POLY(ARYLENE) ETHERS PREPARED FROM FUNCTIONALIZED
3,5-DIFLUOROTRIPHENYLPHOSPHINE OXIDE

A thesis submitted in partial fulfillment
of the requirements for the degree of
Master of Science

By:

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2012
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I HEREBY RECOMMEND THAT THE THESIS PREPARED UNDER MY SUPERVISION BY Courtney M. Sutherland ENTITLED Poly(Arylene) Ethers Prepared From Functionalized 3,5-Difluorotriphenylphosphine Oxide BE ACCEPTED IN PARTIAL FULFILLMENT OF THE REQUIREMENTS FOR THE DEGREE OF Master of Science.

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ABSTRACT

Sutherland, Courtney M. M.S., Department of Chemistry, Wright State University, 2012. Poly(Arylene) Ethers Prepared From Functionalized 3,5-Difluorotriphenylphosphine Oxide

The di-iodinated derivative of 3,5-difluorotriphenyl phosphine oxide, 3,5-DiFTPO-I₂, was synthesized for the modification of poly(arylene ether phosphine oxide)s, PAEPOs. The di-iodinated monomer was polymerized to afford the di-iodinated polymer, a pre-cursor for tailoring solubility and the thermal properties of the PAEPO derivatives via functionalization. The di-iodinated polymer was post-functionalized via the Suzuki Miyaura cross coupling reaction with a variety of boronic acids. The successful conversion of the iodo groups, along with the immense number of possible functional groups that can be introduced to the di-iodinated polymer makes PAEPO-derivative a highly useful thermoplastic with a wide range of potential uses.

The synthesis of 3,5-DiFTPO monomer derivatives was investigated for the use of synthesizing chiral compounds. The synthesis of these monomers (the mono-nitrated 3,5-DiFTPO, the nitrated-iodinated 3,5-DiFTPO monomer, the mono-iodinated 3,5-DiFTPO monomer, and the nitrated-brominated 3,5-DiFTPO monomer) proved successful, conceptually, and provides an avenue for the development of the desired chiral compounds.
# TABLE OF CONTENTS

1. INTRODUCTION.........................................................................................................................1

1.1 Applications and Examples of PAEs.....................................................................................1

1.2 PAE Synthesis.........................................................................................................................2

1.21 Nucleophilic Aromatic Substitution.....................................................................................2

1.22 Oxidative Coupling.............................................................................................................4

1.3 Polymer Morphology.............................................................................................................4

1.4 Thermal Properties...............................................................................................................5

1.5 Influencing the Glass Transition Temperature.......................................................................7

1.6 Pre vs. post polymer functionalization..................................................................................9

1.7 Functionalization of PAEs.....................................................................................................10

1.8 Current Project.....................................................................................................................19

2. EXPERIMENTAL....................................................................................................................24

2.1 Materials.................................................................................................................................24

2.2 Synthesis of Di-Iodinated 3,5-DiFTPO, 1-[Bis-(3-iodo-phenyl)-phosphinoyl]-
3,5-difluorobenzene, 3,5-DiFTPO-I₂, 1..................................................................................25

2.3 Representative Synthesis Procedure of Di-Iodinated Model Compound,

2a-c ...........................................................................................................................................26

2.4 Representative Synthesis Procedure of Iodinated Polymer, 3a-c.................................26

2.5 Representative Synthesis of Post Modified Polymer, 4-6..............................................27
2.6 Synthesis of Pre Modified 3,5-DiFTPO-I₂, 1-[Bis-3-phenyl]-phosphinoyl]-3,5-difluoro-benzene, 7.................................................................28

2.7 Synthesis of Di-Nitrated 3,5-DiFTPO, 1-[Bis-(3-nitro-phenyl)-phosphinoyl]-3,5-difluoro-benzene, 8.................................................................29

2.8 Synthesis of Mono-Nitrated 3,5-DiFTPO, 1,3-Difluoro-5-[(3-nitro-phenyl)-phenyl-phosphinoyl] benzene, 9.................................................................29

2.9 Synthesis of Nitro-Iodo 3,5-DiFTPO, 1,3-Difluoro-5-[(3-iodo-phenyl)-(3-nitro-phenyl)-phosphinoyl]-benzene, 10.........................................................30

2.10 Synthesis of Mono-Iodinated 3,5-DiFTPO, 1,3-Difluoro-5-[(3-iodo-phenyl)-phenyl-phosphinoyl] benzene, 11.................................................................30

2.11 Synthesis of Nitro-Bromo 3,5-DiFTPO, 1-[(3-Bromo-phenyl)-(3-nitro-phenyl)-phosphinoyl]-3,5-difluoro-benzene, 12.................................31

2.12 Synthesis of Di-Brominated 3,5-DiFTPO, 1-[Bis-(3-bromo-phenyl)-phosphinoyl]-3,5-difluoro-benzene, 13.................................................................31

3 RESULTS AND DISCUSSION........................................................................................................................................33

3.1 Iodinated Compounds........................................................................................................................................33

3.1.1 Synthesis of 1-[Bis-(3-iodo-phenyl)-phosphinoyl]-3,5-difluorobenzene, 3,5-DiFTPO-I₂, 1.................................................................33

3.1.2 Di-Iodinated Model Reaction, 2.......................................................................................................................36

3.1.3 Di-Iodinated Polymerization, 3.......................................................................................................................38

3.1.4 Post modified Polymers, 4-6.........................................................................................................................42

3.2 Pre modification of PAEPO; Functionalized Monomer Synthesis.................47
3.2.1 Synthesis of Pre Modified 3,5-DiFTPO-I₂, 1-[Bis-3-phenyl]-phosphinoyl]-3,5-difluoro-benzene, 7

3.2.2 Nitrated Compounds

3.2.2.1 Synthesis of Di-Nitrated 3,5-DiFTPO, 1-[Bis-(3-nitro-phenyl)-phosphinoyl]-3,5-difluoro-benzene, 8

3.2.2.2 Synthesis of Mono-Nitrated 3,5-DiFTPO, 1,3-Difluoro-5-[(3-nitro-phenyl)-phenyl-phosphinoyl]-benzene, 9

3.2.2.3 Synthesis of Nitrated-Iodinated 3,5-DiFTPO, 1,3-Difluoro-5-[(3-iodo-phenyl)-(3-nitro-phenyl)-phosphinoyl]-benzene, 10

3.2.2.4 Synthesis of Mono-Iodinated 3,5-DiFTPO, 1,3-Difluoro-5-[(3-iodo-phenyl)-phenyl-phosphinoyl]-benzene, 11

3.2.2.5 Synthesis of Nitrated-Brominated 3,5-DiFTPO, 1-[(3-Bromo-phenyl)-(3-nitro-phenyl)-phosphinoyl]-3,5-difluoro-benzene, 12

3.2.3 Synthesis of Di-Brominated 3,5-DiFTPO, 1-[Bis-(3-bromo-phenyl)-phosphinoyl]-3,5-difluoro-benzene, 13

4 CONCLUSIONS

5 PROPOSED FUTURE WORK

6 REFERENCES
LIST OF FIGURES

Figure 1: Structures of common poly(arylene ether)s..................................................1

Figure 2: Resonance forms of nitro benzene.................................................................3

Figure 3: Representation of amorphous (left) and crystalline (right) regions.............5

Figure 4: Changes in $T_g$ due to functionalization......................................................8

Figure 5: Comparison of $T_g$ of poly(1-hexene), polypropylene, and polystyrene.....9

Figure 6: Methods of pre and post polymer functionalization.....................................9

Figure 7: Chemical Structure of Poly(arylene ether sulfone), PAES, commercially

known as Udel®..............................................................................................................11

Figure 8: Chemical structure of poly(ether ether ketone), PEEK. .................................12

Figure 9: $p$-PPO and 2,6-dimethyl-$p$-PPO.................................................................14

Figure 10: 75.5 MHz $^{13}$C NMR spectrum (CDCl$_3$) of the iodinated monomer, 1........34

Figure 11: $^{13}$C NMR spectral overlay of 3,5-DiFTPO and 3,5-DiFTPO-I$_2$, 1............35

Figure 12: $^{13}$C NMR spectral overlay for the iodinated monomer, 1, and iodinated

model, 2.........................................................................................................................37

Figure 13: $^{13}$C NMR spectral overlay for the iodinated monomer, 1, and iodinated

polymers, 3....................................................................................................................39

Figure 14: TGA thermograms of iodinated polymers, 3............................................40

Figure 15: DSC traces of iodinated polymers, 3......................................................41

Figure 16: $^{13}$C NMR spectral overlay for the iodinated polymer, 3, and modified

polymers, 4-6. ..............................................................................................................44
Figure 17: TGA thermograms of post functionalized polymers 4-6. .................45

Figure 18: DSC traces of post functionalized polymers, 4-6. .........................46

Figure 19: $^{13}$C NMR spectral overlay for the iodinated monomer, 1, and Suzuki-coupled phenylated monomer, 7. .................................................................49

Figure 20: $^{13}$C NMR spectral overlay for the 3,5-DiFTPO monomer and $di$-nitrated monomer, 8. .................................................................53

Figure 21: $^{13}$C NMR spectral overlay for the 3,5-DiFTPO monomer and the $mono$-nitro monomer, 9. .................................................................55

Figure 22: $^{13}$C NMR spectral overlay for the $mono$-nitrated monomer, 9, and the nitrated-iodinated monomer, 10. .......................................................57

Figure 23: $^{13}$C NMR spectral overlay for the 3,5-DiFTPO monomer and the crude $mono$-iodinated monomer, 11. ...............................................................59

Figure 24: $^{13}$C NMR spectral overlay for the 3,5-DiFTPO monomer, 9, and the nitrated-brominated monomer, 12. .......................................................61

Figure 25: $^{13}$C NMR spectral overlay for the 3,5-DiFTPO monomer and the $di$-brominated monomer, 13. ...............................................................63
LIST OF TABLES

Table 1: Reaction conditions, percentage yield, molecular weight, and thermal analysis data of iodinated model compounds, 2, and iodinated polymers, 3 .......................41

Table 2: Percentage yield, molecular weight data, and thermal data of modified polymers, 4-6. ..........................................................47
LIST OF SCHEMES

**Scheme 1:** Overview of Nucleophilic aromatic substitution (NAS)..........................3

**Scheme 2:** Synthesis of poly(phenylene oxide) via oxidative coupling..................4

**Scheme 3:** Highly halogenated PAES/PEEK..................................................11

**Scheme 4:** Pre functionalized PEEK with tertiary amine ..................................13

**Scheme 5:** Synthesis of pre and post modified PAES....................................15

**Scheme 6:** Synthesis of phosphonated polystyrene.....................................16

**Scheme 7:** Phosphonation of phosphonated and bromo-phosphonated PAES.......17

**Scheme 8:** Synthesis of fluorinated PAEPO derivatives...................................18

**Scheme 9:** Synthesis of poly(arylene thioether phosphine oxide) and sulfonated poly(arylene thioether phosphine oxide)...................................................19

**Scheme 10:** Differences between functionalization of 4,4’-DiFTPO and 3,5-DiFTPO...20

**Scheme 11:** Functionalization of 3,5-DiFTPO via halogenation..........................21

**Scheme 12:** General reactions of 3,5-DiFTPO-I₂, 1...........................................22

**Scheme 13:** Nitration and reduction of 3,5-DiFTPO..........................................23

**Scheme 14:** Synthesis of potentially chiral 3,5-DiFTPO monomer derivative........23

**Scheme 15:** Synthesis of iodinated monomer, 1.............................................33

**Scheme 16:** Synthesis of iodinated model compound, 2.....................................36

**Scheme 17:** Synthesis of iodinated polymers, 3..............................................38

**Scheme 18:** Synthesis of post functionalized polymers 4-6...............................42

**Scheme 19:** Synthesis of pre functionalized monomer with phenyl boronic acid, 7...48
Scheme 20: Synthesis of di-nitrated 3,5-DiFTPO monomer, 8………………………….51
Scheme 21: Synthesis of mono-nitrated 3,5-DiFTPO monomer, 9………………………54
Scheme 22: Synthesis of iodinated/nitrated 3,5-DiFTPO monomer, 10…………………56
Scheme 23: Synthesis of mono-iodinated 3,5-DiFTPO monomer, 11…………………..58
Scheme 24: Synthesis of brominated/nitrated 3,5-DiFTPO monomer, 12………………60
Scheme 25: Synthesis of di-brominated monomer, 13………………………………….62
ACKNOWLEDGEMENT

The material in this thesis was supported, in part by National Science Foundation under CHE-1012392. Thank you to my thesis defense committee members, Dr. Kenneth Turnbull, Dr. William Feld, and Dr. Eric Fossum. A special thank you goes out to Dr. Eric Fossum for the guidance of my thesis project over the last two years.

I could not have completed this program without the love and support of my family, so I thank you all for being by my side through the last two crazy years of my life.

Thank you so much to the wonderful people that I have worked with in Dr. Fossum’s group. I will forever remember all of the help and support you all gave me, as well as the laughter that we shared.

This is dedicated to my beautiful niece and my three amazing nephews, who always keep me grounded and remind of what is most important in life. I love you kids!
1 INTRODUCTION

Poly(arylene ether)s (PAEs) are a class of high-performance engineering thermoplastics used in the aerospace, automobile, engineering, and electrical industries.\(^1\) PAEs are widely used due to their properties; good mechanical properties, excellent resistance to hydrolysis and oxidation, and high thermal stability, including high glass transition temperatures (\(T_g\)) and high decomposition temperatures (\(T_{d5\%}\)).\(^2\) With further functionalization of these materials, the physical and mechanical properties can be altered, allowing for the materials to be tailored for specific uses.

1.1 Applications and Examples of PAEs

Common PAEs include poly(arylene ether sulfone) (PAES), poly(aryl ether ketone), which includes (poly ether ether ketone), (PEEK), poly(phenylene oxide) (PPO), and poly(arylene ether phosphine oxide) (PAEPO).

![Structures of common poly(arylene ether)s.](image)

Figure 1. Structures of common poly(arylene ether)s.
Each class of PAEs has a multitude of uses. For example, PPO is currently being blended with nylon by Saturn, for the use in fenders;\(^3\) PAEPO is being investigated for use in flame retardant materials;\(^4\) PAES is being modified for the use in proton exchange membranes fuel cells (PEMFCs);\(^5\) PEEK is becoming the leading material in medical implants, such as joint implants, shoulder prosthesis, and artificial spinal disks.\(^6\)

### 1.2 PAE Synthesis

The synthesis of PAEs is achieved via two different main pathways, nucleophilic aromatic substitution (NAS) and electrophilic aromatic substitution (EAS), while PPO is typically prepared via an oxidative coupling process.

#### 1.2.1 Nucleophilic Aromatic Substitution

As shown in Scheme 1, NAS occurs in two steps; the first being attack of the electrophile by the nucleophile, forming a resonance-stabilized anion, known as a Meisenheimer complex. The second step is the elimination of the halogen leaving group (LG). The first step is the rate-determining step, due to the loss of the aromaticity of the benzene ring. The second step is fast, as the aromaticity is reestablished. The rate of NAS reactions is dependent on the functional group that is attached to the aromatic ring. An electron-donating group (EDG) slows the reaction by destabilizing the intermediate in addition to decreasing the electrophilic strength of the molecule. An electron-withdrawing group (EWG) enhances the reaction by stabilizing the intermediate formed during the first step as well as increasing the electrophilic strength of the molecule.\(^7\)

The strength of the electrophile is also affected by the LG.\(^6\) Due to its small size and high electronegativity, fluorine is a better leaving group in NAS reactions than are the other halogens. The small size of fluorine does not lead to steric issues, which allows
for the nucleophile to form a new bond while the fluorine is still attached to the ring. Fluorine is also very electronegative causing a strong partial positive charge on the carbon atom of the carbon-fluorine bond and increasing the rate of nucleophilic attack as well as stabilizing the resulting intermediate.\(^9\)

![Scheme 1](image)

**Scheme 1.** Overview of Nucleophilic aromatic substitution (NAS).

NAS, utilized for the synthesis of PAEs, typically occurs with an electron withdrawing group (EWG) located *para* to the LG, however, when a strong EWG is present, the carbon atoms in the *meta* positions are also activated, allowing for NAS to occur in the *meta* position. A functional group is determined to be an EWG or an EDG by the resonance and the inductive effects that the group has on the aromatic ring.

An EWG group, such as NO\(_2\), activates the ring in the *ortho* and *para* positions, due to the partial positive charges caused by the resonance of the substituent with the aromatic ring, as shown below in **Figure 2**.

![Figure 2](image)

**Figure 2.** Resonance forms of nitro benzene.

A strong EWG, such as a sulfone, or a phosphoryl, will activate the ring in the *meta* position, due to the strong inductive effects of the EWG.
The inductive effect of substituents on the aromatic ring during NAS is determined by the polarization effects of the sigma bond between the ipso carbon and the substituent. The polarization is typically due to the electronegativity of the two atoms creating the sigma bond—the more electronegative atom will have a greater pull on the electrons, causing a partial negative charge on the more electronegative atom. In the above scheme, NO$_2$ of nitrobenzene withdraws by resonance, as well as by induction effects, due to the greater electronegativity of the NO$_2$ compared to the carbon atom of the benzene ring.

1.22 Oxidative Coupling

Oxidative coupling is used for the synthesis of poly(phenylene oxide) (PPO). As shown in Scheme 2 the synthesis is achieved by bubbling oxygen through the reaction solution consisting of a phenol and a catalyst, typically an amine with a copper salt. The oxygen abstracts a hydrogen atom from the phenol, creating a phenoxy radical. Coupling and tautomerization of two of these phenoxy radicals forms the dimer, which grows step-wise by repeating the radical formation and coupling again and again, be it with another monomer or one of the growing chains.$^3$

![Scheme 2. Synthesis of poly(phenylene oxide) via oxidative coupling.](image)

1.3 Polymer Morphology

Polymers exist in three different states: amorphous, semi-crystalline, and crystalline. Polymer chains in the amorphous regions are highly disordered, providing a
large amount of chain entanglements. Crystalline regions contain chains that are highly ordered, packed closely next to one another. Semi-crystalline polymers have both amorphous regions and crystalline regions.

Figure 3. Representation of amorphous (left) and crystalline (right) regions.

Fully amorphous polymers are generally more soluble and more pliable than semi-crystalline and crystalline polymers. The level of crystallinity is important to determine the properties of the polymer, altering the solubility, the pliability, and the reaction temperatures of the polymer. Often, semi-crystalline materials are desired for applications due to the improved strength of the material provided by the crystalline regions.

1.4 Thermal properties

The most commonly reported thermal properties of polymers consist of the glass transition temperature ($T_g$), the melting temperature ($T_m$), and the thermal stability, expressed as the 5% degradation temperature ($T_{d5\%}$). Depending on the system, a crystallization temperature ($T_c$) may also be observed. Due to the high temperatures to which materials may be exposed, the thermal properties of a polymer define the limits for its processing and/or use.

The thermal stability of a material, or $T_{d5\%}$, is the measurement of the temperature at which the polymer loses 5% of its mass as a result of degradation. This is crucial, as knowing at which temperature the polymer begins to degrade determines the upper
temperature limit for use. The $T_{d5\%}$ is found by thermogravimetric analysis (TGA), during which a small sample is heated to high temperatures while collecting mass data on the sample.\textsuperscript{10}

The $T_g$ and the $T_m$ are measured by differential scanning calorimetry (DSC). The DSC shows the $T_g$ as an endothermic change in the baseline (change in heat capacity), while the $T_m$ is an actual endothermic peak, and $T_c$ is an exothermic transition. Polymers that have amorphous regions show glass transition temperatures ($T_g$). This is a reversible transition that is unique to every polymer. The $T_g$ is a measure of when the polymer transitions from a glassy, brittle state to a more flexible, rubbery state. Some polymers are used above their $T_g$, while others are used below. For example, rubber elastomers, such as polyisoprene and polyisobutylene are used above their $T_g$’s, in the rubbery state, while hard plastics like polystyrene and PMMA are used below, in their glassy and brittle state.\textsuperscript{11}

The value of $T_g$ depends on the flexibility of the polymer chains; a more flexible polymer chain will exhibit a low $T_g$, while one that is more rigid will have a higher $T_g$. A higher $T_g$ indicates that more energy is needed in order to commence the movement of the chains; the lower $T_g$ means that less heat is needed for the chains to move. The movement of these chains is caused by the rotation of chain segments around the sigma bonds within the polymer chains, also known as the crankshaft motion.\textsuperscript{12} The motion of the chains is increased with a greater amount of free volume for the chains to rotate into.

Semi-crystalline polymers have both amorphous regions with a $T_g$, as well as crystalline regions with a melting temperature ($T_m$) and a crystallization temperature ($T_c$).
PEEK is a semi-crystalline polymer, with a $T_g$, a $T_m$, and a $T_c$. A completely crystalline polymer would exhibit only a $T_m$.

Solid polymers can exist in both a crystalline and amorphous state. By increasing the crystallinity of a polymer, the physical properties are altered, as discussed above.

1.5 Influencing the Glass Transition Temperature

Plasticizers are used to increase the flexibility of the polymers, and thus, decrease the $T_g$. These low molecular weight compounds achieve this depression in $T_g$ by getting between the individual polymer chains, forcing the chains farther apart, weakening the intermolecular forces, and increasing the amount of free volume between the chains. Plasticizers, in general, do not react with the polymers. However, problems arise when the plasticizers react with the polymers, increasing the rigidity of the chains, or when they leach out of the material (e.g. phthalates).\(^{13}\)

Structural modifications of polymeric systems allow the $T_g$ to be altered, tailoring the use temperature for a variety of desired applications. By the introduction of various structural motifs into the backbone of the polymer, the flexibility of the chains can be altered. As shown in Figure 4, more flexible groups, such as aliphatic chains, can be incorporated into the backbone to lower the $T_g$, while more rigid groups, such as phenyl rings, will increase the $T_g$. An extreme example of backbone rigidity is poly(phenylene sulfone). This polymer has such a rigid backbone that the polymer does not exhibit a $T_g$. With heating, the polymer begins to degrade before it transitions from its glassy state to a rubbery state.\(^{14}\)
Figure 4. Changes in $T_g$ due to functionalization.

In the above figure, it is demonstrated that the addition of a flexible functional group decreases the $T_g$ in poly(ethylene adipate), a rigid functional group increases the $T_g$ in poly(ethylene terephthalate), while the rigid backbone of poly(phenylene sulfone) prevents the polymer from having a $T_g$.

Pendant functional groups allow for the tailoring of polymers without altering the backbone. Similar to the alteration of $T_g$ by structural modifications of the backbone, the altering of $T_g$ via pendant functional groups depends on the nature of the functional group. Flexible groups, such as butyl groups, act like a plasticizer, pushing the chains apart, increasing free volume, and decreasing the $T_g$. More rigid, bulky functional groups, such as phenyl rings, decrease the rotational motion, increasing the rigidity of the polymer chains, and increasing the $T_g$. In Figure 5 below, a comparison between poly(1-hexene), polypropylene, and polystyrene shows the effect of the various groups on the $T_g$.\textsuperscript{15, 16}
1.6 Pre vs. post polymer functionalization

The introduction of functional groups into PAE systems can be achieved via either pre or post polymerization methodologies. Pre involves the functionalization of the monomeric units, while post is functionalization after the polymerization process is complete.

Figure 5. Comparison of $T_g$ of poly(1-hexene), polypropylene, and polystyrene.

![Figure 6. Methods of pre and post polymer functionalization.](image)
There are advantages and disadvantages to both forms of polymer modification. Pre functionalization allows for better control over the level of functionalization, granting full control of the conversion of each monomeric unit used in the polymerization process. However, the functional groups added to the monomer must be stable to the polymerization conditions, limiting the possible functional groups that can be employed. Another disadvantage is the purification of the functionalized monomers; if conversion to the functionalized monomer is not 100% complete, the monomer must be isolated, which can result in lower yields. Due to the potential loss of product, pre modification is ideally carried out with high yielding reactions, limiting the list of potential reactions used for functionalization.

Post functionalization is done at the polymer stage, which allows for the use of functional groups that would not have been stable to the polymerization process. However, post is only possible if a solvent can be found to dissolve the polymer in to carry out the reaction. Also, during post functionalization, complete functional group conversion is difficult due to the steric hindrance provided by the polymer chains and the reaction conditions must be carefully chosen to prevent any degradation reactions of the backbone.

1.7 Functionalization of PAEs

PAES has a \( T_g \) of 190 °C, which allows a relatively high continuous use temperature of 180 °C. It is used in electrical and electronic components, medical and agricultural components that require repeated sterilization, and photographic accessories, such as camera lenses. One of the commercially available PAES materials, Udel®, as
seen in Figure 7, is traditionally synthesized by NAS polycondensation of 4,4’-Difluorodiphenyl sulfone and Bisphenol A.

![Chemical Structure of Poly(arylene ether sulfone), PAES, commercially known as Udel®.](image)

**Figure 7.** Chemical Structure of Poly(arylene ether sulfone), PAES, commercially known as Udel®.

PAES derivatives have been synthesized with a wide range of uses in mind, as well as improvement of reaction conditions. For example, Qi et al. studied a highly halogenated copolymer of PAES and PEEK that was synthesized with the overall goal of tailoring the refractive index of the material (Scheme 3). The highly halogenated monomer had an increased reactivity due to the presence of the multiple fluorine atoms, allowing for a decrease in reaction temperature. The halogenated copolymer was synthesized at 45 °C, compared to the non-halogenated polymer synthesis at 160 °C.

![Scheme 3. Highly halogenated PAES/PEEK.](image)
PEEK is used for flexible circuit boards, fabrics and single fibers, injection-molded machine parts, as well as the aforementioned medical implants. PEEK is semi-crystalline with a $T_g$ of 144 °C, and a $T_m$ of 343 °C.$^{17}$

![Chemical structure of poly(ether ether ketone), PEEK.](image)

**Figure 8.** Chemical structure of poly(ether ether ketone), PEEK.

Due to its thermal, mechanical, and chemical stability, PEEK is highly versatile. However, the material is also difficult to process, and insoluble in most organic solvents, which requires the synthesis to be carried out in diphenylsulfone near its boiling point of 373 °C.$^{18, 19}$ In an attempt to improve the processability as well as the physical and mechanical properties of the polymer, PEEK has been functionalized by both pre and post functionalization methods. The majority of functionalized PEEK is synthesized with pre functionalization methods. For post modification of PEEK, the material is dissolved in sulfuric acid, which risks the degradation of the polymer.$^{20}$ With functionalization, reaction conditions and solubility of the semi-crystalline polymer are improved. **Scheme 4** shows the synthesis of PEEK, pre functionalized by integrating a tertiary amine in the backbone, carried out by Gao, Wang, and Zhang in 2006.
The previously semi-crystalline polymer was completely amorphous after the pre-modification, with a $T_g$ of 119.57 °C, a $T_{d5\%}$ of 378 °C, and molecular weight ($M_w$) of 20 kD.²¹

PPO is synthesized via oxidative coupling. The un-substituted $p$-PPO material is not a commercial product, however, 2,6-dimethyl- $p$-PPO is commonly known as PPO.
and was commercialized by General Electric Co. Functionalization of PPO is necessary to improve the processability and properties, similar to the need to functionalize PEEK. Analogous to PEEK, the un-substituted \( p \)-PPO is semi-crystalline with a \( T_g \) of 95 °C and a \( T_m \) of 295 °C. The most common modification of PPO is 2,6-dimethyl-\( p \)-PPO, with a \( T_g \) of 210 °C and no melt temperature, as it is not semi-crystalline, due to the additional methyl groups.\(^{22,23}\)

![O-\( p \)-PPO](image)

**Figure 9.** \( p \)-PPO and 2,6-dimethyl-\( p \)-PPO.

The ideal functional group is one that can be added to the system pre polymerization, and can undergo post modification. This allows for a multitude of possibilities for altering the properties of a polymeric system. A fluorine group is an example of one such functional group that allows for both pre and post modification. The introduction of a halogen group allows for an abundance of polymers with various applications to be synthesized, due to the stability of the halogen groups to NAS. One such example can be seen below in **Scheme 5**. In 2006, Guiver et al. discussed the preparation of PAES with grafting capabilities, achieved via a pre functionalized monomer. The monomer was fluorinated pendant to the backbone, and the polymerization was carried out with the fluorinated monomer. Post polymerization, the thioether was oxidized to the sulfone, creating a strong EWG to activate the pendant fluorine toward NAS. Following the oxidation, a second post modification afforded the sulfonated PAES derivative, with possible use in PEMFCs.\(^{24}\)
Scheme 5. Synthesis of pre and post modified PAES.

The versatility of halogenation has been demonstrated in a review by Bock, Möhwald, and Mühlaupt in 2007. Various methods of phosphonation for the use in PEMFCs were discussed in the review, some achieved via halogenation, followed by phosphonation.
One such method, by Walder et al. utilized a Friedel-Crafts-type reaction, with the overall goal of phosphonating polystyrene. However, a crosslinked polymer was also synthesized alongside the desired phosphonated product, making the final product ineffective for the desired use of PEMFCs.\textsuperscript{25}

\begin{center}
\textbf{Scheme 6.} Synthesis of phosphonated polystyrene.
\end{center}

Jokoby, Peinemann, and Nunes also used a halogen group to achieve phosphonation in 2003. In this post functionalization method, the polymer was brominated in order to achieve lithiation in the ortho position, followed by conversion of the organolithium species to a phosphonate group, as seen in \textbf{Scheme 7}.\textsuperscript{26}
Scheme 7. Phosphonation of phosphonated and bromo-phosphonated PAES.

In the above example, the functionalization of the polymer occurs on the backbone, which is not the ideal modification of polymers. Pendant functionalization is desired, due to the ability to alter the properties of the polymer without initiating structural changes to the backbone of the polymer.

Modification of PAEPO has been of interest to research groups due to the high thermal stability as well as exceptional flame retardance of phosphorus-containing polymers. In 2012, Ghosh et al. synthesized six fluorinated PAEPO derivatives using a pre-functionalized monomer, bis(4-fluoro-3-trifluoromethylphenyl)phenylphosphine oxide, as the starting material, with the overall intent of synthesizing polymers that demonstrate high thermal stability as well as excellent flame retardance. The pre-
functionalized monomer was synthesized with phenylphosphonic dichloride and the Grignard salt of 5-bromo-2-fluorobenzotrifluoride. The monomer, bis(4-fluoro-3-trifluoromethylphenyl)-phenylphosphine oxide, was polymerized with six different diphenols. Scheme 8 shows the synthesis of the modified PAEPO polymers.

Scheme 8. Synthesis of fluorinated PAEPO derivatives.

The functionalized PAEPOs demonstrated $T_g$ values that ranged from 173 °C to 252 °C and the $T_{d5\%}$ values ranged from 428 °C to 471 °C. All polymers were amorphous and soluble in common organic solvents. It was reported that all six functionalized PAEPO derivatives were comparable to or better than the products that are currently being used as engineering thermoplastics.\textsuperscript{27}

In 2008, Ma et al. pre-modified the 4,4’-DiFTPO monomer, by sulfonation, followed by the synthesis of a copolymer of poly(arylene thioether phosphine oxide) and sulfonated poly(arylene thioether phosphine oxide), with the purpose of PEMFC applications. The synthesis of this copolymer appears below in Scheme 9.
Scheme 9. Synthesis of poly(arylene thioether phosphine oxide) and sulfonated poly(arylene thioether phosphine oxide).

The resulting copolymers exhibited high thermal stability with a $T_g$ of 230 °C and above, and a $T_{d5\%}$ of 400 °C and above, depending on the degree of sulfonation of the copolymer. The thermal properties of the pendant functionalized polymer were compared to that of PAEPO with the sulfonation of the backbone, and the pendant sulfonation resulted in higher thermal stability than that of the polymer with the modified backbone.²⁸

The Functionalization of PAEPOs has not been as meticulously delved into when compared with the other PAEs. These phosphorus-containing polymers hold a lot of potential for future use, and further research of these polymers for an array of applications would be highly beneficial.

1.8 Current Project

Current research is focused on 3,5-difluorotriphenylphosphine oxide (3,5-DiFTPO), 1, the geometric isomer of the commercially available 4,4’-diFTPO monomer. The 3,5-DiFTPO monomer contains the strong electron withdrawing phosphoryl group, which sufficiently activates nucleophilic aromatic substitution (NAS) to occur in the meta position with a good leaving group.²⁹ The phosphoryl group is utilized to stabilize the intermediate formed during NAS.
The structure of the 3,5-DiFTPO monomer allows for polycondensation to be undergone to afford PAEs with the activating group pendant to the polymer backbone. Compared to the commercial product that only allows for functionalization on one of the phenyl rings, functionalization of 3,5-DiFTPO allows for the introduction of two pendant functional groups, one on each ring. This approach provides an avenue for the straightforward introduction of two pendant functional groups, unique to the PAEPO system. The structure of the 3,5-DiFTPO monomer has increased access to the phenyl rings for pendant functionalization when compared with 4,4’-DiFTPO. Scheme 10 shows an example of EAS functionalization of the commercial 4,4’-DiFTPO, as well as EAS of 3,5-DiFTPO. Since the phosphoryl is a strong meta director, the EAS reactions are expected to occur in the meta position of the non-fluorinated ring.30

Scheme 10. Differences between functionalization of 4,4’-DiFTPO and 3,5-DiFTPO.

The synthesis of 3,5-DiFTPO is achieved via the reaction of 3,5-difluorophenylmagnesium bromide with chlorodiphenylphosphine, followed by oxidation.
with hydrogen peroxide. Purification is achieved via recrystallization from cyclohexane.\textsuperscript{30}

This particular project is focused on the pre functionalization of 3,5-DiFTPO, as well as the post functionalization of the synthesized polymers. Previous examples have shown the successful functionalization of PAEs.\textsuperscript{24, 31, 32} Functionalization of 3,5-DiFTPO provides an avenue for introducing a high level of functional groups into 3,5-DiFTPO-based PAEs, thus, tailoring the polymeric properties.

**Scheme 11** represents an example of an EAS reaction used to iodinate or brominate 3,5-DiFTPO, with \textit{N}-Bromosuccinimide, NBS, or \textit{N}-Iodosuccinimide, NIS. The \textit{di}-substituted compound can be used as a platform for both pre- and post-polymerization modification reactions, allowing for the incorporation of a multitude of functional groups.

![Scheme 11. Functionalization of 3,5-DiFTPO via halogenation.](image)

As discussed previously, the halogen groups provide an avenue to perform an abundance of reactions for both pre and post modification, such as the Suzuki-Miyaura, Heck, or other cross-coupling reactions, as seen in **Scheme 12.**\textsuperscript{33}
Scheme 12. General reactions of 3,5-DiFTPO-I₂, 1.

Nitration of 3,5-DiFTPO is also accomplished via EAS, followed by the reduction of the nitro groups to amino groups (Scheme 13).
Further modification, post polymerization, such as acetylation, amide synthesis via the Schotten–Baumann reaction, and various click chemistry reactions, are then possible.\textsuperscript{34-36}

The 3,5-DiFTPO monomer is unique in the sense that it contains three phenyl rings, only one of which is a part of the backbone after polymerization. These two rings provide the possibility of introducing two different functional groups, one on each ring, making each ring unique, allowing for the synthesis of a potentially chiral compound, as outlined below in Scheme 14.

\begin{scheme}
\centering
\includegraphics[width=\textwidth]{scheme14}
\end{scheme}

\textbf{Scheme 14.} Synthesis of potentially chiral 3,5-DiFTPO monomer derivative.

The synthesis of chiral monomers introduces possibility for chiral polymers with a vast array of applications for PAEPOs that have yet to be investigated. The exploration of this exciting new research area is important for the improvement of currently utilized thermoplastics, as well as numerous applications that have yet to be discovered.
2 EXPERIMENTAL

2.1 Materials

All $^1$H and $^{13}$C NMR spectra were acquired on a Bruker AVANCE 300 MHz NMR spectrometer operating at 300 and 75.5 MHz, respectively. Samples were dissolved in deuterated chloroform (CDCl$_3$) at a concentration of (~ 60 mg / 0.7 mL). GC/MS analyses were carried out using a Hewlett-Packard (HP) 6890 Series GC and a HP 5973 Mass Selective Detector/Quadrupole system. Size Exclusion Chromatography (SEC) analysis was performed using a system consisting of a Viscotek Model 270 Dual Detector (viscometer and light scattering) and a Viscotek Model VE3580 refractive index detector. Two Polymer Laboratories 5 mm PL gel Mixed C columns (heated to 35 ºC) were used with tetrahydrofuran as the eluent and a Thermoseparation Model P1000 pump operating at 1.0 mL/minute. Thermal Gravimetric Analysis (TGA) and Differential Scanning Calorimetry (DSC) data were obtained on TA Instruments TGA Q500 and DSC Q200, respectively, with a heating rate of 10 ºC/min. Melting points were determined on a MEL-TEMP apparatus and are uncorrected.

$N$-Methylpyrrolidinone (NMP) was purchased from Sigma Aldrich Chemical Co. and was dried over and distilled from CaH$_2$ under nitrogen prior to use. Reagent-grade anhydrous potassium carbonate powder ($K_2$CO$_3$) was purchased from Sigma Aldrich Chemical Co. and dried at 130 ºC in an oven prior to use. Bisphenol A was purchased from Sigma Aldrich Chemical Co., recrystallized from toluene, and dried in vacuo prior to use. Chlorodiphenyl phosphine was purchased from Sigma Aldrich Chemical Co. and distilled in vacuo before use. $N$-bromosuccinimide was purchased from Sigma Aldrich Chemical Co., recrystallized from water, and dried in vacuo. 4-tert-butyl phenol, phenyl
boronic acid, acetyl-phenyl boronic acid, naphthyl boronic acid, and Palladium(II) acetate were purchased from Sigma Aldrich Chemical Co. and used as received. N-iodosuccinimide (NIS) was purchased from Acros Organics and used as received. 1-Bromo-3,5-difluorobenzene, 99%, was purchased from Oakwood Products and was used as received. Ethanol (EtOH), hydrogen peroxide (H₂O₂), hydrochloric acid (HCl), nitric acid (HNO₃), sulfuric acid (H₂SO₄), glacial acetic acid (AcOH), tetrahydrofuran (THF), cyclohexane (C₆H₁₂), dichloromethane (DCM), ethyl ether, and isopropyl alcohol were used as received from Pharmco-Aaper. ACS-certified acetone, sodium bicarbonate (NaHCO₃), and magnesium sulfate (MgSO₄) were used as received from Fischer Scientific. Non-iodized Morton salt was purchased from a local retailer and used as received.

2.2 Synthesis of Di-Iodinated 3,5-DiFTPO, 1-[Bis-(3-iodophenyl)phosphinoyl]-3,5-difluorobenzene, 3,5-DiFTPO-I₂, 1

In a 50-mL RB flask, equipped with a stir bar and a nitrogen gas inlet, were placed 3.00 g (9.60 mmol) of 3,5-DiFTPO and 25 mL of concentrated H₂SO₄. To the vigorously stirred solution were added 5.70 g (25.2 mmol) of N-Iodosuccinimide (NIS) and the reaction was stirred for 12 hours at room temperature. The product was precipitated from water and isolated by filtration. The solid was dissolved in dichloromethane and washed with a 10 % sodium bisulfite (NaHSO₃) solution. The organic layer was dried over MgSO₄ and the solvents removed via rotary evaporation to afford a yellow solid that was recrystallized from cyclohexane, affording 3.8 g of 1 (71%) with a melting point of 95-98 °C. ¹H NMR (CDCl₃, δ): 7.02 (tt, 1H), 7.17 (m, 2H), 7.24 (m, 2H), 7.54 (m, 2H), 7.94 (m, 2H), 8.03 (dd, 2H). ¹³C NMR (CDCl₃, δ): 95.3
(ArCl), 108.2 (t), 115.0 (m), 130.5 (d), 130.8 (d), 133.3 (d), 135.8 (dt), 140.3 (d), 141.8 (d), 162.9 (ddd). Elemental Analysis: Calc. Anal. for C\textsubscript{18}H\textsubscript{11}F\textsubscript{2}I\textsubscript{2}OP: C, 38.19; H, 1.96; Found: C, 38.15; H, 1.99.

2.3 Representative Synthesis Procedure of Di-Iodinated Model Compound, 2

A typical model reaction for 1 will be described at 170 °C. In a 25-mL RB flask equipped with a stir bar, condenser, and nitrogen gas inlet, were placed 0.50 g (0.88 mmol) of 1, 0.37 g (2.6 mmol) of potassium carbonate, 0.27 g (1.8 mmol) of t-butyl phenol, and 1.4 mL of NMP. The reaction flask was immersed in an oil bath and stirred vigorously at 170 °C for 31 hours. The brown solid was isolated by precipitation from water and filtered to afford 0.49 g of a light brown solid, 2 (71%). The same procedure was utilized for the iodinated model compound at 150 °C (49 %), and the iodinated model compound at 160 °C (81 %). \textsuperscript{1}H NMR (CDCl\textsubscript{3}, \(\delta\)): 1.32 (s, 18H), 6.80 (m, 4H), 6.87 (d, 4H), 6.94 (m, 1H), 7.20 (d, 2H), 7.36 (d, 2H), 7.55 (dd, 2H), 7.89 (d, 2H), 8.02 (d, 2H). \textsuperscript{13}C NMR (CDCl\textsubscript{3}, \(\delta\)): 31.5 (s), 34.4 (s), 94.9 (d), 111.5 (d), 115.1 (m), 119.1 (s), 126.9 (s), 130.3 (d), 130.9 (d), 133.7 (d), 133.9 (d), 140.3 (d), 141.3 (d), 147.4 (s), 153.1 (s), 159.7 (d).

2.4 Representative Synthesis Procedure of Iodinated Polymer, 3

A typical polymerization reaction for 1 will be described at 170 °C. In a 25-mL RB flask, equipped with a stir bar, condenser, and nitrogen gas inlet, were placed 1.5 g (2.7 mmol) of 2, 0.62 g (2.7 mmol) of BisA, 1.1 g (3 molar equivalents) of potassium carbonate, and 4.2 mL of NMP. The reaction flask was immersed in an oil bath and stirred vigorously at 170 °C for 40 hours. The polymer was isolated via precipitation from water, affording a light brown powder. The solid was dissolved in THF and precipitated
from isopropyl alcohol to afford 0.49 g of 3 (56 %). The same procedure was utilized for the iodinated polymer at 150 °C (44 %), and the iodinated polymer at 160 °C (42 %). $^1$H NMR (CDCl$_3$, δ): 1.65 (s, 6H), 6.89 (m 7H), 7.17 (m, 6H), 7.54 (t, 2H), 7.84 (m, 2H), 7.99 (d, 2H). $^{13}$C NMR (CDCl$_3$, δ): 31.3 (s), 42.3 (s), 95.0 (s), 112.0 (d), 115.3 (m), 119.0 (s), 128.3 (s), 130.3 (d), 130.9 (d), 133.9 (m), 134.6 (d), 140.3 (d), 141.3 (s), 146.6 (s), 153.5 (s), 159.4 (d).

2.5 Representative Synthesis of Post Modified Polymer, 4-6

Post modification of the iodinated polymer was completed following the phosphine free Suzuki-Miyaura reaction procedure reported by Novak, with minor modifications.$^{37}$ A typical post polymerization reaction for the iodinated polymer will be described using the phenyl boronic acid. In a 25-mL Schlenk flask, equipped with a stir bar, were placed 0.30 g (0.40 mmol) of 3, 0.24 g (1.6 mmol) of phenyl boronic acid, and 5 mL of THF. In another 25-mL Schlenk flask were placed 0.33 g (2.4 mmol) of potassium carbonate, 1 mL of 1 mol % Pd(OAc)$_2$ in acetone, and 1 mL of water. The contents of the Schlenk flasks were subjected to three freeze-pump-thaw cycles, back-filled with nitrogen, and combined in one Schlenk flask. The reaction mixture was immersed in an oil bath and heated at 60 °C for 2 hours, followed by addition of an extra 20 % of the boronic acid, and heating for an additional 46 hours. The reaction mixture was diluted with ~10 mL of THF and washed with brine. The organic layer was isolated and dried over MgSO$_4$, and precipitated from isopropyl alcohol to obtain 0.15 g of 4 (58 %): $^1$H NMR (CDCl$_3$, δ): 1.47 (s, 6H), 6.60 – 7.96 (m, 29H). $^{13}$C NMR (CDCl$_3$, δ): 29.9 (s), 41.2 (s), 110.9 (m), 115.0 (m), 117.7 (s), 126.1 (s), 126.9 (s), 127.2 (s), 127.9 (s), 128.0 (m), 129.6 (m), 131.5 (m), 133.7 (m), 138.8 (s), 140.6 (d), 145.3 (s), 152.6 (s), 153.5 (s), 159.4 (d).
The same procedure was utilized for naphthyl boronic acid (5) and 4-acetylphenyl boronic acid (6).

5 (64 %): $^1$H NMR: 1.42 (s, 6H), 2.41 (s, 6H), 6.50 – 8.0 (m, 23H). (CDCl$_3$, δ): $^{13}$C NMR (CDCl$_3$, δ): 25.6 (s), 29.9 (s), 41.2 (s), 110.9 (s), 114.7 (s), 117.8 (s), 126.3 (s), 127.3 (s), 128.0 (s), 129.6 (d), 130.1 (s), 130.6 (d), 131.0 (d), 131.7 (d), 133.9 (m), 135.4 (s), 139.5 (d), 143.0 (s), 145.4 (s), 152.5 (s), 158.2 (d), 197.0 (s).

6 (70 %): $^1$H NMR (CDCl$_3$, δ): 1.34 (s, 6H), 6.55 – 8.30 (m, 33H). $^{13}$C NMR (CDCl$_3$, δ): 29.8 (s), 41.1 (s), 110.9 (m), 114.9 (m), 117.7 (s), 124.1 (s), 125.3 (s), 125.5 (s), 126.6 (s), 127.1 (s), 127.7 (s), 128.1 (d), 129.8 (m), 130.2 (s), 131.8 (s), 131.9 (m), 132.5 (s), 134.0 (d), 135.9 (s), 140.6 (s), 145.3 (s), 152.6 (s), 158.1 (d).

2.6 Synthesis of Pre Modified 3,5-DiFTPO-I$_2$, 1-[Bis-3-phenyl]-phosphinoyl]-3,5-difluorobenzene, 7

In a 25-mL Schlenk flask, equipped with stir bar, were placed 0.50 g (0.88 mmol) of 1, 0.37 g (2.6 mmol) of phenyl boronic acid, and 1.4 mL of acetone. In another 25-mL Schlenk flask were placed 0.31 g (2.0 mmol) of potassium carbonate, 1 mL of 1 mol % Pd(OAc)$_2$ in acetone, and 2 mL of water. The contents of the Schlenk flasks were subjected to three freeze-pump-thaw cycles, back-filled with nitrogen, and combined in one Schlenk flask. The reaction mixture was immersed in an oil bath and heated at 60 °C for 2 hours, followed by addition of an extra 10 % of the boronic acid, and heating for an additional 4 hours. The reaction mixture was diluted with ~10 mL of toluene and washed with brine. The organic layer was isolated, dried over MgSO$_4$, and solvent was removed in vacuo. GC/MS analysis showed 89 % of 7, and 10 % of the monomer after losing an iodo group. $^1$H NMR (CDCl$_3$, δ): 6.81 (tt, 1H), 7.13 (m, 2H), 7.21 (m, 4H), 7.42 (m, 6H),
7.64 (m, 4H), 7.79 (d, 2H), 7.89 (d, 2H). $^{13}$C NMR (CDCl$_3$, δ): 106.9 (td), 114.0 (m), 126.1 (s), 127.0 (s), 127.9 (s), 128.3 (d), 129.4 (m), 129.6 (d), 130.4 (d), 132.0 (d), 135.6 (dt), 138.5 (s), 141.1 (d), 161.9 (ddd).

2.7 Synthesis of Di-Nitrated 3,5-DiFTPO, 1-[Bis-(3-nitrophenyl)phosphinoyl]-3,5-difluorobenzene, 8

In a 25-mL RB flask, equipped with a stir bar and nitrogen gas inlet, were placed 2.0 g (6.4 mmol) of 3,5-DiFTPO and 10 mL of concentrated H$_2$SO$_4$. The reaction flask was immersed in an ice bath, and 1.6 g (17 mmol) of HNO$_3$ was added drop wise. The solution was allowed to react for 4 hours, at which point the product was precipitated from water. The resulting yellow solid was isolated via filtration and analyzed by GC/MS, which indicated the presence of 87 % of 8 and 13 % of tri-nitrated monomer. The product was recrystallized from isopropanol, producing an off white solid, consisting of 95 % of 8 and 5 % tri-nitrated monomer. $^1$H NMR (CDCl$_3$, δ): 7.11 (tt, 1H), 7.24 (m, 2H), 7.82 (m, 2H), 8.06 (m, 2H), 8.50 (m, 2H), 8.54 (m, 2H). $^{13}$C NMR (CDCl$_3$, δ): 109.0 (td), 115.0 (m), 126.7 (d), 127.7 (d), 130.7 (d), 133.0 (d), 134.2 (dt), 137.4 (d), 148.4 (d), 163.1 (ddd).

2.8 Synthesis of Mono-Nitrated 3,5-DiFTPO, 1,3-Difluoro-5-[(3-nitrophenyl)phenylphosphinoyl]-benzene, 9

In a 10-mL RB flask, equipped with stir bar and nitrogen gas inlet, were added 0.20 g (0.64 mmol) of 3,5-DiFTPO and 2.2 mL of concentrated H$_2$SO$_4$. The reaction flask was immersed in an ice bath, and 0.057 g (0.64 mmol) of HNO$_3$ was added drop wise. The solution was allowed to react for 1 hour, at which point GC/MS analysis showed the presence of 85 % of 9, 5 % of un-reacted monomer, and 10 % of di-nitrated
monomer, 8. The reaction mixture was precipitated from water, and the yellow solid stuck to the bottom and the sides of the beaker. The product was isolated by decanting off the water, and was analyzed by NMR. $^1$H NMR (CDCl$_3$, δ): 6.94 (tt, 1H), 7.14 (m, 2H), 7.40 – 7.77 (m, 6H), 7.96 (m, 1H), 8.32 (m, 1H), 8.45 (m, 1H). $^{13}$C NMR (CDCl$_3$, δ): 108.2 (dt), 114.9 (m), 126.6 (d), 127.0 (d), 129.2 (d), 130.2 (d), 131.8 (d), 133.1 (d), 134.0 (d), 134.3 (d), 135.9 (dt), 137.5 (d), 148.0 (d), 162.9 (ddd).

2.9 Synthesis of Nitrated-Iodinated 3,5-DiFTPO, 1,3-Difluoro-5-[(3-iodophenyl)-(3-nitrophenyl)-phosphinoyl]-benzene, 10

In a 10-mL RB flask, equipped with stir bar and nitrogen gas inlet, were added 0.20 g (0.64 mmol) of 3,5-DiFTPO and 2.2 mL of concentrated H$_2$SO$_4$. The reaction flask was immersed in an ice bath, and 0.057 g (0.64 mmol) of HNO$_3$ was added drop wise. The solution was allowed to react for 1 hour, at which point GC/MS analysis showed the presence of 85 % of 9, 5 % of un-reacted monomer, and 5 % of di-nitrated monomer, 8. The reaction mixture was split in half, and 0.093 g (0.41 mmol) of NIS was added to half and the mixture was allowed to react for 12 hours. The reaction product was precipitated from water and isolated by filtration, affording an offwhite, sticky solid. GC/MS analysis showed 56 % of 10 and 44 % of the iodinated di-nitro monomer. $^1$H NMR (CDCl$_3$, δ): 7.08 (tt, 1H), 7.18 (m, 2H), 7.54 (m, 1H), 7.78 (m, 1H), 8.02 (m, 4H), 8.49 (m, 1H), 8.60 (t, 1H). $^{13}$C NMR (CDCl$_3$, δ): 95.4 (d), 108.4 (m), 115.0 (m), 126.7 (m), 127.6 (m), 130.7 (m), 132.6 (d), 133.3 (d), 133.8 (m), 137.6 (m), 140.4 (m), 141.8 (m), 148.4 (m), 163.0 (m).

2.10 Synthesis of Mono-Iodinated 3,5-DiFTPO, 1,3-Difluoro-5-[(3-iodophenyl)-phenyl-phosphinoyl]-benzene, 11
In a 10-mL RB flask, equipped with stir bar and nitrogen gas inlet, were placed 0.50 g (1.6 mmol) of 3,5-DiFTPO and 5 mL of concentrated H$_2$SO$_4$. To the vigorously stirring solution was added 0.45 g (2.0 mmol) of NIS and the reaction was stirred for 12 hours at room temperature. The product was isolated via precipitation from water and the solid was dissolved in dichloromethane and washed with a 10 % sodium bisulfite (NaHSO$_3$) solution. The organic layer was dried over MgSO$_4$ and the solvents removed via rotary evaporation to afford a yellow, sticky solid. GC/MS analysis showed 95 % of 11, 3 % of the di-iodinated monomer, 1, and 2 % of un-reacted monomer. $^1$H NMR (CDCl$_3$, δ): 6.83 (tt, 1H), 7.07 (m, 2H), 7.40 (m, 5H), 7.72 (m, 1H), 7.94 (d, 1H). $^{13}$C NMR (CDCl$_3$, δ): 95.2 (dd), 107.7 (t), 114.8 (m), 128.8 (m), 130.4 (m), 130.7 (m), 131.8 (m), 132.7 (m), 133.1 (d), 133.9 (d), 136.1 (m), 140.1 (dd), 141.5 (dd), 162.6 (m).

2.11 Synthesis of Nitrated-Brominated 3,5-DiFTPO, 1-[(3-Bromophenyl)-(3-nitrophenyl)phosphinoyl]-3,5-difluorobenzene, 12

The other half of the reaction mixture, from the synthesis of 10, was used for this purpose. In a 10-mL RB flask, equipped with stir bar and nitrogen gas inlet, was added 0.074 g (0.42 mmol) of N-Bromosuccinimide (NBS) to the half of the reaction mixture, and the mixture was allowed to react for 12 hours. The reaction product was precipitated from water and isolated by filtration, affording a white, sticky solid. GC/MS analysis showed 70 % of 12, 16 % of the di-nitrated monomer, 8, and 11 % of the di-brominated, mono-nitrated monomer. $^1$H NMR (CDCl$_3$, δ): 7.00 (tt, 1H), 7.13 (m, 2H), 7.36 (m, 1H), 7.50 (m, 1H), 7.71 (m, 3H), 7.97 (m, 1H), 8.41 (m, 1H), 8.45 (m, 1H). $^{13}$C NMR (CDCl$_3$, δ): 108.8 (td), 115.0 (m), 123.8 (d), 126.7 (d), 127.6 (d), 130.5 (m), 132.1 (d), 132.5 (d), 133.1 (d), 136.3 (d), 137.4 (m), 138.0 (m), 148.4 (dd), 163.1 (ddd).
2.12 Synthesis of Di-Brominated 3,5-DiFTPO, 1-[Bis-(3-bromophenyl)-phosphinoyl]-3,5-difluorobenzene, 13

In a 10-mL RB flask, equipped with a stir bar and nitrogen gas inlet, were placed 0.20 g (0.64 mmol) of 3,5-DiFTPO and 3 mL of concentrated H$_2$SO$_4$. To the vigorously stirring solution was added 0.24 g (1.3 mmol) of NBS and the reaction was stirred for 12 hours at room temperature. The product was isolated via precipitation from water and extracted into chloroform. The organic layer was isolated and the chloroform was removed in vacuo to afford a sticky, white solid. GC/MS analysis showed that the product was 93 % of 13, 4 % of un-reacted monomer, and 3 % of tri-brominated monomer. $^1$H NMR (CDCl$_3$, δ): 6.93 (dt, 1H), 7.11 (m, 2H), 7.31 (m, 2H), 7.48 (t, 2H), 7.62 (d, 2H), 7.74 (d, 2H). $^{13}$C NMR (CDCl$_3$, δ): 108.3 (t), 114.9 (m), 123.6 (d), 130.4 (d), 130.6 (d), 132.8 (d), 134.4 (d), 135.6 (dt), 136.0 (d), 162.8 (ddd).
3 RESULTS AND DISCUSSION

3.1 Iodinated Compounds

The iodinated 3,5-DiFTPO monomer, 1, was synthesized for use in both pre and post polymerization modification processes. The monomers and polymers that were synthesized, using 3,5-DiFTPO-I₂, 1, as the base compound, will be discussed.

3.1.1 Synthesis of 1-[Bis-(3-iodo-phenyl)-phosphinoyl]-3,5-difluorobenzene, 3,5-DiFTPO-I₂, 1

The synthesis of 3,5-difluorotriphenylphosphine oxide, 3,5-DiFTPO, was previously reported by Tienda, et al., via the reaction of 3,5-difluorophenylmagnesium bromide and chlorodiphenylphosphine. The synthesis of 3,5-DiFTPO-I₂, 1, was achieved in the one-step reaction of 3,5-DiFTPO with a slight excess of NIS (Scheme 15).

![Scheme 15. Synthesis of iodinated monomer, 1.](image)

Iodination of the 3,5-DiFTPO monomer occurred meta to the phosphoryl group, as expected with a typical EAS reaction. The 3,5-DiFTPO monomer was dissolved in concentrated H₂SO₄, after which the NIS was added and the reaction was stirred for 12 hours at room temperature. The product was precipitated from water and isolated by filtration. The solid was dissolved in dichloromethane, resulting in a purple solution, due
to the byproduct of the reaction, I₂, a result of the excess of NIS. The purple solution was washed with a 10 % sodium bisulfite (NaHSO₃) solution to reduce the I₂ to I⁻, which was soluble in water, resulting in a light yellow solution. The organic layer was extracted, dried over MgSO₄, and the solvents removed via rotary evaporation to afford a yellow solid that was recrystallized from cyclohexane, affording white crystals. The structure of the iodinated monomer was confirmed by a combination of GC/MS, elemental analysis, and NMR spectroscopy. The ¹³C NMR spectrum of 1 appears below in Figure 10.

Figure 10. 75.5 MHz ¹³C NMR spectrum (CDCl₃) of the iodinated monomer, 1.

The NMR results of the iodinated monomer in Figure 10 show 10 distinct signals. The two fluorine atoms cause carbon atoms a-d to experience varying degrees of splitting, depending on their position in relation to the fluorine-bearing carbon atoms,
while the NMR-active phosphorus atom is coupled to all of the carbon atoms in the structure. Carbon a is a doublet of triplets at 108 ppm, carbon b is a doublet of doublet of doublets at 161-165 ppm, carbon c is a multiplet at 115 ppm, and carbon d is a doublet of triplets at 136 ppm. Carbons e, f, g, h, i, and j were all identified as doublets and were found at 133, 130, 131, 142, 95, and 140 ppm, respectively. The doublet at 95 ppm represents the carbon atom with the iodo group attached. Figure 11 shows the carbon spectra of 3,5-DiFTPO monomer and 3,5-DiFTPO-I₂, 1.

Figure 11. ¹³C NMR spectral overlay of 3,5-DiFTPO and 3,5-DiFTPO-I₂, 1.

The carbon spectrum of 3,5-DiFTPO-I₂, 1, contains the new signal, i, at 95 ppm, representing the carbon of the carbon-iodine bond. With the addition of the iodo group, the phenyl ring is no longer symmetrical, causing the carbon ortho to the iodine and the
phosphoryl group, \( j \), to be seen as an added doublet at 140 ppm. The addition of the iodo group also causes the doublets of the bottom ring on \( 1 \) to shift farther downfield, when compared with 3,5-DiFTPO due to the inductively withdrawing effect of the iodo group.

### 3.1.2 Di-Iodinated Model Reaction, \( 2 \)

In order to ensure that the carbon-iodine bond was stable to typical NAS conditions, model reactions of \( 1 \) were performed, using \textit{tert}-butyl phenol as the nucleophile, as outlined in Scheme 16.

![Scheme 16. Synthesis of iodinated model compound, 2.](image)

Polymerization of 3,5-DiFTPO was previously achieved at 185 \(^\circ\)C. However, when the model reaction was run at 185 \(^\circ\)C, the iodo groups did not appear to survive the reaction conditions. Therefore, three model reactions were carried out to look at temperature effects on the polymerization of \( 1 \). The model reaction, \( 2 \), was heated at 150 \(^\circ\)C for 48 hours, as well as at 160 \(^\circ\)C for 60 hours, and at 170 \(^\circ\)C for 31 hours. The model at 150 \(^\circ\)C was found to be incomplete after 48 hours, therefore, the model at 160 \(^\circ\)C was heated for 60 hours to ensure completion of the reaction. The product of each model reaction, \( 2 \), was precipitated from water and isolated via filtration. The resulting brown solid was analyzed by NMR spectroscopy. Figure 12 shows the carbon spectra of \( 1 \) and the model reaction, \( 2 \), at 150 \(^\circ\)C.
Figure 12. $^{13}$C NMR spectral overlay for the iodinated monomer, 1, and iodinated model, 2.

The NMR spectrum of 2 shows that the C-I bonds of 1 are, in fact, stable to this particular set of NAS conditions, indicated by the presence of i, the signal for carbon atoms of the C-I bonds, at 95 ppm. Due to the displacement of the fluorine atoms by the tert-butyl phenol, the triplet at 108 ppm, a, is reduced to a singlet, m, at 112 ppm, and the doublet of doublet of doublets at 161-165 ppm, b, is observed as a doublet at 159 ppm, l, in the model. The additional singlet at 153 ppm, k, represents the carbon atom of the C-O bond provided by the tert-butyl phenoxy group.
3.1.3 Di-Iodinated Polymerization, 3

The success of the model reactions at all three temperatures, 150 °C, 160 °C, and 170 °C, indicated that the polymerization of 1 should be possible at the same temperatures. Thus, the iodinated polymer, 3, was synthesized via NAS reactions of the iodinated monomer, 1, with Bisphenol A, as outlined in Scheme 17.

\[
\text{Scheme 17. Synthesis of iodinated polymer, 3.}
\]

The polymerization of 1 with Bisphenol A was carried out at 150 °C for 68 hours, 160 °C for 62 hours, and 170 °C for 40 hours. The polymers, 3, were precipitated from water and isolated via filtration. The resulting brown solids were dissolved in THF, followed by precipitation from isopropyl alcohol, to remove any cyclic species and/or low molecular weight materials. The light brown, powdery solids were isolated via filtration, and analyzed by NMR spectroscopy, SEC, DSC, and TGA. Figure 13 displays the $^{13}$C NMR spectra of 1 and the polymers, 3, at all three temperatures.
Figure 13. $^{13}$C NMR spectral overlay for the iodinated monomer, 1, and iodinated polymers, 3, at three temperatures.

The $^{13}$C NMR spectra of the iodinated polymers, 3, show i, the carbon of the C-I bonds at 95 ppm, the newly formed singlet, m, at 112 ppm, the doublet, l, at 159 ppm, representing b, and the singlet, k, of the carbon of the ether bond of the Bisphenol A component of the polymer.
Thermal data of the iodinated polymers, 3, was collected to detect any differences in the thermal properties of the polymers, due to synthesis temperature variance. Figure 14 shows the thermogravimetric analysis, TGA, thermograms of the polymers.

![Figure 14. TGA thermograms of iodinated polymers, 3, at three different temperatures.](image)

The 5 % decomposition temperatures, $T_{d5\%}$, of the iodinated polymers, 3, synthesized at 150 °C, 160 °C, and 170 °C were found to be 384 °C, 353 °C, and 387 °C, respectively. TGA data of 3 shows two degradation steps, the first degradation step representing the iodine loss while the second step can be attributed to the decomposition of the polymer backbone.

Figure 15 shows the glass transition, $T_g$, data of 3, determined by differential scanning calorimetry, DSC.
The collected DSC data showed that the polymers demonstrated similar $T_g$’s of 161 °C, 155 °C, and 153 °C.

Molecular weight and PDI data of the iodinated polymers were determined by size exclusion chromatography (SEC) analysis. The results are summarized in **Table 1**.

**Table 1.** Reaction conditions, percentage yield, molecular weight and thermal analysis data of iodinated model compounds, 2, and iodinated polymers, 3.

<table>
<thead>
<tr>
<th>Compound</th>
<th>Temp (°C)</th>
<th>Time (h)</th>
<th>% yield</th>
<th>$M_w$ (Daltons)</th>
<th>PDI</th>
<th>$T_g$ (°C)</th>
<th>$T_{d5%}$ (°C)</th>
</tr>
</thead>
<tbody>
<tr>
<td>2</td>
<td>150</td>
<td>48</td>
<td>49%</td>
<td>--</td>
<td>--</td>
<td>--</td>
<td>--</td>
</tr>
<tr>
<td>2</td>
<td>160</td>
<td>60</td>
<td>81%</td>
<td>--</td>
<td>--</td>
<td>--</td>
<td>--</td>
</tr>
<tr>
<td>2</td>
<td>170</td>
<td>31</td>
<td>71%</td>
<td>--</td>
<td>--</td>
<td>--</td>
<td>--</td>
</tr>
<tr>
<td>3</td>
<td>150</td>
<td>68</td>
<td>44%</td>
<td>3,000</td>
<td>2.2</td>
<td>161</td>
<td>384</td>
</tr>
<tr>
<td>3</td>
<td>160</td>
<td>62</td>
<td>42%</td>
<td>5,700</td>
<td>1.5</td>
<td>155</td>
<td>352</td>
</tr>
<tr>
<td>3</td>
<td>170</td>
<td>40</td>
<td>41%</td>
<td>8,500</td>
<td>1.8</td>
<td>153</td>
<td>387</td>
</tr>
</tbody>
</table>
3.1.4 Post modified Polymers, 4-6

Post modification of the iodinated polymer was completed following the phosphine free Suzuki Miyaura reaction procedure reported by Novak, with minor modifications.\textsuperscript{37} The introduction of the desired functional groups to polymer 3 was achieved via the \textit{Pd (OAc)}\textsubscript{2} catalyzed cross-coupling reaction with phenyl, naphthyl, and acetyl-phenyl boronic acid, yielding polymers 4-6, as outlined in Scheme 18.

\textbf{Scheme 18.} Synthesis of post functionalized polymers 4-6.

The post polymerization modification of the iodinated polymers, 3, was completed with the goal of displacing the iodo groups on the polymer with an R group. Three boronic acid groups were chosen, phenyl boronic acid, naphthyl boronic acid, and acetyl-phenyl boronic acid. The reactions were performed in a Schlenk flask, utilizing the freeze-pump-thaw method for the removal of gas from the system. The iodinated polymer and the boronic acid were dissolved in THF in one Schlenk flask, while the \textit{K}_2\textit{CO}_3, \textit{H}_2\textit{O}, and \textit{Pd(OAc)}\textsubscript{2} were placed in another Schlenk flask. Both flasks were subjected to three freeze-pump-thaw cycles, and the contents of the two flasks were combined. Each post modification reaction was heated at 60 °C for 24 hours, followed by the addition of an
additional 20 mol % of the boronic acid, and heated for another 24 hours. The reaction mixture was diluted with THF and washed with brine. The organic layer was isolated and dried over MgSO₄, and precipitated from isopropyl alcohol to obtain a grey powder. **Figure 16** shows the $^{13}$C NMR spectra of 3 and the post modified polymers, 4-6.
Figure 16. $^{13}$C NMR spectral overlay for the iodinated polymer, 3, and modified polymers, 4-6.
The $^{13}$C NMR spectrum of the modified polymers indicates the successful conversion of the iodo groups to the phenyl, acetyl-phenyl, and naphthyl groups. The signal of the carbon atom of the carbon-iodine bond at 95 ppm, \textit{i}, is no longer present in the three modified polymers. The most obvious change in the phenylated and the acetyl-phenylated polymer, \textit{4} and \textit{5}, is the presence of the large signals, \textit{p} and \textit{q}, representing the carbon atoms of the additional phenyl ring. These signals are larger than all of the other signals in the spectra of \textit{4} and \textit{5}, due to the symmetry of the additional phenyl ring. The acetyl-phenylated polymer, \textit{5}, also contains the signal of the carbon of the acetyl group at 197 ppm, \textit{s}. The naphthylated polymer, \textit{6}, contains the additional singlet signals associated with the naphthyl group.

Thermal data for the polymers, \textit{4-6}, was collected to show the difference in the thermal properties of the post-modified polymers.

\textbf{Figure 17.} TGA thermograms of post functionalized polymers \textit{4-6}.
The iodinated polymer, 3, showed a $T_{d5\%}$ of 387 °C, while the modified polymers all displayed higher degradation temperatures. The naphthylated polymer, 6, provided a $T_{d5\%}$ of 407 °C, the acetyl-phenylated polymer, 5, showed a $T_{d5\%}$ of 414 °C, and the phenylated derivative, 4, displayed the highest $T_{d5\%}$ at 426 °C. The naphthylated polymer was expected to be the most stable, due to the rigid and bulky functional group; however, the lower $T_{d5\%}$ could be due to the presence of $bi$-naphthyl, formed by the coupling of two naphthyl boronic acid molecules. Further research into the removal of this by-product is necessary.

Figure 18. DSC traces of post functionalized polymers, 4-6.
The iodinated polymer, 3, showed a $T_g$ of 153 °C while the corresponding phenylated derivative, 4, displayed a slight decrease in $T_g$ to 149 °C. The more polar acetyl-phenylated polymer, 5, showed a higher $T_g$ of 156 °C. The bulkier naphthylated polymer, 6, provided the highest $T_g$ of 161 °C.

The modified polymers indicate that the thermal properties can easily be changed via functionalization, but not to a great extent. By way of simply changing the R group attached to the pendant rings on the 3,5-DiFTPO polymer derivatives, the thermal properties of the polymers were altered.

Molecular weight and PDI data of the modified polymers were determined by SEC analysis. The results are summarized in Table 2.

**Table 2.** Percentage yield, molecular weight data, and thermal data of modified polymers, 4-6.

<table>
<thead>
<tr>
<th>Polymer</th>
<th>% yield</th>
<th>$M_w$ (Daltons)</th>
<th>PDI</th>
<th>$T_g$ (°C)</th>
<th>Td5% (°C)</th>
</tr>
</thead>
<tbody>
<tr>
<td>4</td>
<td>58%</td>
<td>4,800</td>
<td>1.5</td>
<td>149</td>
<td>426</td>
</tr>
<tr>
<td>5</td>
<td>64%</td>
<td>6,000</td>
<td>1.7</td>
<td>156</td>
<td>414</td>
</tr>
<tr>
<td>6</td>
<td>70%</td>
<td>6,200</td>
<td>1.9</td>
<td>161</td>
<td>407</td>
</tr>
</tbody>
</table>

The molecular weight of the polymers increased after the modification process, as expected, due to the increase in the repeat unit formula weight. The trend of the molecular weight data was also as expected, with the phenylated polymer, 4, resulting in the lowest molecular weight, and the naphthylated polymer, 6, with the highest molecular weight.

3.2 Pre modification of PAEPO; Functionalized Monomer Synthesis

The second half of this thesis is more exploratory in nature. The possibility of synthesizing various monomers that could be utilized for modification of PAEPOs was explored, without too much emphasis being placed on the purification of the products.
The knowledge learned from delving into the synthesis of these monomers is incredibly useful and opens the door for a vast array of functionalized PAEPOs to be synthesized in the future. The synthesis, purification attempts, and the analysis of the functionalized monomers will be discussed.

3.2.1 Synthesis of Pre Modified 3,5-DiFTPO-I₂, 1-[Bis-3-phenyl]-phosphinoyl]-3,5-difluoro-benzene, 7

The pre modification of the iodinated monomer was performed by following the slightly modified Suzuki Miyarua reaction procedure that was utilized for the previously discussed post modification. Scheme 19 shows the synthesis of the phenylated monomer, 7.

![Scheme 19. Synthesis of pre-functionalized monomer, 7.](image)

Phenyl boronic acid was added to a solution of 1 dissolved in acetone in a Schlenk flask. In another Schlenk flask were placed K₂CO₃, Pd(OAc)₂ in acetone, and water. The contents of the Schlenk flasks were subjected to three freeze-pump-thaw cycles, back-filled with nitrogen, and combined in one Schlenk flask. The reaction mixture was immersed in an oil bath and heated at 60 °C for 2 hours, followed by addition of an extra 10 % of the boronic acid, and heating for an additional 4 hours. The reaction mixture was diluted with toluene and washed with brine. The organic layer was
isolated, dried over MgSO₄, and solvent was removed in vacuo. GC/MS analysis showed 89% of 7 with a [M⁺] m/z of 465, and 10% of the monomer after losing an iodo group. Figure 19 displays the ¹³C NMR spectra of 1 and crude product of 7.

![Figure 19. ¹³C NMR spectral overlay for the iodinated monomer, 1, and Suzuki-coupled phenylated monomer, 7.](image)

The ¹³C NMR spectrum of the pre-modified monomer, 7, shows that the reaction was successful in displacing the iodo groups with a phenyl group. The loss of the signal of the carbon-iodine bond at 95 ppm, i, shows that the iodo groups are no longer present in the monomer. The resonance for the new carbon-carbon bond in 7, i, is shifted to 141 ppm. The new singlet signals, k, l, m and n, indicate the new carbons of the additional phenyl rings.
Recrystallization of the product in cyclohexane was attempted, but was unsuccessful, as the solid that came out of solution when the cyclohexane cooled had the same amount of impurity as the crude product. Additional attempts at recrystallization should be performed to purify this sample for the future use in polymerization.

3.2.2 Nitrated Compounds

The introduction of nitro groups, to the 3,5-DiFTPO monomer, allows for a large range of functionalization, potentially using both pre and post polymerization processes. The nitro groups can be reduced to the amino form, which opens the door for amide synthesis, nitrosylation to form a diazonium cation, as well as the introduction of an azide group using sodium azide, allowing for the azide-alkyne Huisgen reaction to be performed. The nitro groups are not always stable to nucleophilic aromatic substitution conditions, therefore, reduction to the amino might be required.

The *di*-nitrated 3,5-DiFTPO monomer, 8, the syntheses of *mono*-nitrated 3,5-DiFTPO monomer, 9, the nitrated/iodinated 3,5-DiFTPO monomer, 10, the *mono*-iodinated 3,5-DiFTPO monomer, 11, and the nitrated/brominated 3,5-DiFTPO monomer, 12, were attempted with the goal of introducing perpendicular functional groups within one monomer species. The synthetic procedures for each of these monomers, along with their corresponding synthetic and purification difficulties will be discussed.

3.2.2.1 Synthesis of *Di*-Nitrated 3,5-DiFTPO, 1-[Bis-(3-nitro-phenyl)-phosphinoyl]-3,5-difluoro-benzene, 8

The *di*-nitrated 3,5-DiFTPO monomer, 8, was synthesized via a typical nitration, using concentrated sulfuric acid and nitric acid, as outlined in Scheme 20.

The di-nitrated monomer, 8, was synthesized by way of EAS, with an expected substitution meta to the electron withdrawing phosphoryl group. The 3,5-DiFTPO monomer was first dissolved in concentrated H$_2$SO$_4$, the reaction flask was immersed in an ice bath, and HNO$_3$ was added drop wise, as the nitration is an exothermic reaction. The reaction occurred quickly, with mono-nitrated compound being produced after about 30 minutes, di-nitro production being complete after two hours, and tri-nitration following, depending on the amount of HNO$_3$ present in the reaction mixture. However, the reaction requires an excess of HNO$_3$, believed to be due to the lower activity of the nitric acid or slow degradation over its lifetime during storage. On a smaller scale (~ 200 mg of 3,5-DiFTPO monomer), these reactions are difficult to control, as one drop of HNO$_3$ can make a large difference on the stoichiometry of the reaction.

In order to provide more control in the synthesis of the di-nitrated compound, less HNO$_3$ than required was added and the reaction was monitored by removing aliquots for GC/MS analysis to determine how much more HNO$_3$ was necessary in order to push the reaction to completion. After the addition of the nitro group to the ring, the ring is much less reactive to substitution, leading us to believe that the tri-nitrated monomer would be difficult to synthesis. However, tri-nitrated monomer was observed in many of the
product mixtures. Therefore, care had to be taken to prevent pushing the reaction too far. Once the reaction showed a majority of di-nitrated compound, the reaction mixture was precipitated from water resulting in a yellow solid. The solid was isolated by filtration, and analyzed by GC/MS and NMR spectroscopy. GC/MS indicated the presence of 87% of 8, with a [M⁺] m/z of 403, and 13% of tri-nitrated monomer, with a [M⁺] m/z of 448. The product was recrystallized from isopropanol, to afford an off white solid, consisting of 95% of 8 and 5% tri-nitrated monomer, according to GC/MS.

Further recrystallization of 8 was attempted with isopropyl alcohol, again with the goal of completely removing the tri-nitrated compound from the product. However, GC/MS analysis showed that the product obtained from the second recrystallization was 75% of 8 and 25% of tri-nitrated compound. In an attempt to determine if the isopropanol was possible for purification, a third recrystallization with the alcohol was performed, yielding a yellow compound that was 22% of 8 and 78% of the tri-nitrated impurity. This led to the thought that something was occurring with the compound when injected into the GC/MS, causing the di-nitrated compound to appear as tri-nitrated, or vice versa. It is believed that the di-nitrated compound was about 95% pure, due to the NMR analysis. Figure 20 displays the ¹³C NMR spectra of 3,5-Di-FTPO and 8.
Figure 20. $^{13}$C NMR spectral overlay for the 3,5-DiFTPO monomer and di-nitrated monomer, 8.

The $^{13}$C NMR spectrum of the di-nitrated 3,5-DiFTPO, 8, shows that the introduction of the nitro groups was successful, most evident by the presence of the signal for the carbon atom with nitro group present at 148 ppm, i. Due to the strong electron withdrawing properties of the nitro group, the signals of the lower phenyl ring are shifted significantly relative to the 3,5-DiFTPO, however, not always in the downfield direction. The signal for the carbon atom ortho to both the nitro group and the phosphorus was actually shifted upfield to 126 ppm, j. The carbon atom ortho to the phosphorus and para to the nitro group, f, gave rise to a signal that was shifted from 128 ppm in 3,5-DiFTPO to 137 ppm in 8.
The inability to purify the monomer to 100% of 8 caused a slight halt in the project, as pure monomer was desired to carry out the reduction to the amino form before moving forward. Further investigation into the purification of the monomer is necessary before proceeding.

3.2.2.2 Synthesis of Mono-Nitrated 3,5-DiFTPO, 1,3-Difluoro-5-[(3-nitrophenyl)-phenylphosphinoyl]benzene, 9

With the overall goal of synthesizing a potentially chiral compound by producing a monomer with two different functional groups on the bottom rings, the synthesis of a mono-nitrated compound, 9, was attempted, as outlined in Scheme 21.


The 3,5-DiFTPO monomer was first dissolved in concentrated H₂SO₄, immersed in an ice bath, and HNO₃ was added drop wise. After one hour, the reaction mixture was precipitated from water to produce a sticky, yellow solid. The solid adhered to the bottom of the beaker, allowing for the water to be decanted off isolating the final product mixture. GC/MS analysis showed 85% of 9 with a [M⁺] m/z of 358, 10% of di-nitrated monomer, 8, with a [M⁺] m/z of 403, and 5% of un-reacted monomer with a [M⁺] m/z of 313

Purification of 9 was attempted with a variety of solvents. However, the majority of recrystallization attempts did not result in an improvement of the final product. A
mixture of isopropanol: ethanol: chloroform in a ratio of 80:10:10 produced light yellow crystals that were 100% di-nitratated monomer, 8, according to GC/MS. However, GC/MS analysis of what remained in the liquid after the crystals were isolated showed that un-reacted monomer and tri-nitratated monomer were still present, in a ratio similar to the crude product before recrystallization. This leads to the belief that GC/MS analysis of these nitrated products is not reliable, and NMR analysis must be performed on the products to detect the ratios of each compound. Figure 21 shows the $^{13}$C NMR spectra of the 3,5-DiFTPO monomer and the mono-nitratated monomer, 9.

![Figure 21](image)

**Figure 21.** $^{13}$C NMR spectral overlay for the 3,5-DiFTPO monomer and the mono-nitro monomer, 9.

The $^{13}$C NMR spectrum of the mono-nitratated monomer, 9, shows the presence of the carbon of the C-N bond appearing as a doublet at 148 ppm, m. A second doublet is
also observed, indicating that the product also contains di-nitrated monomer, 8. However, the di-nitrated monomer is symmetrical, therefore, the carbon signals of the C-N bonds are twice the size in the symmetrical monomer than in the mono-nitrated monomer, 8. Thus, it is believed that 9 makes up ~ 90% of the final product mixture.

Further investigation, utilizing NMR analysis, should be done on the production of the mono-nitrated monomer.

3.2.2.3 Synthesis of Nitrated-Iodinated 3,5-DiFTPO, 1,3-Difluoro-5-[(3-iodo-phenyl)-(3-nitro-phenyl)-phosphinoyl]-benzene, 10

The mono-nitrated monomer, 9, was used as a precursor for the chiral compounds. After verification by GC/MS that the reaction contained 85% of 9, 10% of di-nitrated monomer, and 5% of un-reacted monomer, the reaction mixture was split in half for the use of two different reactions. To one of the reaction flasks was added NIS and the mixture was stirred overnight at room temperature.

![Scheme 22. Synthesis of iodinated/nitrated 3,5-DiFTPO monomer, 10.](image)

The reaction mixture was isolated by precipitation from water, affording an off-white, sticky solid. GC/MS analysis showed 56% of 10 with a [M⁺] m/z of 484 and 44% of the iodinated di-nitro monomer with a [M⁺] m/z of 530. Figure 22 shows the ¹³C NMR spectra of the mono-nitrated monomer, 9, and the nitrated-iodinated monomer, 10.
Conversion of 9 to 10 was verified by the existence of both C-I and C-N bonds, with signals observed at 95 and 148 ppm, respectively. The NMR spectrum indicates that the product contains a large amount of impurities, due to the impure 9. The resonance for the carbon atom of the C-I bond in 10 is a doublet at 95 ppm, as expected, indicating that only one iodinated compound is present in the product, while the signal for the carbon atom of the C-N bond appears as two unique doublets, signifying that the mono-nitro was not as clean as reported by GC/MS analysis. Purification of this compound was not attempted, as the conclusion was reached that a pure mono-nitratated monomer was required for this reaction to be a success. This did prove, however, that the chiral
compound, 10, can be synthesized from a mono-nitrated monomer, which is promising if the purification of 9 can be achieved.

3.2.2.4 Synthesis of Mono-Iodinated 3,5-DiFTPO, 1,3-Difluoro-5-[(3-iodo-phenyl)-phenyl-phosphinoyl]-benzene, 11

Another attempt at synthesizing the desired chiral compounds was to synthesize the mono-iodinated precursor monomer, and further functionalize this monomer, 11. The idea was that the mono-nitro monomer was difficult to purify, and that the mono-iodinated monomer might be easier to purify. The di-iodinated monomer is easily recrystallized with cyclohexane, therefore attempts at the mono-iodinated monomer were made, as outlined in Scheme 23.

![Scheme 23](image)

**Scheme 23.** Synthesis of mono-iodinated 3,5-DiFTPO monomer, 11.

The 3,5-DiFTPO monomer was dissolved in concentrated H$_2$SO$_4$, and to the vigorously stirring solution was added ~ 1 eq. of NIS. The reaction was stirred for 12 hours at room temperature. The product was isolated via precipitation from water and the solid was dissolved in dichloromethane and washed with a 10 % NaHSO$_3$ solution to reduce the excess I$_2$. The organic layer was dried over MgSO$_4$ and the solvents removed via rotary evaporation to afford a yellow, sticky solid. GC/MS analysis showed 95 % of 11, 3 % of the di-iodinated monomer, 1, and 2 % of un-reacted monomer. **Figure 23**
shows the $^{13}$C NMR spectra of 3,5-DiFTPO and the crude product from the synthesis of 11.

![Chemical structures and NMR spectra](image)

**Figure 23.** $^{13}$C NMR spectral overlay for the 3,5-DiFTPO monomer and the crude mono-iodinated monomer, 11.

The spectral overlay of 3,5-DiFTPO and 11 shows that the conversion to the *mono*-iodinated monomer was a success. The carbon of the C-I bond in 11 is seen at 95 ppm, m, while bonds from the un-substituted ring remain, most evident by the signals f and g at 129 and 132 ppm, respectively. Evidence of the *di*-iodinated monomer, 1, is also present in the NMR spectrum, as seen by a second doublet in the region assigned to carbon atom m. This indicates that both the *mono-* and *di*-substituted compounds are present. The abundance of the second set of signals in this region signifies that more *di*-substituted compound is present than found by GC/MS analysis.
Purification of this product was attempted from cyclohexane, as was used with the di-iodinated monomer. However, no crystals were produced. Recrystallization from isopropyl alcohol was also attempted, but the entire reaction mixture did not dissolve in the hot alcohol. A hot filtration was performed to remove the solid that did not dissolve in the isopropanol. GC/MS results showed that the solid that was not soluble was the same compound as the crude that did dissolve, and crystals were not produced when the solvent cooled. The difficulty of purifying the product may be due to the larger amount of di-substituted product. Further work on purification of this monomer is necessary to move forward.

3.2.2.5 Synthesis of Nitrated-Brominated 3,5-DiFTPO, 1-[(3-Bromo-phenyl)-(3-nitro-phenyl)-phosphinoyl]-3,5-difluoro-benzene, 12

The other half of the mono-nitrated reaction used to synthesize 10 was used as a precursor for the chiral compound containing one nitrated ring and one brominated ring, as outlined in Scheme 24 below.

![Scheme 24. Synthesis of brominated/nitrated 3,5-DiFTPO monomer, 12.](image)

The synthesis of the nitrated-brominated 3,5-DiFTPO monomer was achieved via EAS reaction, substituting meta to the strong electron-withdrawing phosphoryl on the unsubstituted ring. Bromination was achieved using concentrated H2SO4 as the acid catalyst and solvent with N-bromosuccinimide (NBS). To one of the reaction flasks containing
half of the reaction product of 9 was added NBS and the mixture was stirred overnight at room temperature. The reaction product was precipitated from water and isolated by filtration, affording a white, sticky solid. GC/MS analysis showed 70 % of 12 with a [M+] m/z of 438, 16 % of the di-nitrated monomer, 8, with a [M+] m/z of 403, and 11 % of the di-brominated, mono-nitrated monomer with a [M+] m/z of 516. Figure 24 shows the 13C NMR spectra of the mono-nitrated monomer, 9, and the reaction mixture containing the nitrated-brominated monomer, 12.

**Figure 24.** 13C NMR spectral overlay for the 3,5-DiTPO monomer, 9, and the nitratert-brominated monomer, 12.

The 13C NMR spectrum of 12 indicates that the conversion from 9 was successful. The carbon of the C-Br bonds is present at 124 ppm, m, as well as the carbon of the C-N bonds at 148 ppm, i. The purification of this product was not attempted, as a pure mono-
nitratated monomer is necessary as a precursor for the reaction. However, this reaction proved that it is possible to prepare a chiral compound, if the starting materials are sufficiently pure. The success of the bromination indicated that this is a promising future project.

3.2.3 Synthesis of Di-Brominated 3,5-DiFTPO, 1-[Bis-(3-bromo-phenyl)-phosphinoyl]-3,5-difluoro-benzene, 13

The synthesis of the di-brominated 3,5-DiFTPO monomer, was achieved via an EAS reaction, substituting meta to the strong electron-withdrawing phosphoryl group. Bromination was achieved using concentrated H$_2$SO$_4$ with NBS. The synthesis of the di-brominated compound, 13, is outlined below in Scheme 25.


The reaction of 3,5-DiFTPO with NBS was stirred for 12 hours at room temperature, after which the product was isolated via precipitation from water and extraction into chloroform. The organic layer was isolated and the chloroform was removed in vacuo to afford a sticky, white solid. GC/MS analysis showed that the product was 93% of 13 with a [M$^+$/] m/z of 471, 4% of un-reacted monomer with a [M$^+$/] m/z of 313, and 3% of tri-brominated monomer with a [M$^+$/] m/z of 549. Figure 25 shows
the $^{13}$C NMR spectra of 3,5-DiFTPO and the reaction mixture containing the di-brominated monomer, 13.

\[ \text{3,5-DiFTPO} \]

\[ \text{13} \]

\[ \text{13C NMR spectral overlay for the 3,5-DiFTPO monomer and the di-brominated monomer, 13.} \]

The $^{13}$Carbon NMR spectrum of the reaction mixture containing the di-brominated monomer, 13, shows the addition of the bromine atom; by introduction of the bromine \textit{meta} to the phosphorus on the two bottom phenyl rings, the rings are no longer symmetrical, and two new carbon signals are present in the spectrum, i and j. The signal of carbon atom of the C-Br bonds is seen at 123 ppm, i, while the carbon \textit{ortho} to both the phosphorus and the bromine is present at 134 ppm, j. The addition of the inductively-withdrawing and donating-by-resonance bromine atom shifts the other carbon signals
around, most obviously by the shift of the carbon *para* to the phosphorus, shifted from 132 ppm in 3,5-DiFTPO to 136 ppm in 13.
4 CONCLUSIONS

The di-iodinated derivative of the 3,5-DiFTPO monomer has been synthesized via EAS reaction with NIS. The di-iodinated monomer, 1, was polymerized to afford the di-iodinated polymer, 3, allowing for a vast array of potential functionalization of the polymer. Three post-modified polymers, 4, 5, and 6, have been synthesized from 3, via the Suzuki Miyaura reaction, using phenyl boronic acid, acetyl-phenyl boronic acid, and naphthyl boronic acid, respectively. These modified polymers demonstrated higher thermal stability when compared with the iodinated polymer, 3. The successful conversion of the iodo groups, along with the immense number of possible functional groups that can be introduced to 3 makes this functionalized polymer a highly useful thermoplastic with a wide range of potential uses.

Pre-modification of the 3,5-DiFTPO-I₂, was performed to synthesis the phenylated monomer, 1-[Bis-3-phenyl)-phosphinoyl]-3,5-difluoro-benzene, 7, using phenyl boronic acid. Although the purification of the product was unsuccessful, the possibility of the synthesis of the pre-functionalized monomer was verified, indicating that if post-modification is proving difficult, pre-polymerization is a possible route for the introduction of the desired functional group.

The di-nitrated 3,5-DiFTPO, 8, was successfully synthesized, according to NMR spectroscopy. Although the purification of the product was unsuccessful, the purity was improved with recrystallization from isopropyl alcohol. Further research in the purification process is promising.

The di-brominated 3,5-DiFTPO, 13, was synthesized, according to NMR spectroscopy. Similar to the di-nitrated monomer, the di-brominated monomer was not
isolated. The purification of this product was unsuccessful, due to the ease of synthesizing the tri-brominated product. The purified di-brominated 3,5-DiFTPO monomer, 13, would provide another route to the reaction schemes outlined for the di-iodinated monomer, 1.

The remaining compounds were synthesized with the intent of synthesizing a chiral monomer for use in polymerization to afford chiral polymers. The synthesis of these monomers (mono-nitrated 3,5-DiFTPO, 9, the nitrated-iodinated 3,5-DiFTPO monomer, 10, the mono-iodinated 3,5-DiFTPO monomer, 11, and the nitrated-brominated 3,5-DiFTPO monomer, 12) proved successful, conceptually, and provides an avenue for the development of the desired chiral compounds.
5 PROPOSED FUTURE WORK

Future development of this current project is necessary to fully exploit the unique potential of the 3,5-DiFTPO monomer. Using the di-iodinated 3,5-DiFTPO polymer, post-modified polymers synthesized via the Heck reaction, Sonogashira coupling, and the Grignard reaction are possible to achieve functionality that can be tailored to specific applications.

The naphthylated post modified polymer, 6, requires some attention to remove the bi-naphthylated structure, a potential by-product of the coupling reaction. It is believed that the removal of this product will greatly increase the Td5% of this material.

Purification of the pre-modified monomers should be investigated, allowing for the development of the possibly chiral compounds. NMR spectroscopy should be utilized for the analysis of the nitrated compounds, as the previously utilized GC/MS analysis provided unreliable results.
6 REFERENCES


   


6. Medical implants based on PEEK.
   

   


14. Factors Influencing $T_g$.

   http://faculty.uscupstate.edu/llever/Polymer%20Resources/FactorsTg.htm


   http://www.chemicalbook.com/ProductMSDSDetailCB4108290_EN.htm

   (Accessed April 10, 2012).


23. Plastics International: Noryl PPO (Modified Polyphenylene Oxide)


33. Diederich, F.; Stang, P. J. *Metal-Catalyzed Cross-Coupling Reactions*; Wiley-VCH: Weinheim, Germany, **1998**.

