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## Synthesis and characterization of PEEK analogues utilizing 3,5- and 2,4-difluorobenzophenone.

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**SYNTHESIS AND CHARACTERIZATION OF PEEK ANALOGUES UTILIZING 3,5  
AND 2,4-DIFLUOROBENZOPHENONE**

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

By

ZACHARY EWING

B.S. Northern Kentucky University, 2014

2016

Wright State University

WRIGHT STATE UNIVERSITY  
GRADUATE SCHOOL

December 14<sup>th</sup>, 2016

I HEREBY RECOMMEND THAT THE THESIS PREPARED UNDER MY SUPERVISION BY Zachary Ewing ENTITLED Synthesis and Characterization of PEEK Analogues Utilizing 3,5 and 2,4-Difluorobenzophenone BE ACCEPTED IN PARTIAL FULFILLMENT OF THE REQUIREMENTS FOR THE DEGREE OF Master of Science.

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## ABSTRACT

Ewing, Zachary. M.S., Department of Chemistry, Wright State University, 2016.  
Synthesis and Characterization of PEEK Analogues Utilizing 3,5 and 2,4-Difluorobenzophenone

Two routes to semi-crystalline, potentially functionalizable poly(ether ether ketone), PEEK, analogues were explored using varying percentages of 4,4'-difluorobenzophenone and either 3,5-difluorobenzophenone or 2,4-difluorobenzophenone as the electrophilic component in nucleophilic aromatic substitution polycondensation reactions with hydroquinone. PEEK analogues utilizing 3,5-difluorobenzophenone were carried out in a "one-pot" fashion and their properties were compared to the same materials prepared previously by a multi-step synthetic procedure. The use of 2,4-difluorobenzophenone led to completely new PEEK analogues. The polymers were characterized via NMR spectroscopy, Size Exclusion Chromatography, Thermogravimetric Analysis, and Differential Scanning Calorimetry. Molecular weight determinations showed the synthesized polymers to be of a variety of molecular weights, with weight averaged molecular weight ( $M_w$ ) values between 7,500 and 83,000 Da and dispersity ( $\mathcal{D}$ ) values between 2.5 and 2.9. The polycondensation reactions were also accompanied by the formation of cyclic species that could be, and were, removed via precipitation/trituration with isopropanol or mostly avoided by a judicious choice of reaction conditions. Solubility tests showed that the 3,5-homopolymers, which were semi-crystalline, and 2,4-homopolymers, which were completely amorphous, were soluble in many common organic solvents, while the solubility of the copolymers decreased as the percentage of 4,4'-difluorobenzophenone increased. Thermal analysis of the 3,5-difluorobenzophenone polymers possessed 5 % weight loss temperature values ( $T_{d 5\%}$ ) that were similar to those of the previously synthesized polymers<sup>1</sup>, with values between 330 and 500°C. For both polymer systems,

the glass transition temperatures ( $T_g$ ) were between 86 and 129°C, which is consistently lower than those of the materials previously synthesized via the multistep protocols. The 3,5 homopolymer and 75%/25% (PEEK/PAMPPPO) copolymers displayed crystallization temperatures ( $T_c$ ) between 156 and 210°C with melting temperatures ( $T_m$ ) between 252 and 254°C. The 2,4-difluorobenzophenone polymers had  $T_g$  values ranging from 113 to 152°C with  $T_c$  and  $T_m$  values, for polymers containing 35% or less 2,4-difluorobenzophenone, ranging from 220 to 230°C, and 280 to 320°C, respectively.

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## **ACKNOWLEDGEMENTS**

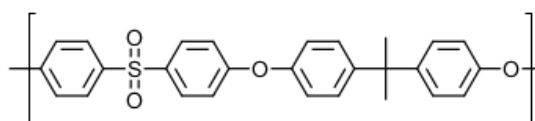
I would like to express my sincere gratitude to my advisor, Dr. Eric Fossum for his guidance, support and kindness over the past two years and some months. The opportunities he has provided have shaped my career path and personally build my confidence. I am very thankful of my committee members, Dr. William Feld and Dr. Daniel Ketcha for their contributions and suggestions towards this thesis. I would also like to thank the past and present members of the Fossum research group, especially Trevor, Brady, Renata, Abraham, James, Luke, Amy, Shannon, Steve, any many more, as well as the faculty and staff members of the Wright State University Department of Chemistry.

## **DEDICATION**

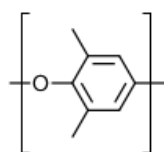
I would like to dedicate this thesis to my parents, Paul and Pam Ewing, for their continued support and love throughout my college career. Without their support, this journey would have been immensely difficult. I would like to particularly thank my brother, Jason Ewing, for giving me someone to beat up and hang out with throughout the years, and to anyone who has affected my life one way or the other.

## 1. INTRODUCTION

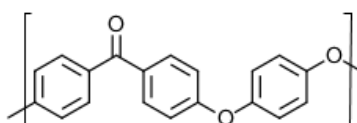
In recent years, engineering thermoplastics have been receiving a lot of attention for their robust physical and chemical properties. These systems have very good chemical resistance, are very thermally stable, and are resistant to oxidation. **Figure 1** highlights a few of the most common engineering thermoplastics. Modification of these systems can lead to enhanced properties, which is now a staple in the research world. For this thesis, the focus will be on a specific set of engineering thermoplastics known as poly(arylene ether)s.



PAES- Udel  
 $T_g = 190\text{ }^\circ\text{C}$  ;  $T_m = \text{N/A}$



PPO- Noryl  
 $T_g = 210\text{ }^\circ\text{C}$  ;  $T_m = \text{N/A}$



PEEK- Victrex  
 $T_g = 143\text{ }^\circ\text{C}$  ;  $T_m = 343\text{ }^\circ\text{C}$

Figure 1: Various PAEs, with  $T_g$  and  $T_m$  data, where applicable.

### 1.1. Poly (arylene ether)s, PAEs

PAE is an umbrella term for a specific set of engineering thermoplastics, the most prolific of which are highlighted in **Figure 1**. They consist of aryl groups covalently linked by ether bonds in the polymer backbone. Many of these systems are available

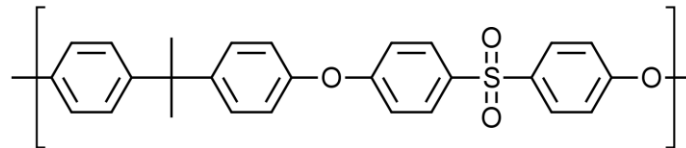
commercially, with the simplest one being poly (2,6-dimethyl-1,4-phenylene oxide), commonly referred to as PPO. Other systems that fall under the PAE umbrella are poly (arylene ether sulfone)s and poly (arylene ether ketone)s, PAES's and PAEK's respectively. These two PAE's are the most widely utilized engineering thermoplastic materials, and are receiving a lot of attention for their properties. PPO and PAES are completely amorphous materials, while PAEK's are semi-crystalline. This means that PPO and PAES materials have poorer solvent resistance when compared to PAEK's.

Their lack of crystallinity is a result of the way they are oriented in space. In PAES, the sulfonyl moiety adopts a tetrahedral structure, bending the repeat unit and disrupting any stacking ability in the polymer. In PPO, a similar thing happens. The methyl groups on the phenyl ring force the repeat unit into a non-planar structure, preventing stacking, and crystallinity, from occurring. In PAEK's, the entire repeat unit can adopt a planar arrangement, allowing for stacking of molecules (or segments of chains, in the case of polymers) to occur, resulting in crystalline regions and the properties that come along with crystallinity.

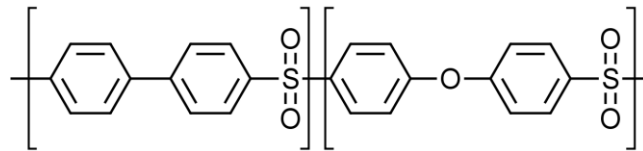
#### **1.1.1. Poly (arylene ether sulfone)s, PAES**

PAES are part of a family of amorphous materials that are useful thermoplastics due to their excellent mechanical properties, thermo-oxidative stability, and high glass transition temperatures ( $T_g$ ). They are soluble in polar aprotic and halogenated solvents due to their amorphous nature. Despite this, they are still used in a wide variety of industrial applications, like membranes, films, composite matrices, etc. PAES's are characterized by the presence of *para*-linked aromatic groups connected by many different groups; mainly ether (-O-), sulfone (-SO<sub>2</sub>-), and alkyl groups, as shown in **Figure 2**. PAES are some of the earliest implemented engineering thermoplastics, being first commercially available in 1965 as UDEL by Union Carbide. UDEL had a continuous-

use temperature of 150°C and a maximum-use temperature of 170°C. This polymer was prepared via nucleophilic aromatic substitution of 4,4'-dichlorodiphenylsulfone and the alkali salt of Bisphenol-A at moderate temperatures in solvents like *N*-methyl-2-pyrrolidinone (NMP), dimethyl acetamide (DMAc), sulfolane, or dimethyl sulfoxide (DMSO).<sup>2</sup>



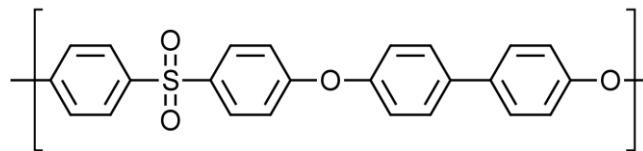
UDEL (Union Carbide)  $T_g = 190\text{ }^\circ\text{C}$



A B

When A predominates= Astel (3M Corp)  $T_g = 285\text{ }^\circ\text{C}$

When B predominates= PES 720P (ICI)  $T_g = 250\text{ }^\circ\text{C}$



Radel (Union Carbide)  $T_g = 220\text{ }^\circ\text{C}$

Figure 2: Various commercially available PAES with associated  $T_g$  values.

### 1.1.2. Poly (phenylene oxide), PPO

PPO is really just a polyether with aromatic groups connected by oxygen linkages either *para*, *ortho*, or both throughout the backbone. Poly (2,6-dimethyl-1,4-phenylene oxide) is referred to as PPO, and is the most common material in the PPO family. PPO is considered a high-performance engineering thermoplastic due to its mechanical strength and high  $T_g$  (210°C), due to the rigid structure of the polymer backbone. PPO was first synthesized, in 1956, by Allan Hay<sup>3</sup> and coworkers. During

research on oxidizing phenols and xylenols, the route to synthesize PPO was discovered. By itself, PPO is difficult to process, but when blended with polystyrene, it becomes a very good polymer system in terms of properties, from high heat resistance, electrical insulation, hydrolytic stability, and other properties associated with thermoplastics, while also becoming easier to process. This polymer blend is now known as Noryl, and is actually a family of blends with different compositions.

### 1.1.3. Poly (arylene ether ketone)s, PAEKs

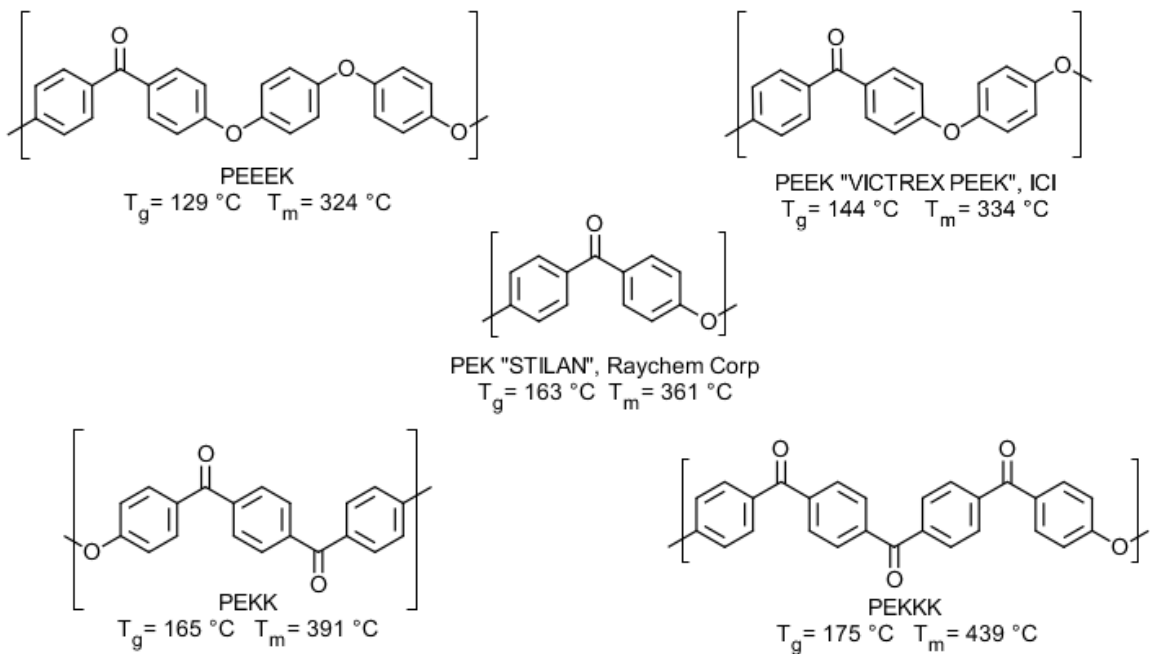


Figure 3: Major PAEK's with  $T_g$  and  $T_m$  values.

PAEKs (see **Figure 3**), such as poly(ether ketone) (PEK), poly(ether ether ketone) (PEEK), poly(ether ether ether ketone) (PEEEK), and poly(ether ketone ether ketone ketone) (PEKEKK), are generally semi-crystalline and insoluble materials that exhibit a unique combination of physical and thermal stability, chemical and solvent resistance, good mechanical properties, good fire resistance, and good electrical performance. It is these properties that make these materials important for applications in the aerospace, automobile, nuclear, electronics, and many other high technology

fields. They can be fabricated by conventional techniques and can also be applied as a matrix resin for high performance reinforced composites. The most widely used PAEKs are PEEK and PEKK, which differ by a single oxygen in the repeat unit, as shown in **Figure 3**, along with other PAEK's. From top to bottom, the repeat units of the polymers have fewer ether bonds and more ketone groups. As a result, the decrease in percentage of flexible ether bonds causes the  $T_g$  of the polymer to increase.

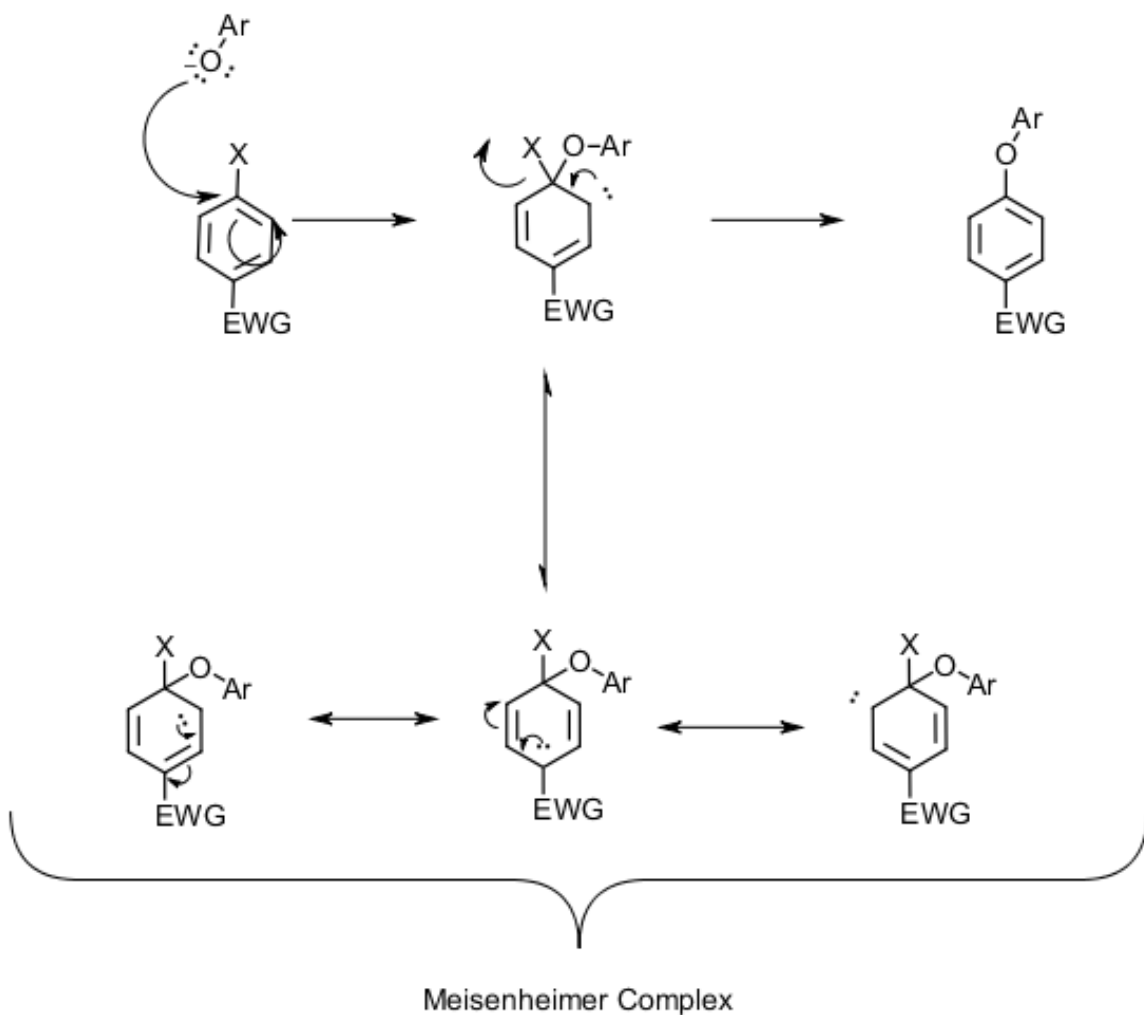
## 1.2. Synthesis of Poly (arylene ether ketone)s

### 1.2.1. Polycondensation via Nucleophilic Aromatic Substitution (NAS)

With the exception of PPO, which is synthesized using oxidative coupling, the aforementioned materials are prepared via Nucleophilic Aromatic Substitution (NAS) chemistry, as outlined in **Scheme 1**. NAS chemistry is done by first reacting a phenol with a base where upon the resulting anion then acts as the nucleophile. The nucleophile attacks the other monomer, usually an aryl halide activated by a strong electron-withdrawing group in the *ortho* or *para* positions, leading to an anionic intermediate known as a Meisenheimer complex. Loss of the halide, with a concurrent re-aromatization, affords the aryl ether bond. This process is repeated over and over, yielding the desired polymer. Aryl fluorides have shown to be the best groups for NAS chemistry, due to their excellent leaving group ability, to yield high molecular weight polymers. In a typical NAS reaction for PAEKs, potassium carbonate is used as the base to prevent side reactions, like hydrolysis, from happening. NAS was first utilized in PAEK systems by Hale *et al.*<sup>4</sup> by using a bisphenolate of hydroquinone and 4,4'-difluorobenzophenone in the presence of NaOH as the base and DMSO as the solvent. This method did not yield high molecular weight polymers due to premature crystallization and, ultimately, the insolubility of the polymers in DMSO. Despite this, they managed to observe a melting temperature of 350°C and a glass transition temperature



of 160°C. With a few modifications, Attwood *et al.*<sup>5</sup> and Rose<sup>6</sup> changed the solvent to diphenyl sulfone and used the weak base Na<sub>2</sub>CO<sub>3</sub>. When carried out near the previously observed melting point of the polymer, this reaction yielded high molecular weight PEEK.



*Scheme 1: General mechanism for Nucleophilic Aromatic Substitution (NAS) chemistry.*

The first patent for the polymer PEEK synthesized in this fashion was filed in 1975, and granted in 1982 to Imperial Chemical Industries, ICI, under the name VICTREX™. Upon careful optimization of reaction conditions to prevent high

temperature side reactions, like ether exchange and cleavage from happening, high molecular weight polymers could be obtained.<sup>7</sup>

Unfortunately, the only monomers that have been shown to yield high molecular weight polymers are the expensive difluoro monomers, making the synthesis of PEEK less industrially friendly. Dichloro monomers have failed to yield high molecular weight polymer due to side reactions like single electron transfer.<sup>8</sup>

### 1.3. Isomers of Poly (ether ether ketone), PEEK

It is well known that changing the structure of a polymer can drastically change the properties of the system, whether it be solubility, crystallinity,  $T_g$ , etc. With the robust properties of PEEK already demonstrated, researchers wondered if these properties could be enhanced by changing the way the polymer was structured, leading to many geometric isomers of PEEK. An example of each is shown in **Figure 4**, with boxes demonstrating possible sites for functionalization on the benzophenone rings, as well as the possibility in all three to add to the bisphenol ring.

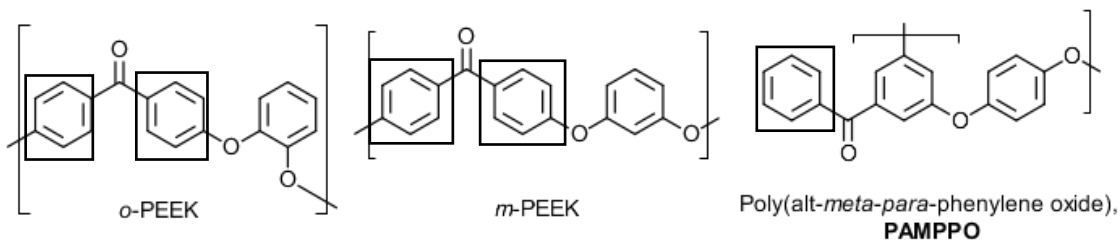


Figure 4: Examples of isomers of traditional PEEK, with a box showing functionalization sites in each case. \*PAMPPO was originally called *m*-PEEK by Fortney and Fossum<sup>1</sup>

#### 1.3.1. *o*-PEEK

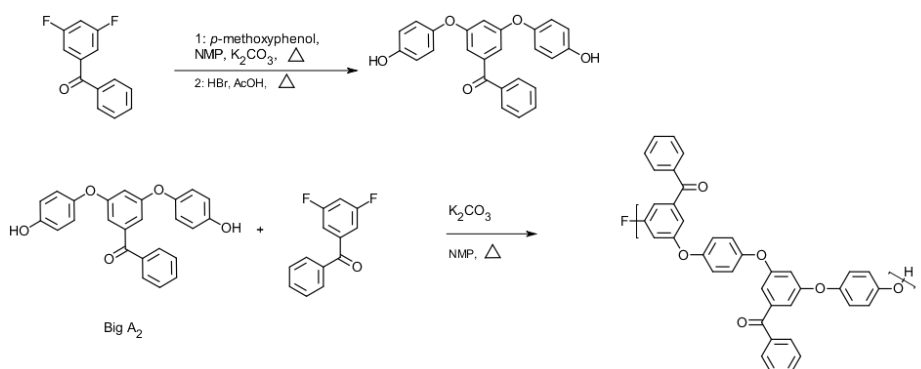
In a paper published by Ben-Haida *et al.*,<sup>9</sup> *o*-PEEK is described. *o*-PEEK differs from traditional PEEK by the bisphenol used. In the place of hydroquinone, Ben-Haida *et al.* used catechol (1,2-dihydroxybenzene) in diphenyl sulfone along with 4,4'-difluorobenzophenone, in the presence of potassium carbonate, and heated to 200°C for

4 hours, then 320°C for 4 hrs. The result was a completely amorphous polymer with a  $T_g$  of 145°C and weight average molecular weight ( $M_w$ ) of 240,000 Da and a dispersity of 2.7. *o*-PEEK was soluble in a wide array of organic solvents, including dichloromethane (DCM), tetrahydrofuran (THF), and DMAc. They also prepared copolymers of traditional PEEK with *o*-PEEK showing similar results with respect to  $T_g$  data, with 30% *o*-PEEK being semi crystalline.

### 1.3.2. *m*-PEEK

Preceding Ben-Haida *et al.*, Rao *et al.*<sup>9</sup> attempted polymerization of a new PEEK derivative involving resorcinol and 4,4'-difluorobenzophenone. To keep with the naming scheme, from this point forward this polymer will be referred to as *m*-PEEK. Running the reaction for 2 hours at 230°C in sulfolane yielded a completely amorphous polymer with a  $T_g$  of 119°C. The researchers, however, did not test the solubility of *m*-PEEK. X-ray diffraction (XRD) data was used to confirm the lack of crystallinity as determined by differential scanning calorimetry (DSC) data. Thermogravometric analysis (TGA) was used to obtain a degradation temperature ( $T_{d 5\%}$ ) of 500°C in a nitrogen atmosphere, and slightly below 500°C in an air atmosphere.

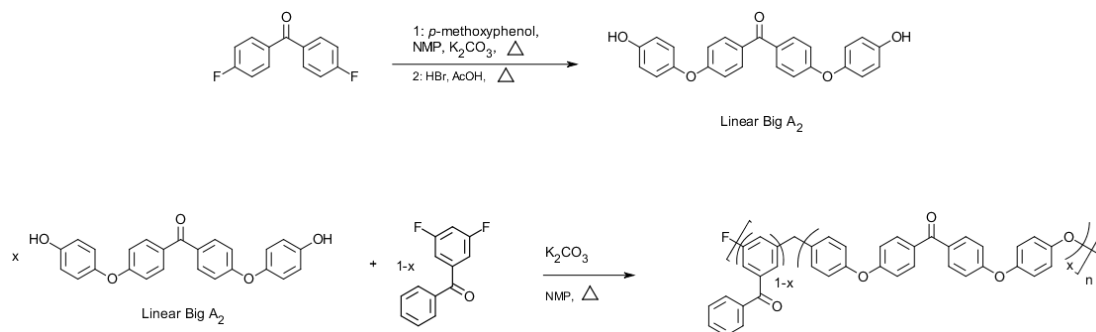
### 1.3.3. PAMPPO



Scheme 2: Summarized synthesis of PAMPPO without the use of hydroquinone.

Rather than change the phenol group, Fortney and Fossum<sup>1</sup> changed the aryl halide to synthesize another form of *m*-PEEK. To avoid confusion with the resorcinol

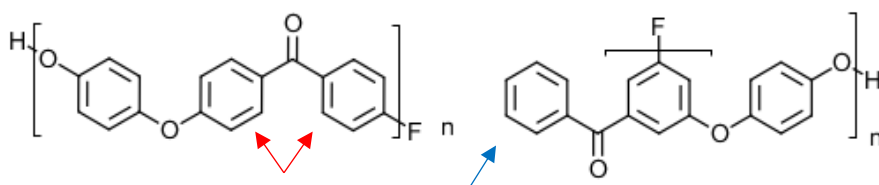
version of *m*-PEEK, Fortney and Fossum's *m*-PEEK will be called poly (alt-*meta-para*-phenylene oxide), or PAMPPPO. Fortney and Fossum had difficulties utilizing hydroquinone in the process, so they developed a "work-around" as summarized in **Scheme 2**. Initial PAMPPPO synthesis required the synthesis of a Big A<sub>2</sub> monomer, which was prepared by reacting 3,5-difluorobenzophenone with excess 4-methoxyphenol in the presence of excess base in toluene and NMP at 150°C, to insure dryness, and then at 185°C. The resulting material was isolated, purified, and then deprotected with hydrobromic acid and glacial acetic acid. Finally, the "Big A<sub>2</sub> PAMMPO" monomer was reacted with 3,5-difluorobenzophenone and excess base, in NMP at 185°C, to afford a completely amorphous polymer with a T<sub>g</sub> of 105°C and 5% weight loss temperatures of 428°C and 426°C, under nitrogen and air, respectively. PAMPPPO was soluble in most organic solvents, including NMP, chloroform, THF, and DMAc, but not toluene.



*Scheme 3: Summarized synthesis of copolymers of PEEK and PAMPPPO without the use of*

Fortney and Fossum also made copolymers of traditional PEEK and PAMPPPO, to attempt to regain crystallinity in the system, while keeping some solubility in solvents other than concentrated acid. **Scheme 3** outlines the synthesis of these systems. The copolymers ranged from 0% to 90% PEEK, and it was discovered that the 75% PEEK copolymer allowed for the highest amount of PAMPPPO while maintaining crystallinity. This sample, however, was only soluble in hot NMP. The copolymers were synthesized in a special manner due to the lack of reactivity in the 3,5-system compared to the 4,4'-

system. If all 3 reactants: hydroquinone, 3,5-, and 4,4'-difluorobenzophenone, were put into the reaction vessel at once, highly crystalline and insoluble material would result. Therefore, the 3,5-difluorobenzophenone had to be incorporated, or the 4,4'-difluorobenzophenone had to be “controlled”, before the system could be polymerized. Following the same procedure as before, with the exception of using 4,4'-difluorobenzophenone in place of the 3,5-difluorobenzophenone, Fortney and Fossum<sup>1</sup> synthesized a monomer that contained two phenol units and one 4,4'-difluorobenzophenone unit. Then, they took this unit and reacted with 3,5-difluorobenzophenone and 4,4'-difluorobenzophenone to synthesize alternating copolymers of varying ratios. This approach is not as industrially friendly, but is a step toward a cheaper alternative to an easier to process, semi-crystalline PEEK polymer. This introduction of the 3,5-system provides a site for reaction that is pendent to the backbone of the polymer, allowing modifications to be made via functionalization of the pendent ring either pre- or post- polymerization, without directly affecting the backbone of the polymer, as shown in **Figure 5**.

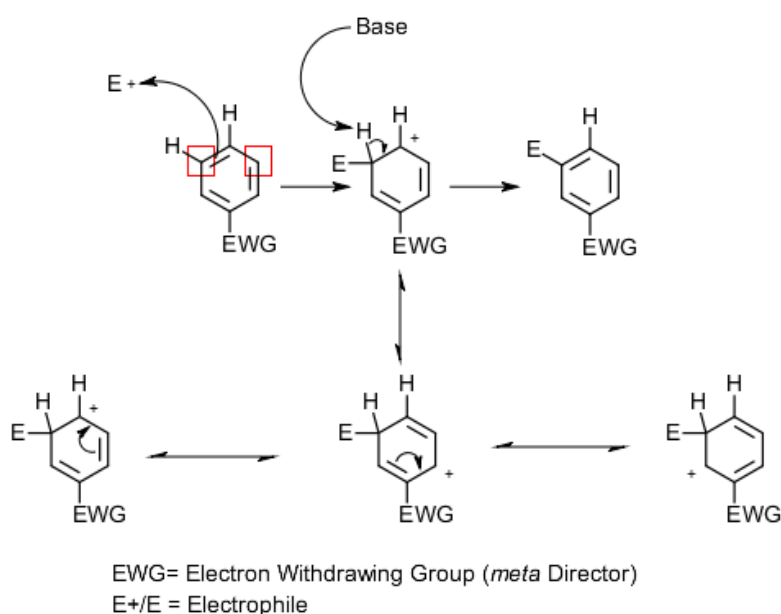


*Figure 5: Visualization of the benefit of a pendent functionalization site. Red arrows show modification of the backbone, while the blue arrow shows modification that does not affect the backbone.*

#### 1.4. Functionalization Chemistry

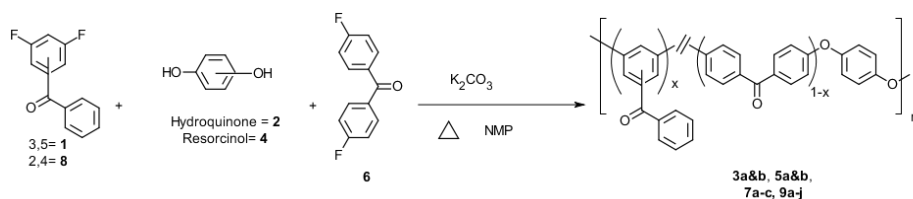
Functionalization of PAE systems is often done via Electrophilic Aromatic Substitution (EAS). This allows for “pre-functionalization” of the monomer species with a group that can survive harsh reaction conditions and be present in the final compound. From there, the group can be further converted into a variety of functionalities that can increase solubility, provide anti-fouling characteristics, afford proton exchange

capabilities, and many other functions. EAS processes cannot be done in a “post” fashion to yield a functional group on the pendant moiety exclusively, due to the presence of the aryl ethers, and the electron rich aromatic rings to which they are attached. These sites are much more likely to undergo EAS chemistry than the location that is desired, the pendent moiety. **Scheme 4** shows the general reaction mechanism for EAS with a *meta*-director, which is similar to the mechanism for *ortho-para* directors, with the only difference being the resulting R-group’s location.



*Scheme 4: General mechanism for Electrophilic Aromatic Substitution, with red boxes indicating area of attack.*

## 1.5. Current Project



*Scheme 5: General Reaction scheme for whole project.*

As represented in **Scheme 5**, the goals of this project are threefold and include: 1) the preparation of PAMPPO in a “one-pot” fashion, 2) the synthesis of PAMPPO-PEEK copolymers in a “one-pot” fashion, and 3) the exploration of “one-pot” syntheses of 2,4-difluorobenzophenone-PEEK polymers. As mentioned previously, PEEK is not very soluble in many solvents, which is part of the reason it is such a great thermoplastic. However, this insolubility causes problems when it comes to processing the material. Therefore, if the polymer could become more soluble while maintaining crystallinity, it would make for a much more attractive material. It was shown that incorporating 3,5-difluorobenzophenone into the PEEK polymer increased the resulting copolymers’ solubility in some more common organic solvents. The major issue with the method employed by Fortney to synthesize PAMPPO-PEEK copolymers was the multi-step nature of the synthesis, due to problems associated with hydroquinone. This project, as outlined in **Figure 6**, aims to address these issues with hydroquinone in three different goals. The first goal of this project seeks to eliminate the need to synthesize, isolate, and purify a Big A<sub>2</sub> monomer before moving on to polymerization, which might afford a more industrially friendly process to obtain these polymers. The second goal of this project is to utilize a “one-pot” method to prepare PEEK-PAMPPO copolymers. If these materials could be synthesized in this manner, they would become more desirable to industry.

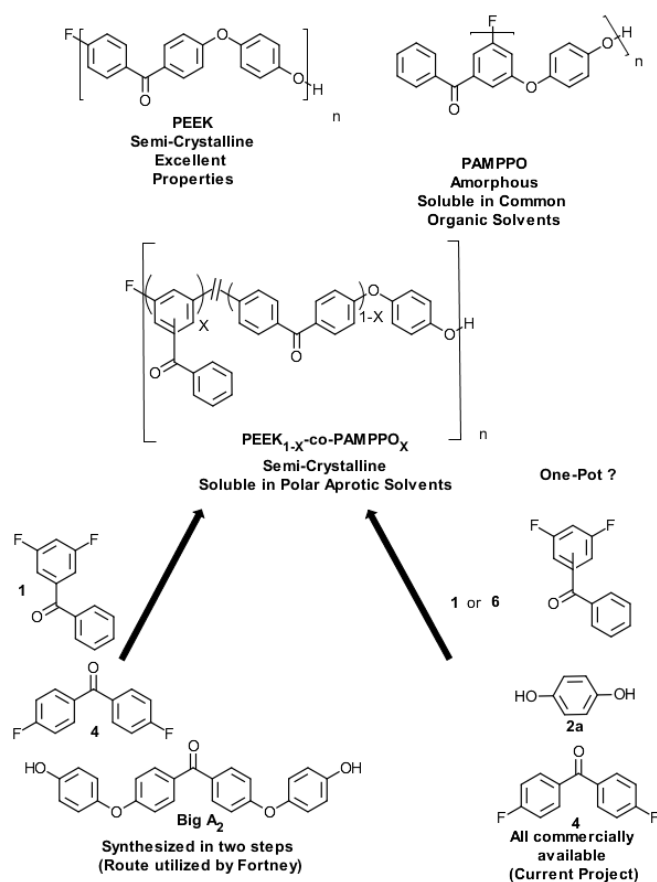


Figure 6: Representation of the main goal of this project.

Finally, the third goal attempts to utilize the new “one-pot” method to a slightly different system, making sure that the method can be utilized in similar systems effectively. This system will also address the poor reactivity of the 3,5-system, showing that polymerization can take as little as 12 hours. This new monomer, 2,4-difluorobenzophenone, is introduced and compared to the 3,5-system. The 2,4-system is much more reactive toward NAS reactions, than is the 3,5-system, but maintains the pendent site for functionalization. Unfortunately, the way in which the fluorines are positioned allows for EAS functionalization to occur on the fluorinated ring, as shown in **Figure 7**.



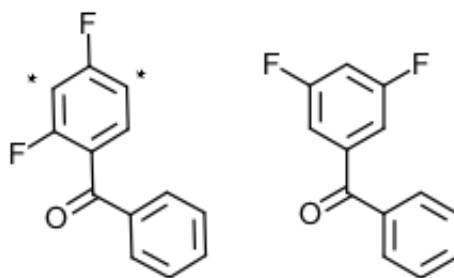
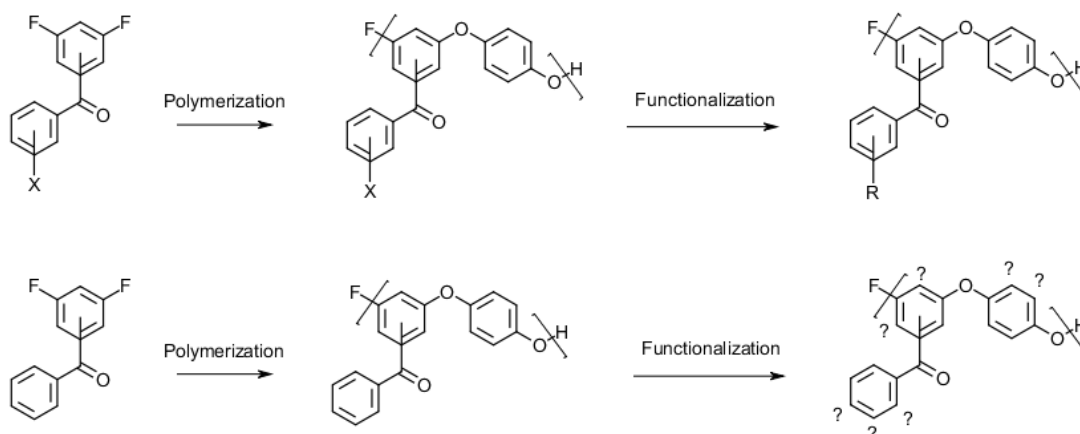


Figure 7: 2,4-difluorobenzophenone (left) and 3,5-difluorobenzophenone (right), two starting materials in this project.

A potential danger to these systems lies in their backbones being modified in an EAS type reaction. The rings associated with the bisphenol in the polymer are much more susceptible to an EAS attack, practically guaranteeing modification of the backbone. Another risk to these systems lies in the reactivity of the pendent moiety. An EAS post-polymerization functionalization could result in modification of the backbone of the polymer and not the pendent moiety. However, this issue can be easily avoided by the reaction of 1,3-difluorobenzene with a benzoyl chloride derivative that already possesses the desired functional group. This results in a monomer that can then be polymerized without worry, as depicted in **Scheme 6**. This can also be done using a 2,4-difluorobenzoyl chloride and a benzene with the desired functional group already attached. To the best of our knowledge, only one other paper on a 2,4-difluorobenzophenone system exists. Kricheldorf *et al.*<sup>11</sup> has used 2,4-difluorobenzophenone to produce macrocyclic and hyperbranched polymers but there

have been no papers utilizing 2,4-difluorobenzophenone in a linear system.



Scheme 6: Example of ability to do "pre" and "post" functionalization, but not exclusively "post" functionalization. X= group that can survive polymerization, R= Desired functional group.

## 2. EXPERIMENTAL

### 2.1. Materials

All reactions were carried out under a nitrogen atmosphere. Reagent grade anhydrous potassium carbonate ( $K_2CO_3$ ) was dried at  $130^\circ C$  in an oven before use. 3,5-difluorobenzophenone was synthesized according to a literature procedure.<sup>11</sup> Hydroquinone and resorcinol were purchased from Sigma Aldrich Chemical Co. and used as received. 4,4'-difluorobenzophenone and 2,4-difluorobenzophenone were purchased from Oakwood Products and used as received. *N*-Methylpyrrolidinone (NMP) was purchased from Sigma Aldrich Chemical Co., dried and distilled over  $CaH_2$  under nitrogen prior to use. To help clarify the different structures, **Figure 8** shows the different

monomers/polymers with their names and identifying name (i.e. **3a**, **5b**, etc).

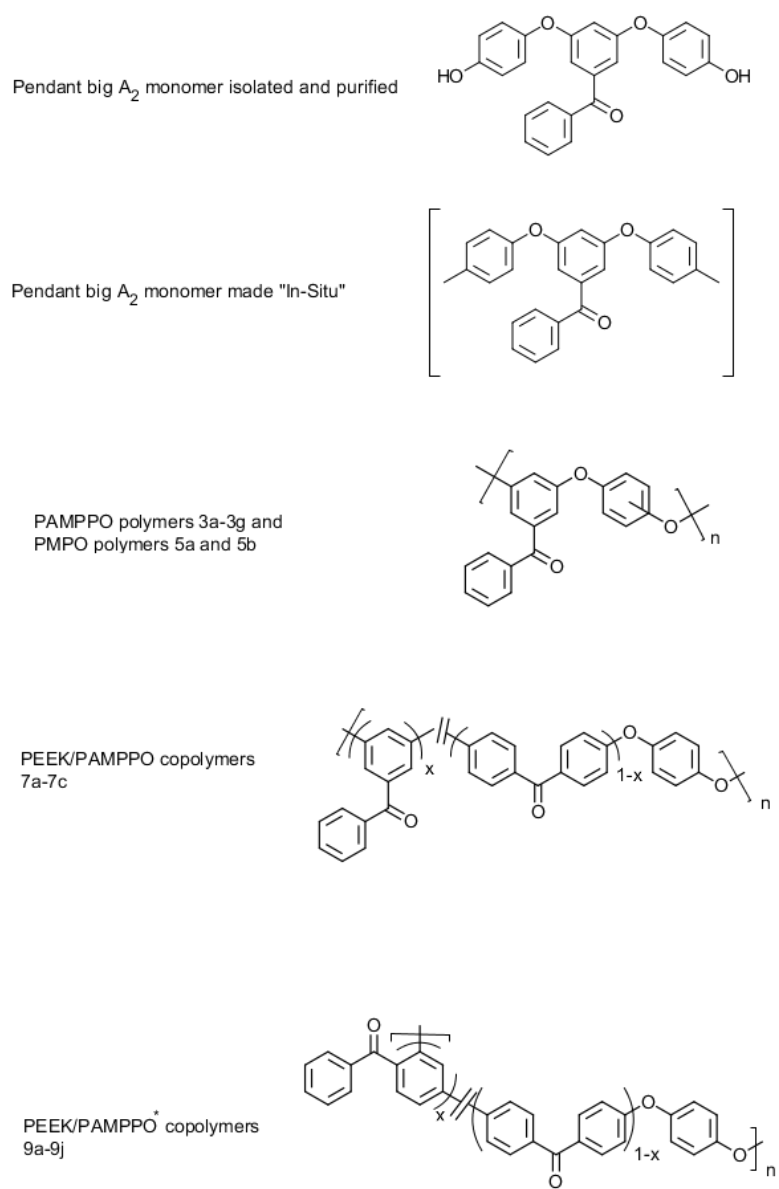


Figure 8: Names of monomers and polymers with their names and structures for clarification

## 2.2. Instrumentation

<sup>1</sup>H and <sup>13</sup>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*<sub>6</sub> or CDCl<sub>3</sub>), at a concentration of ~30mg/0.6mL.

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  $\mu\text{m}$  PL gel Mixed C columns (heated to 35°C) were used with tetrahydrofuran/5% (v/v) acetic acid as the eluent and a GPCMax VE-2001 with pump operating at 1.0 mL/minute. Weight average molecular weights,  $M_w$ , were determined via the light scattering signal while the dispersity was determined via the refractive index (RI) signal. Calibration was done using polystyrene standards.

DSC and TGA analyses were carried out under nitrogen (or air) on TA Instruments DSC Q200 and TGA Q500, respectively, at a heating rate of 10°C/min.

### **2.3. General Procedure for the Synthesis of PAMPPO via “Batch-wise”**

#### **Approach**

For PAMPPO synthesized in a “batch-wise” manner, the synthesis of **3f** is presented as an example. This reaction was run using the same monomers, but utilizing many different reaction conditions, as denoted by the letters a-g. In a 10 mL round bottomed flask were placed 3,5-difluorobenzophenone, **1**, (0.454 g, 2.08 mmol), hydroquinone, **2**, (0.229 g, 2.08 mmol), potassium carbonate (0.852 g, 6.24 mmol), NMP (3.25 mL), and a stir bar. The reaction mixture was connected to a reflux condenser and a gas inlet adapter. The system was purged with nitrogen and placed in a silicone oil bath. The reaction vessel was heated to 185°C for 24 hrs, at which point an aliquot was taken and analyzed via NMR spectroscopy. The reaction mixture was precipitated from ~900 mL of vigorously stirred water and an off-white solid was collected via vacuum filtration to yield 0.453 g (75.6%).  $^1\text{H}$  NMR (DMSO- $d_6$ ,  $\delta$ ): 6.96 (b, 3H); 7.49 (b, 3H); 7.62 (b, 3H); 7.73 (b, 3H);  $^{13}\text{C}$  NMR (DMSO- $d_6$ ,  $\delta$ ): 111.7, 113.2, 121.5, 128.9, 129.9, 133.2,

136.7, 140.1, 152.3, 159.1, 194.4;  $^{13}\text{C}$  DEPT 90 NMR (DMSO- $d_6$ ,  $\delta$ ): 111.7, 113.2, 121.5, 128.8, 129.9, 133.2.

#### 2.4. General Procedure for the Synthesis of PAMPPO via “Step-wise” Approach

For PAMPPO synthesized in a “step-wise” manner, the synthesis of **3e** is presented as an example. In a 10 mL round bottomed flask were placed 3,5-difluorobenzophenone (0.228 g, 1.04 mmol), hydroquinone (0.229 g, 2.08 mmol), potassium carbonate (0.852 g, 6.24 mmol), NMP (3.25 mL), and a stir bar. The reaction mixture was connected to a reflux condenser and a gas inlet adapter. The system was purged with nitrogen and placed in a silicone oil bath. The reaction vessel was heated to 185°C for 24 h, at which point an aliquot was taken and analyzed via NMR spectroscopy. To the reaction mixture, 3,5-difluorobenzophenone (0.114 g, 0.52 mmol) was added and the reaction vessel was heated again at 185°C for 24 h, at which point another aliquot was taken and analyzed via NMR spectroscopy. This process was repeated for a third time and, after confirmation of complete reaction via NMR spectroscopy, the reaction mixture was precipitated from ~900 mL of vigorously stirred water and the resulting off-white solid was collected via vacuum filtration to yield 0.256 g (55.7%).  $^1\text{H}$  NMR (DMSO- $d_6$ ,  $\delta$ ): 6.96 (b, 3H); 7.49 (b, 3H); 7.62 (b, 3H); 7.73 (b, 3H);  $^{13}\text{C}$  NMR (DMSO- $d_6$ ,  $\delta$ ): 111.7, 113.3, 121.5, 128.8, 129.9, 133.2, 136.7, 140.1, 152.3, 159.1, 194.3;  $^{13}\text{C}$  DEPT 90 NMR (DMSO- $d_6$ ,  $\delta$ ): 111.7, 113.2, 121.5, 128.8, 129.9, 133.2.

#### 2.5. Synthesis of PMPO (5a) via “Batch-wise” Approach

In a 10 mL RB flask, equipped with a reflux condenser, gas inlet and magnetic stir bar, were placed 3,5-difluorobenzophenone, **1**, (0.300 g, 1.38 mmol), resorcinol, **4**, (0.151 g, 1.38 mmol), potassium carbonate (0.570 g, 4.13 mmol), NMP (2.15 mL), and a magnetic stir-bar. The reaction vessel was placed in a silicon oil bath and heated at

185°C for 24 h. An aliquot was removed for NMR analysis and the reaction mixture was precipitated from ~900 mL of vigorously stirred water and a brown solid was collected via vacuum filtration to yield 0.274 g (66.0%). <sup>1</sup>H NMR (DMSO-*d*<sub>6</sub>, δ): 6.92 (b, 2H); 7.04 (b, 2H); 7.50 (b, 5H); 7.72 (b, 2H); 7.82 (b, 1H); <sup>13</sup>C NMR (DMSO-*d*<sub>6</sub>, δ): 108.9, 110.4, 113.1, 116.5, 128.7, 129.9, 131.6, 133.2, 136.7, 140.3, 157.6, 158.4, 194.2; <sup>13</sup>C DEPT 90 NMR (DMSO-*d*<sub>6</sub>, δ): 108.9, 110.4, 113.1, 116.5, 128.7, 129.9, 131.6, 133.2.

## 2.6. Synthesis of PMPO (5b) via “Step-wise” Approach

In a 10 mL RB flask, equipped with a reflux condenser, gas inlet and magnetic stir bar, were placed 3,5-difluorobenzophenone, **1**, (0.150 g, 0.69 mmol), resorcinol, **4**, (0.151 g, 1.38 mmol), potassium carbonate (0.570 g, 4.13 mmol), NMP (2.15 mL), and a magnetic stir-bar. The reaction vessel was placed in a silicon oil bath and heated at 185°C for 24 h. An aliquot was removed for NMR analysis, and 3,5-difluorobenzophenone (0.075 g, 0.35 mmol) was added to the reaction mixture, which was heated at 185°C for a further 24 h. Another aliquot was taken for NMR analysis, and this was repeated a third time. The reaction mixture was precipitated from ~900 mL of vigorously stirred water and a brown solid was collected via vacuum filtration to yield 0.136 g (33.0%).

## 2.7. General reaction procedure for 3,5-system (copolymers 7a, 7b, & 7c)

For polymerizations utilizing **1**, the procedure for the synthesis of P<sub>75</sub>-co-PAMPPPO<sub>25</sub> via the “batch-wise” approach (**7b**) is presented as an example. For future reference, these copolymers and other copolymers will be referenced in this manner: Polymer reference number (i.e. **7b**), (%PEEK/%non-PEEK). In a 10 mL round bottomed flask were placed 3,5-difluorobenzophenone, **1**, (0.300 g, 1.38 mmol), hydroquinone, **2**, (0.606 g, 5.50 mmol), potassium carbonate (2.28 g, 16.5 mmol), NMP (2.15 mL), and a stir bar. The reaction mixture was connected to a reflux condenser and a gas inlet

adapter. The system was purged with nitrogen, immersed in a silicone oil bath and heated to 185°C for 24 h at which point an aliquot was removed for NMR analysis. To the remaining reaction mixture was added 4,4'-difluorobenzophenone, **6**, (0.900 g, 4.13 mmol) and NMP (6.45 mL), followed by heating to 150°C for 24 h. The reaction mixture was precipitated from ~900 mL of vigorously stirred water and a light gray material was collected via vacuum filtration to yield 1.55 g (97.5%).

*\*This reaction was also run similarly to reactions **3f** and **5b**, where 4,4'-difluorobenzophenone was added in portions instead of all at once.*

**7a**, (50%/50%): <sup>1</sup>H NMR (DMSO-d<sub>6</sub>, δ): 7.06 (b, 5H); 7.27 (b, 5H); 7.54 (b, 5H); 7.80 (b, 5H); <sup>13</sup>C NMR (DMSO-d<sub>6</sub>, δ): 111.0, 113.3, 117.1, 121.6, 122.2, 128.8, 129.9, 132.4, 133.2, 136.7, 140.1, 152.3, 159.1, 161.4, 193.4, 194.4; <sup>13</sup>C DEPT 90 (DMSO-d<sub>6</sub>, δ): 111.6, 113.3, 117.2, 121.6, 122.2, 128.8, 129.9, 132.4, 133.2.

**7b**, BW (75%/25%): <sup>1</sup>H NMR (DMSO-d<sub>6</sub>, δ): 7.06 (b, 5H); 7.27 (b, 5H); 7.54 (b, 5H); 7.80 (b, 5H); <sup>13</sup>C NMR (DMSO-d<sub>6</sub>, δ): 111.0, 113.3, 117.1, 121.6, 122.2, 128.8, 129.9, 132.4, 133.2, 136.7, 140.1, 152.3, 159.1, 161.4, 193.4, 194.4; <sup>13</sup>C DEPT 90 (DMSO-d<sub>6</sub>, δ): 111.6, 113.3, 117.2, 121.6, 122.2, 128.8, 129.9, 132.4, 133.2.

**7c**, SW (75%/25%): <sup>1</sup>H NMR (DMSO-d<sub>6</sub>, δ): 7.06 (b, 5H); 7.27 (b, 5H); 7.54 (b, 5H); 7.80 (b, 5H); <sup>13</sup>C NMR (DMSO-d<sub>6</sub>, δ): 111.0, 113.3, 117.1, 121.6, 122.2, 128.8, 129.9, 132.4, 133.2, 136.7, 140.1, 152.3, 159.1, 161.4, 193.4, 194.4; <sup>13</sup>C DEPT 90 (DMSO-d<sub>6</sub>, δ): 111.6, 113.3, 117.2, 121.6, 122.2, 128.8, 129.9, 132.4, 133.2.

## 2.8. General reaction procedure for 2,4-system (polymers **9a-j**)

For polymers utilizing **8**, the procedure for the synthesis of poly(oxy-1,3-[4-benzoyl]-oxy-1,4-phenylene-oxy-co-PEEK) (**9h**, 75:25) is presented as an example. In a 10 mL round bottomed flask were placed 2,4-difluorobenzophenone, **8**, (0.300 g, 1.38

mmol), 4,4'-difluorobenzophenone, **6**, (0.900 g, 4.13 mmol), hydroquinone, **2**, (0.606 g, 5.50 mmol), potassium carbonate (2.28 g, 16.5 mmol), NMP (8.60 mL), and a stir bar. The reaction flask was connected to a reflux condenser and a gas inlet adapter. The system was purged with nitrogen and immersed in a silicone oil bath and heated to 185°C for 24 h. An aliquot was taken for NMR analysis and the reaction mixture was precipitated from ~900 mL of vigorously stirred water and a light gray material was collected via vacuum filtration to yield 0.406 g (81.6%).

*\*The following polymers will have names ranging from **9a** to **9j**, followed by (x/y) where x is the percentage of 4,4'-difluorobenzophenone and y is the percentage of 2,4-difluorobenzophenone.*

**9a** (0/100): <sup>1</sup>H NMR (DMSO-*d*<sub>6</sub>, δ): 7.01 (b, 2H); 7.57 (b, 6H); 7.85 (b, 4H); <sup>13</sup>C NMR (DMSO-*d*<sub>6</sub>, δ) 100.6, 110.8, 112.5, 121.6, 124.4, 128.7, 129.5, 132.7, 133.2, 138.1, 151.3, 159.1, 163.1, 194.1; <sup>13</sup>C DEPT 90 NMR (DMSO-*d*<sub>6</sub>, δ): 100.6, 110.8, 124.4, 128.7, 129.5, 132.7, 133.2.

**9b** HC (0/100): <sup>1</sup>H NMR (DMSO-*d*<sub>6</sub>, δ): 7.01 (b, 2H); 7.57 (b, 6H); 7.85 (b, 4H); <sup>13</sup>C NMR (DMSO-*d*<sub>6</sub>, δ) 100.6, 110.8, 112.5, 121.6, 124.4, 128.7, 129.5, 132.7, 133.2, 138.1, 151.3, 159.1, 163.1, 194.1; <sup>13</sup>C DEPT 90 NMR (DMSO-*d*<sub>6</sub>, δ): 100.6, 110.8, 124.4, 128.7, 129.5, 132.7, 133.2.

**9c** SW (0/100): <sup>1</sup>H NMR (DMSO-*d*<sub>6</sub>, δ): 7.01 (b, 2H); 7.57 (b, 6H); 7.85 (b, 4H); <sup>13</sup>C NMR (DMSO-*d*<sub>6</sub>, δ) 100.6, 110.8, 112.5, 121.6, 124.4, 128.7, 129.5, 132.7, 133.2, 138.1, 151.3, 159.1, 163.1, 194.1; <sup>13</sup>C DEPT 90 NMR (DMSO-*d*<sub>6</sub>, δ): 100.6, 110.8, 124.4, 128.7, 129.5, 132.7, 133.2.

**9d** (20/80): <sup>1</sup>H NMR (DMSO-*d*<sub>6</sub>, δ): 6.87 (b, 2H); 7.06 (b, 9H); 7.57 (b, 7H); 7.87 (b, 2H); <sup>13</sup>C NMR (DMSO-*d*<sub>6</sub>, δ): 100.4, 110.8, 117.3, 121.6, 122.2, 124.5, 128.6, 129.5, 132.1,



132.3, 132.6, 133.3, 138.1, 151.3, 152.1, 159.1, 161.3, 163.2, 193.2, 194.1; <sup>13</sup>C DEPT  
90 NMR (DMSO-*d*<sub>6</sub>, δ): 100.6, 110.8, 124.4, 128.7, 129.5, 132.7, 133.2.

**9e** (50/50): <sup>1</sup>H NMR (DMSO-*d*<sub>6</sub>, δ): 6.87 (b, 2H); 7.06 (b, 9H); 7.57 (b, 7H); 7.87 (b, 2H);  
<sup>13</sup>C NMR (DMSO-*d*<sub>6</sub>, δ): 100.4, 110.8, 117.3, 121.6, 122.2, 124.5, 128.6, 129.5, 132.1,  
132.3, 132.6, 133.3, 138.1, 151.3, 152.1, 159.1, 161.3, 163.2, 193.2, 194.1; <sup>13</sup>C DEPT  
90 NMR (DMSO-*d*<sub>6</sub>, δ): 100.6, 110.8, 124.4, 128.7, 129.5, 132.7, 133.2.

**9f** (60/40): <sup>1</sup>H NMR (DMSO-*d*<sub>6</sub>, δ): 6.87 (b, 2H); 7.06 (b, 9H); 7.57 (b, 7H); 7.87 (b, 2H);  
<sup>13</sup>C NMR (DMSO-*d*<sub>6</sub>, δ): 100.4, 110.8, 117.3, 121.6, 122.2, 124.5, 128.6, 129.5, 132.1,  
132.3, 132.6, 133.3, 138.1, 151.3, 152.1, 159.1, 161.3, 163.2, 193.2, 194.1; <sup>13</sup>C DEPT  
90 NMR (DMSO-*d*<sub>6</sub>, δ): 100.6, 110.8, 124.4, 128.7, 129.5, 132.7, 133.2.

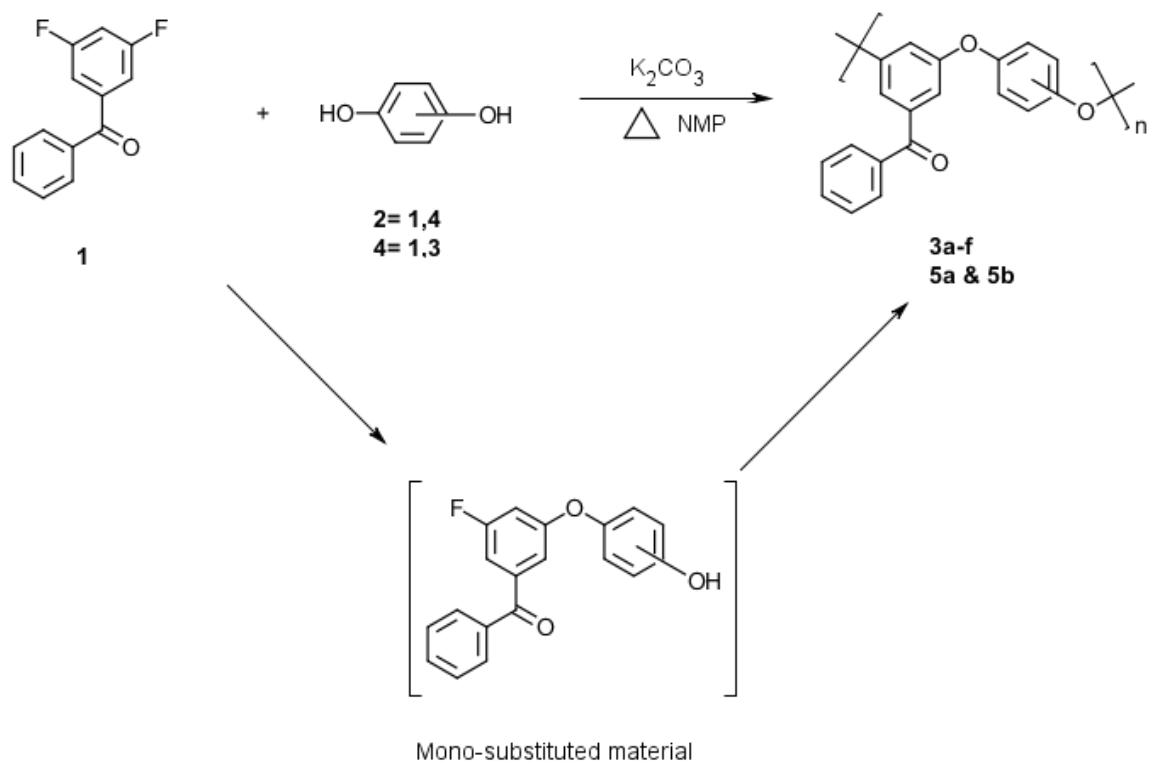
**9g** (65/35): <sup>1</sup>H NMR (DMSO-*d*<sub>6</sub>, δ): 6.87 (b, 2H); 7.06 (b, 9H); 7.57 (b, 7H); 7.87 (b, 2H);  
<sup>13</sup>C NMR (DMSO-*d*<sub>6</sub>, δ): 100.4, 110.8, 117.3, 121.6, 122.2, 124.5, 128.6, 129.5, 132.1,  
132.3, 132.6, 133.3, 138.1, 151.3, 152.1, 159.1, 161.3, 163.2, 193.2, 194.1; <sup>13</sup>C DEPT  
90 NMR (DMSO-*d*<sub>6</sub>, δ): 100.6, 110.8, 124.4, 128.7, 129.5, 132.7, 133.2.

**9h**, **9i**, and **9j** were too insoluble to obtain NMR data.

*\*Reaction 9b was run similarly to 9a, but at a higher (2.55 M) reaction concentration (HC). Reactions 9c and 9i were run similarly to reactions 3f, 5b, and 7c, where a monomer (4,4'-difluorobenzophenone in this case) was held back and added in portions (SW).*

### 3. RESULTS AND DISCUSSION

#### 3.1. Characterization and identification of PAMPPO



Scheme 7: General reaction scheme for **3a-f**, **5a**, and **5b**.

The overall goal of the project was to synthesize PEEK analogues that were previously prepared via a multi-step approach, but by using a much simpler “in situ” approach, as outlined in **Scheme 7**. The initial work involved the synthesis of PAMPPO via the reaction of 3,5-difluorobenzophenone and hydroquinone. The polymerizations were carried out using a variety of conditions and monomer addition methods as summarized in **Table 1**. Initially, entry **3a**, a 1:1 ratio of 3,5-difluorobenzophenone (**1**) and hydroquinone (**2a**) were reacted at low temperature (150°C) for 24 hrs to form, presumably, mostly mono-substituted material. After this initial reaction phase, the system temperature was increased (185°C) to allow for di-substitution to take place and the polycondensation to proceed. After roughly 96 hours relatively low weight average molecular weight ( $M_w$ ), approximately 3,000 Da, material was present. This was thought

to be due to 2 factors: the formation of cyclic species (discussed more in-depth later) and incomplete reaction.

**Table 1.** Reaction methods utilized for the synthesis of **3a-f**, **5a**, and **5b**.

	A Monomer	B Monomer	Ratio (A:B)	Temp.	Time	Addition Method	M <sub>w</sub> /Đ
<b>3a</b>	2	1	1:1	150°C 185°C	24h 72h	A	2,990 Da/2.5
<b>3b</b>	2	1	1:1	150°C 185°C 200°C	24h 24h 24h	A	5,019 Da/2.5
<b>3c</b>	2 95%/ 5% Phenol	1	1(.95/.5):1	150°C 185°C 200°C	24h 24h 24h	A	1,482 Da/2.6
<b>3d†</b>	2	1	1:1	150°C 185°C	24h 96h	A	10,661 Da/2.5
<b>3e</b>	2	1	1:1	185°C	96h	B	7,666 Da/2.5
<b>3f</b>	2	1	1:1	185°C	24h	C	19,563 Da/2.5
<b>3g</b>	2	1	1:1	185°C	24h	D	N/A
<b>5a</b>	4	1	1:1	185°C	24h	C	10,390 Da/2.9
<b>5b</b>	4	1	0.5:1	185°C	96h	B	10,000 Da/2.9

Base for every reaction= K<sub>2</sub>CO<sub>3</sub>, in a stoichiometric ratio of 3 to 1 to the phenol amount. Solvent for every reaction= NMP. Monomer concentration= 0.64M in NMP. († Monomer concentration 2.55M in NMP) Addition Methods: A= low temp high temp, B= Step-wise, C= High temp only, D= Dilute

Increasing the final reaction temperature to 200°C (entry **3b**), to help drive the polycondensation forward, showed a slight increase in the final product's M<sub>w</sub>, to 5,000 Da. End-capping agents, which have been shown to limit the size of chains, were introduced. They limit the size of chain by effectively “terminating” one side of a monomer, allowing growth out of one side of the chain. This effect could, theoretically, help inhibit the formation of cyclic species. The addition of the end-capping agent, phenol, in entry **3c**, showed a decrease in the observed M<sub>w</sub>. Increasing the concentration of monomers from 0.64 to 2.55 M (entry **3d**), which was expected to help limit the formation of cyclic species by enhancing intermolecular rather than intramolecular reactions, afforded an increase of M<sub>w</sub> to approximately 10,500 Da.

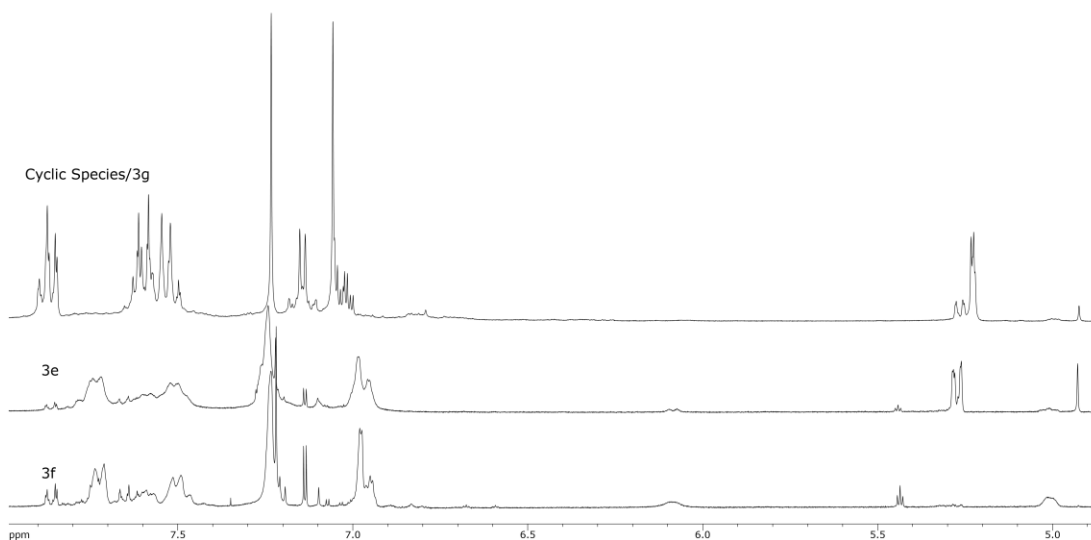


Figure 9: Comparison of a step-wise synthesis (**3e**) and a batch-wise synthesis (**3f**) in terms of cyclic species by the peak located around 5.4 ppm

Method **3e** introduced the use of a step-wise addition method, which involved withholding one of the monomer units (3,5-difluorobenzophenone in this case), essentially running the reaction at a 2:1 ratio. After adequate reaction time, the remainder of the monomer was added all at once, or in portions. This allowed for smaller molecules with the same end groups to be formed in the reaction vessel that are not able to form cyclic species. Then the small molecules were allowed to react with additional monomer, extending the chains. This effectively lowers the amount of cyclic species present, but does not remove them completely, as shown via  $^1\text{H}$  NMR spectroscopy<sup>13</sup> in **Figure 9**, which compares both **3e** and **3f** to **3g**. The only difference between these two NMR spectra is the addition method.

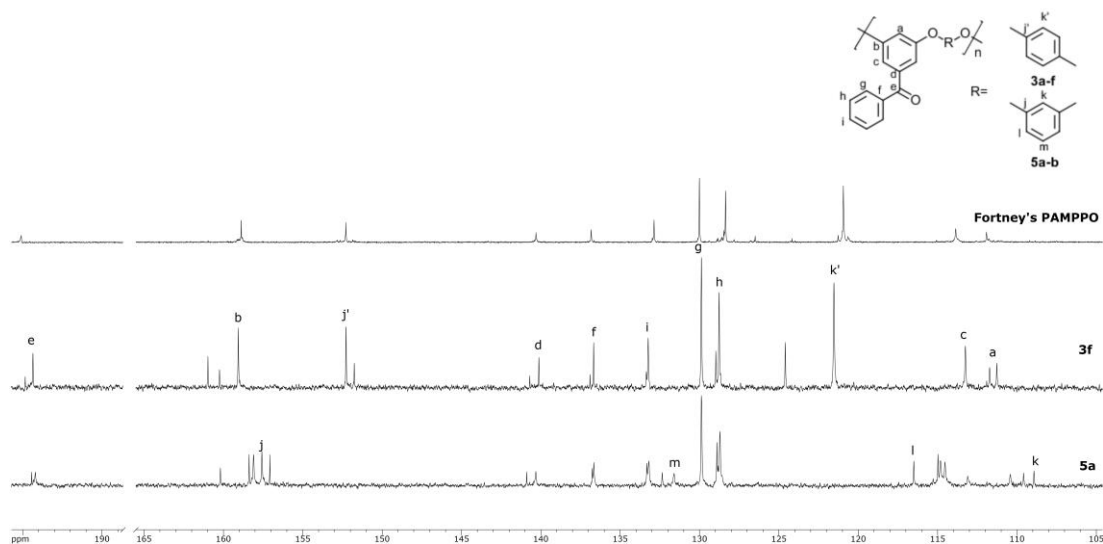
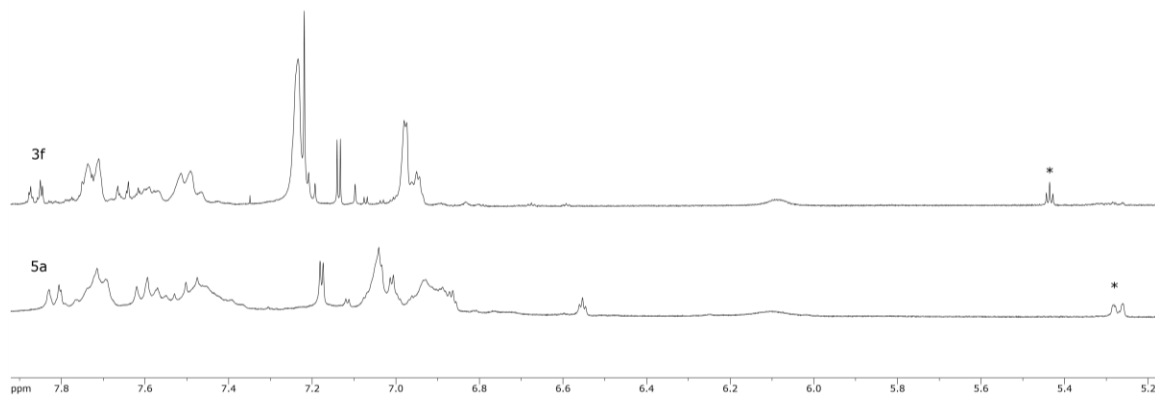


Figure 10: 75.5 MHz  $^{13}\text{C}$  CPD NMR ( $\text{DMSO-d}_6$ ) overlay **3f** and **5a** compared to Fortney's PAMPPO. Note: The NMR sample is a mixture of the sample and NMP in  $\text{DMSO-d}_6$ .

Similar to methods **3e** and **3a**, **3f** was run at  $185^\circ\text{C}$ , as in **3e**, and all of the reactants were added at once, as in **3a**. This resulted in a higher molecular weight material, with an  $M_w$  of approximately 19,500 Da. In order to increase the symmetry along the backbone resorcinol (**4**) was used in place of hydroquinone, which should afford exclusively poly(1,3-phenylene oxide). Reaction of **4** with **1** was carried out using conditions similar to those for **3e** and **3f** to afford polymers **5a** and **5b**, respectively. Each of the polymers had a  $M_w$  value of approximately 10,000 Da. The structures were confirmed via  $^{13}\text{C}$  NMR spectra as shown in **Figure 10**. This spectrum shows 11 signals for the hydroquinone series, represented by **3f**, and 13 signals for the resorcinol series, represented by **5b**. Of these peaks, 9 are shared between the two systems, which are labeled *a-i*. Carbons *a* and *c* appear at around 111 and 113 ppm respectively, while carbon *b* appears around 160 ppm. This shift is due to the inductive electron withdrawing ability of the oxygen attached to carbon *b*. Carbons *d*, *f*, and *l* appear around 140, 136, and 133 ppm, respectively, and carbons *g* and *h* appear near 130 and 128 ppm, respectively. Carbon *e* appears around 195 ppm, due to the carbonyl. For **3e** and **3f**, carbons *j* and *k* appear near 152 and 122 ppm. These peaks are the only peaks that are

not reflected in **5a**. Due to the configuration of resorcinol (1,3 versus 1,4), the phenol ring is not as symmetrical, giving rise to more unique peaks in **5a**. Carbons *j*, *k*, *l*, and *m* are located around 158, 109, 117, and 131 ppm. As mentioned earlier, cyclic species show unique signals in both  $^1\text{H}$  and  $^{13}\text{C}$  NMR spectra, some of which are highlighted in the  $^1\text{H}$  NMR spectrum in **Figure 11** and can be seen in the  $^{13}\text{C}$  NMR spectrum.



*Figure 11: 300 MHz  $^1\text{H}$  NMR of **5a** showing the presence of cyclic species*

The thermal properties of representative sample polymers **3e**, **3f**, **5a**, and a replication of Fortney's PAMPPO were evaluated using TGA and DSC analyses. All thermal data for the selected polymers is tabulated in **Table 2** and overlaid in **Figure 12**. The TGA traces all showed 5% weight loss temperatures in excess of 300°C, with the highest 5% weight loss temperature being observed for the highest molecular weight material, **3f**. The DSC traces show  $T_g$ 's for **3e**, **3f**, and **5a**, as well as both  $T_c$ 's and  $T_m$ 's

for **3e** and **3f**, which indicates the presence of crystalline regions.

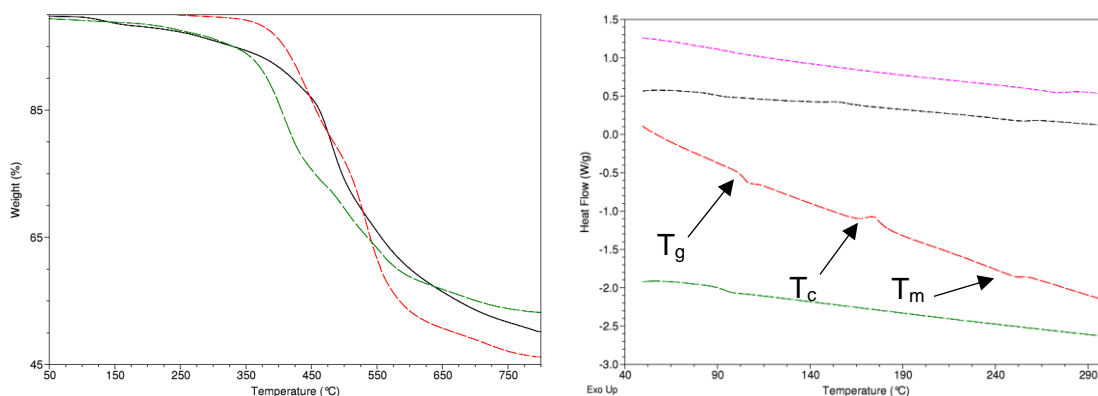
**Table 2.** TGA and DSC data of previously reported materials, **3e**, **3f**, and **5a**.

Compound	DSC 2 <sup>ND</sup> HEATING CURVE <sup>Y</sup>					TGA <sup>Z</sup>
	$T_g$ (°C)	$T_c$ (°C)	$\Delta H$ ( $T_c$ ) (J/g)	$T_m$ (°C)	$\Delta H$ ( $T_m$ ) (J/g)	$T_d$ 5% (°C)
PAMPPPO <sup>a</sup>	105	-	-	-	-	428
<b>3e</b>	87	156	-0.63	254	1.31	329
<b>3f</b>	104	174	-3.73	252	1.26	408
<b>5a</b>	95	-	-	-	-	329

y- Heating ramp of 10 °C/min

z- Heating ramp of 10 °C/min

a- As reported by Fortney and Fossum<sup>1</sup>



**Figure 12:** (Left) TGA overlay showing similar degradation patterns for **3e**, **3f**, and **5a**. (Right) DSC trace (second heat) for **3e** (—), **3f** (---), **5a** (—) and Fortney's PAMPPPO (---).

Powder diffraction was also used to determine the morphologies of the synthesized polymers, and is shown in **Figure 13**. The powder diffraction effectively shows the amount of order, and subsequently crystalline character, in a polymer system. Polymers that are amorphous generally show an “amorphous halo” which looks like a semi-circle in the diffractogram. Polymers that are semi-crystalline will show sharp peaks protruding from the semi-circle, indicating to what degree the sample is crystalline. As shown in **Figure 13**, **5a** shows an amorphous halo, while both **3e** and **3f** show hints at

slight crystallinity.

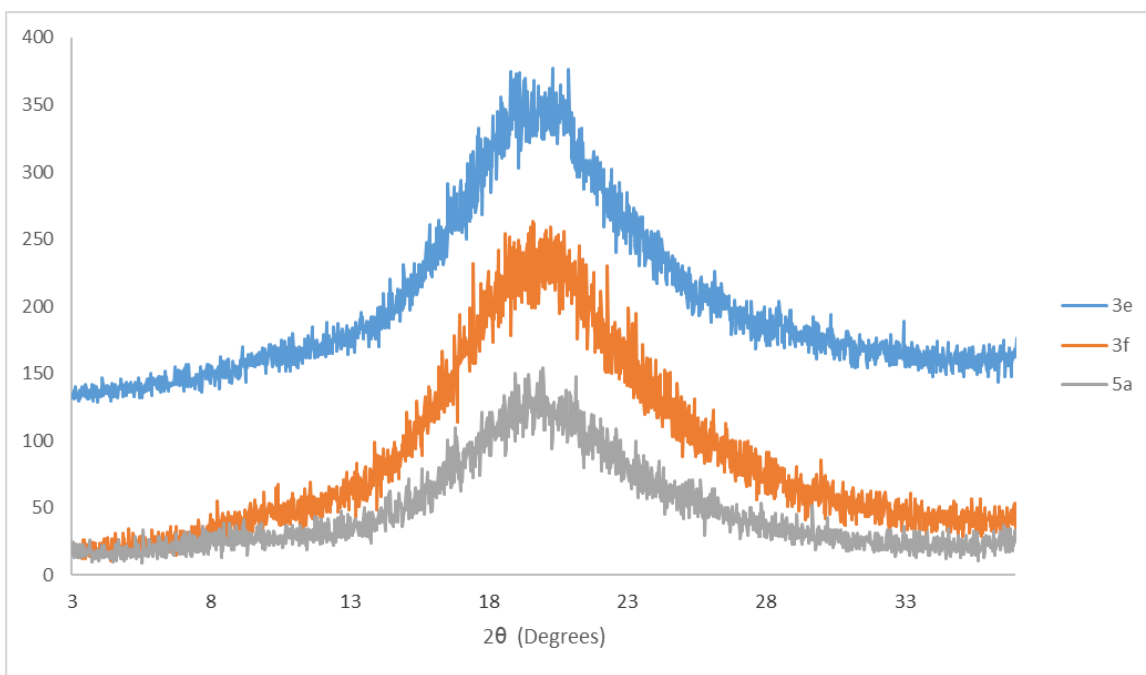


Figure 13: Powder diffraction data for 3e, 3f, and 5a

The formation and removal of cyclic species is cause for concern in this system, as cyclic formation tends to lower the  $M_w$  value for the system. Currently, the method for removing cyclic species is to reprecipitate in an alcohol multiple times, as once will not remove all the cyclic species, which is shown in **Figure 14**. The quantity of cyclic species can be roughly estimated by integrating the entire aromatic region against the peak at 5.4 ppm. The respective values of this peak, from 0-2 times reprecipitated are



0.01, 0.004, and 0.001 when the aromatic region is set to 1.

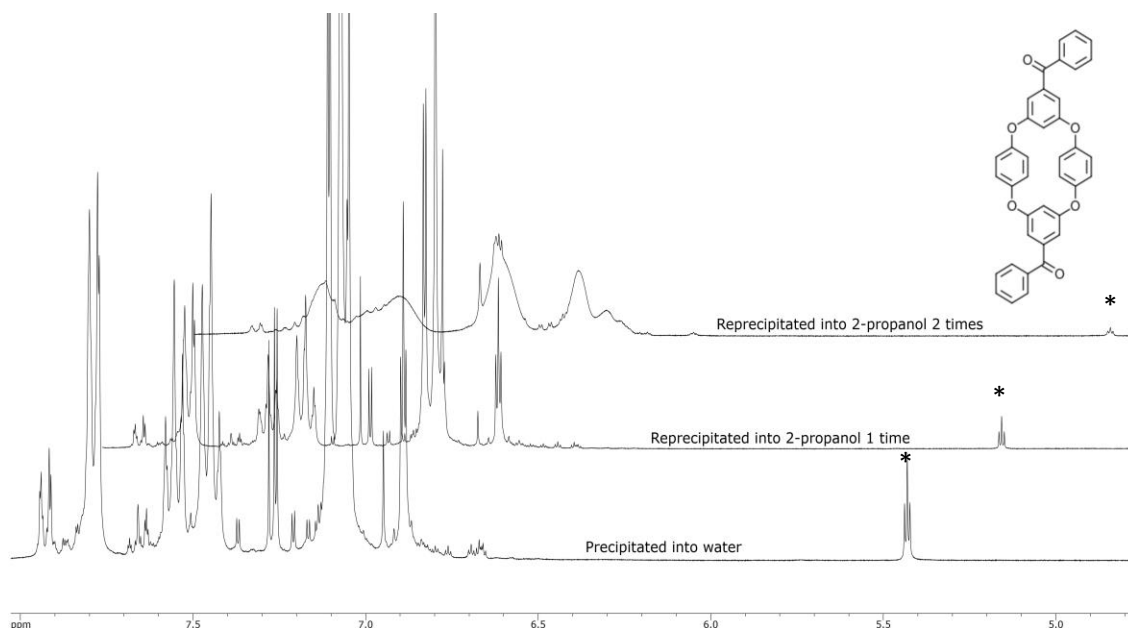
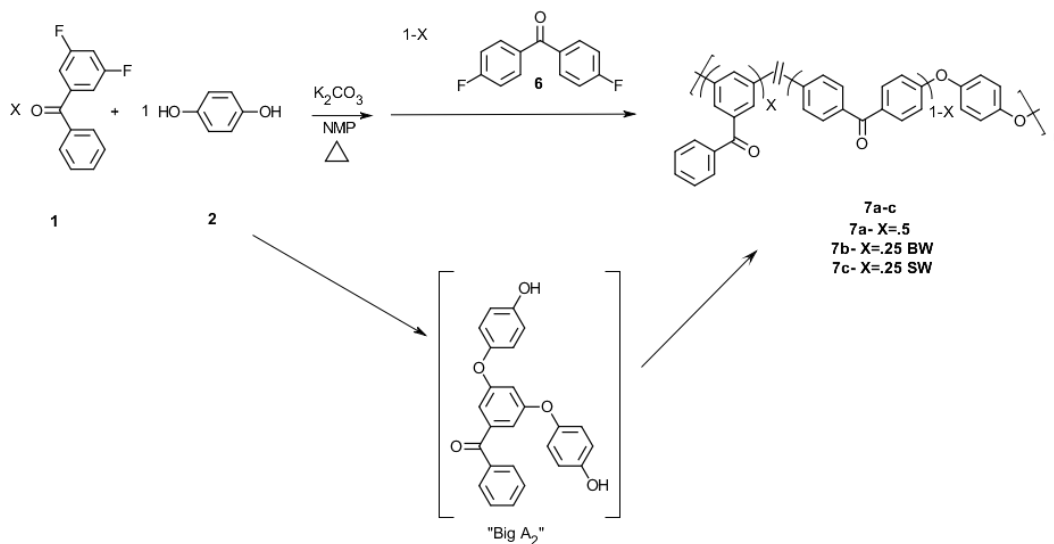


Figure 14: Comparison of **3f** before (bottom), after 1 reprecipitation (middle), and after 2 reprecipitations in isopropanol. Note: The NMR sample is a mixture of the sample and NMP in DMSO- $d_6$ .

### 3.2. Characterization and identification of PEEK/PAMPPPO copolymers



Scheme 8: General reaction scheme for **7a**, **7b**, and **7c**.

The next phase of the project was to recreate the copolymers synthesized by Fortney and Fossum,<sup>1</sup> but using an “in situ” approach, as outlined in **Scheme 8**. This

work involved the synthesis of PAMPPO-co-PEEK copolymers via the reaction of 3,5-difluorobenzophenone (**1**) with hydroquinone (**2**) and 4,4'-difluorobenzophenone (**6**). These polymerizations were carried out using a variety of conditions and monomer addition methods as summarized in **Table 3**. Due to the fact that **6** is much more reactive than **1**, the reaction could not be run in a truly “batch-wise” manner, otherwise small, insoluble PEEK oligomers would have formed and fallen out of solution. Therefore, as shown in entry **7a**, a 0.5:1 ratio of 3,5-difluorobenzophenone and hydroquinone was reacted at 185°C for 24 h to form “Big A<sub>2</sub>”<sup>1</sup> *in situ*. After this initial reaction phase, the system temperature was lowered to 150°C, the 4,4'-difluorobenzophenone was added to make the final reaction ratio be 1:1, and the polycondensation was allowed to proceed.

**Table 3.** Reaction Conditions for **7a**, **7b**, and **7c**.

	Ratio (2:1:6)	Temp.	Time	Addition Method	Observations
<b>7a</b>	1:0.5:0.5	185°C 150°C	24h 24h	A	Amorphous
<b>7b</b>	1:0.25:0.75	185°C 150°C	24h 24h	A	Semi-Crystalline
<b>7c</b>	1:0.25:0.75	185°C 150°C 150°C 150°C	24h 24h 24h 24h	B	Semi-Crystalline

Base for every reaction= K<sub>2</sub>CO<sub>3</sub>, in a stoichiometric ratio of 3 to 1 to the phenol amount. Solvent for every reaction= NMP. Monomer concentration =0.64M in NMP. Addition Methods: A= “Batch-wise” synthesis, B= “Step-wise” Synthesis

<sup>13</sup>C NMR spectroscopy (see **Figure 15**) confirmed the structure of the 50% copolymer, and is compared to Fortney and Fossum’s 50% copolymer. Peaks *j* and *k*, which are associated with the carbon atoms in the hydroquinone portion of the repeat unit, and *m*, which is associated with the carbon atom the farthest away from the

carbonyl, appear to have multiple signals associated with them relative to Fortney and Fossums 50% copolymer. This is due to the slightly different environments these bonds are in. For example, *j* is always connected to the oxygen, but after that oxygen, there could be a 3,5-benzophenone system, or a 4,4'-benzophenone system, which will alter the environment, and in turn the chemical shift, that this C-H bond has.

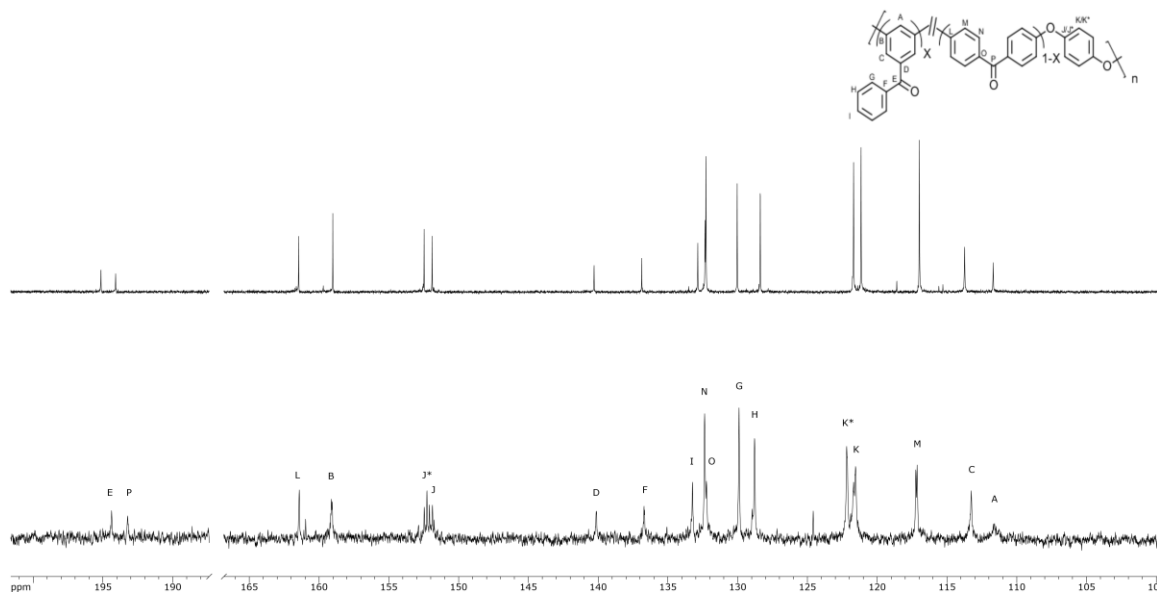


Figure 15: 75.5 MHz  $^{13}\text{C}$  CPD ( $\text{DMSO-}d_6$ ) overlay of **7a** (bottom) and Fortney and Fossum's 50% copolymer. Note: The NMR sample is a mixture of the sample and NMP in  $\text{DMSO-}d_6$ .

Both DSC and X-Ray diffraction analyses had shown hints of semi-crystalline character in the 25% copolymer synthesized by Fortney.<sup>1</sup> As such, 3,5-difluorobenzophenone and hydroquinone were reacted in a 0.25:1 ratio (entry **7b**) at 185°C to form “Big  $A_2$ ” *in situ*. After this initial reaction phase, the system temperature was lowered to 150°C, 4,4'-difluorobenzophenone was added to make the final reaction ratio be 1:1, and the polycondensation was allowed to proceed. This reaction was also run in a “step-wise” manner (**7c**), where 3,5-difluorobenzophenone and hydroquinone were initially reacted in a 0.25:1 ratio at 185°C to form “Big  $A_2$ ” *in situ*, at which point the reaction temperature was lowered to 150°C and 1 of 3 portions of the 4,4'-difluorobenzophenone were added. Subsequent portions were added after the reaction

mixture had heated for 24 h, until the reaction stoichiometric ratio reached 1:1.

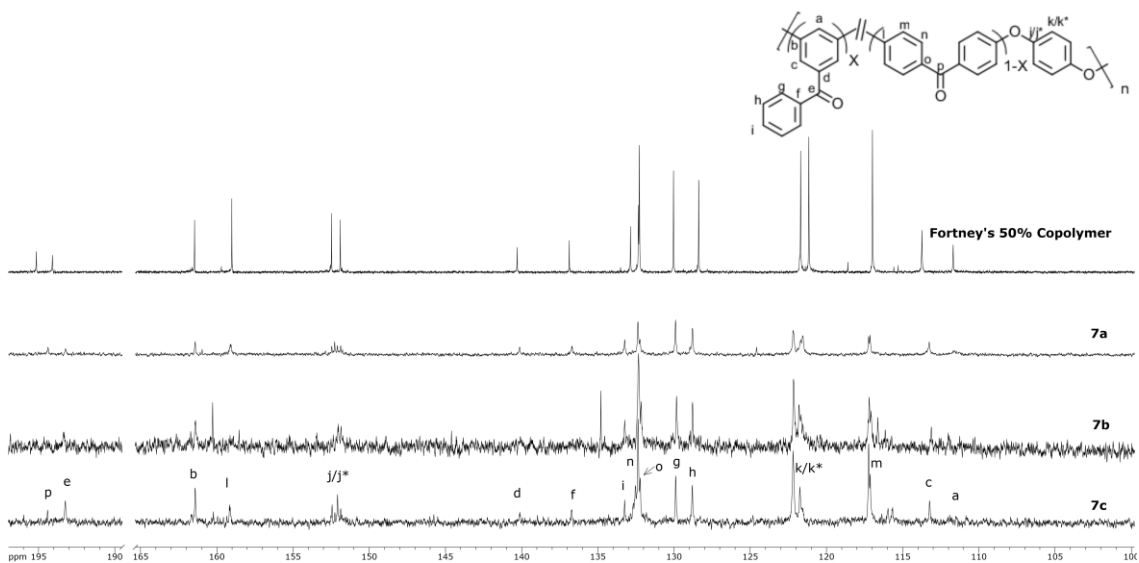


Figure 16: 75.5 MHz <sup>13</sup>C NMR (DMSO-d<sub>6</sub>) of **7a**, **7b**, and **7c**.

The structures of these copolymers were confirmed via <sup>13</sup>C NMR spectroscopy (**Figure 16**), and are compared to Fortney and Fossums 50% copolymer. Due to the increased level of PEEK in these materials, the polymers became insoluble in most organic solvents. This can be seen in **Figure 16**, as the signals for both 25% copolymers are much weaker than their 50% counterparts. The poor solubility led to a lack of SEC

data for the 25% copolymers, as well as poor NMR spectra quality.

**Table 4.** TGA and DSC data for **7a**, **7b**, and **7c**, compared to previously synthesized materials.

Compound	DSC COOLING CURVE <sup>x</sup>			DSC 2 <sup>nd</sup> HEATING CURVE <sup>y</sup>				TGA <sup>z</sup>
	T <sub>g</sub> (°C)	T <sub>c</sub> (°C)	ΔH (T <sub>c</sub> ) (J/g)	T <sub>g</sub> (°C)	T <sub>c</sub> (°C)	T <sub>m</sub> (°C)	ΔH (T <sub>m</sub> ) (J/g)	T <sub>d 5%</sub> (°C)
50% <sup>a</sup>	128	-	-	126	-	-	-	480
<b>7a</b>	121	-	-	127	-	-	-	444
25% <sup>a</sup>	136	-	-	137	-	-	-	508
<b>7b</b>	124	206	-22.4	128	-	281	18.6	498
<b>7c</b>	125	210	-16.7	124	-	282	8.83	440

x- Cooling rate at 10 °C/min

y-Heating rate at 10 °C/min

z-Heating rate at 10 °C/min

a- As reported by Fortney and Fossum{{2 Fortney,Andria 2012;}}

The thermal properties of copolymers **7a**, **7b**, and **7c** were evaluated using TGA and DSC analyses. All thermal data for these polymers are tabulated in **Table 4**, as well as overlaid in **Figure 17** and **Figure 18**. The TGA traces all showed 5% weight loss temperatures in excess of 400°C, with the highest 5% weight loss, 498°C, being observed for **7b**. The DSC analysis confirmed the presence of crystalline regions in both **7b** and **7c**, while showing a completely amorphous nature for **7a**. Compared to that of PEEK (143°C), the T<sub>g</sub>'s of these systems are low, between 124 and 127°C, but are much closer to Fortney and Fossum's previously synthesized polymers. These differences in thermal properties can be attributed to the addition of the pendant "side group" to the main backbone of the polymer. This change alters the spacing and size of the repeat unit, increasing the free volume of the polymer and, therefore, lowering the T<sub>g</sub>.

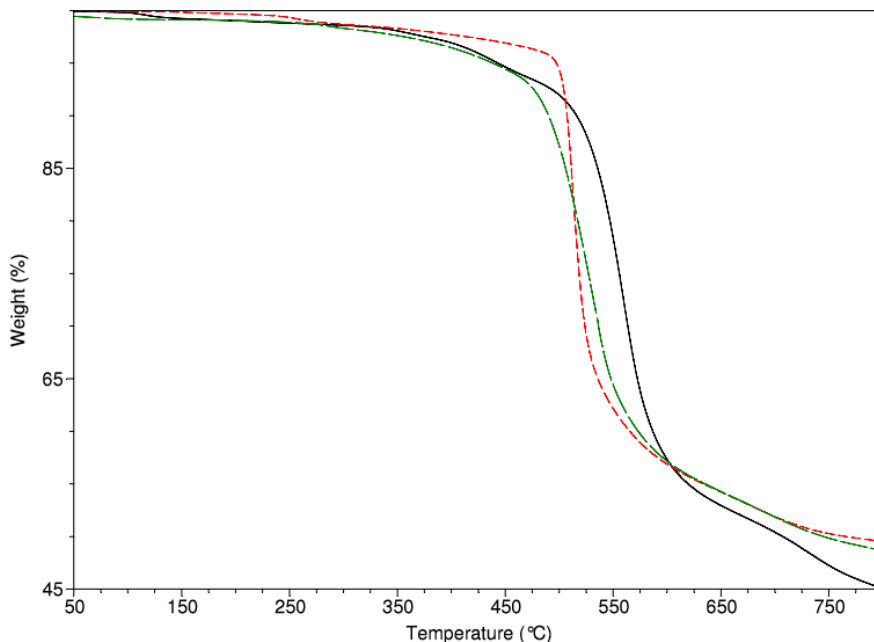


Figure 17: TGA trace showing similar degradation patterns for polymers **7a** (—), **7b** (---), and **7c** (---).

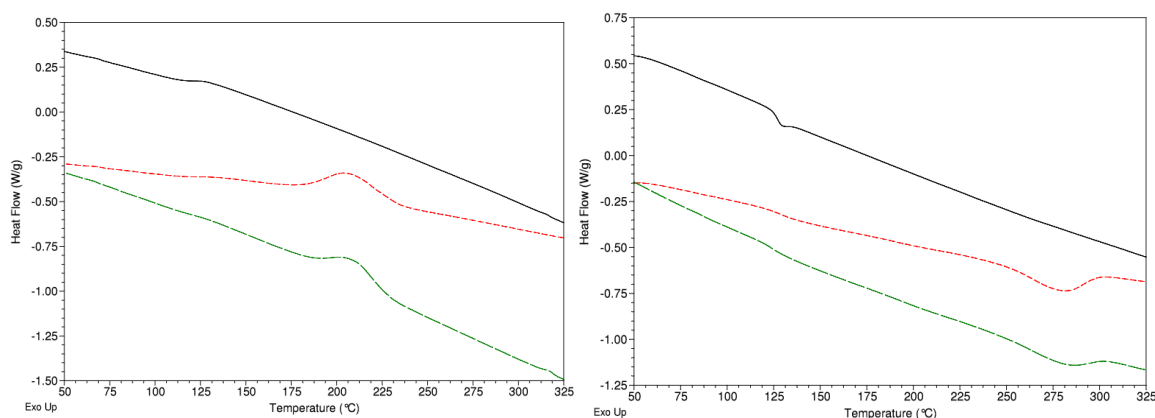


Figure 18: (Left) DSC cooling trace showing crystallization temperature ( $T_c$ ) upon cooling and (Right) DSC second heating trace showing  $T_g$  and  $T_m$  peaks of **7a** (—), **7b** (---), and **7c** (---).

For **7b** and **7c**, the  $T_m$  values are lower than the value for PEEK itself, which is 343°C. The structure of the polymer affects the  $T_m$  of the system. Due to the pendant group of these copolymers, the ability of the polymer to form long crystalline regions is reduced, forcing smaller crystalline regions and, as a result, lower  $T_m$  values. Smaller crystalline regions do not require as much heat to melt compared to their longer counterparts. Powder diffraction was also used to determine the morphologies of the

synthesized copolymers, and is outlined in **Figure 19**. **7a** shows an amorphous halo, which reflects the amorphous nature of this polymer. However, **7b** and **7c** starts to show peaks that arise from the amorphous halo, which reflects the semi-crystalline nature of these polymer systems.

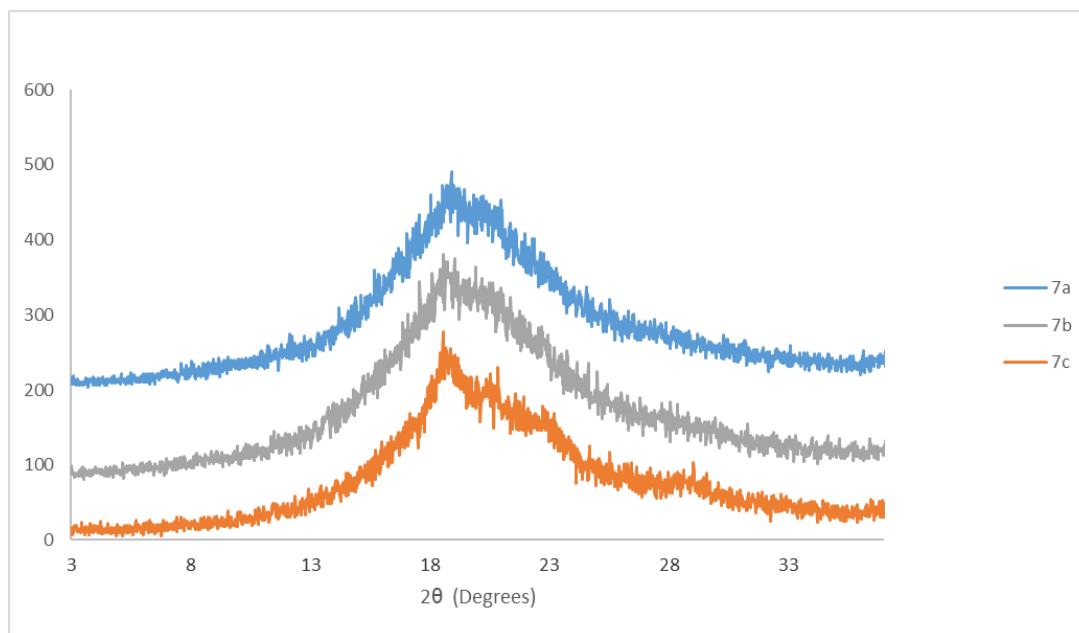


Figure 19: Powder diffraction data for 7a-7c

With the addition of the 4,4'-difluorobenzophenone monomer, the tendency to form cyclic species is considerably reduced. This is due to the geometry of the 4,4'-difluorobenzophenone monomer compared to that of the 3,5-difluorobenzophenone monomer. The reactive groups are located farther away from one another and, therefore, require more repeat units to be able to bend around and allow the chain to find its own end. When the polymer chain becomes long enough for this to happen, the likelihood for the polymer chain to find another free monomer instead of its own end is very high. Despite the reduced chance of forming cyclic species, they still can form, as can be seen in **Figure 20**, which is shown in **7a** much better than in **7b** or **7c**, due to the poor solubility of **7b** and **7c**. **Figure 20** also shows the reduction of the formation of cyclics due to the addition of the 4,4'-difluorobenzophenone. The process for removal is

the same as in the homopolymer's case. However, the process of removal involves dissolving in another solvent and then precipitating into a solvent intended to remove cyclics. This is to ensure maximum removal of cyclics, but cannot be done for insoluble materials, therefore the presence of cyclic materials may always be present in lower 3,5 monomer percentage polymers. In order to counter this, one could simply replace vigorously stirred water with vigorously stirred isopropanol during the initial precipitation process.

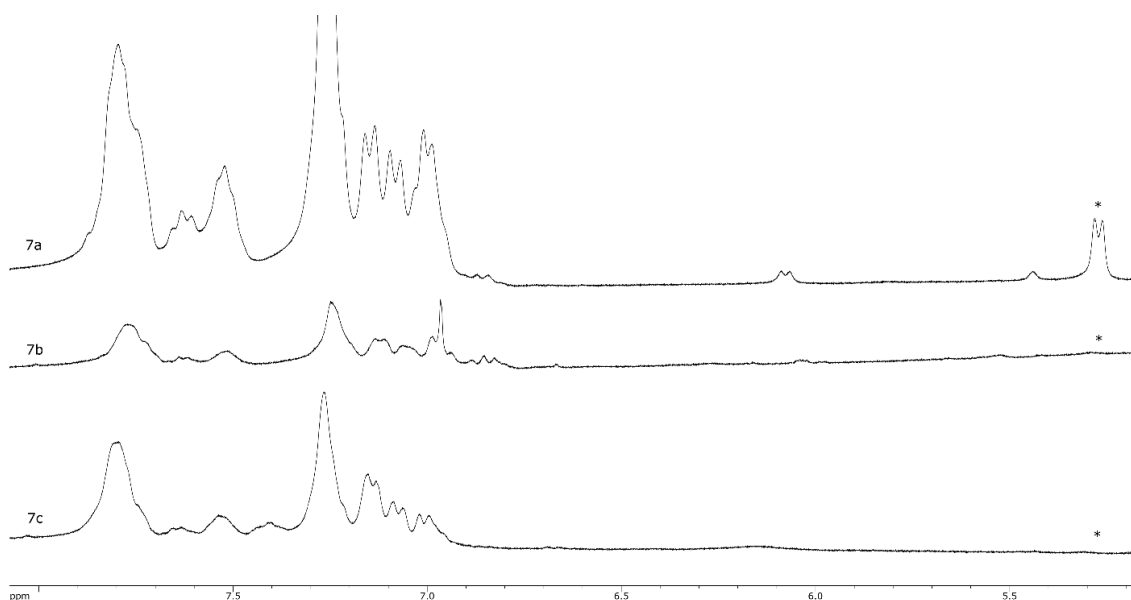
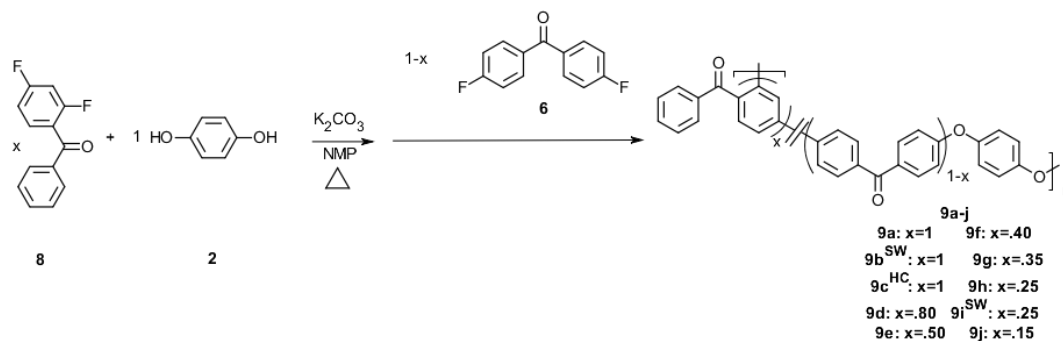


Figure 20: 300 MHz  $^1\text{H}$  NMR showing cyclization peaks around 5.3 ppm disappearing.

### 3.3. Characterization and Identification of PEEK/PAPOPO



Scheme 9: General reaction scheme for the 2,4 system. "HC"- reaction was run at higher concentration (2.55 M). "SW"- reaction was run in a "step-wise" manner.

As depicted in **Scheme 9** the final goal of the project was the synthesis of



PAPPO-*co*-PEEK copolymers via the reaction of 2,4-difluorobenzophenone (**8**) with hydroquinone (**2**) and 4,4'-difluorobenzophenone (**6**). The 2,4-difluorobenzophenone is more reactive and less expensive than 3,5-difluorobenzophenone, but still provides a pendent benzoyl group for the introduction of functional groups. The polymerizations with **8** were carried out using a variety of different conditions and monomer addition methods as summarized in **Table 5**.

**Table 5.** Reaction conditions for **9a-j**.

<i>Compound</i>	Ratio ( <b>2a/8/6</b> )	Temp.	Time	Observations	M <sub>w</sub> /Đ
<i>9a</i>	1/1/0	185 °C	12 hrs	Amorphous	Low Molecular Weight/2.5
<i>9b</i> <sup>HC</sup>	1/1/0	185 °C	12 hrs	Amorphous	83,000 Da/2.6
<i>9c</i> <sup>SW</sup>	1/1/0	185 °C 185 °C	12 hrs 12 hrs	Amorphous	6,600 Da/2.5
<i>9d</i>	1/0.8/0.2	185 °C	12 hrs	Amorphous	-
<i>9e</i>	1/0.5/0.5	185 °C	12 hrs	Amorphous	-
<i>9f</i>	1/0.4/0.6	185 °C	12 hrs	Amorphous	-
<i>9g</i>	1/0.35/0.65	185 °C	12 hrs	Semi-crystalline	-
<i>9h</i>	1/0.25/0.75	185 °C	12 hrs	Semi-crystalline	-
<i>9i</i> <sup>SW</sup>	1/0.25/0.75	185 °C	12 hrs	Semi-crystalline	-
<i>9j</i>	1/0.15/0.85	185 °C	12 hrs	Semi-crystalline	-

*Base for every reaction= K<sub>2</sub>CO<sub>3</sub>, in a stoichiometric ratio of 3 to 1 to the phenol amount. Solvent for every reaction= NMP. Monomer concentration =0.64M in NMP, except the reaction denoted by "HC", which had a reaction concentration of 2.55M. All reactions were run in "batch-wise" fashion, except for the reaction denoted by "SW", which denotes reaction was run in "step-wise" fashion.*

Initially, a 1:1 ratio of 2,4-difluorobenzophenone and hydroquinone was reacted at 185°C for 12 hours to yield the homopolymer (**9a**). Unfortunately, <sup>1</sup>H NMR and SEC data showed the reaction product to be more cyclic species and oligomers than expected. In **Figure 21** the aromatic proton peaks are relatively sharp compared to the spectrum of **3f**. The formation of cyclic species is confirmed by the low M<sub>w</sub> value

obtained by the SEC, <1,000 Da.

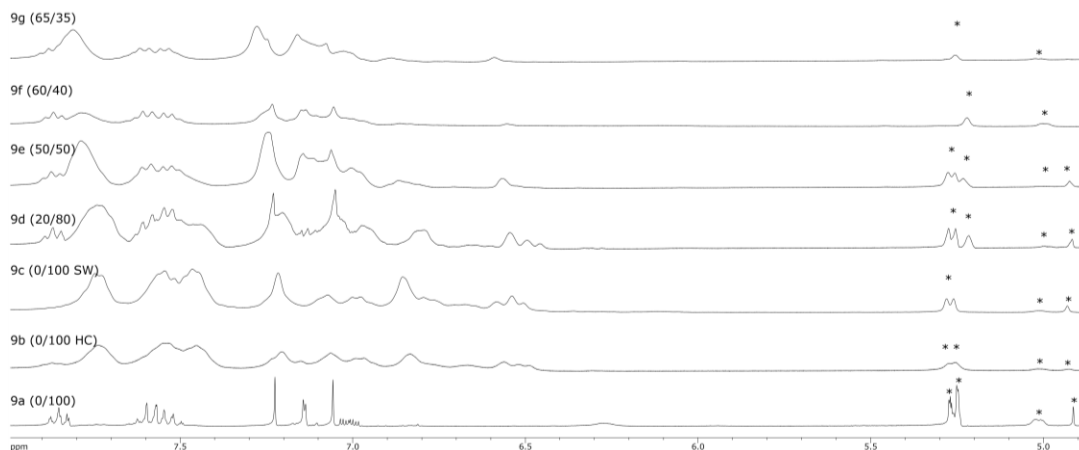


Figure 21: 300 MHz  $^1\text{H}$  NMR of polymers **9a-9g**, showing reduction in cyclic formation.

Kriecheldorf *et al.*<sup>11</sup> has studied cyclic species associated with the 2,4-monomer and has shown that 2,4-difluorobenzophenone monomer has a higher tendency to cyclize than its 2,6 counterpart. This was due to the conformation adopted by the different monomer systems when substituted, either “M” or “V” conformation, which are shown in **Figure 22**. Monomers like 2,4-difluorobenzophenone prefer to form into a “V” conformation, which is more prone to cyclization than the 2,6-difluorobenzophenone’s “M” conformation. The 2,4-difluorobenzophenone’s carbonyl group also pushes the group in the 2 position away from it, causing intramolecular interactions to become more

frequent.

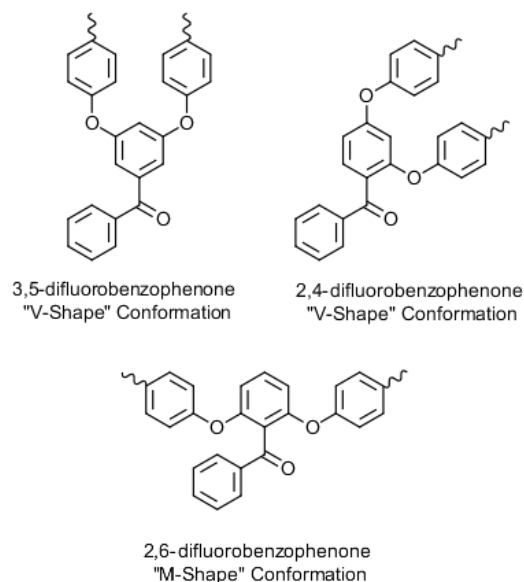


Figure 22: Different intermediate conformations

In order to limit the formation of cyclic species the same reaction was run again, but at a higher concentration, 2.55 M (**9b**), which should encourage inter- rather than intramolecular reactions. This method still formed cyclic species, but a considerably lower percentage (See **Figure 21** and **Table 6**). As an added benefit, reaction **9b** also provided a high molecular weight material, Mw = 83,000 Da. As another measure to limit the formation of cyclic species, a third homopolymer reaction was run, this time with a "step-wise" approach (**9c**), in which the hydroquinone was added in portions. This yielded lower molecular weight polymer, but with fewer cyclic species. The lower molecular weight material may be due to the increased importance of accurate measurements in the step-wise reaction, as mentioned for the "step-wise" 3,5-homopolymer. As was done with the 3,5-system, a series of copolymers were prepared in order to determine the level of incorporation of the 2,4-monomer that would provide a PEEK analogue with measurable crystallinity. Since the 2,4-difluorobenzophenone and the 4,4'-difluorobenzophenone should have similar reactivities, the copolymer reactions

**Table 6:** Relative amounts of cyclic signals, derived from  $^1\text{H}$  NMR spectra, across all soluble polymers.

<b>Polymer</b>	<i>Percentage 4,4'-comonomer</i>	<i>Integration of Aromatic Region Versus Cyclic peaks</i>
<b>9a</b>	0	5:2.25
<b>9b</b>	0	1:0.1
<b>9c</b>	0	1:0.05
<b>9d</b>	20	1:0.07
<b>9e</b>	50	1:0.09
<b>9f</b>	60	1:0.08
<b>9g</b>	65	1:0.08

could be run in a truly “batch-wise” approach. The first of the copolymers (**9d**) was synthesized by reacting 2,4-difluorobenzophenone, 4,4'-difluorobenzophenone, and hydroquinone in a 0.2/0.8/1 (i.e. 20 % PEEK) ratio at a monomer molarity of 0.64 M. After 12 hours at 185°C, the reaction mixture was added dropwise to water and was collected via vacuum filtration, which yielded a fine beige powder. The remaining reactions were run as stated in **Table 5**, with the only notable exception being entry **9i**, where the 2,4-difluorobenzophenone was added in a step-wise manner. This was done to show the difference, if any, that addition methods could have on the formation of cyclic species in a copolymer. As previously mentioned, **Figure 21** shows the  $^1\text{H}$  NMR spectra of reactions **9a-g** to highlight the relative quantities of cyclic species present. As 4,4'-difluorobenzophenone is added (going from the bottom to the top in the figure) the relative number of cyclic species is lowered, and **Table 6** contains the integration values of the aromatic region versus the integrations of the signals associated with the cyclic species. This is due to the 4,4'-difluorobenzophenone making the reactive sites become further away, preventing the polymer from forming cycles.

$^{13}\text{C}$  NMR spectroscopy was used to confirm the structures of polymers **9a-9j**. **Figure 23** shows a  $^{13}\text{C}$  NMR overlay of the soluble polymers in the 2,4 system, showing the similarities of all polymers synthesized in this manner. As more 4,4' monomer was incorporated the solubility decreased and characterization via NMR spectroscopy became more difficult. For all of the polymers, there were carbon signals that were

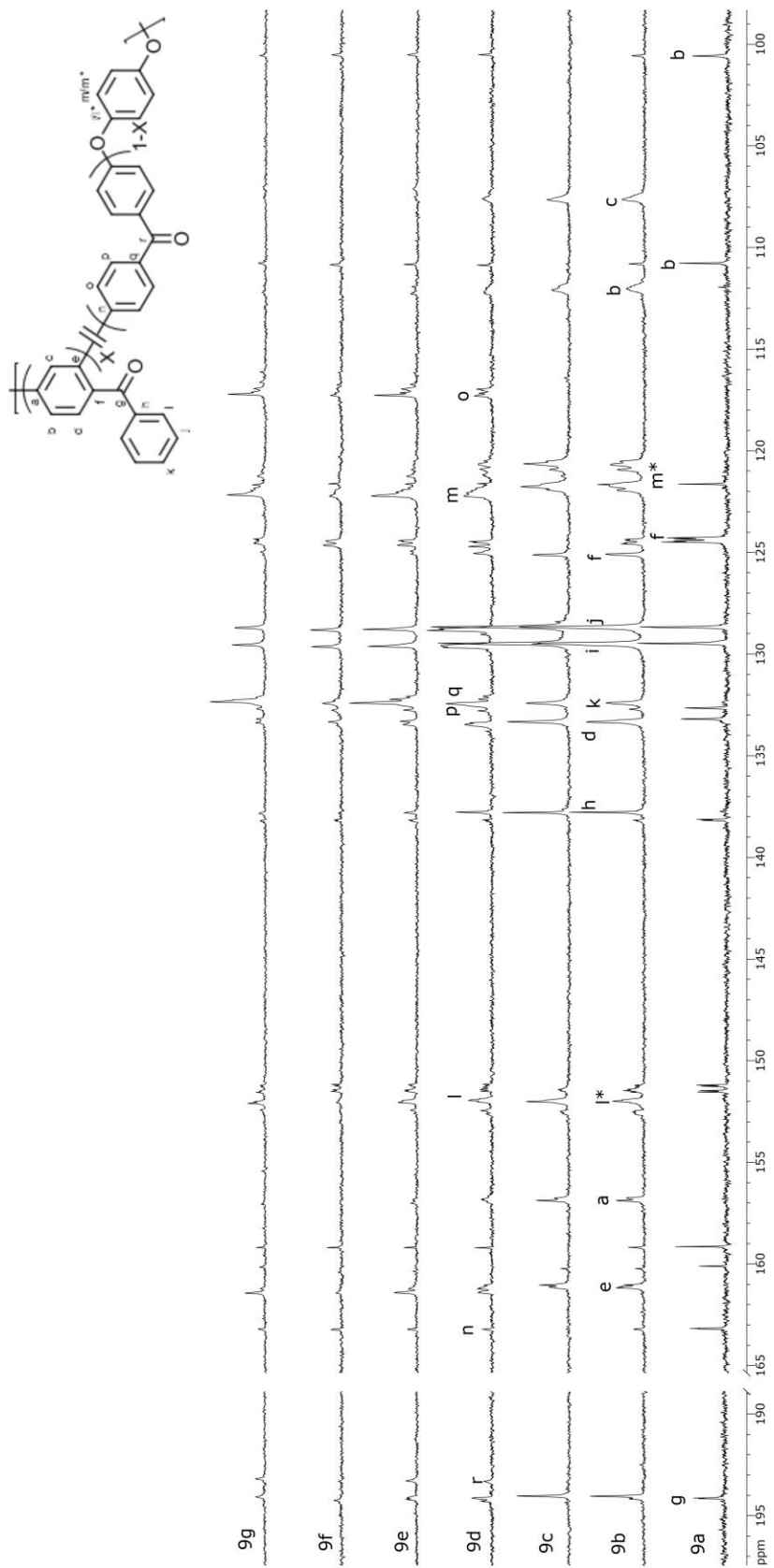
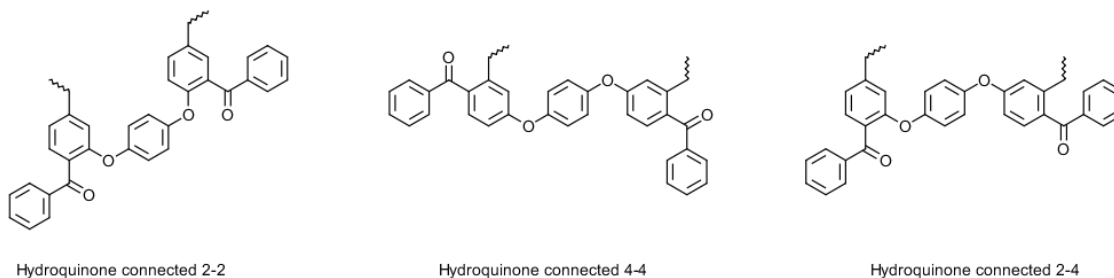


Figure 23: 75.5 MHz  $^{13}\text{C}$  CPD (DMSO- $d_6$ ) Overlay of Spectra for polymers **9a-g**

present in every polymer. These can be found in **Figure 23** and are as follows: carbon **a** appears at approximately 159 ppm; carbon **b** appears at approximately 111 ppm; carbon **c** appears at approximately 101 ppm; carbon **d** appears at approximately 133 ppm; carbon **e** appears at approximately 163 ppm; carbon **f** appears at approximately 121 ppm. Carbons **g, h, i, j, k, q,** and **r** appear in approximately the same place for the 2,4 polymers as in the 3,5 polymers. For the copolymers exclusively, carbon **l** appears at approximately 162 ppm, carbon **m** and appears at approximately 116 ppm, carbon **n** appears at approximately 133 ppm, carbon **o** appears at approximately 133 ppm and close to the peak for carbon **n**, and carbon **p** appears at approximately 193 ppm. It is important to mention that due to the structure of the 2,4 monomer, multiple  $^{13}\text{C}$  NMR signals can be observed for a single carbon atom in the polymer. Examples of this are shown in **Figure 24**, and are highlighted by peaks **l** and **m** in **Figure 23**.



*Figure 24: Due to the structure of the 2,4 monomer, many different connectivity's can occur*

The thermal properties of **9a-9j** were evaluated with DSC and TGA and the data is summarized in **Table 7**. The TGA traces are displayed in **Figure 25** and show that all of the polymers possessed  $T_{d-5\%}$  values in excess of 400°C, with the highest value associated with the most “PEEK like” copolymer, **9i**, at 448°C.

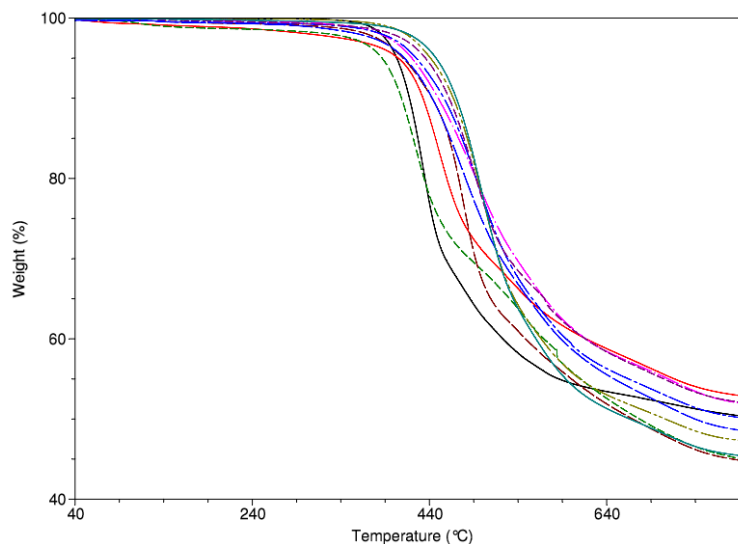


Figure 25: TGA traces of the 2,4 system, showing similarity in degradation temperatures. 9a (—), 9b (· · · · ·), 9c (— · — · —), 9d (— · — · —), 9e (— · — · —), 9f (— · — · —), 9g (— · — · —), 9h (— · — · —), 9i (— · — · —),

DSC analysis showed that polymers **9a-9f** were completely amorphous materials, while the presence of crystalline regions was confirmed for polymers **9g, 9h, 9i, and 9j**, as shown by the presence of the  $T_c/T_m$  peaks in **Figure 26**.

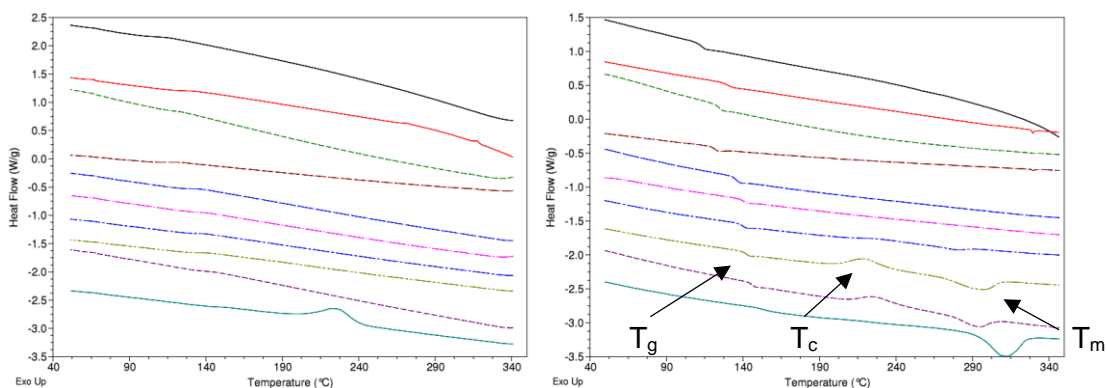


Figure 26: (left) DSC cooling traces of the 2,4 system and (right) second heat outlining  $T_g$ ,  $T_c$ , and  $T_m$ , where applicable. 9a (—), 9b (· · · · ·), 9c (— · — · —), 9d (— · — · —), 9e (— · — · —), 9f (— · — · —), 9g (— · — · —), 9h (— · — · —), 9i (— · — · —), 9j (— · — · —)

Powder diffraction was also used to determine the synthesized polymers morphologies, which are highlighted in **Figure 27**. These traces show for polymers 9a-9f an amorphous halo, which denotes a completely amorphous polymer. For polymers 9g-9j, the traces exhibit peaks that protrude out from the amorphous halo, indicating

order, or crystallinity.

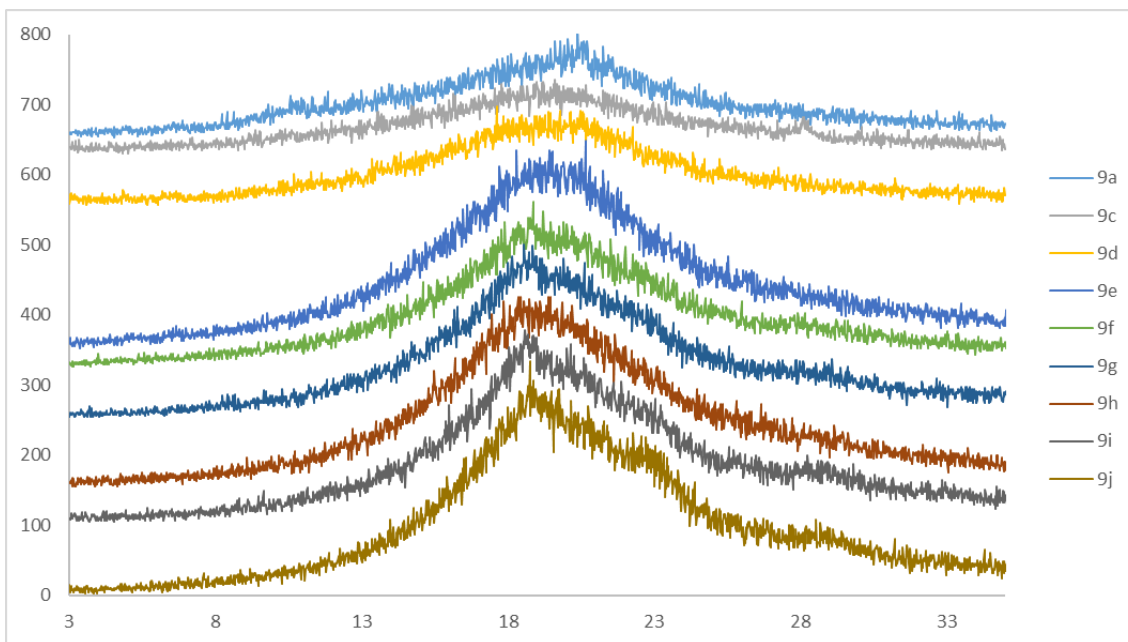


Figure 27: Powder diffraction data of polymers 9a-9j

Compared to the copolymers of the 3,5 system, the 2,4-difluorobenzophenone copolymers had consistently higher  $T_g$  values, from 126°C to 149°C. For direct comparison, the 3,5-homopolymer that was run “batch-wise” had a  $T_g$  value of 104°C, compared to 116°C for the 2,4-homopolymer, and the 3,5 75% PEEK copolymer had a  $T_g$  value of ~125°C, while the 2,4 75% PEEK copolymer had a  $T_g$  value of ~138°C. The  $T_g$  increase can be attributed to the increased amount of 4,4'-difluorobenzophenone and, therefore, increased amount of steric strain in the polymer system due to a decrease in the ratio of flexible ether bonds to less flexible carbonyl units in the backbone. This causes the system to require more energy to start being able to move around and



become more rubber like, resulting in the higher  $T_g$  temperature.

**Table 7.** DSC and TGA data for polymers **9a-i**

Compound	DSC COOLING CURVE <sup>x</sup>			DSC 2 <sup>nd</sup> HEATING CURVE <sup>y</sup>					TGA <sup>z</sup>
	$T_g$ (°C)	$T_c$ (°C)	$\Delta H$ ( $T_c$ ) (J/g)	$T_g$ (°C)	$T_c$ (°C)	$T_m$ (°C)	$\Delta H$ ( $T_c$ ) (J/g)	$\Delta H$ ( $T_m$ ) (J/g)	$T_{d 5\%}$ (°C)
9a	116	N/A	-	113	-	-	-	-	403
9b <sup>HC</sup>	127	N/A	-	124	-	-	-	-	387
9c <sup>SW</sup>	126	N/A	-	122	-	-	-	-	411
9d	131	N/A	-	136	-	-	-	-	412
9e	133	N/A	-	141	-	-	-	-	421
9f	133	N/A	-	140	229	280	-2.36	2.18	426
9g	137	N/A	-	143	220	295	-18.5	15.9	442
9h <sup>SW</sup>	138	N/A	-	146	226	294	-15.4	10.4	435
9i	149	223	-31.1	152	-	312	-	-	448

HC-Denotes reaction concentration of 2.55M

SW- Denotes reaction run in a "Step-wise" fashion.

x- Cooling rate at 10 °C/min

y-Heating rate at 10 °C/min

z-Heating rate at 10 °C/min

The decrease and disappearance in crystalline character can be attributed to many different factors relating to the introduction of the 2,4-difluorobenzophenone. This monomer unit disrupts the ability of the polymer to pack efficiently, causing a loss in crystalline character. Free volume is also increased for the polymer system that includes the 2,4-difluorobenzophenone, due to the pendent moiety attached to the backbone of the polymer, which lowers the packing efficiency of the polymer system. The 2,4-difluorobenzophenone causes the polymer system to become less symmetric which results in the system becoming more disordered and lowers packing efficiency. Lastly, this monomer not only sticks out away from the backbone of the polymer, but it also pushes out of the plane of the backbone, further disrupting the packing ability of the polymer system. This is due to the relative distance between the group attached at the 2 position and the carbonyl group, which forces the 2,4-moiety out of plane. These

statements can also be made for the 3,5-difluorobenzophenone monomer to a greater degree, except for the last statement. As shown by the amount of pendent monomer incorporated that still allows crystallinity in the polymer system, 2,4-difluorobenzophenone can be incorporated up to 35% before causing the copolymer system to become amorphous, while the 3,5-difluorobenzophenone can only be incorporated up to 25% before causing the polymer system to become amorphous.

#### **4. CONCLUSIONS**

Two routes to semi-crystalline, potentially functionalizable poly(ether ether ketone), PEEK, analogues were explored using varying percentages of 4,4'-difluorobenzophenone and either 3,5-difluorobenzophenone or 2,4-difluorobenzophenone in nucleophilic aromatic substitution polycondensation reactions with hydroquinone. The PEEK analogues, prepared in a "one-pot" fashion, were semi-crystalline when up to 25% of 3,5-difluorobenzophenone, or up to 35% 2,4-difluorobenzophenone, were incorporated into the polymer. The 3,5-homopolymers, which were semi-crystalline, and 2,4-homopolymers, which were completely amorphous, displayed very good solubility in a variety of common organic solvents, such as chloroform, tetrahydrofuran, *N*-methylpyrrolidinone, etc. The solubility of the copolymers decreased at higher percentages of 4,4'-difluorobenzophenone, but were still soluble in *N*-methylpyrrolidinone.

#### **5. PROPOSED FUTURE WORK**

The next step for these polymer systems is to attempt one-pot style synthesis with a group capable of functionalization, like an aryl bromide, followed by further modification to a carboxylic acid, alkyl chain, chromophore, etc., to meet a variety of

applications. The backbone of the polymer can be further investigated to discover the optimum balance between thermal properties and solubility.

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