Facile Synthesis of Functionalized Poly (Arylene Ether Sulfone)s

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Facile Synthesis of Functionalized Poly (Arylene Ether Sulfone)s

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

Master of Science

By

Mehmet Tatli
B.S., Cumhuriyet Universitesi, 2007

2012
Wright State University
I HEREBY RECOMMEND THAT THE THESIS PREPARED UNDER MY SUPERVISION BY Mehmet Tatli ENTITLED Facile Synthesis of Functionalized Poly(arylene ether sulfone)s BE ACCEPTED IN PARTIAL FULFILLMENT OF THE REQUIREMENTS FOR THE DEGREE OF Master of Science.

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Abstract

Tatli, Mehmet. M.S., Department of Chemistry, Wright State University, 2012. Facile Synthesis of Functionalized Poly(arylene ether sulfone)s

The synthesis of poly(arylene ether sulfone)s, with a pendant aryl iodide, was achieved via nucleophilic aromatic substitution (NAS) polycondensation of 3-iodo-3',5'-difluoro-diphenylsulfone (2) with Bisphenol-A. Monomer 2 was prepared by the reaction of 3, 5-difluorodiphenylsulfone with N-iodosuccinimide (NIS). Model reactions indicated that the iodo group was stable to NAS conditions. Both GC/MS analysis and NMR spectroscopy indicated quantitative displacement of the two fluorine atoms while the iodo group remained untouched. Furthermore, the modification of the iodo polymer was achieved via Suzuki-Miyaura cross-coupling reaction with phenyl, naphthyl, and phenylacetyl boronic acids. The thermal properties of the polymers were evaluated via DSC and TGA. The iodo polymer possessed a glass transition temperature, \( T_g \), of 144 °C while the corresponding phenyl derivative displayed a slight decrease in \( T_g \) to 131 °C. The much bulkier naphthyl derivative provided a higher \( T_g \) of 150 °C. The more polar acetyl derivative showed a much higher \( T_g \) of 165 °C. All the polymers exhibited high \( T_{d,5\%} \) values between 400 °C and 500 °C. Moreover, conversion of the iodo moiety to an azide group was achieved by using sodium azide in a straightforward manner with the structure being confirmed by IR and NMR spectroscopies. In addition, the iodo group was replaced with a phenyl group, at the monomer stage, in order to prove that the system not only could be functionalized via “post” but also “pre” modification processes.
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1 INTRODUCTION:

1.1 Poly (arylene ether)s, PAE

Poly(arylene ether)s, PAE, consist of aromatic rings linked by ether bonds and, due to their excellent thermal stability and mechanical properties, have been commonly used in many industrial applications. They are also good for use as engineering thermoplastics and show excellent resistance towards hydrolysis and oxidation. Common and commercially available examples of PAE (Figure 1) are poly(2, 6-dimethylphenylene oxide) PPO, poly(ether ether ketone) PEEK, and poly(arylene ether sulfone) PAES.

![Diagram of PPO, PEEK, and PAES structures]

**Figure 1.** The general structures of PPO, PEEK, and PAES.
The PPO and PAES materials are generally amorphous while PEEK is semi-crystalline. The PEEK displays good solvent resistance, but requires high moulding temperatures. The PAES is more soluble than PEEK and requires only moderate moulding temperatures.¹

1.1.1 Poly (phenylene oxide), PPO

Poly(2,6-dimethyl-1,4-phenylene oxide), PPO, is a commercially available and widely used polymer in membrane preparation because of its excellent mechanical properties and resistance against oxidizing reagents. Some major uses of the polymer are in the automotive industry, business machine cases and electrical components, and gas separation membranes.² The polymer is synthesized by oxidative coupling polymerization³ (Scheme 1) and is used as an engineering thermoplastic.

![Scheme 1. Synthetic route to PPO.](image)

The stiffness, tensile strength, and impact strength of PPO are high and maintained over a broad temperature range of -45 °C to 120 °C. PPO exhibits a
glass transition temperature ($T_g$) of 208 °C and this is related to the rigid structure of the polymer. The polymer also carries good hydrolytic stability and, as an engineering thermoplastic, it shows one of the lowest water absorptions.\textsuperscript{2}

1.1.2 Poly(ether ether ketone), PEEK

Another well-known class of PAE is PEEK, which is a linear, semicrystalline, aromatic polymer that has been used as an engineering thermoplastic due to its excellent mechanical properties and stability at high temperatures. PEEK can be synthesized by two methods, electrophilic aromatic substitution (Friedel-Crafts acylation) and nucleophilic aromatic substitution, NAS.

Rose\textsuperscript{4} introduced a synthetic route to synthesize a poly (arylene ether ketone) series, including PEEK, via electrophilic aromatic substitution (Scheme 2). The reaction is carried out in a strong acid system, trifluoromethanesulfonic acid, by catalyzing the condensation of carboxylic acid with the phenyl ether resulting in a high molecular weight. However, this system is not favorable for industrial applications because of the cost and reaction conditions.
Scheme 2. Synthesis of poly (arylene ether ketone)s, including PEEK and poly(ether ether ketone ether ketone), PEEKEK, via electrophilic aromatic substitution.

Another very common method to synthesize PEEK is nucleophilic aromatic substitution, which involves aromatic halides. The first PEEK, synthesized via NAS, was introduced by Johnson et al. who utilized bisphenolate and 4, 4’-difluorobenzophenone in the presence of the base NaOH with DMSO as the solvent. Due to solubility issues with PEEK, the polymer chains precipitated during the reaction and the polymerization process stopped, therefore, only low molecular weight PEEK was obtained. The observed melting temperature (T_m) was 350 °C and the T_g around 160 °C. On further research, Attwood et al. changed the solvent to diphenyl sulfone and the base to Na_2CO_3 in order to obtaining high molecular weight PEEK as depicted in Scheme 3.
Scheme 3. Synthesis of PEEK via NAS in diphenyl sulfone with Na$_2$CO$_3$ as the base.

The Imperial Chemical Industries Limited (“ICI”) first filed a patent in 1978 to make and commercialize PEEK which is called VICTREX® PEEK and got the patent in 1982. A similar route to that employed by Johnson et al. was followed in the synthesis of VICTREX® PEEK. The polymer has been used for a variety of applications such as coatings, adhesives, ultra filtration membranes, and toughening agents.$^6,^7$

PEEK is insoluble in all common organic solvents at room temperature, but it can be dissolved in concentrated sulfuric acid. Due to the solubility issues, modifying the solubility characteristics of PEEK has received considerable attention. Another application of poly (aryl ether ketone)s, PAEK, is as a membrane polymer in gas separation. Their good mechanical properties make them attractive to be used in gas separation membranes. Wang et al. introduced a new series of PAEK, with different backbones, to understand the behavior of the polymers and analyze their gas transportation properties (Figure 2)$^8$. 
Figure 2. PAEK and various repeat units that were used in Wang’s study. 

Table 1. Poly(arylene ether ketone)s, **PAEK**, studied and their $T_g$ values. 

<table>
<thead>
<tr>
<th>Polymer</th>
<th>Repeat Unit$^a$</th>
<th>$T_g$, °C</th>
</tr>
</thead>
<tbody>
<tr>
<td>P1a</td>
<td>P1/a</td>
<td>159</td>
</tr>
<tr>
<td>P1b</td>
<td>P1/b</td>
<td>212</td>
</tr>
<tr>
<td>P2a</td>
<td>P2/a</td>
<td>178</td>
</tr>
<tr>
<td>P2b</td>
<td>P2/b</td>
<td>228</td>
</tr>
<tr>
<td>P2c</td>
<td>P2/c</td>
<td>233</td>
</tr>
<tr>
<td>P3a</td>
<td>P3/a</td>
<td>190</td>
</tr>
<tr>
<td>P3b</td>
<td>P3/b</td>
<td>260</td>
</tr>
</tbody>
</table>

$^a$ See structures from Figure 2.

All the polymers that were synthesized had sufficiently high $T_g$ values to be used in membranes (Table 1). The gas transportation properties of the polymers showed differences as the repeat units changed. Much bulkier
naphthalene based polymers showed higher permeability since they disrupt chain packing and increase the free volume. All of the synthesized polymers were amorphous.

1.1.3 Poly(arylene ether sulfone)s, PAES

Poly(arylene ether sulfone)s, PAES, have been known for the last 40 years. Their outstanding thermal stability, good electrical properties and resistance towards hydrolysis and oxidation make them attractive for industry. Some commercially available PAES are listed in Table 2.

Table 2. Commercially available PAES.

<table>
<thead>
<tr>
<th>Structure</th>
<th>( T_g ) (°C)</th>
<th>Name</th>
</tr>
</thead>
<tbody>
<tr>
<td><img src="image1.png" alt="Structure" /></td>
<td>190</td>
<td>UDEL (Union Carbide)</td>
</tr>
<tr>
<td><img src="image2.png" alt="Structure" /></td>
<td>250</td>
<td>PES 720P (ICI)</td>
</tr>
<tr>
<td><img src="image3.png" alt="Structure" /></td>
<td>285</td>
<td>Astrel (3M Corp)</td>
</tr>
<tr>
<td><img src="image4.png" alt="Structure" /></td>
<td></td>
<td>Radel (Union Carbide)</td>
</tr>
</tbody>
</table>
Similar to the syntheses of PEEK, PAES can be synthesized by two methods, electrophilic aromatic substitution (Friedel-Crafts acylation) and nucleophilic aromatic substitution. The electrophilic substitution has three steps. The first one is the formation of the cation, $\text{ArSO}_2^+$, as is shown in Scheme 4 and the second one is the electrophilic cation attack on the aromatic carbon resulting in formation of an intermediate followed by elimination of a proton in order to generate a new sulfone linkage (Scheme 5).

![Scheme 4](image1)

**Scheme 4.** Formation of sulfonium cation.

![Scheme 5](image2)

**Scheme 5.** Synthesis of PAES via electrophilic substitution.
The other route, which is the most common way to synthesize PAES, is nucleophilic aromatic displacement. The substitution occurs with both strong and weak bases. The first synthesis of PAES, via NAS with a strong base, was done by R. N. Johnson et al. in the 1960’s and is shown in Scheme 6.

\[
\text{HO-} \quad \text{CH}_3 \quad \text{C} \quad \text{CH}_3 \quad \text{OH} + 2 \text{ eq NaOH (50 \% aqueous soln)}
\]

DMSO/Chlorobenzene, N\textsubscript{2}
1) 60-80 °C
2) 120-140 °C
3) 155-160 °C, -H\textsubscript{2}O

\[
\begin{align*}
\text{Na}^+ \text{Na}^+ & \quad \text{CH}_3 & \quad \text{CH}_3 & \quad \text{O}^+ \text{Na}^+ \\
\text{O} & \quad \text{O} & \quad \text{Cl} & \quad \text{Cl}
\end{align*}
\]

160-165 °C
1 to 5 hours


Scheme 7 represents the NAS synthesis of PAES with a weak base (K\textsubscript{2}CO\textsubscript{3} and KHCO\textsubscript{3}), first studied and revealed by a Canadian patent to Clendening et al. in 1970.
1.2 Nucleophilic Aromatic Substitution

PAE are typically synthesized via nucleophilic aromatic substitution (NAS). This reaction occurs based on the displacement of aryl halides with a nucleophilic attack.\textsuperscript{18, 19} A typical NAS reaction is shown in Scheme 8. In the first and rate-determining step, a nucleophile attacks the electropositive carbon to which the leaving group is attached. The electrophilicity of the carbon is due to the presence of strongly electron withdrawing groups such as sulfonyl, phosphoryl or carbonyl, located in the \textit{para} position. As a result of the nucleophilic attack, a stabilized anionic intermediate (Meisenheimer complex) is formed, followed by the loss of the halide in the second step.
**Scheme 8.** Mechanism for a typical NAS reaction of an activated aryl fluoride.

The NAS reactions of 3, 5-difluoro aromatic systems were first studied by Kaiti *et al.* The nucleophilic aromatic substitution takes place in the *meta*-position, relative to activating groups. The synthesis of PAE via *meta*-activated NAS polycondensation reactions with various activating groups has been introduced by the same group, and is shown in **Scheme 9**.

**Scheme 9.** Synthesis of PAE via *meta*-activated NAS polycondensation reactions.
1.3 “Pre” and “Post” Modification Chemistry

The ability to introduce functional groups into polymer systems provides the polymer chemist with a very useful tool to tailor the chemical and physical properties to meet a specific application. Functional groups can be introduced at the monomer stage (“pre”) or after the polymerization process is completed (“post”). Both “pre” and “post” chemistry have been used to modify polymers for many years. A general route of these chemistries is shown in Scheme 10. In the case of “pre”, monomers are functionalized first and then go through the polymerization process. In “post”, the modification is done at the polymer level and functional groups are either located on electron poor rings with anionic reactions or on electron rich rings with electrophilic chemistry (Figure 3).

Scheme 10. “Pre” and “post” modification.
1.4 Functionalization of Poly (arylene ether)s

The synthesis of functionalized monomer systems has been receiving considerable attention in polymer chemistry. Of particular interest is the incorporation of functional groups into monomer systems that undergo polycondensation reactions. Some common functionalization types are sulfonation\textsuperscript{21, 22}, halogenation, nitration, etc.

With PAE systems, the functional groups could be added either prior to polymerization or after the polycondensation reaction. Each process has its own advantages and disadvantages. “Pre” modification might lead to some undesired side reactions due to interference with the polymerization process, which could be fixed by modifying the functional group to prevent undesired side reactions. At the polymer level, the functionalization may suffer because of extreme reaction conditions in addition to the fact that multiple steps might be required. Thus, synthesis of an efficient functionalized monomer system that allows for both “pre” and “post” modification would be an ideal situation.
1.4.1 Sulfonated PAE

Similar to PAES, PPO, and PEEK, sulfonated PAE are expected to maintain their excellent mechanical properties, which allow them to be used for industrial purposes such as fuel cell applications and reverse osmosis desalination processes. Sulfonation techniques were initially revealed by Quentin et al. and, since then, subsequent research has gone into improving the techniques. The PAES could be synthesized by two ways, “pre” which is first to sulfonate the monomer prior to polymerization and “post” which is to sulfonate after polymerization. R.L Orifice and A. Brennan studied the synthesis of sulfonated PAES via “post” chemistry (Scheme 11).
Scheme 11. Sulfonation of PAES via “post” chemistry.

Wang et al. introduced a new route to sulfonate PAES via “pre” chemistry. As is shown in Scheme 12, they used commercially available 4, 4-dichlorodiphenylsulfone (DCDPS) and 4, 4-biphenol to synthesize the 3, 3-disulfonated-4, 4-dichlorodiphenylsulfone (SDCDPS). The ether group is an ortho and para activator since it is an electron donating group\(^{28}\). However, the sulfonic acid group is only located in the ortho position because the para position is blocked. Direct sulfonation of PAES has more advantages as the location and sulfonation level are better controlled in these systems\(^{29,30}\).
Scheme 12. Synthesis of sulfonated PAES via “pre”.

Since the sulfonyl group is a meta-director, the sulfonate groups are located in the meta position after the “pre” modification. According to Wang et al., having two sulfonic acid groups (possible only via “pre” chemistry) on the electron poor ring increases the stability and the acidity of the polymers. Sulfonated PAES have been used in fuel cell applications, desalination processes as well as sulfonated PEEK, and PPO. In particular, ongoing fuel cell research has indicated that sulfonated PAES have been receiving more attention because they show reasonably close results to Nafion® which has a high proton conductivity and chemical stability compared to other sulfonated PAE. 

Sulfonated PAES are also used as desalination membrane polymers. Park et al. synthesized a series of disulfonated PAES random copolymers with various ratios of sulfonated sulfonyl monomer and non-sulfonated sulfonyl or phosphonyl
monomer to monitor the water permeability and salt rejection in saline membranes.\textsuperscript{24} They concluded that the fresh water that goes through the membrane increases when the sulfonated monomer level increases; however, the salt rejection (salt that is kept by the membrane) decreases. On the other hand, when more of the polar monomer unit (phosphonyl monomer) is used, the results obtained were \textit{vice versa} because the more polar group interacts with \textit{SO}_3\textit{H} through H-bonding.\textsuperscript{24}

\section*{1.4.2 Halogenated PAE}

Introducing halogens into monomer systems is another example of functionalization. There are several ways to halogenate organic compounds such as electrophilic halogenation, free radical halogenation, ketone halogenations, and halogen addition. Aromatic compounds usually undergo electrophilic aromatic substitution (EAS), saturated hydrocarbons prefer free radical halogenations, while alkenes and alkynes undergo addition reactions.\textsuperscript{34}

EAS with \textit{N}-Bromosuccinimide (NBS) or \textit{N}-Iodosuccinimide (NIS) is an effective way to functionalize aryl compounds. Rajesh et al. studied the bromination reactions of a series of deactivated aromatic compounds using NBS and concentrated sulfuric acid (\textbf{Scheme 13}).\textsuperscript{35}
Scheme 13. Bromination via NBS.

The reactions were carried out in concentrated sulfuric acid at 60 °C and the yields were obtained mostly in the range of 80-90 %. They used electron-withdrawing groups such as CHO, COOH, NO$_2$, and CN, which are all meta-directors. Therefore, the bromine group was placed in the meta-position on the ring. In 2004, Prakash et al. introduced a synthetic route for halogenations of deactivated aromatic compounds with $N$-halosuccinimides in which BF$_3$•H$_2$O was used instead of H$_2$SO$_4$ and the reactions were done in the range of temperature of 0°C and 105°C. Depending on the activating groups on the aromatic compounds, ortho, meta, and para isomers were acquired.$^{36}$

Functionality can be added to PAE in the same way using iodine and bromine. This could be done by modifying the target monomer, followed by polymerization. Halogenated PAE have been used as waveguide materials.$^{37}$ To be used as waveguide materials, highly halogenated PAEK and PAES were synthesized with different bromine ratios by Qi et al. (Scheme 14).$^{37}$
Scheme 14. Synthesis of halogen-rich PAEK and PAES.

The researchers concluded that polymers containing more C-Br bonds have a better tuning of the refractive index, which is an important parameter for waveguide materials. In other words, by changing the brominated monomer ratio, the refractive index could be easily tuned.

Halogenation could be also done at the “post” stage for PAE. An example of “post” halogen addition was shown by lithium-halogen exchange reaction, followed by phosphonation in Scheme 15. The goal was to obtain a polyelectrolyte poly sulfone to be used for fuel cell applications and to make the polymers more applicable for further functionalization attempts by introducing bromine groups.38
1.4.3 Nitrated PAE

Functionality can also be added to PAE via nitration. The reaction occurs under EAS conditions similar to halogenation reactions. Nitration is usually followed by reduction to the corresponding amine (aniline), which then gives a good opportunity for further modifications such as chain extension and crosslinking reactions to change polymer properties. Pak et al. studied the synthesis of copolymers that contain pendant aryl amines on the backbone of PAES via NAS using bis (4-fluorophenyl)-3-aminophenylphosphine oxide (amino DFTPPO), 4, 4’-dichlorodiphenylsulphone (DCDPS) and bisphenol A.
The purpose of the study was to increase the toughness of epoxy thermosets, used as a toughening agent in thermosetting resins. The ratio of amino to non-amino monomers was varied to alter the concentration of amine groups, which helps to modify epoxy thermosets. Furthermore, the amino groups were also converted to maleimides in order to obtain crosslinked materials. As a result, maleimide functionalized PAES improved the toughness and 2.5 mol % concentration of the aminophenyl unit was found to be ideal to obtain tough epoxy resins.

Scheme 16. Synthesis of amino and maleimide containing PAES copolymers.
PPO has been used in gas separation membranes because it carries excellent physical properties to be used in membranes and provides high gas permeability values. In order to explore the gas transportation properties of functionalized PPO, Bhole et al. nitrated PPO and reduced it to obtain aminated PPO and observed the change in the properties.\textsuperscript{40} As a result, they reported that permeability went down with nitrated PPO and even more when aminated due to a higher packing density. However, selectivity increased because of restricted segmental motions in the nitrated and aminated PPO (Scheme 17).

\textbf{Scheme 17.} Nitration followed by reduction to aminated PPO.\textsuperscript{40}

\section*{1.4.4. Suzuki-Miyaura Cross Coupling Reaction}

A very effective and widespread way to form a C-C bond was introduced by Suzuki and Miyaura in 1981. This reaction occurs in the presence of a palladium catalyst and a base that activates the boron compound to allow the bond formation between aryl halides and phenyl boronic acids (Scheme 18).\textsuperscript{41}
Scheme 18. Suzuki-Miyaura Cross Coupling Reaction.\textsuperscript{41} 

Scheme 19 shows the catalytic mechanism for the Suzuki coupling reaction. The reaction starts with oxidative addition of palladium to the halide, which ends with the formation of organopalladium species. Reacting this species with a base generates an intermediate, which then reacts with the boronate complex to form another organopalladium species. Finally a reductive elimination gives the Ar'-Ar.
1.4.5 Click Chemistry

A very effective and well known cycloaddition reaction allows for the facile modification of azide or alkyne containing polymers. The Huisgen 1, 3-dipolar cycloaddition reaction\textsuperscript{42a,42b} was fully explored by Kolb \textit{et al} in 2001\textsuperscript{43}. In 2002, Sharpless and his co-workers introduced a new approach that leads to the formation of 1,2,3-triazoles via the Cu-catalyzed Huisgen reaction of nonactivated alkynes and alkyl/aryl azides.\textsuperscript{44a} There are several advantages of the Sharpless “click” reaction that allow for functional group variability, solubility in common organic solvents, uses in different interfaces such as liquid/liquid, solid/liquid, etc, while obtaining nearly quantitative yields.
In Scheme 20, a catalytic mechanism for the cycloaddition reaction of alkynes and azides is illustrated. Initially, a Cu$^+$ species and the terminal alkyne generate the Cu acetylide (II) followed by formation of $\pi$-complex between the same reagents (III, IV), which results in a reduction of the pK$_a$ of the acetylene to approximately 9.8 units. Thus, the azide ion attack occurs on the acetylene (V).$^{42b}$ The azide group displaces another ligand and binds to the copper. Then, an unusual six-membered metallacycle is generated (VI). Ring condensation to a triazolyl-copper species (VII) is followed by protonolysis which gives the triazole product (VIII).
Click chemistry has been widely used in polymer science, drug discovery, nanotechnology, materials science, and bioconjugations. In polymer chemistry, click chemistry is used to form new architectures such as block, star, graft, dendritic and polymeric networks having azide/alkyne functionality in the side or end chains. Moreover, it is also used to functionalize polymer via “post” chemistry. Norris et al. synthesized crosslinked polysulfone copolymer membranes via click chemistry in order to improve conductivity and fuel cell performance of fuel cell membranes. They used an azide containing polysulfone, which was prepared by using n-butyl lithium and p-toluenesulfonyl azide, partially sulfonated polysulfone, and a crosslinker (1, 7-octadiyne) as is shown in Scheme 21.\textsuperscript{45}
The researchers noted that similar conductivities and lower methanol permeabilities, compared to Nafion, were obtained with the synthesized copolymer via 1, 3-cycloaddition reaction.

1.5 Current Project

Why functionalized polymers? When polymer chemists work on specific polymers for specific applications, they seek a set of particular properties. However, those properties sometimes might not be readily available. In this case,
giving polymer chemists the ability to introduce functional groups to polymers or modify polymers in order to improve the properties would provide the solution. In this study, it was thought to introduce functional groups to widely known PAE, which have been receiving attention due to their high thermal stability, resistance against oxidation-hydrolysis, and good engineering thermosplastic properties.

This particular project is focused on the use of 3, 5-difluoro aromatics, which are designed to undergo NAS reactions activated by a strongly electron withdrawing group located in the meta position. One aromatic ring possesses two fluorine atoms in the meta positions, while the other aromatic ring is unsubstituted, which allows the straightforward preparation of PAE, which carry functional groups located on a pendant aromatic ring. In particular, 3, 5-difluorodiphenyl sulfone, 1, is utilized as the base monomer in this study.

The initial functional groups, bromides and iodides, are to be introduced to this monomer using electrophilic aromatic substitution reactions, EAS. Since the sulfone is a strong meta director the EAS reactions are expected to occur in the meta position of the non-fluorinated ring. Scheme 22 presents examples of EAS reactions with N-Bromo succinimide (NBS) and N-Iodo succinimide (NIS). This should be the first example of a PAE system in which the halogen resides on the electron poor ring, but is introduced at the monomer stage, rather than using more sophisticated reactions at the “post” stage.
Scheme 22. Functionalization of 3, 5-difluorodiphenyl sulfone via halogenation.

![Scheme 22](image)

The bromo and iodo groups provide an avenue to perform both “pre” and “post” functionalization chemistry via the Suzuki-Miyaura, Heck, or other cross-coupling reactions.\(^{46, 47}\) (Scheme 23). Jo et al. introduced new functional groups to polysulfone via complex iridium-catalyzed borylation followed by the reaction with functionalized aryl bromides.\(^{48}\) In the “proof of concept” phase of this project, various functional groups will be added to PAES via the Suzuki-Miyaura cross-coupling reaction of an iodinated PAES with phenyl, naphthyl, and phenylacetyl boronic acids. Subsequently, a variety of other conversions of the iodo group as well as the introduction of nitro, amino, and alkynyl groups will be explored.
Scheme 23. General reactions of aryl halides.
2 EXPERIMENTAL

2.1 Materials

Powdered K$_2$CO$_3$ was dried at 130 °C in an oven before use. 3, 5-Difluorodiphenylsulfone, I, was synthesized via the previously reported route.$^{20}$ Bisphenol A, was purchased from Sigma Aldrich and recrystallized from toluene and dried under vacuum prior to use. Pd (OAc)$_2$ and the boronic acids were also purchased from Sigma Aldrich, and NIS was purchased from Acros Chemicals.

$^1$H and $^{13}$C NMR spectra were acquired using an AVANCE 300 MHz instrument operating at 300, and 75.5 MHz, respectively. Samples were dissolved in appropriate deuterated solvents (DMSO-$d_6$ or CDCl$_3$), at a concentration of (~30 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 µm PL gel Mixed C columns (heated to 35 °C) were used with THF as the eluent and a Thermoseparation Model P1000 pump operating at 1.0 mL/minute. DSC and TGA analysis were carried out under nitrogen (or air) on TA Instruments DSC Q200 and TGA Q500, respectively, at a heating rate of 10 °C/ min.
2.2 Synthesis of 3'-Iodo 3, 5-Difluorodiphenylsulfone (2)

Into a 50 mL RB flask, equipped with a stir bar, were added 4.00 g (15.7 mmol) of 3, 5-difluorodiphenyl sulfone (1) and 20 mL of concentrated H₂SO₄. To the vigorously stirred solution was slowly added 4.40 g (24.7 mmol) of N-iodosuccinimide (NIS) and the resulting mixture was allowed to react for 12 hours at room temperature. After the reaction was done the reaction mixture was slowly poured into a large excess of water and the resulting solid was isolated via filtration. The solid was redissolved in approximately 50 mL of dichloromethane and then washed with a dilute sodium bisulfite solution. The organic layer was dried over MgSO₄ and the solvents removed via rotary evaporation resulting in a yellowish product (5.6 g). The crude product was recrystallized from isopropanol to afford 3.3 g (60 %) of 2 with a melting point of 158-159 °C. ¹H NMR (CDCl₃, δ): 7.05 (tt, 1 H), 7.28 (t, 1 H), 7.48 (m, 2 H), 7.91 (ddd, 1 H), 7.96 (dt, 1 H), 8.27 (t, 1 H). ¹³C NMR (CDCl₃, δ): 109.4 (t), 111.4 (d), 94.5 (ArC-I), 127 (s), 131 (s), 136.4 (s), 142.0 (s), 142.9 (s), 144.3 (s), 162.9 (dd). MS (EI): [M⁺] m/z calculated for C₁₂H₇F₂O₂SI, 380.15; found 380. Elemental Analysis: Calc. Anal. for C₁₂H₇F₂O₂SI: C, 37.91; H, 1.86; Found: C, 37.93; H, 1.82.

2.3 Synthesis of the Iodo Model Compound (3)

Into a 25 mL RB flask, equipped with a magnetic stir bar, condenser, and gas inlet, were placed 300 mg (0.789 mmol) of 2, 237 mg (1.58 mmol) of t-butyl phenol, 327 mg (2.37 mmol) of K₂CO₃, and 3 mL of NMP. The resulting mixture was stirred at 150 °C for 4 hours at which point GC/MS and NMR spectroscopy
indicated quantitative conversion to the desired product. The reaction mixture was precipitated from water to obtain a white solid (3) in 60 % isolated yield. $^1$H NMR (CDCl$_3$, $\delta$): 1.35 (s, 18 H), 6.69 (t, 1 H), 6.85 (d, 4 H), 7.10 (d, 2 H), 7.16 (t, 1 H), 7.31 (d, 4 H), 7.76 (ddd, 1 H), 7.84 (dt, 1 H), 8.11 (t, 1 H). $^{13}$C NMR (CDCl$_3$, $\delta$): 31.4 (s), 34.4 (s), 94.3 (ArC-I), 110.0 (s), 112 (s), 119 (s), 127 (s), 131 (s), 136 (s), 142 (s) 143 (s), 143.2 (s), 147.8 (s), 152.8 (s), 160 (s).

2.4 Polymerization of Iodo monomer 2 to yield the iodo polymer (4)

In a 50-mL RB flask, equipped with a stir bar, condenser, and nitrogen gas outlet, were placed 4.1 mL of NMP, 1.1 g (3 mole equivalent) of potassium carbonate, 1.00 g (2.63 mmol) of 2, and 0.600 g (2.63 mmol) of Bis-A. The reaction flask was immersed in an oil bath and stirred vigorously at 150 °C for 12 hours. The solution was left to cool to room temperature. The polymer was isolated by precipitation from acidic water and filtration afforded a powdery grey precipitate. The solid was dissolved in THF, precipitated from ethanol, filtered, and dried to afford 1.15 g (72 %) of 4 as an off-white solid. $^1$H NMR (CDCl$_3$, $\delta$): 1.69 (s, 6 H), 6.81 (t, 3 H), 6.91 (d, 4 H), 7.19 (d, 2 H), 7.24 (d, 4 H), 7.83 (bd, 1 H), 7.87 (bd, 1 H), 8.15 (b, 1 H). $^{13}$C NMR (CDCl$_3$, $\delta$): 31.0, 42.4, 94.3 (ArC-I), 111.0, 112.5, 119.2, 127.0, 128.5, 130.9, 136.2, 142.4, 142.9, 143.3, 147.0, 153.0, 159.7.
2.5 General Procedure for Post Polymerization Modification

A slightly modified version of the phosphine free procedure reported by Novak was used for the Suzuki Miyaura reaction. A typical post polymerization reaction for the iodo polymer will be described using phenyl boronic acid. In a 25-mL Schlenk flask, equipped with a stir bar, were placed 200 mg (0.352 mmol) of 4, 85.8 mg (0.704 mmol) of phenyl boronic acid, and 5 mL of THF. Another Schlenk flask was charged with 291 mg (2.100 mmol) of K$_2$CO$_3$, 2 mol % Pd (OAc)$_2$ in acetone, and 1 mL of water. The Schlenk flasks were degassed three times using freeze-pump-thaw cycles, back-filled with nitrogen, and the contents combined through a cannula. The resulting mixture was allowed to react for two hours at 60 $^\circ$C followed by addition of an extra 10 % of the boronic acid and heating for an additional 24 hours. The reaction mixture was diluted with ~10 mL THF, washed with brine, and the layers were separated. The organic layer was dried with MgSO$_4$; the volume was decreased to ~5 mL under pressure, and precipitated from methanol to obtain 134 mg of 5 (74 %): $^1$H NMR (CDCl$_3$, $\delta$): 1.65 (s, 6 H), 6.78 (t, 1 H), 6.90 (d, 4 H), 7.19 (d, 4 H), 7.25 (d, 2 H), 7.41 (m, 3 H), 7.53 (m, 3 H), 7.79 (m, 2 H), 8.07 (t, 1 H). $^{13}$C NMR (CDCl$_3$, $\delta$): 30.9, 42.4, 111.0, 112.5, 119.2, 126.0, 126.7, 127.0, 128.5, 129.0, 129.8, 132.0, 139.0, 141.7, 142.7, 144.0, 146.8, 153.0, 159.7.

6 (55 %): $^1$H NMR (CDCl$_3$, $\delta$): 1.50 (s, 6 H), 6.69 (t, 1 H), 6.79 (d, 4 H), 7.06 (d, 4 H), 7.19 (d, 2 H), 7.42 (m, 2 H), 7.47 (t, 1 H), 7.57 (m, 1 H), 7.79 (m, 5 H), 7.92 (b, 1 H), 8.12 (t, 1 H). $^{13}$C NMR (CDCl$_3$, $\delta$): 30.9, 42.4, 111.0, 112.5, 119.2,
124.8, 126.3 (d), 126.7 (d), 127.6, 128.2, 128.4, 128.9, 129.8, 132.2, 133.0, 133.5, 136.2, 141.7, 142.7, 144.0, 146.8, 153.0, 159.7.

7 (55 %): $^1$H NMR (CDCl$_3$, δ): 1.66 (s, 6 H), 2.62 (s, 3 H), 6.78 (t, 1 H), 6.87 (d, 4 H), 7.20 (d, 4 H), 7.24 (d, 2 H), 7.57 (t, 1 H), 7.64 (d, 2 H), 7.81 (m, 1 H), 7.85 (m, 1 H), 8.03 (d, 2 H), 8.10 (t, 1 H). $^{13}$C NMR (CDCl$_3$, δ): 26.7, 30.9, 42.4, 111.0, 112.5, 119.1, 126.2, 127.2, 127.4, 128.5, 129.0, 130.0, 132.1, 136.7, 141.4, 142.0, 143.4, 143.8, 146.9, 153.2, 159.7, 197.3.

2.6 Synthesis of 3-(3, 5-difluorophenylsulfonyl) biphenyl (2a)

In a 25-mL Schlenk flask, equipped with a stir bar, were placed 200 mg (0.526 mmol) of 2, 75.6 mg (0.620 mmol) of phenyl boronic acid, and 1.4 mL of THF. Another Schlenk flask was charged with 180 mg (1.29 mmol) of K$_2$CO$_3$, 1 mol % Pd (OAc)$_2$ in acetone, and 1.4 mL of water. The Schlenk flasks were degassed for three times using freeze-pump-thaw cycles, back-filled with nitrogen, and the contents combined. The resulting mixture was allowed to react for two hours at 60 °C followed by addition of an extra 10 % of the boronic acid and heating for additional 4 hours. The reaction mixture was diluted with ~10 mL of toluene, washed with brine, and the layers were separated. The organic layer was dried with MgSO$_4$; dried under pressure, and recrystallized from isopropanol to obtain 2a (43 %) with a melting point of 111-112 °C. $^1$H NMR (CDCl$_3$, δ): 6.92 (tt, 1 H), 7.37 (m, 2 H), 7.42 (m, 3 H), 7.55 (m, 3 H), 7.75 (d, 1 H), 7.83 (d, 1 H) 8.07 (t, 1 H). $^{13}$C NMR (CDCl$_3$, δ): 108.9 (t), 111.3 (d), 126.4 (s), 126.7 (s), 127.2 (s), 128.5 (s), 129.2 (s), 130.1(s), 132.5 (s), 138.9 (s), 140.9 (s), 143.1 (s), 145 (s).
162.9 (dd). MS (EI): [M$^+$] m/z calculated for C$_{18}$H$_{12}$F$_2$O$_2$S, 330.35; found 330.
Calculated Analysis for C$_{18}$H$_{12}$F$_2$O$_2$S Calculated: C, 65.44; H, 3.66. Found: C, 65.58; H, 3.74.

2.7 Polymerization of 2a to form the phenylated polymer (5)

In a 50-mL RB flask, equipped with a stir bar, condenser, and nitrogen gas outlet, were placed 0.83 mL of NMP, 175 mg (0.530 mmoles) of 2a, 121 mg (0.530 mmol) of BisA, and 220 mg (3 mole equivalent) of potassium carbonate. The reagents were stirred vigorously at 150 °C for 12 hours. The solution was left to cool to room temperature. The polymer was isolated by precipitation from acidic water and filtration afforded a powdery grey precipitate. The solid was dissolved in THF, precipitated from ethanol, filtered, and weighed to afford 175 mg (59 %) of 5 as an off-white solid. $^1$H NMR (CDCl$_3$, δ): 1.65 (s, 6 H), 6.78 (t, 1 H), 6.90 (d, 4 H), 7.19 (d, 4 H), 7.25 (d, 2 H), 7.41 (m, 3 H), 7.53 (m, 3 H), 7.79 (m, 2 H), 8.07 (t, 1 H). $^{13}$C NMR (CDCl$_3$, δ): 30.9, 42.4, 111.0, 112.5, 119.2, 126.0, 126.7, 127.0, 128.5, 129.0, 129.8, 132.0, 139.0, 141.7, 142.7, 144.0, 146.8, 153.0, 159.7.

2.8 Synthesis of 3’-Ethynyl- 3, 5-Difluorodiphenylsulfone (2b)

*Step 1:* 0.265 g (1.18 mmoles) of zinc bromide was flame-dried under vacuum, and dissolved in 2 mL of THF. Then, into this solution, 0.5 M Grignard solution (acetylene magnesium bromide) was added in order to form a zinc bromide-acetylene compound.
**Step 2:** To a Schlenk flask, wrapped by aluminum foil, was added 300 mg (0.789 mmol) of the iodinated monomer and 43.5 mg (0.0395 mmol) of the catalyst (tetrakis (triphenylphosphine) palladium), followed by flushing with nitrogen. Then, the zinc bromide acetylene compound from step 1 was added through a canula to the same flask. The solution was stirred overnight and quenched in a beaker with 50:50 brine solution - Et₂O. The ether layer was separated and dried over MgSO₄. The ether layer was taken into a round bottom flask and evaporated under vacuum to obtain a solid, which was dissolved in methanol. The solution was filtered multiple times through gravity and Buchner funnels to remove any remaining PPh₃. The methanol was dried off under vacuum to obtain the desired acetylene monomer. The crude monomer was recrystallized first from hexanes, followed by another recrystallization from ethanol/water to obtain 2b (34 %) with a melting point of 128-129 °C. ¹H NMR (CDCl₃, δ): 3.20 (s, 1 H), 7.00 (tt, 1 H), 7.40 (m, 2 H), 7.45 (t, 1 H), 7.63 (ddd, 1 H), 7.83 (ddd, 1 H), 7.96 (s, 1 H). ¹³C NMR (CDCl₃, δ): 80 (s), 81(s), 109 (t), 111 (dd), 124 (s), 127 (s), 129 (s), 131 (s), 137 (s), 140 (s), 144 (t), 162.5 (d). MS (EI): [M⁺] m/z calculated for C₁₄H₈F₂O₂S, 278.27; found 278. Calculated Analysis for C₁₄H₈F₂O₂S: C, 60.43; H, 2.90. Found: C, 60.18; H, 3.09.

2.9 Model reaction of 2b to form 2c

In a 5 ml round bottomed flask, equipped with a stir bar, were placed 0.36 mmol of 2b, 0.72 mmol of t-butyl phenol, 1.08 mmol of K₂CO₃, and 0.56 ml of DMSO. The reaction setup was purged with nitrogen and heated to 120 °C for 12
hours. The reaction mixture was precipitated in water and extracted with chloroform to obtain a greenish powdery solid.

2.10 Synthesis of 3’-Nitro-3, 5-Difluorodiphenylsulfone (2d)

In a 250 mL flask, equipped with a stir bar, were placed 4.00 g (15.7 mmol) of 3, 5-DFDPS and 32.5 mL of H$_2$SO$_4$. Then, into the same flask, 1.35 mL (21.2 mmol) of HNO$_3$ was added dropwise and the resulting mixture was allowed to stir, cooled in an ice bath, for one hour. The reaction mixture was precipitated from crushed ice and isolated by filtration. The crude solid was recrystallized from 100 ml of 88 % isopropanol, 5 % hexane, 5 % toluene, and 2 % chloroform to obtain 2.96 g (63 %) of 2d as light yellow crystals. $^1$H NMR (CDCl$_3$, $\delta$): 7.09 (tt, 1 H), 7.54 (m, 2 H), 7.81 (t, 1 H), 8.30 (dt, 1 H), 8.50 (dt, 1 H), 8.79 (t, 1 H). $^{13}$C NMR (CDCl$_3$, $\delta$): 109.8 (t), 111.7 (d), 123.1 (s), 128.4 (s), 131.1 (s), 133.3 (s), 142.6 (s), 143.5 (t), 148.7 (s), 162.9 (dd). MS (EI): [M$^+$] m/z calculated for C$_{12}$H$_7$F$_2$NO$_4$S, 299.25; found 299. Calculated Analysis for C$_{12}$H$_7$F$_2$NO$_4$S

Calculated: C, 48.16; H, 2.36. Found: C, 47.92; H, 2.26.

2.11 Synthesis of the Azide Polymer (8)

In a 50 mL Schlenk flask, equipped with stir bar and nitrogen inlet, were placed 300 mg (0.528 mmoles) of 4, sodium azide (68.9 mg, 1.06 mmol), sodium ascorbate (20.92 mg, 0.106 mmol) and N,N'-Dimethylethylenediamine (8.55 µl, 0.079 mmol). The entire set-up was flushed with nitrogen and 4.5 ml of NMP and 0.25 ml of water were added. The polymer was given time to dissolve. When it was fully dissolved, a single freeze-pump-thaw was performed. Then, copper
sulfate (13.9 mg, 0.053 mmol) was added followed by the drop wise addition of 0.25 mL water. The set-up was flushed with nitrogen and a second freeze-pump-thaw was performed. The solution was allowed to react for 2 days. The reaction mixture was precipitated from water to obtain 155 mg of a yellowish fine solid (61 %). $^1$H NMR (CDCl$_3$, δ): 1.72 (s, 6 H), 6.82 (t, 1 H), 6.94 (d, 4 H), 7.23 (m, 7 H), 7.50 (m, 2 H), 7.61 (t, 1 H). $^{13}$C NMR (CDCl$_3$, δ): 31.0, 42.4, 110.9, 112.5, 118.1, 119.2, 123.9, 128.5, 130.8, 141.7, 142.9, 143.4, 147.0, 153.2, 159.7. IR (KBr) 2108 cm$^{-1}$ (N=N=N stretch).

2.12 Synthesis of the Triazole Polymer (9)

Into a Schlenk flask, 150 mg (0.310 mmoles) of 4a, 1.65 ml of NMP, and a magnetic stir bar were placed and stirred until the entire polymer was dissolved. Then, 46 microliter (0.310 mmoles) of 1-octyne was added to the solution and a freeze-pump-thaw was performed followed by the addition of 10.7 mg (0.067 mmol) of anhydrous copper sulfate into the same flask. The reaction mixture was stirred for 30 minutes at room temperature, then the reaction mixture was heated in an oil bath to 60 °C and left to react for 12 hours. The reaction mixture was then precipitated from water and filtered to obtain 110 mg (60 %). $^1$H NMR (CDCl$_3$, δ): 0.80 (m, 3 H), 1.23 (m, 8 H), 2.71 (t, 2 H), 6.72 (t, 1 H), 6.84 (d, 4 H), 7.15 (m, 8 H), 7.48 (dt, 1 H), 7.71 (s, 0.5 H), 7.85 (dd, 1 H), 8.12 (s, 0.5 H).
3 RESULTS & DISCUSSION

3.1 Monomer synthesis for “post” modification

3.1.1 Synthesis of 3’-iodo 3, 5-difluorodiphenylsulfone (2)

The first monomer synthesized in lab was 3’-iodo 3, 5-difluorodiphenylsulfone (2) using the base monomer 3, 5-difluorodiphenylsulfone (1), which was previously synthesized by Kaiti et al.\textsuperscript{20} The iodination reaction occurred via a typical electrophilic aromatic substitution pathway using a slight excess of NIS (Scheme 24). From the \textsuperscript{13}C NMR data for 1, it can be seen that the most electron rich carbon on the monomer is the carbon between the two fluorine atoms, thus the electrophilic substitution is expected to take place on the substituted ring. However, due to steric issues, the incoming electrophile is forced to the unsubstituted ring onto which the iodo group was directed to the \textit{meta} position.

![Scheme 24](image)

Scheme 24. Synthesis of 2 via EAS.

After the reaction, the GC/MS showed that 94 % conversion to a mono-iodinated species was obtained. The other 6 % was found to be roughly equal
quantities of a di-iodo compound and the starting material. The reaction mixture was slowly poured into water and the resulting solid was isolation by filtration. The crude product was subjected to a workup procedure, which included dissolving in dichloromethane, washing with 5% sodium bisulfite solution, and drying over magnesium sulfate, followed by recrystallization twice from isopropanol to obtain white crystals (60%) with a 158-159 °C melting point.

The structure of the monomer was confirmed by $^1$H and $^{13}$C CPD NMR spectroscopy, GC/MS and elemental analysis. The $^1$H and $^{13}$C NMR spectra of 2 are shown in Figures 4 and 5, respectively.

**Figure 4.** 300 Mz $^1$H NMR spectrum (CDCl$_3$) of the iodo monomer (2).
Figure 5. 75.5 MHz $^{13}$C NMR spectrum of the iodo monomer (2).

For the iodo monomer, there can be seen that there is some splitting in some of the signals, due to coupling with the fluorine atoms. A triplet can be seen at $< 110$ ppm. The signal for carbon b appears as a doublet of doublets, centered at 163 ppm. Carbon c gives rise to a doublet of doublets at 112 ppm, while carbon atom d appears as a triplet at 144 ppm. All of the remaining peaks in the spectrum appear as singlets; the key feature is the C-I resonance located at 94.5 ppm.

3.1.2 Synthesis of the Iodo Model Compound (3)

After successfully introducing the iodo group to 1, a model reaction was applied to determine if the iodo group would be stable under typical NAS
conditions. The reaction was carried out with 2 equivalents of t-butylphenol as the nucleophlic reaction partner (Scheme 25).

![Scheme 25. Synthetic scheme for iodo model compound (3).](image)

Initial analysis via GC/MS indicated that the fluoro groups on the structure served as the leaving groups while the iodo group was undisturbed under the NAS conditions. The product structure was further confirmed by its $^1$H and $^{13}$C NMR spectra. A $^{13}$C NMR overlay of the iodo monomer (2) and iodo model (3) is shown in Figure 6.
Figure 6. 75.5 MHz $^{13}$C NMR spectral overlay of 2 and 3.

The overlay confirms the successful displacement of the fluoride groups in the iodo monomer while maintaining the iodo group. The major changes in the spectrum are the collapse of the triplets and doublet of doublets to singlets, which indicate the quantitative conversion to the corresponding aryl ether bonds. Moreover, the new peaks at 153 ppm and 160 ppm, which represent the carbon atoms of the C-O bonds, could be seen in the spectrum of the model product. The most important feature of the spectrum is the presence of a carbon atom of the C-I bond, present at 94.5 ppm, indicating that the iodo group was stable under the reaction conditions and it should be possible to carry it directly into the corresponding polymer.
3.1.3 Polymerization of the Iodo Monomer (2) to form Iodinated PAES (4)

The iodo polymer (4) was successfully synthesized after the reaction of 2 with Bisphenol A, in the presence of K$_2$CO$_3$, at 150 °C for 15 hours (Scheme 26). The reaction mixture was first precipitated from water followed by reprecipitation from methanol to obtain 4 as a brownish solid (72%).


As was confirmed for the model reaction, the polymerization occurred by replacement of the fluorine groups and the iodo group was successfully carried into the polymer despite the harsh NAS conditions. The $^{13}$C NMR spectral overlay of 2 and 4 is shown in Figure 7. The NMR results showed that the C-I bonds survived the NAS conditions as the signal for their carbon atoms was observed at 94.5 ppm, and the triplet, present at 109.4 ppm, which represents the carbon atom between the two fluorine atoms, was reduced to a singlet. The doublet of doublets that represents the carbon atom of the C-F bond was gone and the new signals for the carbon atoms in the C-O peaks were observed at 153 ppm and 160 ppm.
The molecular weight of the polymer was found to be 20,100 g/mol with a PDI of 2.1. The polymer showed good solubility in THF, chloroform, DCM, DMAc, and NMP, but was insoluble in methanol, DMSO, toluene and partially soluble in DMF.

### 3.1.4 Synthesis of PAES Series via “Post” Suzuki Modification

After carrying the iodo group into the polymer, the next step was to explore the possibility of “post” modifications. With this purpose in mind, the Suzuki-Miyaura cross coupling reaction was applied to polymer 4 following literature procedures. The introduction of the initial “proof of concept” functional groups was achieved via the Pd(OAc)$_2$ catalyzed cross-coupling
reaction with phenyl, naphthyl, and 4-acetylphenyl boronic acid, respectively, as outlined in Scheme 27.

Scheme 27. Synthesis of PAES series via Suzuki coupling reaction.

Figure 8 presents the $^{13}$C NMR spectra of 4 as well as the modified polymers 5, 6, and 7. After the coupling reaction the signal arising from carbon i, representing the C-I bond at 94.5 ppm, was no longer observed, but a new signal, representing carbon atom of the C-C bond in the biphenyl system (polymer 5), was now present at 143 ppm.
Figure 8. 75.5 MHz $^{13}$C NMR spectral overlay for 4, 5, 6, and 7.

The other indications are that carbons j and h shifted from 136 ppm and 147 ppm to 126 ppm and 132 ppm and a new carbon, o, was observed at 142 ppm. The structure of polymer 6 was also confirmed by the NMR overlay. The indications are that the signals for carbon atoms i, j, and h are shifted to the same region as in the case of 5. In addition, the signals of the new carbon atoms; o, p, r, s, u that belong to the naphthyl group were seen at 136 ppm, 125 ppm, 134 ppm, 129 ppm, and 127 ppm. Polymer 7 had a distinct peak for carbon atom r at 197
ppm for the carbonyl. Peak i on the phenyl acetyl group was observed in the same spot as it was in the phenyl polymer. Peak p was seen at 141 ppm.

Using differential scanning calorimetry (DSC), gel permeation chromatography (GPC), and thermal gravimetric analysis (TGA), the properties of the synthesized polymers were evaluated and the determined glass transition temperature, \( T_g \), 5 % decomposition temperature, \( T_{d5\%} \), polydispersity index (PDI), and number average molecular weight (\( M_n \)) values are given in Table 3.

**Table 3. Polymer Characterization Data for Polymers 4 – 6.**

<table>
<thead>
<tr>
<th>Polymers</th>
<th>( M_n ) (g/mol)</th>
<th>PDI</th>
<th>( T_g ) (°C)</th>
<th>( T_{d5%} ) (°C) ( (N_2) )</th>
<th>( T_{d5%} ) (°C) ( (Air) )</th>
</tr>
</thead>
<tbody>
<tr>
<td>4</td>
<td>20,100</td>
<td>2.1</td>
<td>133</td>
<td>427</td>
<td>404</td>
</tr>
<tr>
<td>5</td>
<td>19,700</td>
<td>2.4</td>
<td>131</td>
<td>492</td>
<td>478</td>
</tr>
<tr>
<td>6</td>
<td>21,700</td>
<td>2.3</td>
<td>149</td>
<td>507</td>
<td>482</td>
</tr>
<tr>
<td>7</td>
<td>20,700</td>
<td>2.4</td>
<td>165</td>
<td>466</td>
<td>454</td>
</tr>
</tbody>
</table>

The molecular weights of polymers 4, 5, 6, and 7 were found to be 20,100, 19,700, 21,700, and 20,700 Daltons and PDI values of 2.1, 2.4, 2.3, and 2.4, respectively. The results are fairly close to each other because the groups that replaced the iodo group are not very different in molecular weight.

### 3.1.5 Thermal Analysis:

The thermal properties of polymers 4, 5, 6, and 7 were evaluated via TGA and DSC and the thermograms are depicted in Figure 9. It can be seen that the
iodo polymer has two degradation steps. The first degradation step represents the iodine loss while the second steps can be attributed to the backbone decomposition. On the other hand, the phenyl, naphthyl, and phenyl acetyl polymers have only one degradation step, presumably, backbone decomposition.

![TGA thermograms of polymers 4, 5, 6, and 7](image.png)

**Figure 9.** TGA thermograms of polymers 4, 5, 6, and 7 (under a nitrogen atmosphere).

The $T_d$ 5% values are in order 427 °C, 492 °C, 507 °C, and 466 °C. Polymer 4 has the lowest decomposition temperature since the iodo group makes it less stable compared to the other polymers. Polymer 5 showed a higher $T_d$ 5% due to having a phenyl ring that makes the polymer more stable and better heat resistant. Polymer 7 provided a lower $T_d$ 5% compared to polymer 5 since due to possessing a less stable acetyl group. The naphthyl containing polymer 6 showed the highest decomposition temperature since the backbone is bulkier, and it is a more aromatic structure compared to that of polymers 4, 5, and 6. The TGA data for the
polymers under air showed a similar trend of $T_{d,5\%}$ values, 404 °C for 4, 478 °C for 5, 482 °C for 6, and 454 °C for 7.

The glass transition temperatures of the polymers were determined as well and the DSC overlay of the polymers is shown in Figure 10. Polymer 4 possessed a glass transition temperature, $T_g$, of 144 °C while the corresponding phenyl derivative (5) displayed a decrease in $T_g$ to 131 °C. A higher $T_g$ for 4 could be explained by having less free volume. Polymer 6 provided a higher $T_g$ of 149 °C due to containing a bulkier group, naphthyl. Finally, polymer 7 showed the highest $T_g$ of 165 °C because of having a more polar side group.

![Figure 10. DSC traces of polymers 4, 5, 6, and 7.](image-url)
3.1.6 Azide Modification of the Iodo Polymer (4) to form 8

With the goal of broadening the range of functional groups that could be readily introduced to PAES materials, the conversion of the iodo group into an azide group was explored. Following a well-established literature procedure, the iodo group was quantitatively replaced with an azide group using sodium azide (NaN₃) and copper sulfate as the catalyst (Scheme 28).

![Scheme 28. Synthetic procedure for the azide polymer (8).](image)

According to the ¹³C NMR spectroscopy data (Figure 11), the reaction was completed after running at room temperature for 24 hours. The signs that indicated the completion were the absence of the peak at 94.5 ppm, corresponding to the carbon atom of the C-I bond and the presence of a new peak representing the carbon atom with the azide group attached at 142 ppm. Moreover, the peaks representing carbons f, j, and h at 125 ppm, 135 ppm, and 142 ppm on the spectrum of the iodo polymer were shifted after the reaction, and these peaks were observed at 119 ppm and as two closely associated peaks at 125 ppm on the spectrum of the azide polymer. TGA and DSC data were not collected due to the presence of copper in the polymer, which might cause some issues in the TGA and DSC instruments and result in unclear data. The molecular weight of the
azide polymer was found to be 17,500 g/mol with a 2.3 PDI value, which was made from an iodo polymer with a MW of 19,000 g/mol.

Figure 11. 75.5 MHz $^{13}$C NMR overlay of 4 and 8.

The synthesis of 8 was also confirmed by infrared spectroscopy. Figure 12 indicates the N$_3$ stretch at ~2108 cm$^{-1}$, which is in the reported range of an N=N=N stretch for aryl azides.$^{47}$
3.1.7 Synthesis of Triazole polymer (9)

After the azide polymer was successfully synthesized, it was thought that the polymer could be “clicked” with an alkyne to convert the azide moiety to a triazole group. For this purpose, the azide polymer was “clicked” with 1-Octyne using CuSO₄ as the catalyst in NMP at 60 °C for 12 hours (Scheme 29). The successful conversion was proven by ¹H NMR spectroscopy (Figure 13). There are two possible product structures obtained as shown in the Scheme 29.
Scheme 29. Synthetic procedure for the triazole polymer (9).

The $^1$H NMR spectral overlay of 8 and 9 provides a better sense for clarifying the successful conversion. The shifts can be easily seen once the groups (azide, and triazole) are altered. The distinct peaks of the triazole polymer represent the aliphatic protons which are labeled as b, c, and d and seen at 2.31 ppm, 1.25 ppm, and 0.81 ppm. The proof of the presence of the two possible structures obtained after the reaction is the two singlets (a' and a) that are seen at 7.71 ppm and 8.12 ppm. There are also some NMP residual peaks in the aliphatic region, which are marked with an asterisk.
Figure 13. 300 MHz $^1$H NMR spectral overlay of 8 and 9.

3.2 Monomer Functionalization Prior to Polymerization

3.2.1 Synthesis of Phenylated Monomer (2a)

After the post modification on polymer 4 was successfully achieved by Suzuki coupling reactions and azide displacement, the next aim was to modify the monomer 2, first via Suzuki coupling and Sonogashira-type coupling reactions, and then perform the polycondensation reactions to prove that the modifications could not only be done at the polymer stage, but also at the monomer stage.
The first attempt was to modify monomer 2 via Suzuki coupling using phenyl boronic acid as shown in Scheme 30. The previous literature procedures were followed except that the solvent used was THF. The catalyst solution was prepared in acetone.

![Scheme 30](image)

**Scheme 30.** Synthetic procedure for the preparation of 2a.

The reaction occurred under nitrogen by reacting 2 with 1.2 equivalents of the boronic acid, 2.5 equivalents of K$_2$CO$_3$, and 1 mol percent of the catalyst at 60 °C for 6 hours. A workup procedure was applied, which was washing with brine solution, drying over MgSO$_4$, filtering, and drying under vacuum followed by recrystallization from isopropanol to obtain white crystals (43 %) with a melting point of 111-112 °C. The structure of 2a was confirmed by a combination of elemental analysis, GC/MS, and $^1$H and $^{13}$C NMR spectroscopy. Figure 14 shows that the peak i at 94 ppm, representing the carbon of the C-I bond peak is gone and the corresponding peak i in the product now can be seen at 141 ppm, indicating the formation of a new C-C bond. The other peaks that belong to the new phenyl ring on the monomer and the other signs of the successful conversion
are labeled on the overlay as k, l, m, and n at 139 ppm, 127 ppm, 129.5 ppm, and 129 ppm, respectively.

![Figure 14. 75.5 MHz $^{13}$C NMR spectral overlay of 2 and 2a.](image)

3.2.2 Polymerization of 2a

The step after the synthesis of the monomer 2a was to polymerize the monomer using Bis-A under the same polycondensation reaction conditions utilized for the iodo monomer (Scheme 31). The structure of the polymer was confirmed by comparing its $^{13}$C NMR spectrum to the spectrum of the “post” phenylated material and the two spectra were identical. The molecular weight was found to be 15,725 Da with a 2.1 PDI. The $T_{d5\%}$ and $T_g$ were found as 472 °C and 134 °C.
The molecular weight of “post” phenylated polymer was recorded as 19,700 with a 2.4 PDI. The $T_g$ and $T_d$ 5% were found to be 131 °C and 492 °C. When the results are compared to the same polymer synthesized via “post”, they are reasonably close to each other, which indicate that the same polymer can be synthesized by both “pre” and “post” chemistry.

Scheme 31. Polymerization of 2a.

3.2.3 Synthesis of 3’-Ethynyl-3, 5-Difluorodiphenylsulfone Monomer (2b)

Another “pre” modification that was performed with the iodo monomer was alkynylation via the Negishi reaction. This particular functional group was chosen because of the further functionalization availability that the alkyne group could provide. One of the reactions is the “click” reaction with azides, which is fast and provides an almost quantitative yield of triazole adduct. The low cost and variety of many azides also make the reaction more interesting. Moreover, when one thinks of introducing different groups to polymers in order to change the properties, the Negishi ethynylation followed by “click” reaction becomes a good choice. The purpose of this reaction was to replace the iodo group with alkynes. This was done by following the previous literature procedures. The alkyne used...
in the experiment was ethynyl zinc bromide which was obtained by reaction of zinc bromide ($\text{ZnBr}_2$), flame dried before it was used, and ethynyl magnesium bromide (Scheme 32). Both reagents were transferred airlessly through a cannula into the reaction vessel.

\[
\text{H} - \text{C} = \text{C} - \text{MgBr} \xrightarrow{\text{ZnBr}_2} \frac{\text{THF, rt}}{} \text{H} - \text{C} = \text{C} - \text{ZnBr}
\]

**Scheme 32.** The displacement of MgBr by ZnBr$_2$.

The Negishi reaction on the iodinated monomer (Scheme 33) was achieved with a 99% conversion after 12 hours and the proton NMR spectrum proved the structure, as can be observed in Figure 15. The triplet of triplets that represents the proton between the fluorine atoms was seen at 7.05 ppm and the signal for the alkyne proton was observed at 3.20 ppm.

\[
\begin{align*}
\text{F} & \quad \text{F} \\
\text{O} & \quad \text{S} = \text{O} \\
\text{I} & \\
\hline
\text{F} & \quad \text{F} \\
\text{O} & \quad \text{S} = \text{O} \\
\text{C} = \text{C} & \quad \text{H}
\end{align*}
\]

**Scheme 33.** Negishi reaction of 2.
Figure 15. 300 MHz $^1$H NMR spectrum (CDCl$_3$) of 2c.

Table 4. Results of the Negishi reaction on 2.

<table>
<thead>
<tr>
<th>Reaction No</th>
<th>Isolated Yield (%)</th>
<th>MP</th>
<th>Crystal color</th>
<th>Purity$^1$(%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1$^{st}$ reaction</td>
<td>25</td>
<td>123</td>
<td>Light yellow</td>
<td>97.5</td>
</tr>
<tr>
<td>2$^{nd}$ reaction</td>
<td>30</td>
<td>127 – 130</td>
<td>Light yellow</td>
<td>99.0</td>
</tr>
<tr>
<td>3$^{rd}$ reaction</td>
<td>34</td>
<td>128 – 130</td>
<td>Light yellow</td>
<td>99.2</td>
</tr>
</tbody>
</table>

$^1$ The percentage of the desired product in the crystals is logged (percentage is calculated by GC/MS integration).

The same reaction was performed three times to improve the isolated yield by recrystallizing the product using different solvents and the results are shown in Table 4. The products of first two reactions were recrystallized from only hexanes multiple times while the third reaction was recrystallized first from
hexanes followed by recrystallization from ethanol/water to obtain the highest purity and yield.

The GC-MS trace of the crude product showed that only a trace amount of iodinated monomer was left. The cleanup of the product was performed via a hot filtration from hexanes. However, the hexanes evaporated quickly, which resulted in the loss of product on the outside of the filter and the glassware. This might be the one of the reasons for the low yield. Moreover, another cause of the low yield was impurities which can mainly be attributed to triphenylphosphine oxide. Since this byproduct and the desired monomer were soluble in many of the same solvents, a number of extractions had to be performed to remove all impurities.

3.2.4 Model Reaction of 2b to form 2c

With the monomer synthesized, the next step was to polymerize the monomer. However, a model reaction with t-butyl phenol had to be performed to determine the reactivity of the monomer before the polymerization step. To keep the consistency in model reaction conditions, the reaction was run at 150 °C. However, a gummy solid which was insoluble in all organic solvents obtained. Then, DSC and TGA were run to determine the thermal stability of the monomer and the melting point was found to be 139 °C by DSC. However, on the second heating ramp, the melting point was not observed at 139 °C, which confirmed that the monomer is not stable at higher temperatures. Therefore, the reaction was run at 120 °C.
Scheme 34. Expected model reaction of 2b.

The second reaction was run at 120 °C for 12 hours (Scheme 34). The reaction mixture was precipitated from water followed by extraction with chloroform and then evaporated. For characterization, proton and carbon NMR spectra were acquired and the results indicated that the t-butyl phenoxide reacted with the acetylene group (Figure 16), rather than displacing the fluorine atoms.

Figure 16. Predicted structure obtained after the model reaction of 2b.
The $^1$H NMR spectrum in Figure 17 showed the presence of the two protons on the alkene.

![Figure 17. 300 MHz $^1$H NMR spectrum of the model product of 2c](image)

Under normal circumstances, it is not expected that phenol would react with the acetylene group. However, in this case the sulfonyl group, with a very strong electron withdrawing character, might be strong enough to lead to the unexpected reaction between the acetylene group and $t$-butyl phenol. As it had been seen from DSC that the monomer was not stable at high temperatures, this also helps to explain the issues with the model reaction. As a conclusion, it can be said that the acetylene monomer is not suitable for polycondensation reactions,
but could be utilized by performing a click reaction first and then doing the polycondensation process.

### 3.2.5 Nitration of 1 to form 2d

Besides the halogens and alkynes, a nitro group could also be introduced to the monomer system. The nitro group brings variability for further functionalization. One common example is reducing the nitro group to an amine group. However, this has to be done before polymerization in our 3, 5 systems because the nitro group can be unstable against NAS conditions. One could expect that the amine group is more stable against NAS conditions and could be carried into polymer systems. It is also possible to convert the amine group into amides, imines, diazonium salts, etc. to observe in what essence different groups could change the polymer properties.

The nitration of 1 was done in an ice bath for 1 hour using nitric acid and sulfuric acid (Scheme 35). The reaction mixture was poured into crushed ice/water and filtered. The GC/MS showed ~85 % mono-nitro and ~15 % di-nitro compound. After recrystallization from a mixture of isopropanol-chloroform-toluene-hexanes, yellowish crystals were obtained (64 %). In Figure 18, the doublet of doublets that represents the carbon of the C-F bond and the triplet that indicates the carbon between the two fluorine atoms were observed in order at 161 ppm and 110 ppm. Moreover, a new peak can be seen at 147 ppm, which represents the carbon atom of the new C-N bond.
Scheme 35. Nitration of 1 to form 2d.

Figure 18. 75.5 MHz $^{13}$C NMR spectrum of 2d.
4 CONCLUSIONS

Synthesis of the iodo monomer (2), polymerization of the iodo monomer, and “post” polymerization modification via the Suzuki Miyaura reaction, of the iodo polymer were successfully carried out. These results provide the starting point for a wide variety of facile modifications of poly(arylene ether sulfone)s. It should now be relatively straightforward to introduce a multitude of functional groups, at the same position, so as to modify the chemical and mechanical properties of the polymers without altering the backbone. It was seen that the glass transition temperatures, $T_g$, of the iodo polymer, 4, phenyl polymer, 5, naphthyl polymer, 6, and acetyl polymer, 7, were different. The bulkier naphthyl polymer showed a higher $T_g$ compared to the iodo polymer and phenylated polymer while the more polar acetyl polymer had the highest $T_g$. From the thermal gravimetric analysis, TGA, data, the $T_{d,5\%}$ values are in order 427 °C, 492 °C, 507 °C, and 466 °C. It was concluded that bulkier and more aromatic polymers exhibited higher $T_{d,5\%}$ values. The polymers showed good solubility in THF, chloroform, DCM, DMAc, NMP, but were insoluble in methanol, DMSO, and toluene. For the “pre” chemistry purposes, the phenylated monomer, 2a, ethynylated monomer, 2b, and nitrated monomer, 2d, were synthesized. After a successful polymerization of 2a, it was concluded that PAES could also be modified, in some cases, prior to polymerization.
5 PROPOSED FUTURE WORK

There are several future studies proposed on the iodinated PAES. The iodo group could be replaced with an aliphatic group (via boronic acid coupling) to observe how non-aromatic, flexible side chains alter the properties of the polymer. Moreover, the nitro group should be reduced to an amine group before polymerization followed by modifications of the aminated polymer. The azide polymer should be “clicked” with a variety of alkynes and the properties of the polymers determined. Other types of aryl halide coupling reactions, such as the Heck reaction, Grignard coupling reaction, etc., should be explored, perhaps using the less expensive bromide instead of the iodide.
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