Content

Solvato-controlled doping permits intimate mixing of polymer and oxidant species while avoiding reaction between the two. This technique is therefore well suited to controlling the amount of dopant introduced into a film of conjugated polymer. The doping level (and hence conductivity, $\sigma$) of the resulting polymer film can now be determined a priori since conductivity is dependent on the number of charge carriers present (as introduced by oxidation with AgOTf). The dependence of conductivity for a P3HT film on the doping level (the ratio of AgOTf to monomer units) was investigated as described in Section 2.3.3.4.1.

Figure 3.8 shows a plot of $\log(\sigma)$ vs. the molar ratio of AgOTf to thienylene units. From this plot, molar ratios of less than 0.2 result in films of relatively low conductivity (0.01 - 0.8 S/cm), while ratios of $\geq 0.25$ provide polymer films of maximum conductivity (2 S/cm). This doping level corresponds to one Ag(I) dopant (and one OTf$^-$ anion) for every four thiophene rings. This is consistent
with the doping level found for P3DDT films doped by immersion into AgOTf solutions.\textsuperscript{44}

![Graph showing the conductivity of 98% HT P3DDT films vs. molar ratio of AgOTf:thienyl groups present in the films.]

**Figure 3.8**: Plot of the conductivity of 98% HT P3DDT films vs. molar ratio of AgOTf:thienyl groups present in the films.

### 3.3.5 Effect of Regioregularity on Solvato-Controlled Doping

Since the reduction potential of the dopant has a dramatic effect on its ability to dope a given polymer, it is logical that the oxidation potential of the polymer will also play an important role in the doping reaction. It has already been mentioned that the oxidation potential for P3ATs decreases as the head-to-tail (HT) dyad content increases. This arises from the increased torsion between adjacent thiophene rings in polymers of low HT dyad content, which in turn
decreases the effective conjugation length, and so increases the oxidation potential of the polymer. Figure 3.9 illustrates the change in the UV-vis spectra of P3HT films with both 80% HT and 0% HT dyad content upon exposure to AgOTf. The 0% HT P3HT film is only marginally doped by treatment with AgOTf, whereas the P3HT film with 80% dyad content exhibits a large decrease in the \( \pi \rightarrow \pi^* \) absorption (490 nm) and the broad band due to bipolarons (780 nm) has increased significantly, thus indicating that oxidative doping has occurred. In poly(3-dodecylthiophene) films of even higher (98%) HT dyad content (Figure 3.7: Inset), silver(I) doping causes an even larger decrease in the \( \pi \rightarrow \pi^* \) absorption and indicates that doping has proceeded to a greater extent.

![Figure 3.9: UV-vis spectra of (a) a neutral 80% HT P3HT film, (b) a 80% HT P3HT film treated with AgOTf, (c) a neutral 0% HT P3HT film, and (d) a 0% HT P3HT film treated with AgOTf.](image-url)
The effectiveness of silver(I) doping of poly(3-hexylthiophene)s with varying HT dyad content may be visualized by a schematic of the energy of each redox couple as shown in Figure 3.10.

![Energy Diagram](image)

**Figure 3.10**: Schematic representation of the standard reduction potential for Ag⁺ and oxidized P3HT with varying dyad content (100%HT, 80%HT, and 0%HT).

### 3.3.6 Solvato-Controlled Doping of Other Conjugated Polymers

The solvato-controlled doping process is widely applicable, and is not limited to alkyl-substituted poly(thiophene)s. Figure 3.11 shows a series of UV-vis absorption spectra which demonstrate the stabilizing effect of a coordinating ligand on the oxidation state of polyaniline (PANI) when exposed to AgOTf.
**Figure 3.11:** UV-vis absorption spectra showing the stabilizing effect of the addition of pyridine added to a n-methyl pyrrolidinone (NMP) solution of PANI and AgOTf. **a)** a pristine PANI solution, **b)** PANI solution containing 10 % (vol.) pyridine and 0.5 equivalents AgOTf, and **c)** PANI solution with 0.5 equivalents of AgOTf.

Upon addition of 0.5 equivalents of AgOTf (with respect to aniline repeat units) the absorption spectrum for polyaniline changes from that described by curve (a) to that depicted by curve (c), in which the broad absorption at 640 nm has decreased in intensity and a new band has appeared at 430 nm. The new absorbance at 430 nm and the peak emerging above 800 nm have been attributed to radical cations located on the nitrogen, and within the aromatic ring of polyaniline, respectively. The species believed to be responsible for these new absorptions are shown in Figure 3.12.76 The spectral changes, and therefore the oxidation of PANI, are clearly inhibited by the introduction of pyridine to this
system as demonstrated by the similarity of curve (b) to the absorption spectrum for the pristine polymer.

![Chemical structures]

**Figure 3.12**: Radical cations in PANI responsible for the electronic absorptions at a) 430 and b) >800 nm.

Ether-substituted poly(thiophene)s, such as poly(3-butoxythiophene) (P3BuOT), can also be doped by the solvato-controlled doping method. As shown in Figure 3.13, the UV-vis spectra showing solvato-controlled doping of P3BuOT are similar to those obtained for P3ATs. For any of these three polymers (P3HT, PANI, and P3BuOT), the solvent and volatile ligands can be removed in a single casting step to provide electronically conductive films.
Figure 3.13: UV-vis absorption spectra for (a) a CHCl₃ solution of P3BuOT with 25 mol% AgOTf and 10 vol% pyridine, and (b) a conductive film cast from this solution.

3.4 Lifetime of Doped Films

Oxidation of conjugated polymers by Lewis acids, or other means, results in electrically conducting films that exhibit finite lifetimes of conductivity. In the case of thin films of doped P3HT, the decay of conductivity may often be approximated by a first order rate law of the form:

\[
\frac{d \sigma}{dt} = -k \sigma \tag{8}
\]
where $\sigma$ represents conductivity, and $k$ is a constant. Integration of the rate equation (with respect to time) results in an expression for the conductivity as a function of time:

$$\ln \left( \frac{\sigma}{\sigma_0} \right) = -kt$$  \hspace{1cm} (9)

where $\sigma$ and $\sigma_0$ represent the conductivity (S/cm) at time $t$ and at the doping time, respectively. The half-lifetime of the conductivity ($t_{1/2}$) is defined as the time required for the conductivity to decrease by a factor of 2. It is obtained from the slope of the $\ln(\sigma/\sigma_0)$ vs. time plot, and is calculated via equation 10:

$$t_{1/2} = \frac{\ln(0.5)}{\text{slope}}$$  \hspace{1cm} (10)

Figure 3.14 shows a series of lifetime plots for films of regioregular P3HT when oxidized by a) the solvato-controlled doping technique using AgOTf, b) immersion in a FeCl$_3$ solution, and c) immersion in a nitrosonium triflate (ONOTf) solution. These films were stored under an ambient atmosphere and in the absence of light.
AgOTf-Doped, \( t_{1/2} = 117 \) h
FeCl₃-Doped, \( t_{1/2} = 8 \) h
ONOTf Doped, \( t_{1/2} = 3 \) h

**Figure 3.14:** Lifetime plots for 100 nm P3DDT films doped by a) AgOTf, b) FeCl₃ and c) ONOTf.

Using equation 4, the half-lifetimes for AgOTf doped P3DDT films (100 nm thick) have been estimated at 117 hours, or almost 15 times larger than films doped by FeCl₃ (8 hours). Half-lifetime values obtained for P3HT films doped by immersion into an oxidizing AgOTf solution are consistently smaller than those observed for films of the same polymer cast and oxidized in a single step by the solvato-controlled doping method. The stability of oxidatively doped polymer films is one of the major aspects currently inhibiting their widespread application and commercialization. The enhanced stability of silver triflate doped films represents a significant improvement, and an examination of the factors responsible for this stability may prove useful in the design of new polymer-dopant systems. Four possibilities come to mind when considering the differences between
conventionally-doped and silver(I)-doped P3HT, these include: i) the reduction potential of the oxidizing agent; ii) the difference in counter-ions (OTf⁻ vs. FeCl₄⁻); iii) the presence of metallic silver particles in the AgOTf-doped films; and iv) the enhanced morphology of films doped by the solvato-controlled doping method.

3.4.1 In-situ Conductivity of P3HT

The standing potential of P3HT films doped by AgOTf and FeCl₃ were measured against a Ag/AgCl reference electrode in a 0.1 M chloroform solution of tetrabutylammonium trifluoromethanesulfonate (section 2.3.3.5) and were found to be +0.80 V and +1.0 V, respectively. This difference in standing potential is significant and reproducible, and the two doping agents produced films of distinctly differing stability. It was therefore necessary to determine whether the doping potential (i.e. the potential to which a polymer film is oxidized) has a significant impact on the lifetime of conductivity. The potential region in which P3HT is electrically conductive was measured by an in-situ technique. Polymer films would later be oxidized to potentials within this region and their stability would be determined.
The resulting graph demonstrates that P3HT attains a maximum conductivity when oxidized to potentials greater than, or equal to, +0.55 V (Ag/AgCl). This plateau region encompasses the potentials exhibited by P3HT films doped by both AgOTf and FeCl3; furthermore, the conductivities of the two films are similar. To determine whether the applied potential strongly affects lifetime, films of P3HT were oxidized to potentials which spanned this region, their UV-vis spectra were collected, and their conductivities were monitored over time.
3.4.2 Doping Level at Various Applied Potentials

Figure 3.16 shows the evolution of the UV-vis absorption spectrum for a regioregular P3HT film oxidized at potentials ranging from +0.40 to +1.00 V (Ag/AgCl). From this data, an increase in the applied potential results in a decrease in intensity for the \( \pi \rightarrow \pi^* \) absorption at 557 nm and an increase in the intensity of the bipolaron absorption at 840 nm. Thus, the concentration of bipolaron charge carriers is correlated to an increase in the applied potential.

![Figure 3.16: Evolution of UV-vis absorption spectrum of a 95% HT P3HT film doped at various potentials (vs. Ag/AgCl) in a 0.1 M LiOTf/CH\(_3\)CN solution.](image)

Figure 3.17 shows the change in the absorbance due to changes in the concentrations of the neutral (557 nm) and oxidized segments (840 nm) present in a regioregular P3HT film as the applied potential is increased. For both
species, the largest rate of change occurs between +0.4 and +0.5 V (Ag/AgCl). The absorbance, i.e. concentration, of bipolaron charge carriers (840 nm) is seen to level off after this point, thus explaining the plateau in the conductivity observed for P3HT in this potential region. From these results, it seems likely that the application of potentials beyond +0.55 V results mostly in capacitive charging of the polymer, rather than further oxidation. Also, since the absorbance (concentration) due to bipolarons actually decreases slightly at applied potentials greater than +0.8V, it appears that over-oxidation or quenching of charge carriers is occurring beyond this point.

Figure 3.17: Absorbance due to the a) $\pi \rightarrow \pi^*$ (556 nm), and b) bipolaron (840 nm) species in a regioregular P3HT film doped in 0.1 M LiOTf/CH₃CN at applied potentials ranging from 0.0 to +1.0V (Ag/AgCl).
3.4.3 Lifetimes of Electrochemically Doped P3HT Films

Figure 3.18 shows the decay of the normalized conductivity vs. time for films of regioregular P3HT when doped to +0.75V with the triflate anion. The non-linear decay in conductivity illustrates that either a multi-order reaction, or several decay mechanisms affect the net conductivity of a doped P3HT film, and makes direct interpretation of the data difficult. In fact, this initial loss in conductivity has been previously observed in poly(3-methylthiophene) films electrochemically doped with the triflimide anion ((CF₃SO₂)₂N⁺). Raman spectra of these triflimide-doped films showed that surface de-doping was rapid (for periods up to one month) and is the source of this initial loss of conductivity. It is possible that the initial loss in conductivity in these triflate-doped P3HT films is caused by the same effect.

![Figure 3.18: Decay of the normalized conductivity in regioregular P3HT doped at +0.75 V (Ag/AgCl) with the triflate anion.](image)
From Figure 3.18, there are two distinct time frames during which the decay in conductivity appears to follow first order behavior. A measure of the stability in each of these linear regions is approximated by the half-lifetime of the conductivity ($t_{1/2}$, equation 3.3) for each of these two regions. This is calculated from the slope of each linear region as previously described in Section 3.4. Figure 3.19 shows a plot of $t_{1/2}$ versus the applied potential for triflate-doped P3HT films, which demonstrates that there is little sensitivity to the doping potential for the two linear regions. From the positive slope of the top linear fit, there appears to be a small gain in long-term stability with greater applied potentials while the negative slope of the bottom line indicates that short-term stability is affected in the opposite manner. These small gains (or losses) in stability are, however, negligible when compared to the large increase in stability obtained when P3HT films are doped by silver triflate. Thus, it is concluded that the applied potential has little effect on the stability of an electrically conductive P3HT film.
Figure 3.19: Half-lifetimes (of conductivity) for thick P3HT films electrochemically doped with LiOTf in acetonitrile to various applied potentials for a) short-term stability and b) long-term stability.

Since the applied potential appeared to have little effect on the stability of doped films, the differences between electrochemically and chemically oxidized films were investigated. Using the same counter-ion, trifluoromethanesulfonate (OTf$^-$), P3HT films electrochemically oxidized in the presence of lithium triflate were found to exhibit less stability than films of the same polymer oxidized by the nitrosonium cation (NO$^+$) from a solution of ONOTf, and both of these methods produced films of much lesser stability than AgOTf. Wang and Rubner reported a
similar observation for the stability of P3HT films when chemically doped from a solution of FeCl₃, compared to those electrochemically doped with Bu₄N⁺FeCl₄⁻.⁴³

The difference in stability between chemically and electrochemically oxidized films may not be entirely unexpected since the final compositions of the electrochemically doped films are not the same. Unlike P3HT films oxidized electrochemically or chemically by FeCl₃, oxidation by the nitrosonium ion is a clean reaction. It has been found that nitrosonium salts commonly react with aromatic systems (via a single electron oxidation reaction) to produce nitric oxide and radical cations, the latter of which have been isolated as their salts.⁷⁷ This reaction is generalized as:

\[
\text{Ar} + \text{NO}^+\text{BF}_4^- \xrightarrow{\text{CH}_3\text{CN}} \text{Ar}^{++}\text{BF}_4^- + \text{NO}_{(g)}
\]

Therefore, the lack of stability found in films oxidized by nitrosonium triflate most likely is not caused by any side reactions with by-products from the doping reaction. The 100 nm silver clusters are the only remaining possible source of the enhanced stability found in silver-triflate doped P3HT films.
4. **Conclusions**

In this work, silver triflate was used for oxidizing conjugated polymers to produce conductive polymer films by a new process called solvato-controlled doping. Unlike most other approaches, this method provides electrically conductive polymer films from a single solution, via a single step. Solvato-controlled doping is based on the temporary passification of an oxidizing agent (e.g. silver(I)) by coordinating ligands (e.g. pyridine). The coordinating ligands decrease the reduction potential of the oxidant sufficiently, so as to make the redox reaction with the polymer thermodynamically unfavorable. Thus, the oxidant solution may be mixed with a solution of the conjugated polymer, and the polymer remains neutral and soluble. Upon evaporation of the ligands, the redox reaction becomes favorable, and the oxidized, electrically conductive polymer film results. The resulting films were structurally sound and free of cracks.

Solvato-controlled doping with silver triflate proved successful for other conjugated polymers which included poly(3-hexylthiophene), poly(3-dodecylthiophene), poly(3-butoxythiophene), and polyaniline. The resulting electrical conductivity in the poly(3-alkylthiophene) films was much more persistent and environmentally stable than in films oxidized by conventional dopants like iodine or ferric chloride. Silver(I)-oxidized P3AT films exhibited lower standing potentials than films oxidized by these other reagents. While keeping the counter-ion the same, the effect of the doping potential on the lifetime of conductivity in these films was investigated. There was no observed correlation
between these two parameters. Transmission electron microscopy indicated that silver(I)-doped P3AT films contained 100 nm clusters of smaller (10 nm) silver particles. Nitrosonium triflate solutions were then used to dope polymer films by immersion. The resulting films were almost 40 times less stable than silver triflate doped films. Since all other parameters were identical (and since the doping potential had little effect), the 100 nm silver clusters are proposed as the source of enhanced stability in these films.
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