AN ABSTRACT OF THE THESIS OF

Chelsea A. McConnell for the degree of Honors Baccalaureate of Science in Chemical Engineering presented on May 23, 2014. Title: Functionalization of Poly(3-hexylthiophene-2,5-diyl) for Nanoelectromechanical Devices.

Abstract approved: _____

Timothy M. Swager

Innovative nanoelectromechanical switches (NEMS) have the prospects to reduce device actuation voltages as compared to traditional semiconductor devices. Current research on NEMS seeks to avoid irreversible adhesion at the nanoscopic level, which results in device failure. Minimizing leakage currents and increasing device longevity are additional goals of this approach. The switches derive their switching by modulating a tunneling current through a nanometer-scale gap of an organic thin film between two electrodes. Compressing the film decreases the tunneling gap and creates an increase the current; conversely, the restoring force of the compressed (strained) organic layer turns off the switch. This squeezable switch has been termed a "squitch".[1] The properties of the squitch are highly dependent on the organic material sandwiched between the electrodes. Modified poly(3-hexylthiophene-2,5-diyl) (P3HT) is being explored for the design of this organic layer due to its conductive properties and compatibility with gold electrode surfaces. Recent and ongoing work in the Swager group has resulted in a simple, two-step, post-polymerization procedure for the modification of P3HT. This procedure involves bromination of P3HT with N-bromosuccinimide followed by lithium-halogen exchange and quenching of the anion with electrophiles. This method was used to create

ketone-modified P3HT and also allows for a variety of functional groups to be installed

by varying the electrophile. Several functional groups including long, branched, and

unsaturated alkyl chains or poly(ethylene) glycol groups were examined in order to adjust

the electronic and packing properties of P3HT, to achieve the desired mechanical

properties for compression, and to reduce the actuation (switching) voltage below one

volt.

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Functionalization of Poly(3-hexylthiophene-2,5-diyl)

for Nanoelectromechanical Devices

by

Chelsea A. McConnell

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Chelsea A. McConnell, Author

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for Nanoelectromechanical Devices

1. Introduction

High performance physical switches, if made sufficiently small and efficient, offer advantages over conventional semiconductor switches. One class of the switches are those that are characterized as nanoelectromechanical (NEM) switches. These devices currently display near-zero leakage currents.[1] This feature is desired because it saves energy and produces environmentally friendly technology that could have widespread utility. An enabling feature of these devices is their abrupt switching behavior. The trade-off is the actuation voltages, or "turn-on" voltages, for NEM switches are high and exceed conventional semiconductor devices that are limited by the thermodynamics of the electrons. Device components can also experience permanent adhesion, or stiction, which causes device failure.[1]

NEM switches have many desired applications for low power electronics. Reducing actuation voltage and preventing stiction while maintaining the other desired features of these switches will enable significant technological progress in this area. A novel NEM switch, termed a "squitch," with these characteristics has been proposed. This device facilitates tunneling current through a nanometer-scale gap occupied by an organic thin-film inserted between two electrodes.[1] The success of this device is dependent on improvements in its performance and to this end we were interested in the development of improved deformable electro-active polymers for use as the active organic layer.

Poly(3-hexylthiophene-2,5-diyl) (P3HT) is a semiconducting polymer that has found applications involving organic field effect transistors (OFETs) and organic solar cells (OSCs).[2] Its success in these areas has made it an ideal candidate for this application.

1.1 Objective and Thesis Statement

The development and modification of electro-active polymers for use in novel NEM switches is necessary for this technology to progress. However, an appropriate synthesis method must be developed to functionalize such polymers and thereby allow their electromechanical properties to be tuned. The objective of this project is to examine the feasibility of a post-polymerization procedure for the modification of P3HT via bromination of P3HT with N-bromosuccinimide followed by lithium-halogen exchange and quenching of the anion with an electrophile.

2. Background

Most NEM switches are turned on when there is direct contact between two electrostatically attracted electrodes. The switch is turned off when the applied electrostatic force is released and the top electrode breaks contact with the disparate electrode. Stiction occurs when the spring restoring force is not strong enough to overcome the adhesion force. This causes the two electrodes to remain in contact (switched on) leading to device failure. The squitch is considered a novel NEM device because instead of direct contact it employs a tunneling current through a nanoscale organic thin film placed between two electrodes. An applied voltage is used to create an attractive electrostatic force that compresses the organic thin film reducing the tunneling gap and allowing for an exponential increase in current. The switch is turned off when the compression is released and the organic layer is restored to its original width.[1]

The four main goals of this technology are to: reduce device failure due to stiction, minimize leakage current, reduce the actuation voltage below one volt, and provide a nanosecond switching time between on and off states. The use of the organic layer to control/mediate a tunneling current versus direct contact between the two opposing electrodes will allow these goals to be achieved and for NEM switches to compete with traditional semi-conductor based technologies.[1]

2.1 Organic Thin Film Requirements

The organic thin film must be compressible to provide the restoring force to turn off the squitch. It must also be composed of an insulating material to reduce leakage current in the off-state.[1] A theoretical analysis shows that to achieve the goal of a one volt actuation voltage, a 4 nm thick layer compressed by 50% to create a 2 nm tunneling gap is required, as seen in *Figure 1*.[1] Controlling the thickness of the film at the nanaoscale is consequently required. Materials that form self-assembled monolayers (SAMs) meet both of these requirements. SAMs are formed when molecular constituents adsorb from solution onto the surface of a solid substrate and organize into crystalline or semicrystalline structures.[3] This process occurs spontaneously because the constituents lower the interfacial free energy between the substrate and environment. The constituents are functionalized to have a specific substrate affinity.[3] Thiolated SAMs, particularly alkanethiols and dithiols, are of interest for this application because they have an affinity for gold electrode surfaces.[1] Alkanethiols are also of interest because they have a large energy gap between the highest occupied molecular orbital (HOMO) and the lowest unoccupied molecular orbital (LUMO), making them good insulators.[1] The conduction mechanism through molecular junctions of this group of molecules is direct tunneling which is the desired charge transfer mechanism for squitch devices.[1] Success in recent devices has been achieved using as poly(ethylene glycol)-dithiol (PEGdithiol) as shown in *Figure 2(a)*.
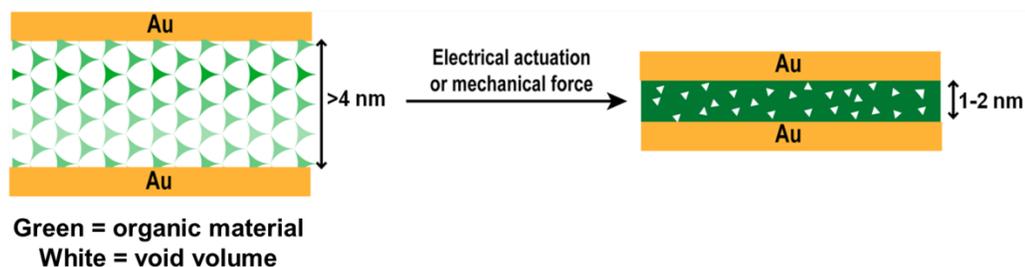
Green = organic material
White = void volume

Figure 1: Current flow through the device is controlled by the tunneling distance through a nanoscale self-assembled organic layer. The distance between electrodes decreases when the structure is mechanically compressed and tunneling occurs. Reducing actuation voltage below one volt for organic thin films composed of alkanethiols or diothiols requires a 50% compression from 4 nm to 2 nm.[1]

The dominant attractive forces between the two electrodes are van der Waals forces due to the nanoscale sized gap.[1] Quantum mechanical forces, such as Casimir forces, are not significant at this scale.[1] Overcoming the attractive forces is required for the squitch to turn off when the electrostatic force is removed. Young's modulus, the ratio of normal stress to normal strain that determines the spring constant of a material, is the material property of most interest concerning this requirement.[4,1] The spring constant directly relates to the elastic force the material exerts on the electrodes when compressed. The Young's modulus must be high enough to exceed the van der Waals forces to turn off the device, however based upon theoretical analysis it has been determined that a low Young's modulus is necessary to achieve the target actuation voltage.[1] This tradeoff results in a narrow range of acceptable values for the Young's modulus in order to achieve both of these goals.
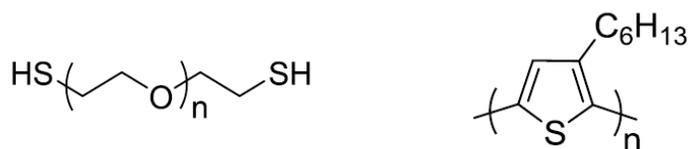
Figure 2: (a) Structure of PEGdithiol; success in recent devices has been achieved with this molecule. Dithiols are of interest for this application because they have an affinity for gold electrode surfaces.[1] (b) Structure of P3HT. P3HT is a semiconducting polymer that has large carrier mobilities due to its π-conjugated polythiophene backbone.

2.2 Investigation of Poly(3-hexylthiophene-2,5-diyl) (P3HT)

P3HT is a semiconducting polymer that is widely used in electronic applications. It belongs to a class of semicrystalline polymers referred to as regioregular poly(3-alkyl thiophene)s (P3AT)s. It is of particular interest for applications in squitch technology due to its high carrier mobilities, stability, precedent use in devices, and tunable Young's modulus.[2] P3HT is also highly soluble in chloroform which is desirable for solution processing methods via spin coating or inkjet printing. As noted earlier P3HT is conductive as opposed to insulating, which will allow for larger film thicknesses because electrons can be transferred from polymer to polymer when compressed. Larger thicknesses are conducive to standard device fabrication techniques, such as spin coating.

The structure of P3HT is shown in *Figure 2(b)* and is composed of a π-conjugated polythiophene backbone. The hexyl side chains account for the observed solubility. The chemical differences between the conjugated polythiophene backbone and the alkyl side chains results in partitioning of the structure at the molecular level. This results in a self-assembled layered structure in which the π-stacked polythiophene backbone alternates

with alkyl side chains.[2] The semicrystalline structure of P3HT also produces a secondary lamellar structure characterized by the alternation of crystalline and amorphous domains.[2]

Two crystal structures have been observed regarding P3ATs and are referred to as Forms I and II. These two forms differ in the side chain conformation and are characterized by different layer periodicities.[2] The layer spacing is dependent on the number of carbon atoms on the side chain.[2] Both forms are a result of processing techniques. Form 1 is a result of casting and spin coating with chlorinated solvents and Form II is created in other thin film processing techniques.[2] A strong dependence between the charge transport capabilities and the morphology/crystallinity of P3HT films has been reported.[5,6] Processing conditions for low molecular weight films have been observed to modify the mobilities up to a factor of 100.[6] Controlling the carrier transport of such films is important for successful squitch device fabrication. One study has found that the morphology and crystallinity of P3HT films can also be significantly altered by varying the processing solvent.[7] Processing from solvents with high boiling points in particular, are known to improve the charge mobility because low-boiling solvents evaporate quickly and limit the crystallization time during the spin-coating process. The use of 1,2,3-tricholorbenzene (TCB) was observed to improve the mobility by a factor of 10 compared to chloroform.[7] Significant improvements were also observed with the use of cyclohexylbenzene.[7]

The Young's modulus was emphasized earlier for its importance in providing the elastic restoring force to turn off the device. Therefore, the primary goal of this functionalization is to modify the Young's modulus of P3HT to achieve ideal "squitching" properties while

simultaneously lowering the actuation voltage. This previous research, however, also highlights the importance of increasing the solubility of P3HT to improve charge transport and processing capabilities. Achieving both of these properties is ideal for applications in NEM switches.

2.3 Reaction Scheme

A simple, two-step, post-polymerization procedure for the modification of regioregular P3HT is shown in *Figure 3*. The first step involves bromination of P3HT with N-bromosuccinimide followed by lithium-halogen exchange and quenching of the anion with an electrophile to produce ketone-modified P3HT. The bromination of P3HT to create poly(3-bromo-4-hexylthiophene) (P3B4HT) has been well studied and has resulted in yields up to 99%.[8] Electrophilic substitution occurs at the 4th position of the thiophene ring which is the only unsaturated center with a C-H bond.. This reaction is also enhanced by the electron donating effect of the 3-alkyl side chain.[8] Aldehydes and anhydrides were chosen as electrophiles to react with the generated lithiated-P3HT because they are readily available and will offer opportunities for novel modified P3HTs. *Figure 3* shows the formation of ketone-modified P3HT using a generic anhydride.

Figure 3: The Swager group has developed a simple, two step, post-polymerization procedure for the modification of P3HT. This procedure involves bromination of P3HT with N-bromosuccinimide followed by lithium-halogen exchange and quenching of the anion with an electrophile. An anhydride is used in this scheme to create ketone-modified P3HT.

3. Materials and Methods

All chemicals were purchased from Aldrich, Acros, and TCI unless otherwise noted. P3B4HT was synthesized according to literature procedures.[8] To a flame dried flask, P3B4HT (10 mg, 0.0412 mmol, 1 equiv.) and THF (5 mL, dry) were added. The P3B4HT was allowed to dissolve and then cooled to -78 ºC with a dry ice and acetone bath. After 20 minutes, n-butyl lithium (0.3 mL of 1.6 M solution, 0.412 mmol, 10 equiv.) was added to the mixture. A color change from yellow to red was observed. After 1 h, the mixture was removed and allowed to warm for 30 min, at which point the electrophile (100 equiv.) was added. The reaction mixture was stirred overnight.

3.1 Electrophile Scope

The anhydrides investigated include acetic anhydride, maleic anhydride, isovaleric anhydride, hexanoic anhydride, 1,8 napthalic anhydride, benzoic anhydride, 4-methylbenzoic anhydride, 4-methoxybenzoic anhydride, 4 fluorobenzoic anhydride, and 4-(Trifluoromethyl) benzoic anhydride. Other promising electrophiles include: benzaldehyde, ethylene sulfide, di-tert-butyl dicarbonate, trimethylsilyl (TMS) chloride, and triisopropylsilyl (TIPS) chloride.

Characterizable products isolated from reactions with acetic anhydride, maleic anhydride, TMS chloride, and TIPS chloride were purified by precipitation in cold methanol. All benzoyl-modified P3HT products were washed five times with a 20% sodium hydroxide solution, dried over magnesium sulfate, and precipitated in cold methanol.

Compounds were characterized by IR (Thermo Scientific equipped with an ATR probe) and NMR spectroscopy (Bruker Avance 400 MHz). Photoluminescence (Horiba) was performed on all benzoyl-modified P3HT in order to conduct a para-substituent study.

4. Results and Discussion

Our initial attempts at the modification of P3HT via the strategy in **Figure 3** employed acetyl chloride. Unfortunately, no carbonyl peaks were observed in the IR spectrum of the product and the methyl peak was absent in the NMR spectrum. When the electrophile was switched to acetic anhydride, analysis of the polymer product by IR and NMR suggested successful modification of P3HT.

4.1 Anhydride Scope

The reaction between acetic anhydride and P3B4HT resulted in a red-brown compound with limited solubility in chloroform. The IR spectrum is shown in **Figure 4** with the carbonyl peak at 1778 cm^{-1}. A 25% conversion was observed. The ^{1}H NMR spectrum is shown in **Figure 5**. Significant NMR peaks include the methyl singlet at 2.79 and the hexyl chain peaks at 2.28, 1.68, 1.32, and 0.88 ppm.
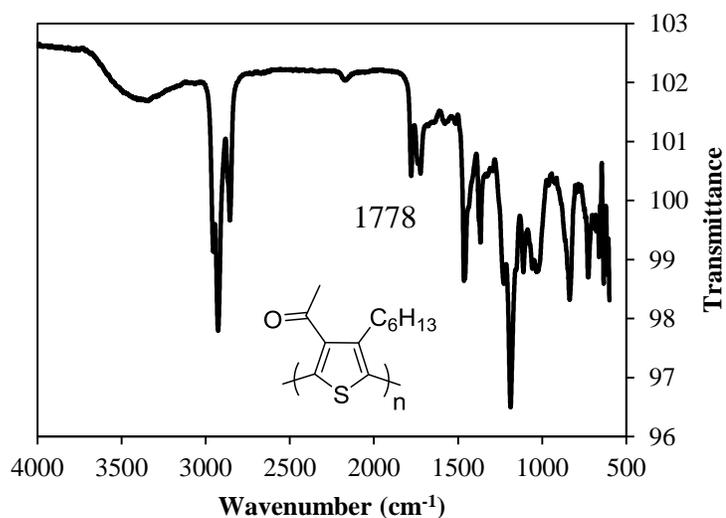
Figure 4: *IR spectra of acetyl substituted P3HT. The carbonyl peak is at 1778 cm^{-1}*
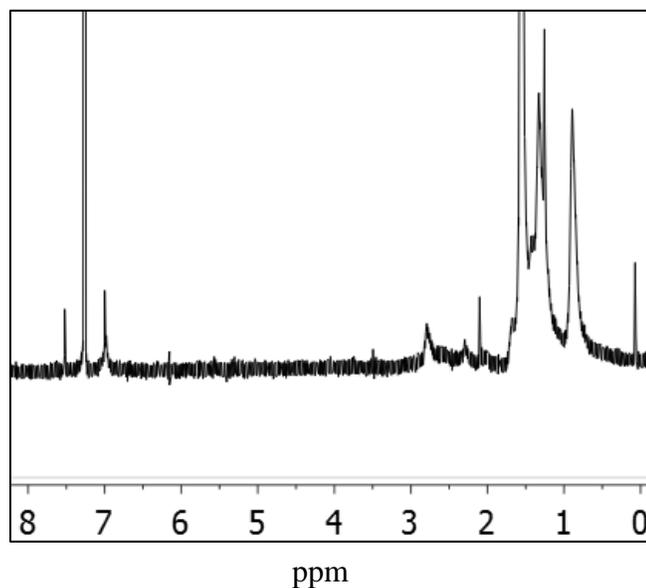
Figure 5: ^1H *NMR spectrum of acetyl substituted P3HT. Significant NMR peaks include the methyl peak at 2.79 and the hexyl chain peaks at 2.28, 1.68, 1.32, and 0.88 ppm.*

Reaction with maleic anhydride also appears to be successful. The IR spectrum is shown in *Figure 6* with a broad OH peak and broad carbonyl peak at 1713 cm^{-1}. This compound was insoluble and therefore an NMR spectrum and accurate conversion could not be obtained.
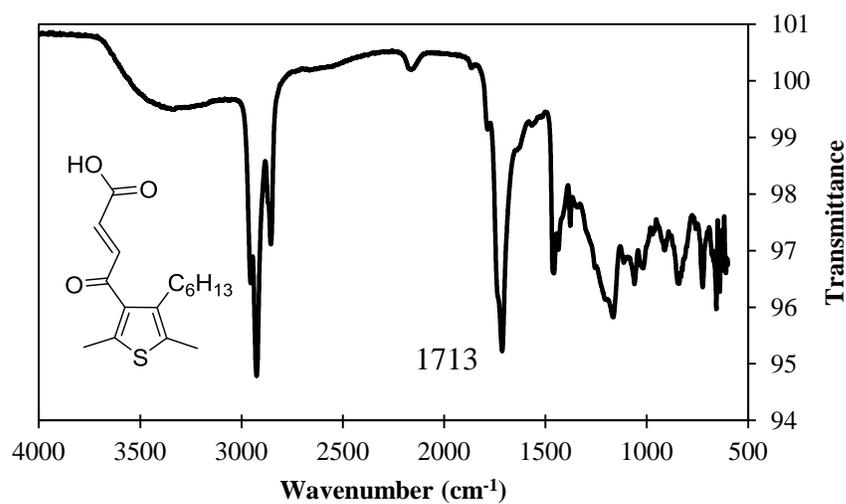
Figure 6: *IR spectra of maleic substituted P3HT. A broad OH peak and broad carbonyl peak at 1713 cm^{-1} were observed.*

4.2 Benzoyl-modified P3HT

Reaction with benzoic anhydride resulted in benzoyl-modified P3HT with 50% conversion. This compound precipitated well in methanol and was highly soluble in chloroform. The IR spectrum is shown in *Figure 7* with the carbonyl peak at 1681 cm^{-1} and aryl stretching peaks at 1203 and 1175 cm^{-1}. The ^{1}H NMR spectrum is shown in *Figure 8.* Significant NMR peaks include aryl peaks at 7.96, 7.52, and 7.37, and hexyl chain peaks at 2.25, 1.25, and 0.84 ppm.
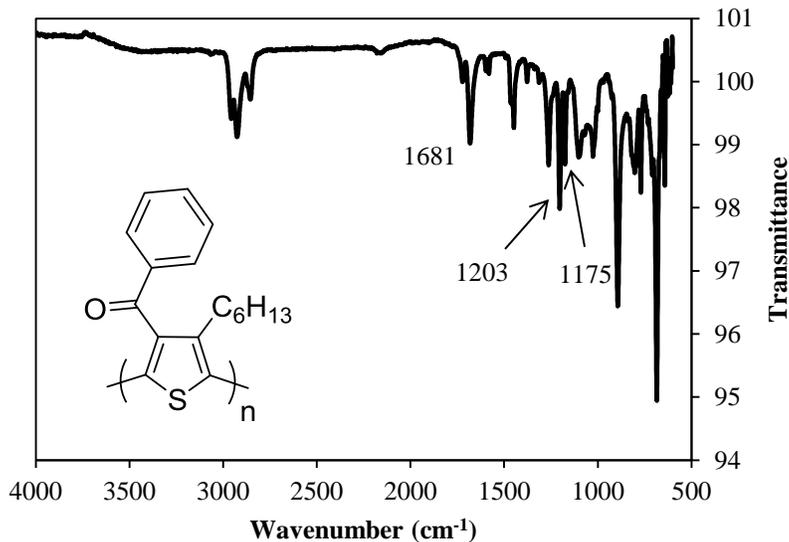
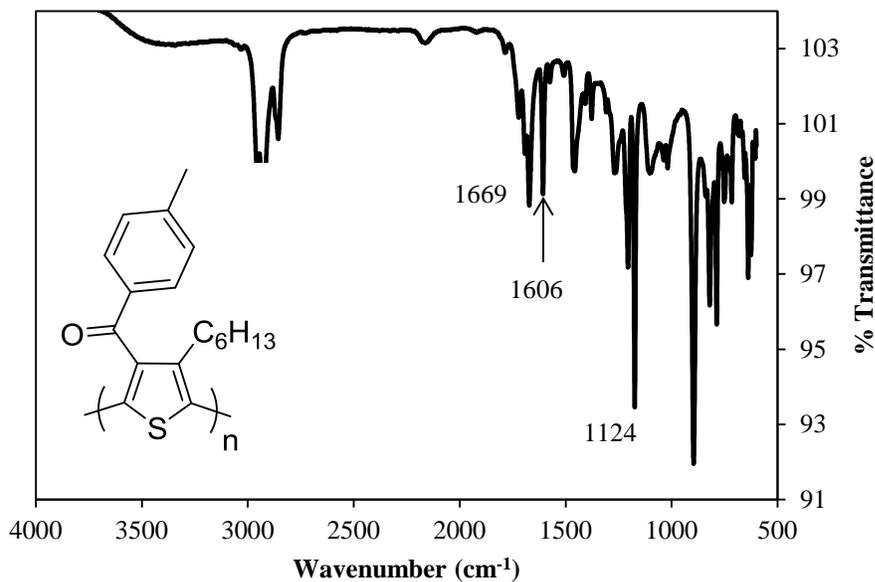*Figure 7: IR spectra of benzoyl-modified P3HT. The carbonyl peak is at 1681 cm^{-1} and aryl stretching peaks are at 1203 and 1175 cm^{-}.^{1}*
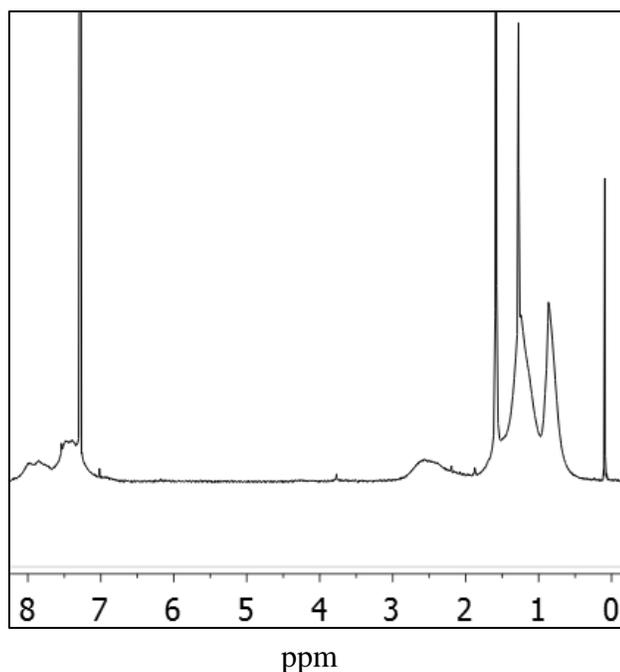
Figure 8: ^{1}H NMR spectrum of benzoyl-modified P3HT. Significant NMR peaks include aryl peaks at 7.96, 7.52, and 7.37, and hexyl chain peaks at 2.25, 1.25, and 0.84 ppm.

The desirable solubility characteristics and simple purification of benzoyl-modified P3HT promoted further investigation into similarly substituted compounds. Benzoic anhydrides with various para-substituents can be easily obtained or synthesized in order to complete a para-substituent study of benzoyl-modified P3HT. This analysis would determine if the electronic properties of P3HT can be modified using this method. The following part of this thesis details the characterization of compounds that were synthesized from this class of anhydrides.

The IR spectrum of methyl-benzoyl-modified P3HT is shown in *Figure 9* with the carbonyl peak at 1669 cm^{-1} and aryl stretching peaks at 1606 and 1124 cm^{-1}. Fifty percent conversion was achieved. The ^{1}H NMR spectrum is shown in *Figure 10* Significant

NMR peaks include aryl peaks at 7.85 and 7.72, the methyl peak at 2.36, and hexyl chain

peaks at 2.58, 1.56, 1.25, 0.84 ppm.

Figure 9: *IR spectrum of methyl-benzoyl-modified P3HT. The carbonyl peak is at 1669 cm^{-1} and aryl stretching peaks are at 1606 and 1124 cm[-].[1]*
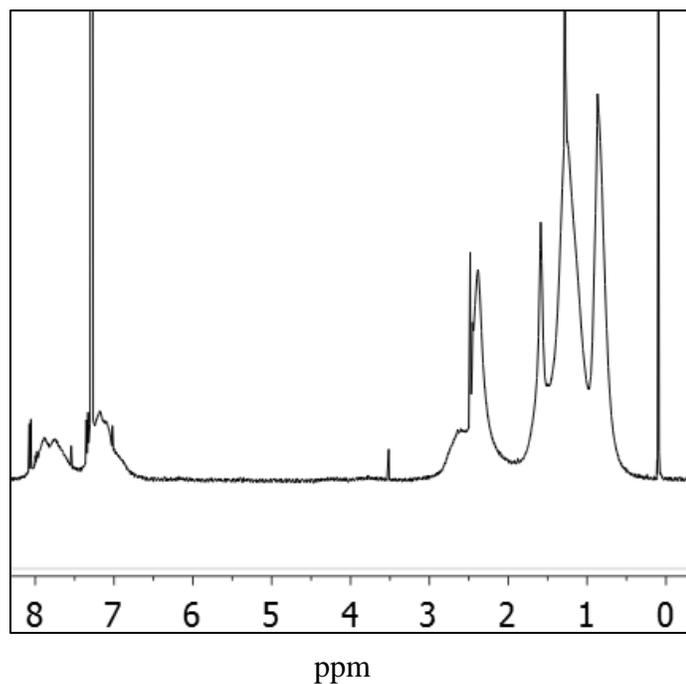

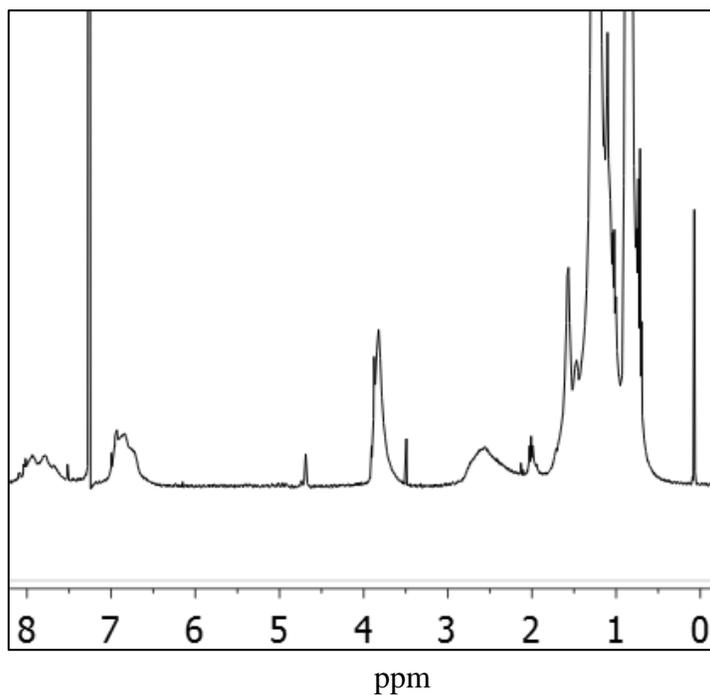***Figure 10:*** *^{1}H NMR spectrum of methyl-benzoyl-modified P3HT. Significant NMR peaks include aryl peaks at 7.85 and 7.72, the methyl peak at 2.36, and hexyl chain peaks at 2.58, 1.56, 1.25, 0.84 ppm.*

The IR spectrum of methoxy-benzoyl-modified P3HT is shown in *Figure 11* with the

carbonyl peak at 1669 cm^{-1}, C-O-C peaks at 1260 and 1039 cm^{-1}, and aryl stretching

peaks at 1601 and 1165 cm^{-1}. Sixty-five percent conversion was achieved. The ^{1}H NMR

spectrum is shown in *Figure 12*. Significant NMR peaks include aryl hydrogen peaks

7.94, 7.79, and 6.83, the methyl singlet at 3.82, and the hexyl chain peaks at 2.55, 1.25,

and 0.84 ppm.
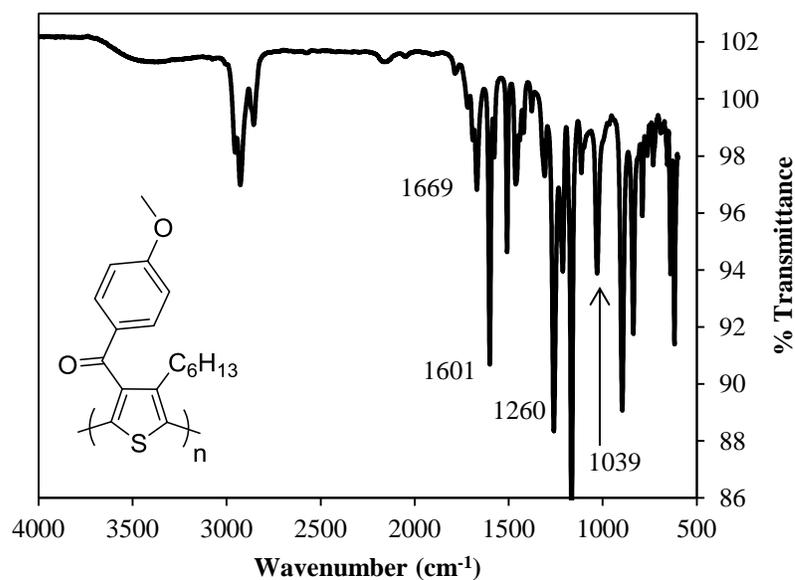
Figure 11: IR spectrum of methoxy-benzoyl-modified P3HT. The carbonyl peak is at 1669 cm^{-1}, C-O-C peaks are at 1260 and 1039 cm^{-1}, and the aryl stretching peaks are at 1601 and 1165 cm^{-1}.

Figure 12: *^{1}H NMR spectrum of methoxy-benzoyl-modified P3HT. Significant NMR peaks include the aryl peaks at 7.94, 7.79, and 6.83, the methyl singlet at 3.82, and the hexyl chain peaks at 2.55, 1.25, and 0.84 ppm.*

The IR spectrum of fluoro-benzoyl-modified P3HT is shown in ***Figure 13*** with the carbonyl peak at 1678 cm^{-1}, aryl fluoride at 1236 cm^{-1}, and aryl stretching peaks at 1599 and 1155 cm^{-1}. Sixty-one percent conversion was achieved. The ^{1}H NMR spectrum is shown in ***Figure 14***. Significant NMR peaks include aryl peaks at 7.99, 7.83, and 7.04, and hexyl chain peaks 2.59, 1.25, 0.83 ppm.
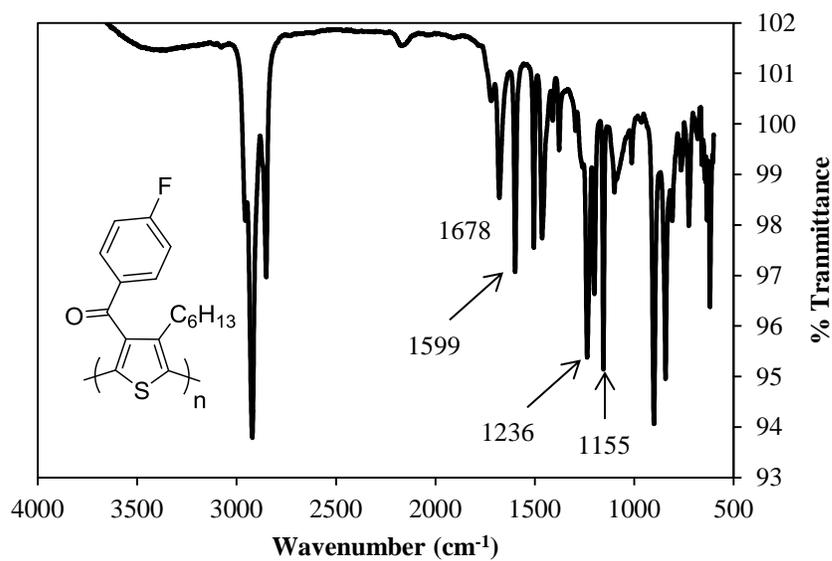
Figure 13: *IR spectrum of fluoro-benzoyl-modified P3HT. The carbonyl peak is at 1678 cm⁻¹, the aryl fluoride peak is at 1236 cm⁻¹, and the aryl stretching peaks are at 1599 and 1155 cm⁻¹.*
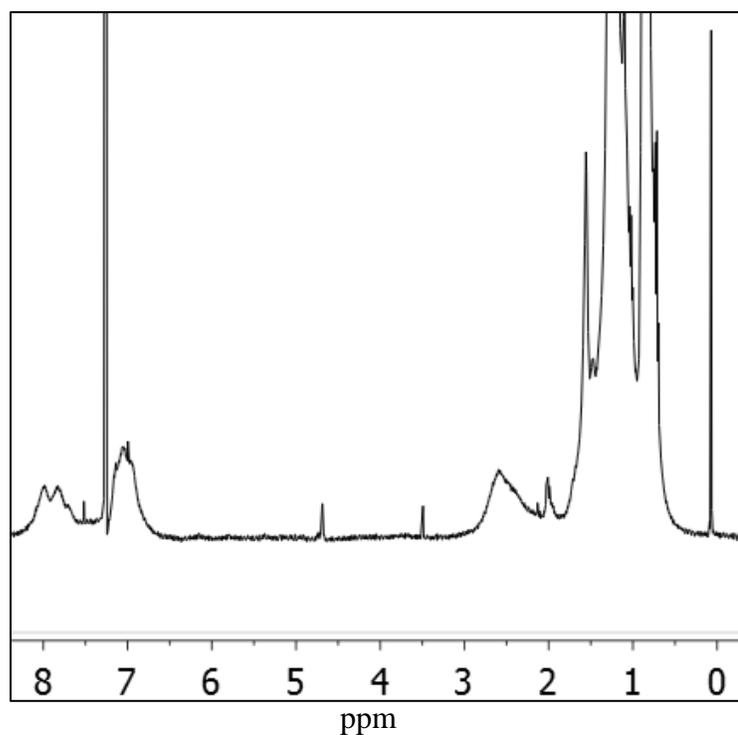

Figure 14: *¹H NMR spectrum fluoro-benzoyl-modified P3HT. Significant NMR peaks include aryl peaks at 7.99, 7.83, and 7.04, and hexyl chain peaks at 2.59, 1.25, 0.83 ppm.*
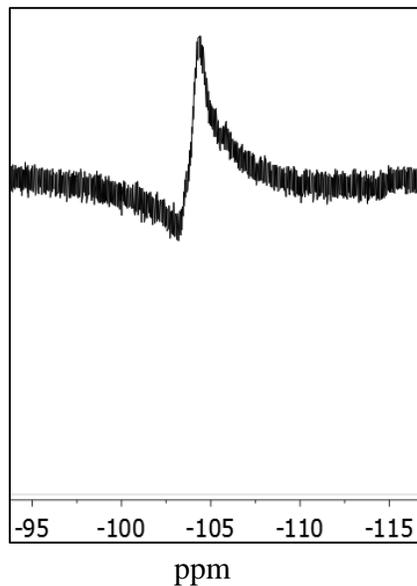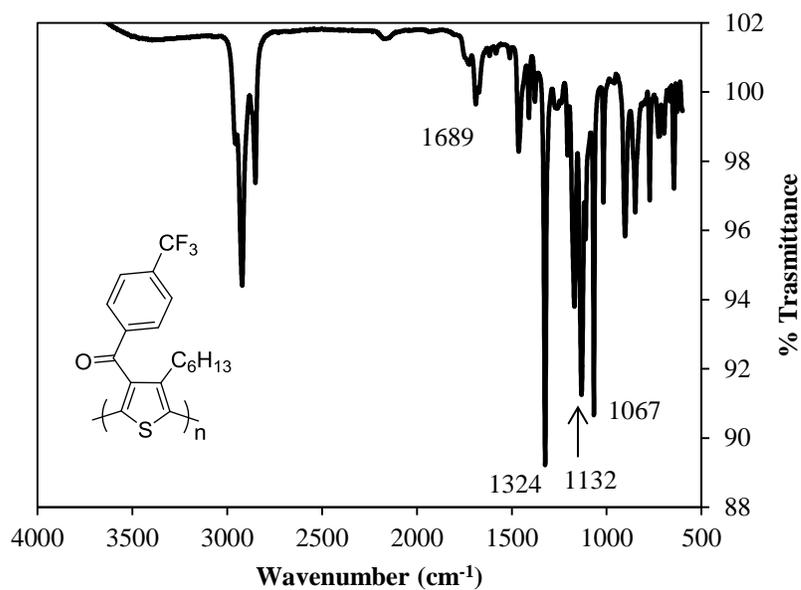
Figure 15: ^{19}F *NMR spectrum of fluoro-methyl-benzoyl-modified P3HT. A singlet at -104.5 ppm is observed.*

The IR spectrum of trifluoromethyl-benzoyl-modified P3HT is shown in *Figure 16* with the carbonyl peak at 1689 cm^{-1}, -CF$_3$ at 1324 cm^{-1}, and aryl stretching peaks at 1132 and 1067 cm^{-1}. Seventy-five percent conversion was achieved. The ^{1}H NMR spectrum is shown in *Figure 17*. Significant NMR peaks include aryl peaks at 7.75 and 7.64 and hexyl chain peaks at 2.59, 1.26, and 0.83 ppm.

Figure 16: IR spectrum of trifluoromethyl-benzoyl-modified P3HT. The carbonyl peak is at 1689 cm^{-1}, -CF_3 is at 1324 cm^{-1}, and the aryl stretching peaks are at 1132 and 1067 cm^{-1}.
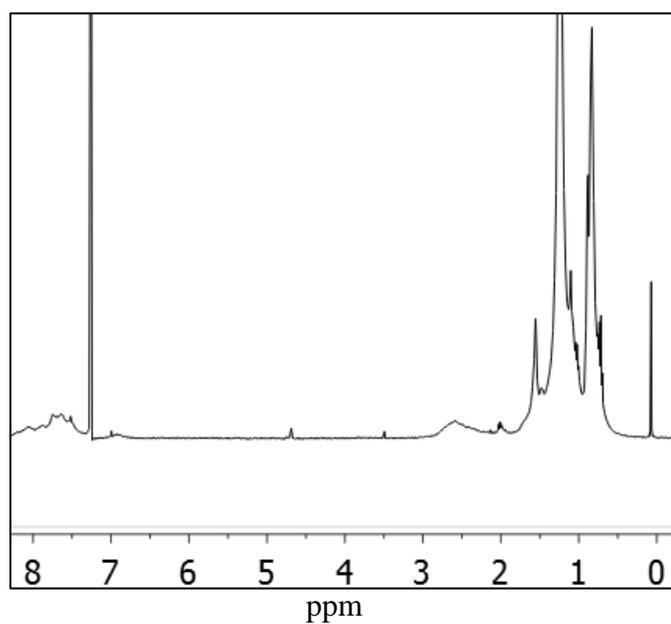

Figure 17: ^{1}H NMR spectrum trifluormethyl-benzoyl-modified P3HT. Significant NMR peaks include aryl peaks at 7.75 and 7.64 and hexyl chain peaks at 2.59, 1.26, and 0.83 ppm.

The ¹⁹F NMR spectrum of this compound is shown in *Figure 18* with a distinctive peak at -62.3 ppm.
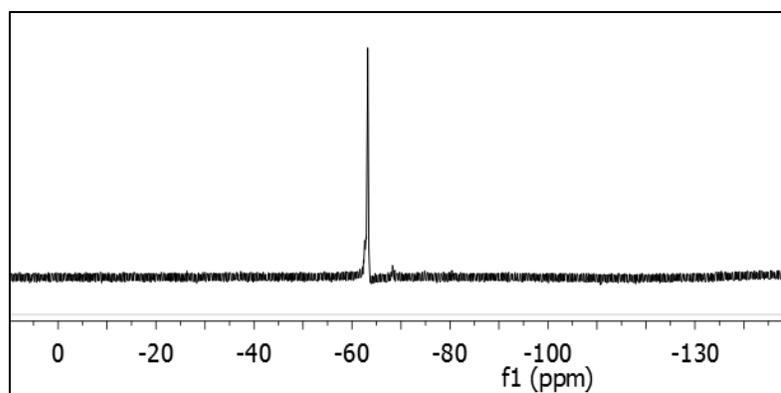

Figure 18: ¹⁹F NMR spectrum of trifluoromethyl-benzoyl-modified P3HT. A singlet at -62.3 ppm is observed.

Elemental analysis was performed on all of these compounds. The results are shown in *Table 1.* The low bromine content indicates the lithium-halogen exchange was successful. All experimental values were more than 5% different than calculated values.

Table 1: *Elemental analysis on benzoyl-modified P3HT. The low bromine content indicates the lithium-halogen exchange was successful. NA indicates the element is not applicable for a particular compound.*

Electrophile	% Cabron	% Hydrogen	% Sulfur	% Bromine	% Fluorine
Benzoic Anhydride	73.57	7.4	NA	NA	NA
4-Methylbenzoic anhydride	70.8	9.5	10.26	0.09	NA
4-Methoxybenzoic anhydride	78.84	10.97	5.41	0.04	NA
4-Fluorobenzoic anhydride	78.48	10.39	5.54	0.06	3.26
4-(Trifluoromethyl) benzoic anhydride	73.06	9.14	4.94	0.07	7.33

4.3 Para-substituent Study of Benzoyl-modified P3HT

The electronics of an aryl ring can be modified by attaching substituents. The electronic

perturbations caused by substituents can be measured using substituent constants, or

sigma parameters commonly used for Hammet plots, according to the substituent

position.[9] A para-substituent study of benzoyl-modified P3HT was conducted to

determine if the electronic properties can be varied by changing the para-substituent. The

electronic properties or modified P3HT compound were assayed by analyzing their IR

carbonyl stretch and photoluminescence spectra. *Figure 19* shows the IR carbonyl stretch

versus the respective sigma para values. The linear trend observed suggests that the
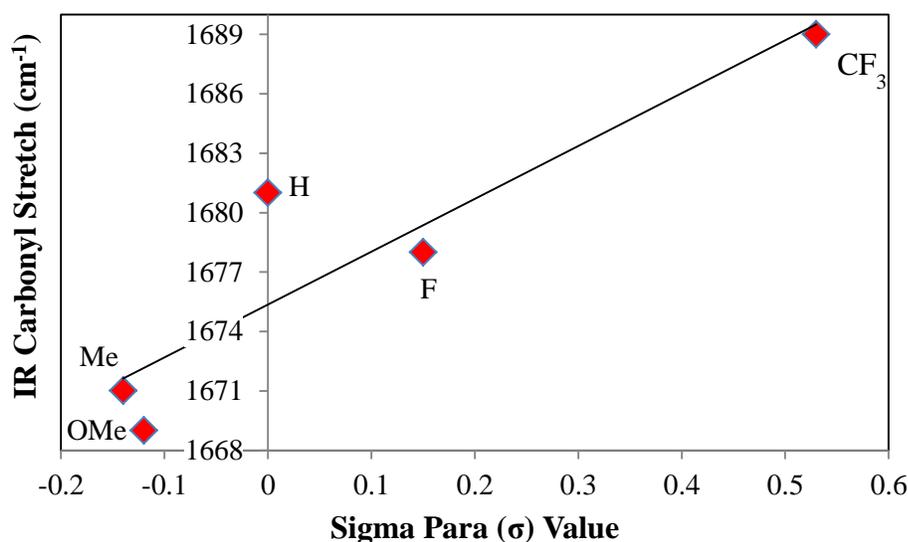
electronic properties could be modified.

Figure 19: Plot of the IR carbonyl stretch of benzoyl-modified P3HT versus the respective sigma para values. A linear trend is observed indicating the electronic properties can be modified by varying the para-substituent.

Figure 20 shows the normalized photoluminescence versus wavelength. The maximum wavelength did not change significantly. Thus, it is proposed that the aryl ring is not in conjugation with the P3HT backbone as shown in *Figure 21 (a)*. Polymer stacking is less likely to occur if the aryl ring is out of plane as compared to *Figure 21 (b)* where the polymer is planar and more prone to stacking. This hypothesis is supported by the observed high solubility and processability of benzoyl-modified P3HT versus acetyl P3HT.
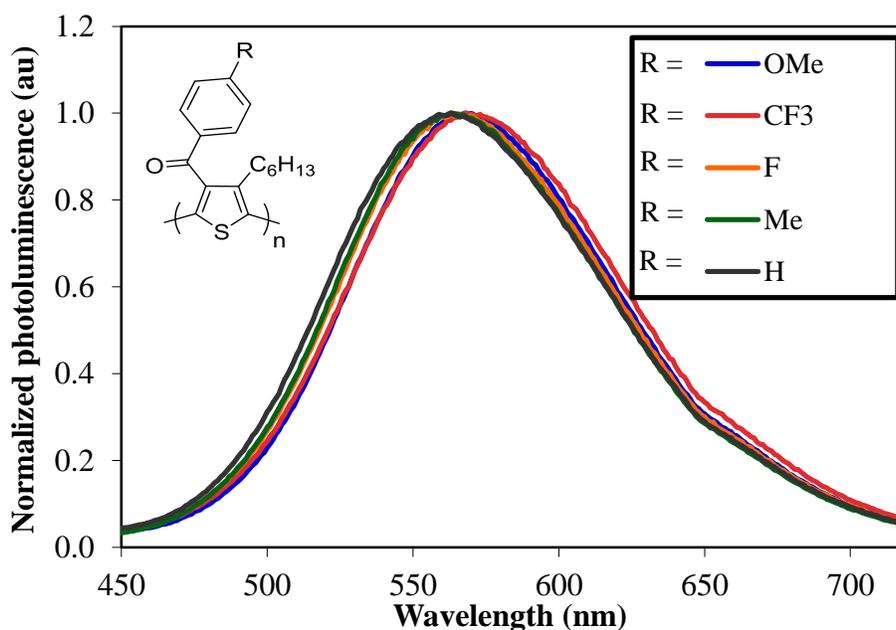

Figure 20: Para-substituent study via photoluminescence of benzoyl-modified P3HT. The potential lack of planarity may explain the small changes observed in maximum wavelength.
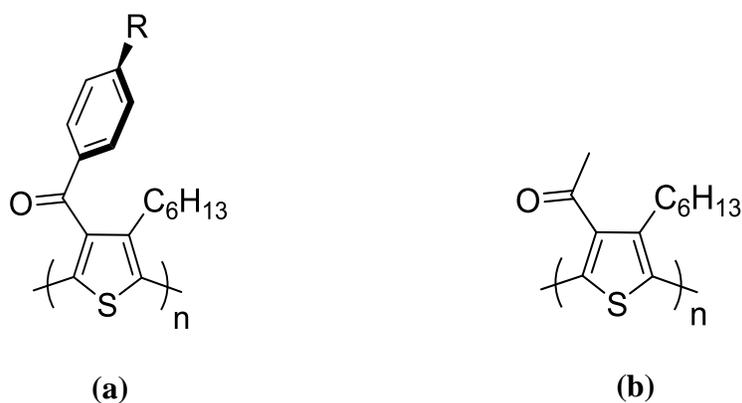
***Figure 21: (a)** Proposed orientation of benzoyl-modified P3HT. Polymer stacking is less likely to occur if the aryl ring is out of plane. This is compared to **(b)** where the polymer is planar, which promotes stacking and may be responsible for the sparingly soluble characteristics that were observed.*

4.4 Silyl Compounds

Silyl compounds are commonly used as protecting groups for a variety of organic synthesis pathways and are electron donating in nature as opposed to the electron withdrawing nature of ketone groups installed by using anhydrides as the electrophile. Trimethylsilyl (TMS) chloride and triisopropylsilyl (TIPS) chloride were investigated as viable electrophiles in the lithium-halogen exchange reaction. The IR spectra of the resulting substituted silyl compounds are shown in ***Figure 22*** and ***Figure 23***. These compounds were insoluble in most common organic solvents including chloroform, THF, DCB, and toluene; therefore, NMR spectra could not be obtained. The lack of an NMR spectrum did not allow for an accurate conversion to be calculated. Elemental analysis was performed on the TIPS substituted compound. The compound composition was 73.5% carbon, 8.1% hydrogen, 9.5% sulfur, 0.2% bromine and 0.5% silicon. The low bromine content below 1% suggests the lithium-halogen exchange was successful. A

large enough sample could not be collected to perform elemental analysis on the TMS

substituted compound. Future work will involve a scale up of this process that may allow

for a larger sample size and improved purification procedure.
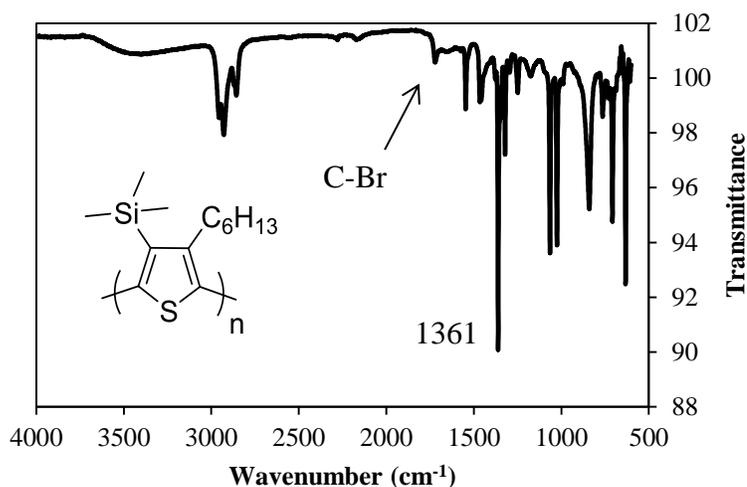

Figure 22: *IR spectra of TMS substituted P3HT displaying the SiCH$_3$ peaks at 1361 (s) and 1465 (w) cm^{-1}. The disappearance of the C-Br stretch is observed around 1730 cm^{-1}.*
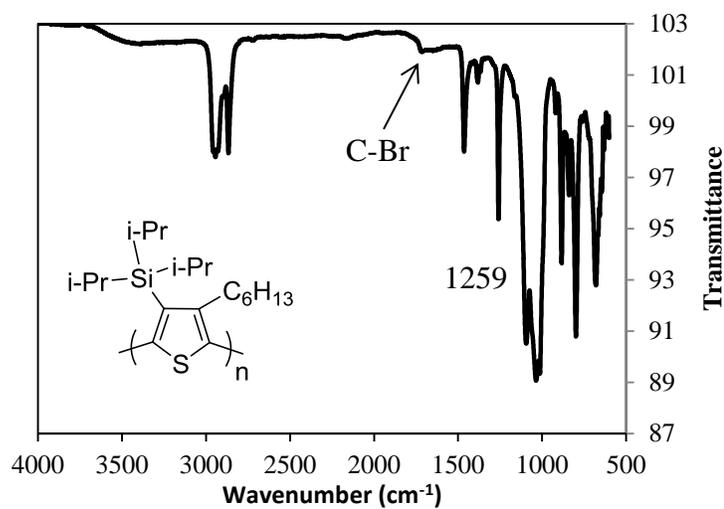

Figure 23: *IR spectra of TIPS substituted P3HT displaying the SiCH$_2$ peak at 1259 (m) cm^{-1}. The disappearance of the C-Br stretch is observed around 1730 cm^{-1}.*

5. Future Work

Other electrophiles were employed to investigate the scope of this reaction scheme.

Benzaldehyde as shown in *Figure 24* was not successful. Aldehydes do not appear to be

a successful group of electrophiles, but further research is needed to confirm this

conclusion. Aldehydes are prone to oxidation to acids and any acid impurities would

prevent successful electrophile addition. Di-tert-butyl dicarbonate was also unsuccessful.

Ethylene sulfide was explored concerning its potential to modify P3HT via a ring

opening reaction. A distinct color change was observed which produced a bright orange

compound. The inability to purify this compound did not allow for successful

characterization. It is hypothesized that the side reactions of ethylene sulfide may have

occurred resulting in the crosslinking of P3HT as well as the formation of other products.

This research has thoroughly explored the use of anhydrides as viable electrophiles for

the post-polymerization modification of P3HT. The exception to this statement was 1,8

napthalic anhydride which resulted in an unsuccessful reaction. This result may be

attributed to the steric hindrance of this molecule. Reactions involving isovaleric

anhydride and hexanoic anhydride were also unsuccessful, but are of great interest

concerning squitch development. The branched alkyl chain of isovaleric anhydride is of

interest due to its solubility characteristics and desirable squitching properties. Long

chains are desirable because they are hypothesized to prevent polymer to polymer

conduction in the off state. The long alkyl chain of hexanoic anhydride is likewise of

interest to provide an optimal compression and subsequent restoring force in squitch

devices. Future research should focus on improving synthetic methods concerning these

reactions. The reaction with hexanoic anhydride exhibited a color change, but the product could not be purified adequately for accurate characterization. Scale-up of this reaction is expected to improve the difficulties encountered with precipitation of the product in methanol as the 10 mg scale is not conducive to this procedure.
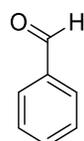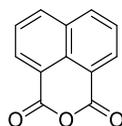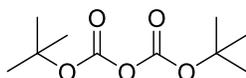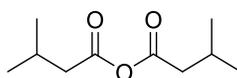

(a)   (b)   (c)
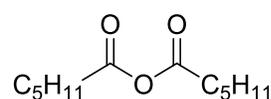
(d)   (e)   (f)

Figure 24: *Unsuccessful electrophiles include (**a**) benzaldehyde (**b**) 1,8 napthalic anhydride (**c**) ethylene sulfide (**d**) di-tert-butyl dicarbonate. Compounds needing improved synthetic methods include (**e**) isovaleric anhydride (**f**) hexanoic anhydride.*

6. Conclusions

This research has successfully explored the scope of the lithium-halogen exchange mediated functionalization of P3HT. Anhydrides and chlorosilanes are effective electrophiles for this reaction and result in ketone- and silyl-modified P3HT, respectively. A series of benzoyl-modified P3HT polymers were synthesized to study the electronic effects of the modification and there was little difference in the photophysical properties of the prepared polymers. It is proposed that the aryl group does not remain in conjugation with the polymer backbone due to these results and the observed favorable solubility properties of benzoyl-modified P3HT.   Future work involves optimizing the reaction and purification conditions to improve modification with longer alkyl chains. These modifications are the most promising for use in squitch devices.

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