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THE SYNTHESIS OF 3,5-DIFLUOROBENZOPHENONE DERIVATIVES AND THEIR CORRESPONDING PEEK COPOLYMERS

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

By

RACHAEL STUCK
B.S., Wright State University, 2010

2017
Wright State University

WRIGHT STATE UNIVERSITY

THE GRADUATE SCHOOL

April 29th, 2017

I HEREBY RECOMMEND THAT THE THESIS PREPARED UNDER MY SUPERVISION BY Rachael Stuck ENTITLED The Synthesis of 3,5-Difluorobenzophenone Derivatives and their Corresponding PEEK Copolymers BE ACCEPTED IN PARTIAL FULFILLMENT OF THE REQUIREMENTS FOR THE DEGREE OF Master of Science .

_____

Eric Fossum, Ph.D.
Thesis Director

_____

David A. Grossie, Ph.D.
Chair, Department of Chemistry

Committee on Final Examination

_____

Eric Fossum, Ph.D.

_____

Daniel M. Ketcha, Ph.D.

_____

Kenneth Turnbull, Ph.D.

_____

Robert E.W. Fyffe, Ph.D.
Vice President for Research and
Dean of Graduate School

ABSTRACT

Stuck, Rachael M.S., Department of Chemistry, Wright State University, 2017.
The Synthesis of 3,5-Difluorobenzophenone Derivatives and their Corresponding PEEK Copolymers.

Poly(aryl ether ketone)s (**PAEK**) are high performance thermoplastics, which are chemically robust, semi-crystalline, and stable at high temperatures. Of the family of **PAEKs**, poly(ether ether ketone) (**PEEK**) is a well-known semi-crystalline thermoplastic widely used for electronics, energy, industrial, and medical applications due to its resistance to solvents, radiation, heat, and other environmental factors. The traditional **PEEK** is prepared from 4,4'-difluorobenzophenone (**2**) and disodium hydroquinone. However, a challenge is processability, since due to its highly crystalline nature, **PEEK** possesses very limited solubility. An approach to solve these issues is to pre-functionalize **PEEK** polymers synthesized by nucleophilic aromatic substitution from 3,5-difluorobenzophenone (**1**) and hydroquinone, which results in a pendant benzoyl group. By using varying ratios of 3,5-difluorobenzophenone (**1**) and 4,4'-difluorobenzophenone (**2**) the degree of crystallinity in the polymer can be tailored. Herein, a series of semi-crystalline **PEEK** analogues bearing functional groups on the pendant benzoyl moiety, were synthesized and characterized in order to investigate the effects of structural variances on the thermal and solubility behavior.

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Lastly, I would like to thank all the wonderful people in my life for their support and inspiration. I am so thankful for my family and friends, who have been so understanding and accommodating. I would like to dedicate this work in memory of my grandparents. Their influence has fostered my curiosity and pursuit of knowledge.

INTRODUCTION

Polymers make up many aspects of our daily life from the protein we eat to the gas station coffee in a styrofoam cup. Polymers can have many advantages to natural materials. Thermoplastics are lightweight compared to steel or fire retardant compared to wood. Engineered thermoplastics are designed to have specific properties for applications in our daily life. These materials are a valuable resource, and can be produced cheaply. The various applications and possibilities for these materials are the reason for the increased research and growth in this field.

Aromatic Polyethers

Thermoplastics are polymers, which soften at a given temperature to form a homogenous liquid. After molding and cooling a thermoplastic returns to solid form. Thermoplastics are employed in a variety of markets for various applications such as aerospace, automotive, and medical components. Poly(arylene ether)s, **PAE**s, are a class of high performance thermoplastics with excellent physical properties. **PAE**s are identifiable by aryl ether linkages in the "backbone" of the polymer chain. Poly(phenylene oxide), or **PPO,** is one of the first commercially used **PAEs**. Other common **PAE**s are poly(aryl ether ketone), **PAEK,** and poly(arylene ether sulfone), **PAES** (**Figure 1**).[1]

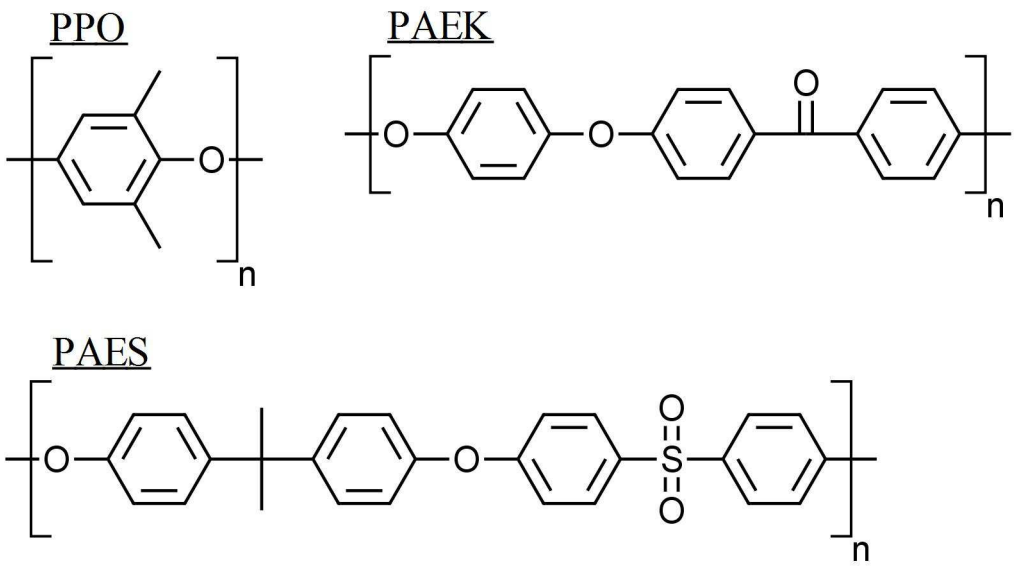
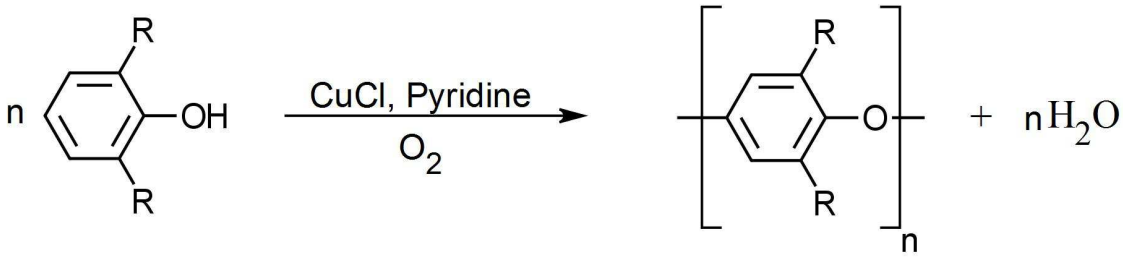


Figure 1. Commercial Poly(arylene ether)s

Poly(phenylene oxide), PPO

One of the most widely used engineering plastics is **PPO**, also known as poly(phenylene ether). Hay *et al*. synthesized **PPO** in 1959 by oxidative polymerization (**Scheme 1**). The linear, amorphous, thermoplastic is formed from 2,6-dimethylphenol using a copper amine catalyst system.[2]



Scheme 1. Oxidative Polymerization to PPO by Hay *et al.*[2]

The mechanical and physical properties allow for it to be utilized in numerous applications. **PPO** has a high glass transition temperature (T_g) of 212°C, low moisture absorption, excellent electrical insulation, dimension stability, flame resistance, and is utilized in applications for food packaging, construction materials, automotive panels,

and electronic components.[1] Another **PAE** that has excellent mechanical properties and chemical resistance is **PAEK**.

Poly(aryl ether ketone), PAEK

Poly(ether ketone), **PEK**, Poly(ether ether ketone), **PEEK**, and Poly(ether ketone ketone), **PEKK**, are **PAEKs**, which contain 1,4-phenylene ether and 1,4-phenylene ketone linkages. (**Figure 2**) All of them are high performance thermoplastics with good thermal stability, chemical resistance, and excellent mechanical properties.[1,3] The changes in the ratio of ether/ketone linkages give rises to differences in T_g, and alter the polymer chain conformation, which, in turn, influences the level of crystallinity.

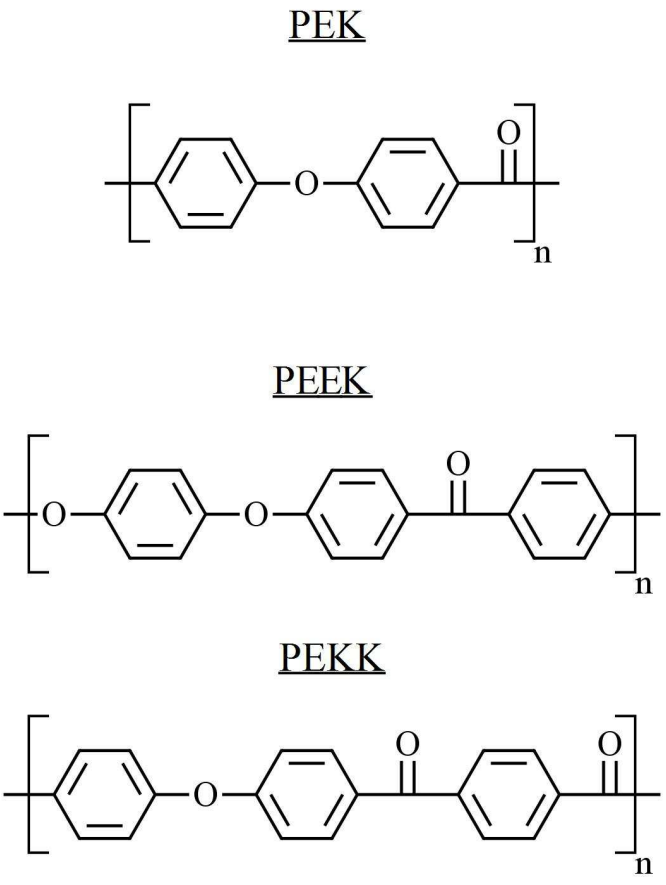


Figure 2. Common **PAEKs**

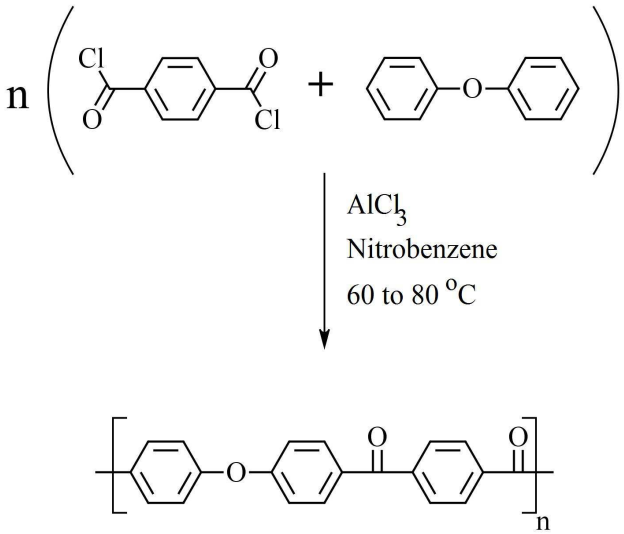
Unlike amorphous polymers, the crystalline nature of **PAEKs** gives rise to melting points (T_m), which are relatively high. The T_g and T_m values, as well as the commercial suppliers, of common **PAEKs** are listed in **Table 1**. Due to the level of crystallinity present in many PAEK systems, the formation of high molecular weight materials requires high temperatures or specialty solvents.

Table 1. Commercially Available **PAEKs** and Their Thermal Properties

Polymer	**Supplier**	**T_g (°C)**	**T_m (°C)**
PEEK	"Victrex" ICI	143	343
PEK	"Stilan" Raychem Corp.	163	361
PEKK	Dupont	165	391

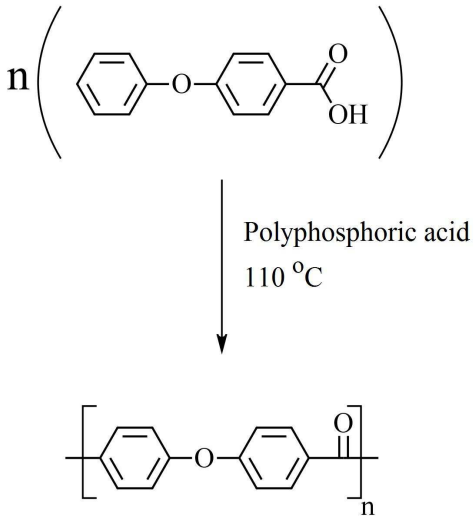
PAEK Synthesis Routes

Polycondensation reactions, by electrophilic or nucleophilic substitution, are the two main routes for the synthesis of **PAEK**s. Polymerization by Friedel-Crafts acylation was proposed in 1962 by Bonner at DuPont.[4] An aromatic diacid chloride was reacted with diphenyl ether, in the presence of a Lewis Acid (**Scheme 2**). Based on the relatively low inherent viscosity of 0.13dL/g, the polymer was presumed to have a low molecular weight.[4]



Scheme 2. Polymerization to **PEKK** by Friedel-Crafts Acylation[4]

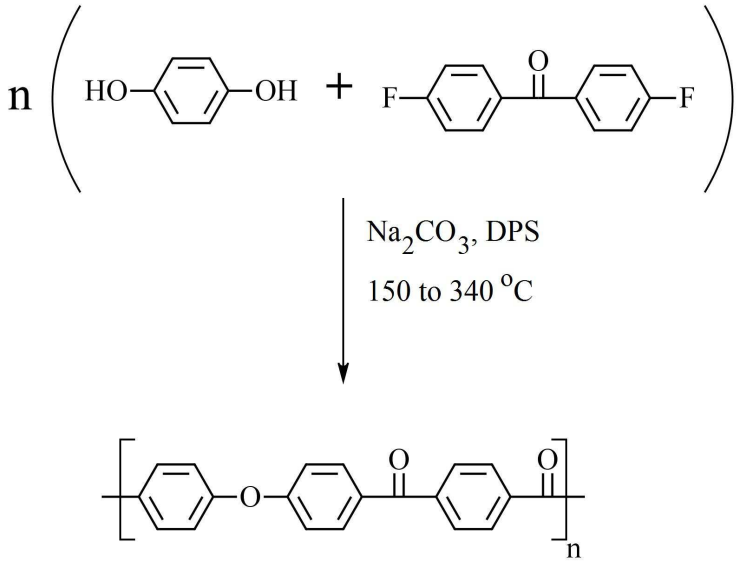
Direct polycondensation to form **PEEK**, by Ueda *et al*., utilized phosphorus pentoxide (P_2O_5), methanesulfonic acid, and aromatic acid to afford **PEEK** with an inherent viscosity of ~1.1dL/g.[5] The molecular weight could be controlled by the quantity of P_2O_5, and gave increased molecular weights when compared to some other synthetic routes. Several others have also reported electrophilic routes to **PEEK** with inherent viscosity values ranging from 0.04-1.5dL/g.[3]



Scheme 3. Synthesis of PEK by Direct Condensation[6]

The synthesis of **PEK** homopolymer was carried out by Iwakura *et al*., who utilized *p*-phenoxybenzoic acid, with polyphosphonic acid (PPA) as the solvent and catalyst (**Scheme 3**).[6] The PPA assisted the polymerization by preventing the polymer system from crystallizing out of solution as the molecular weight increased. In general, the **PAEKs** are soluble in strong acids, and some acids (methanesulfonic acid, polyphosphoric acid, and hydrogen fluoride) have been employed to aid polycondensation.[1] Other polycondensation routes utilize polar solvents, such as dimethylsulfoxide (DMSO), *N*-methyl-2-pyrrolidone (NMP), and diphenylsulfone (DPS), and nucleophilic conditions.

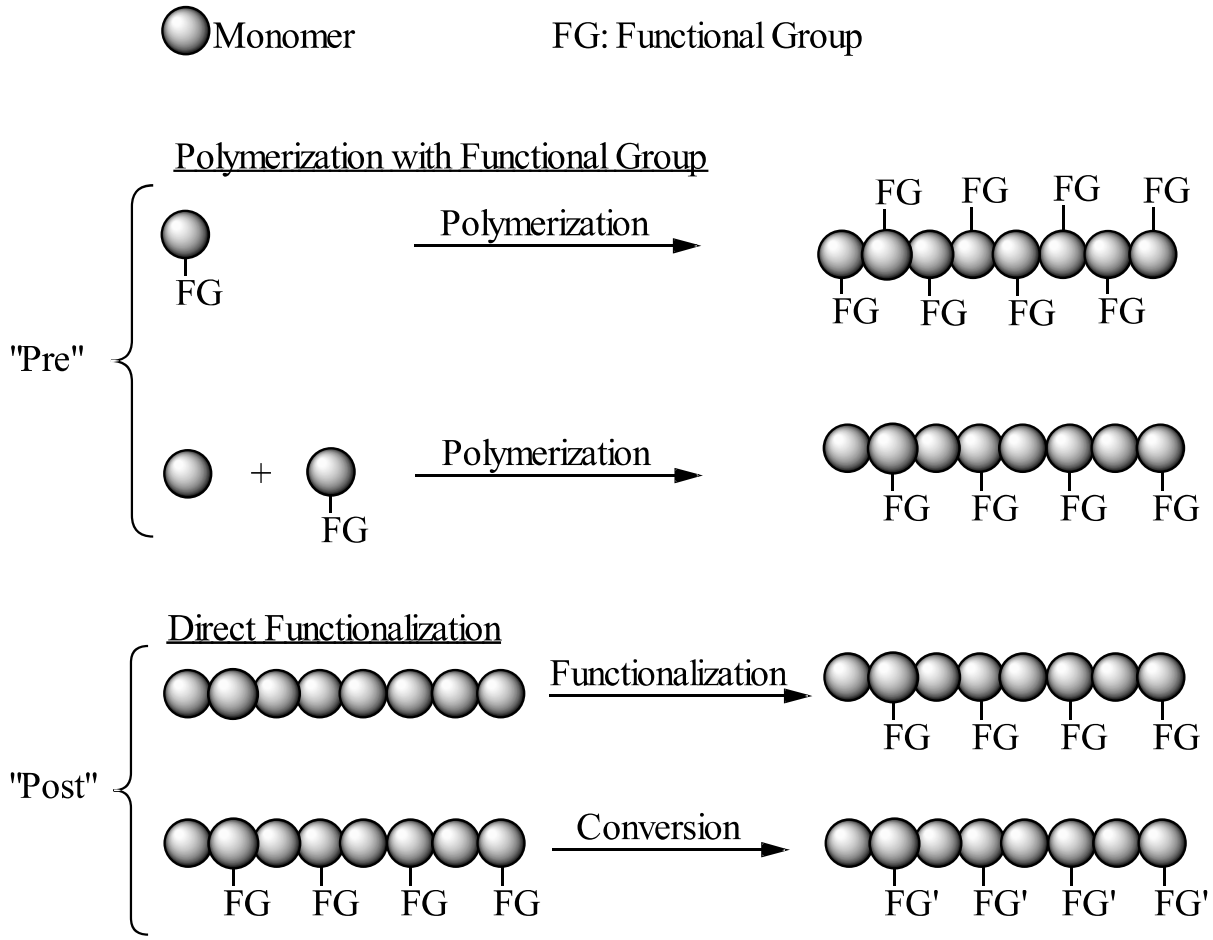
Scheme 4 illustrates a nucleophilic aromatic substitution, NAS, polycondensation reaction of a difluoro-aromatic ketone with disodium bisphenolate as reported in 1967 by Johnson *et al*.[7] A high polarity organic solvent, DMSO, and no catalyst were reported for the process, but the use of DMSO caused premature crystallization resulting in lower molecular weight. The use of diphenyl sulfone (DPS) permitted higher reaction temperatures during the synthesis and was utilized by Rose and Staniland.[8] Commercialized by ICI, **PEEK**, with the trade name Victrex, has a high molecular weight and is robust with chemical resistance and thermal stability.



Scheme 4. Nucleophilic Aromatic Substitution Polymerization by Rose *et al.* [8]

Polymer Functionalization

Monomers are microscopic components of polymers. Alteration of these components will affect the macroscopic properties. Modifications to monomers or functional groups allow for slight changes to the polymer system and customization of thermal, mechanical, and chemical properties for specific applications. Introduction of functional groups is achieved through two routes; before polymerization or "pre" and after polymerization or "post" as shown in **Scheme 5**.



Scheme 5. Two Routes for Polymer Functionalization

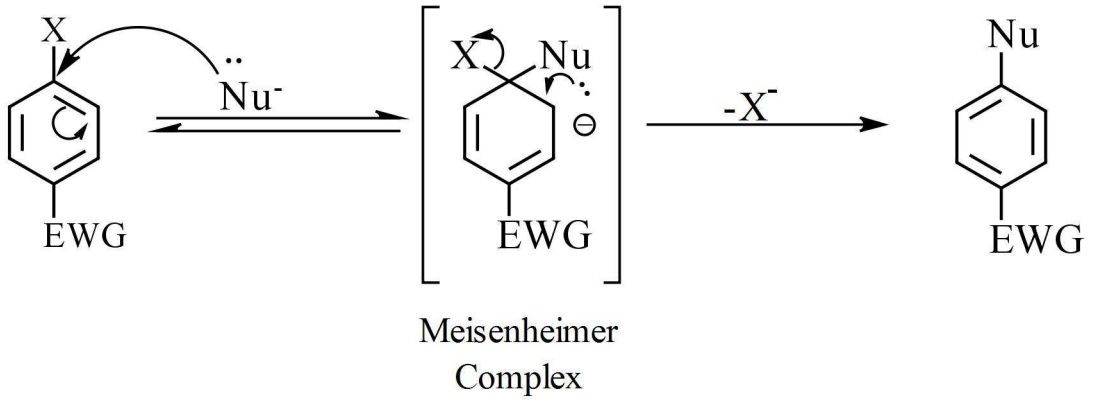
Both routes for functionalization have advantages and disadvantages. In both systems, the location of functional group attachment can be on the electron rich positions, with electrophilic substitution, or electron poor positions with anionic synthesis routes. Modifications of the monomer allow for the polymer to contain a select amount of functional groups with a specific motif. However, monomer functionalization is limited to groups that are inert to the polymerization process. Polymer modification often requires harsh reaction conditions, lacks functional group attachment selectivity and control, but the range of functional groups is quite expansive given that they do not need to survive the reaction conditions.

Another approach to modification combines the best characteristics of each route, functionalized monomers and further modification after the polymerization. The approach provides specific sites for further functionalization, and affords better synthetic utility. The sites would be present in specific quantities at specific locations, and would allow for a wider variety of functional groups to be utilized. Initial monomer functionalization would contain a potentially inert substituent, such as a nitro, methoxy, or halide group. After polymerization, the substituent could be altered to a more beneficial functional group, such as an amine, alcohol, carboxylic acid, etc.

Nucleophilic Aromatic Substitution (NAS)

The most common pathway to polymers like **PAEs** is by way of NAS polycondensation reactions. The general process for NAS is the displacement of a leaving group, such as an aryl halide by a nucleophile (**Scheme 6**). An electron-withdrawing group, normally located *ortho* or *para* to the halide, assists the reaction. Initially, the nucleophile attacks the electropositive *ipso* carbon in the rate-determining step, at which point an intermediate known as a Meisenheimer complex is formed. The *ortho* or *para* electron withdrawing substituent stabilizes the intermediate by resonance and inductive effect and also activates the electrophilic site. Loss of the halide, and rearomatization of the benzene ring, completes the reaction.

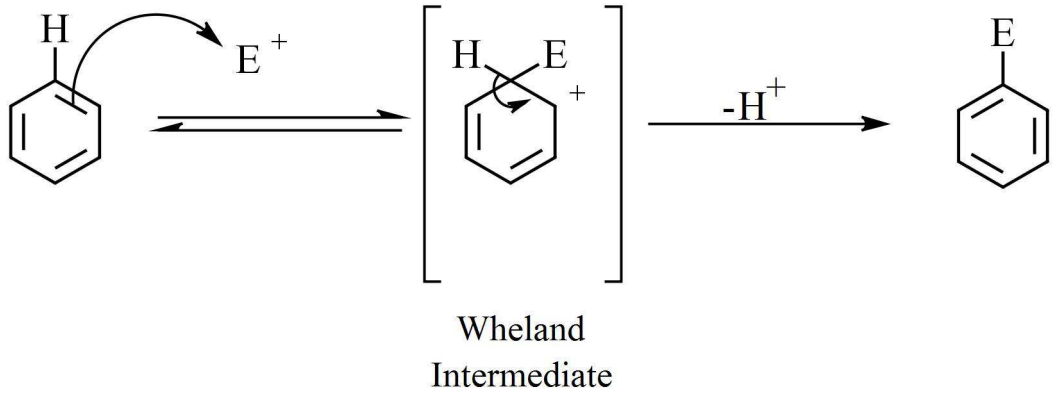
Kaiti *et al.* demonstrated that, with a strong enough electron-withdrawing group, *meta*-activated NAS polycondensation reactions also occur.[9] *Meta* substitution was demonstrated with phenolate ions and activated aryl halides *meta* to a sulfone, ketone, or phosphine.[10,11]



Scheme 6. General NAS Reaction with Electron Withdrawing Group (EWG)

Electrophilic Aromatic Substitution (EAS)

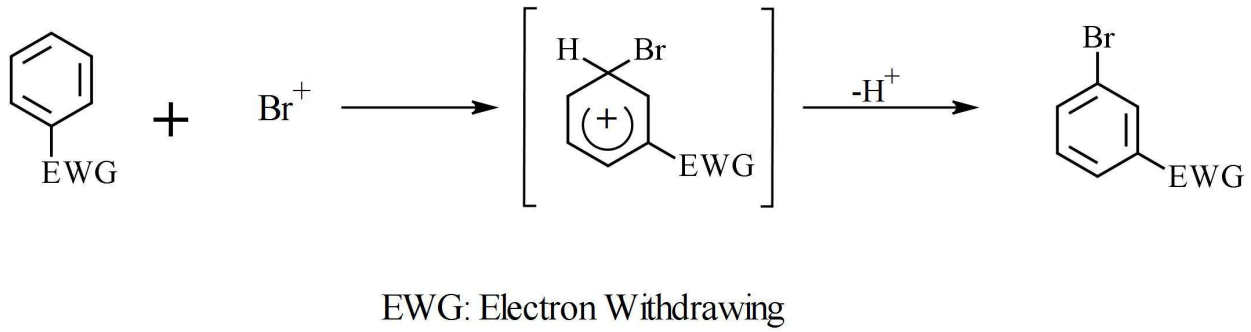
As previously shown, EAS is utilized for PAE polymerization and is also a route to functionalized monomers and polymers. The general mechanism for EAS is shown in **Scheme 7**. In the rate-determining step, the π electrons attack the electrophile, which results in the destabilization of the benzene ring and the formation of a carbocation, known as a Wheland intermediate. A Lewis base then abstracts the proton on the carbon atom to which the electrophile is attached, reforming the aromatic structure.



Scheme 7. General EAS Reaction

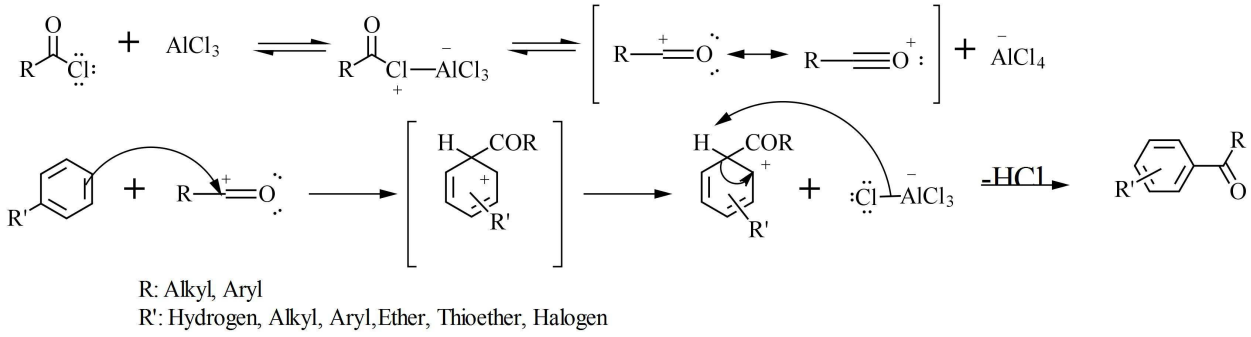
Common EAS reactions include nitration, halogenation, sulfonation and Friedel Crafts acylation. Nitration requires sulfuric acid to form the nitronium ion, and the Lewis

base for this reaction is water. Bromination with NBS and sulfuric acid allows for EAS to occur on a deactivated system. Bromination is directed to the *meta* position with respect to an EWG, as shown in **Scheme 8**.



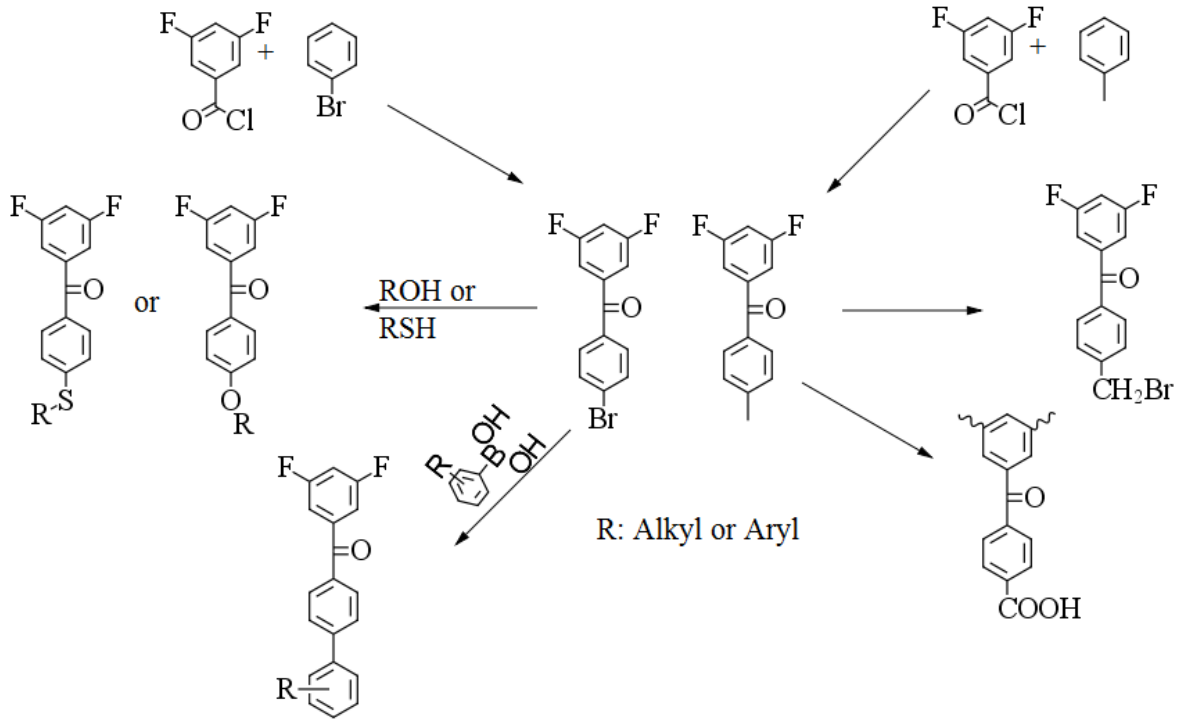
Scheme 8. General EAS Reaction with *meta* Directing EWG

Halogen groups will direct acylation primarily to the *para* position. The mechanism for acylation is similar to **Scheme 8**, but slightly more complex, as depicted in **Scheme 9**. A Lewis acid, commonly aluminum chloride, is used to form the necessary electrophile. The acylium ion is then attacked by the arene and a chloride ion deprotonates the arenium ion to form hydrochloric acid, leaving behind the substituted aromatic ring. Some functional groups unaffected by acylation are halogens, ethers, thioethers, and tertiary amines.



Scheme 9. General Acylation Reaction

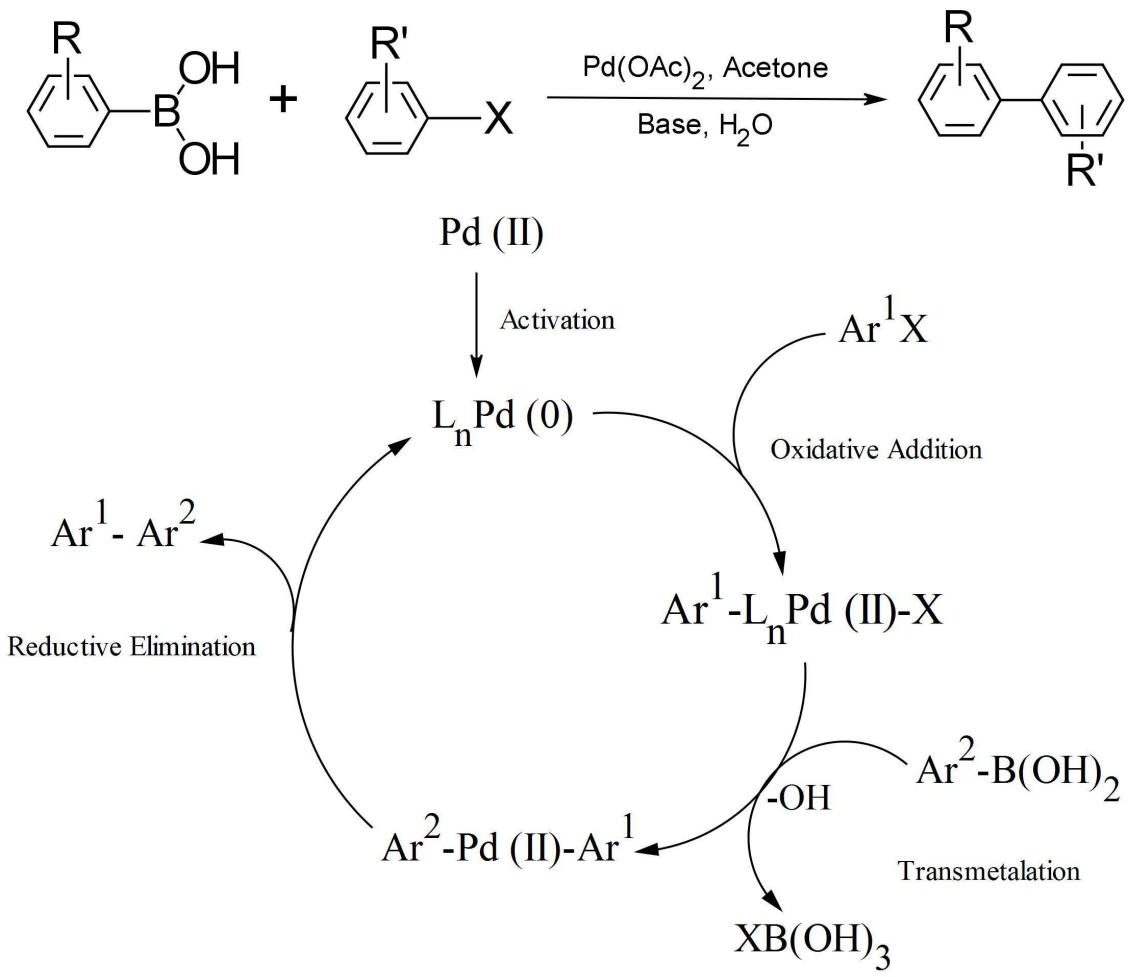
EAS is a route to initially functionalize as well as synthesize the monomers. The functional groups previously mentioned can be further functionalized with Suzuki coupling, Sonogashira Cross coupling, reduction of the nitro group, and further reactions with a methyl group. **Scheme 10** shows some functionalization routes, which could be employed in either pre or post polymerization routes.



Scheme 10. Synthetic Route for 'pre' and 'post' Functionalization of Benzophenones

Suzuki Coupling

The cross coupling of organic boronic acids with organic halides is catalyzed by palladium and known as Suzuki-Miyaura coupling.[12] **Scheme 11** shows a slightly modified procedure that was demonstrated by Wallow *et al*. and was employed in the current work.[12]



Scheme 11. Modified Suzuki-Miyaura Coupling Reaction with Palladium Cycle

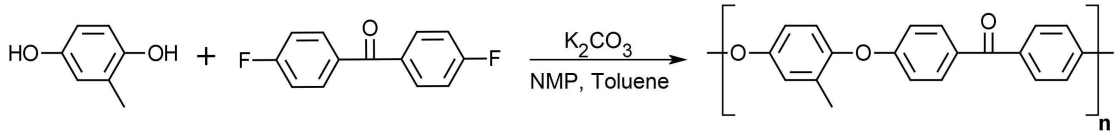
For the coupling to occur, the catalyst must complete a redox cycle. The palladium cycle is a multistep process. The organoboronic acid and halide cross coupling with the palladium catalyst begin with an oxidative addition between palladium and the aryl halide. The intermediate undergoes transmetallation with base and the boron-ate complex. The desired product is then obtained by reductive elimination which intern reestablishes the palladium catalyst.

Modified PEEK with a Functionalized Monomer and/or Preformed Polymer

Modifications of the monomer or preformed polymer are two general routes to functionalize polymers. A functionalized monomer in the polymer synthesis can later be used for further modification. Due to the chemical resistance of **PEEK**, modification is limited. **PEEK** is soluble in strong protic acids, such as sulfuric acid, which will result in sulfonation of the preformed polymer.[13] Another approach to modification was demonstrated by Pramanik *et al*. where initial acylation was conducted for further functionalization to pendant acetyl groups, which were then be converted to pendant carboxylic acids, amides, and/or amines.[14] The modification kept the ether/ketone linkages intact, while other modifications utilized the carbonyl group to form soluble derivatives. An example by Colquhoun *et al*. demonstrated post modification at the carbonyl to form poly(ether dithioketal)s.[15]

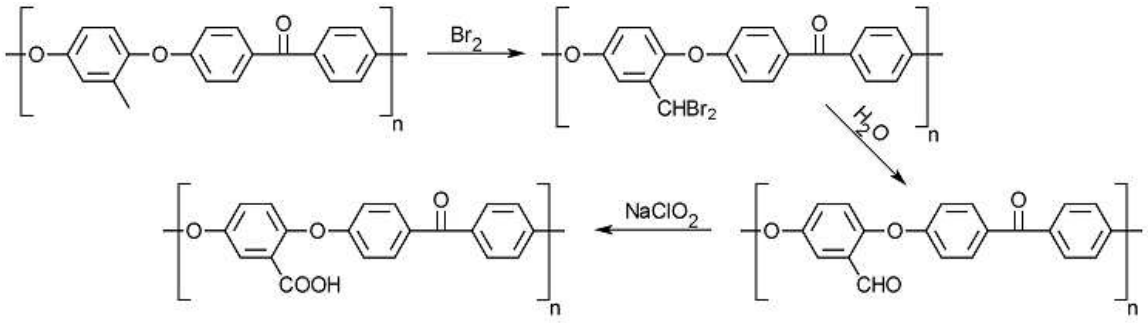
An example of a functionalized **PEEK**, which uses both approaches of 'pre' and 'post' modification was published by Wang *et al*.[16,17] Toluhydroquinone replaced hydroquinone to form methyl-substituted poly(aryl ether ether ketone), **MePEEK.** The resulting polymer had one pendant methyl group per repeat unit, which caused only minor disruption in backbone conformation. In comparison, Mohanty *et al*. has synthesized **PEEK** with *t*-butyl substituents, and the resulting amorphous polymer showed a higher glass transition (T_g: 175 °C) and better solubility in common organic solvents, but lacked crystallinity.[18] **MePEEK**, while less soluble, had a double melting endotherm between 200 to 250 °C, and low molecular weight polymer was predisposed to crystallize in chlorinated hydrocarbons. **MePEEK** fractions had T_g values ranging from 124 to 154 °C, and were directly proportioned to the molecular weight. The

polymerization was similar to that of Rose *et al*. with slight variations as shown in **Scheme 12**.



Scheme 12. Synthetic route for **MePEEK**

Further functionalization of **MePEEK** by Wang *et al*. transformed the polymer to a dibromomethyl substituted version, which was converted, through hydrolysis and oxidation, to other functional groups (**Scheme 13**).[16] The aldehyde and carboxylic acid **PEEK** displayed T_g values of 175 and 210 °C, respectively. The higher glass transition temperatures were ascribed to interactions of the polar groups amongst polymer chains. The polymers exhibited lower decomposition temperatures (T_{de}), and the findings suggested that it was due to the loss of the carboxyl group (T_{de}: 445 °C) and the carboxylate (T_{de}: 312 °C).[16]



Scheme 13. Functionalization of Preformed **MePEEK**

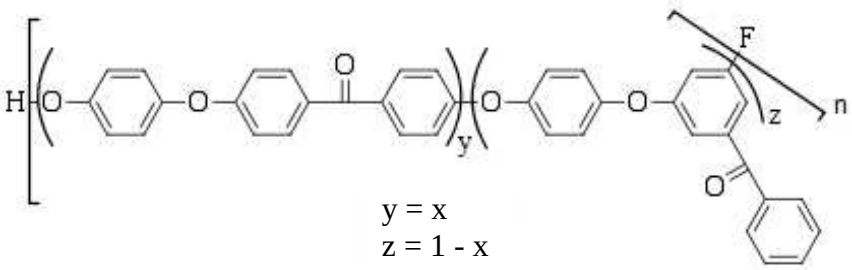
PEEK Modifications with Constitutional Isomers

Without functionalization, traditional (*para*) **PEEK** has been modified structurally to alter physical and thermal properties with constitutional isomers. An amorphous analog of **PEEK** prepared with 4,4'-difluorobenzophenone and catechol was

reported by Ben-Haida *et al*. to form *ortho*-**PEEK** (***o*-PEEK**).[18] The step-growth polymerization of ***o*-PEEK** was synthesized at 145 °C with a suspension of potassium carbonate (K_2CO_3) in a mixture of dimethylacetamide (DMAc) and toluene. The isolated cyclic ***o*-PEEK** oligomer underwent ring-opening polymerization to obtain block copolymers of **PEEK** to ***o*-PEEK**, which contained 30 to 50 % ***o*-PEEK**. A semi-crystalline polymer, which contained 30 % ***o*-PEEK,** had a T_g of 131 °C and T_m of 273 °C.[18]

With 3,5-difluorobenzophenone and 4,4'-dihydroxydiphenyl ether, *meta*-**PEEEK** (***m*-PEEEK**) was synthesized by van Beek and Fossum.[10] A later variation of the bisphenol was made by Fortney and Fossum utilizing 4-methoxyphenol to form *meta*-**PEEK** (***m*-PEEK**). To overcome cyclization and oxidative issues, a larger bisphenol oligomer was formed with the benzophenone and 4-methoxyphenol, and the subsequent product underwent demethylation and protonation to obtain a bisphenol for later polymerization. The thermal data for the amorphous polymer were 105 °C for T_g and 428 °C for $T_{(d5\%, N2)}$.[19] Further exploration of ***m*-PEEK**, with varying ratios of **PEEK**, was later conducted by Fortney and Fossum.[19] An alternating *para* to *meta* benzophenone system was formed by initial reaction with 4-methoxyphenol, and later deprotected to form a larger diol monomer (**4**). Various molar ratios of the two difluorobenzophenones were then utilized to tailor the thermal properties of the polymer system. Copolymers of **PEEK** to ***m*-PEEK** were obtained with ratios 50:50, 75:25, 80:20, 85:15, and 90:10, respectively. Molar ratios of $\geq$ 80% of the 4,4'-difluorobenzophenone showed crystallinity by DSC and X-Ray diffraction as well as the 75% having a potential for annealing. The level of crystallinity directly affected the

solubility, and the more crystalline materials had limited solubility. **Figure 3** illustrates the copolymers with some corresponding thermal data.



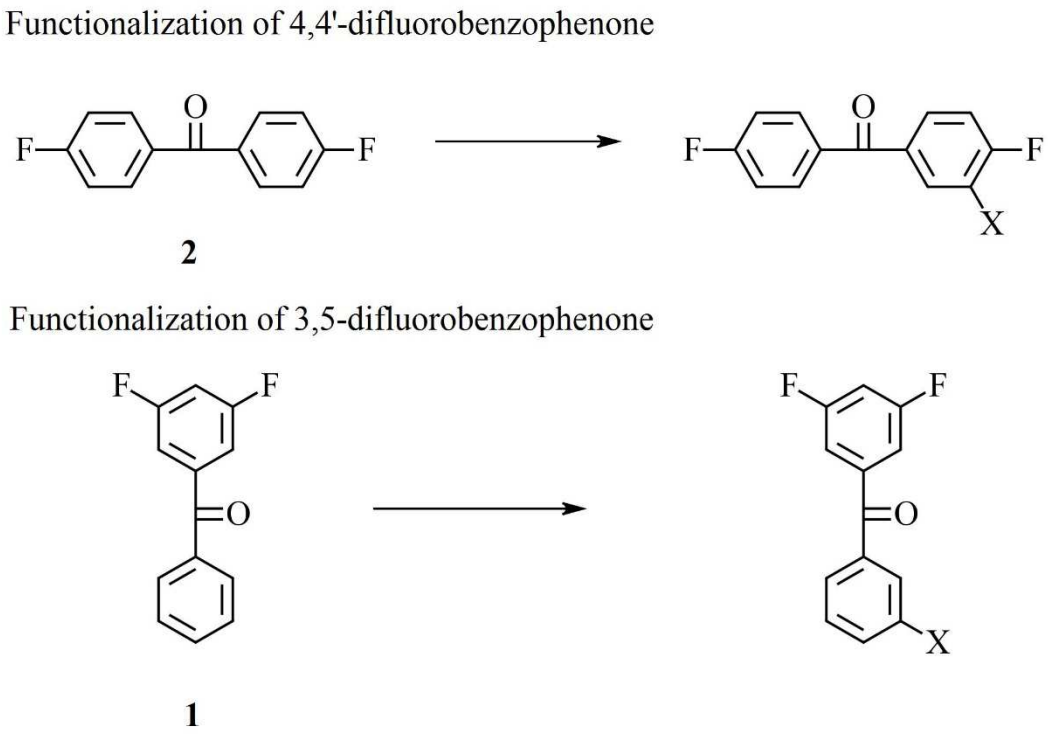
y = x
z = 1 - x

x	T_g	T_m
0.8	138	284
0.85	143	307
0.9	147	316

Figure 3. Semi-Crystalline **PEEK**:***m*-PEEK** Copolymer Structure with Thermal Data (°C)[19]

Current Work

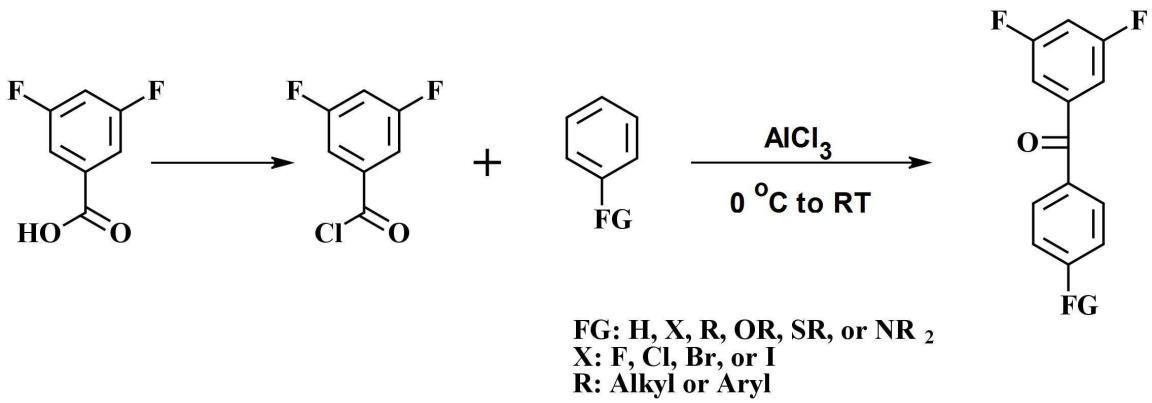
Similar to Fortney and Fossum, the current research was to focus on varying ratios of the ***m*-PEEK** to **PEEK**.[19] However, the goal was to use functionalized monomers for the polymerization. Also the preformed polymers with pendant functional groups were to be utilized for further functionalization. The objective was to tailor the thermal and physical properties of the polymer systems. Initially, the constitutional isomer 3,5-difluorobenzophenone (**1**) was substituted to obtain a functional group in the *meta* position on the pendant phenyl ring. The substituent was less sterically hindered than the substitution on the 4,4'-difluorobenzophenone (**2**) and this is further illustrated by **Scheme 14**.



Scheme 14. Functionalization Differences between **1** and **2**

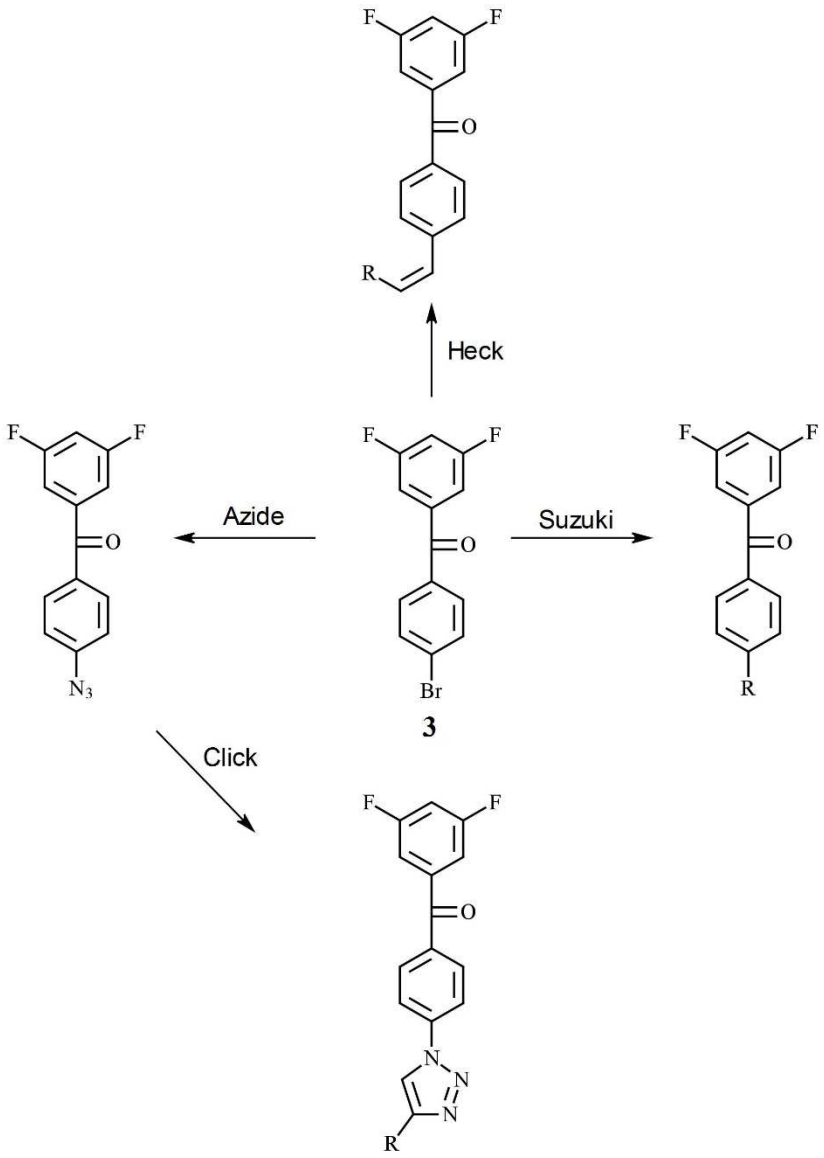
The substitution is an EAS with bromination or iodination of **1** utilizing *N*-bromosuccinimide (NBS) or *N*-iodosuccinimide (NIS), respectively. The halogenated monomer could then be further modified after polymerization to incorporate additional functional groups. Another EAS system would utilize nitric acid for the nitration of **1**.

The synthesis of **1** is achieved via Friedel-Crafts acylation, and can also be utilized for placement of functional groups in the *para* position. **Scheme 15** shows the formation of functionalized derivatives of **1**, via acylation. Functional groups available via this methodology include halogens, alkyl, aryl, ether, and thioether groups.



Scheme 15. General Acylation for **1** and Functionalized Monomers

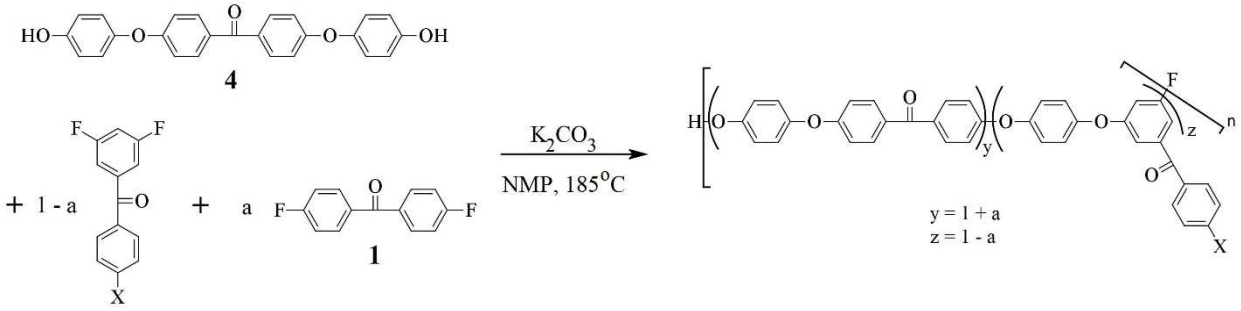
The aryl halide can then be further functionalized with a variety of other conversions of the bromo or iodo groups (either before or after the polymerization) as illustrated in **Scheme 16**, using 4'-bromo-3,5-difluorobenzophenone (**3**) as an example. Further functionalization of the aryl halide is explored via Suzuki-Miyaura cross-coupling. The synthetic route is a modification of published work by Wallow *et al.*[12] Heck-Matsuda reaction is another palladium catalyzed coupling, which attaches an activated alkene in the presence of a base with low to mild heat. Also NAS with sodium azide would replace a halogen, and the thermal Huisgen 1,3 cycloaddition of an alkyne with aryl azide would result in triazole formation by click chemistry.



Scheme 16. Further Functionalization of Aryl Halide **3** Prior to Polymerization

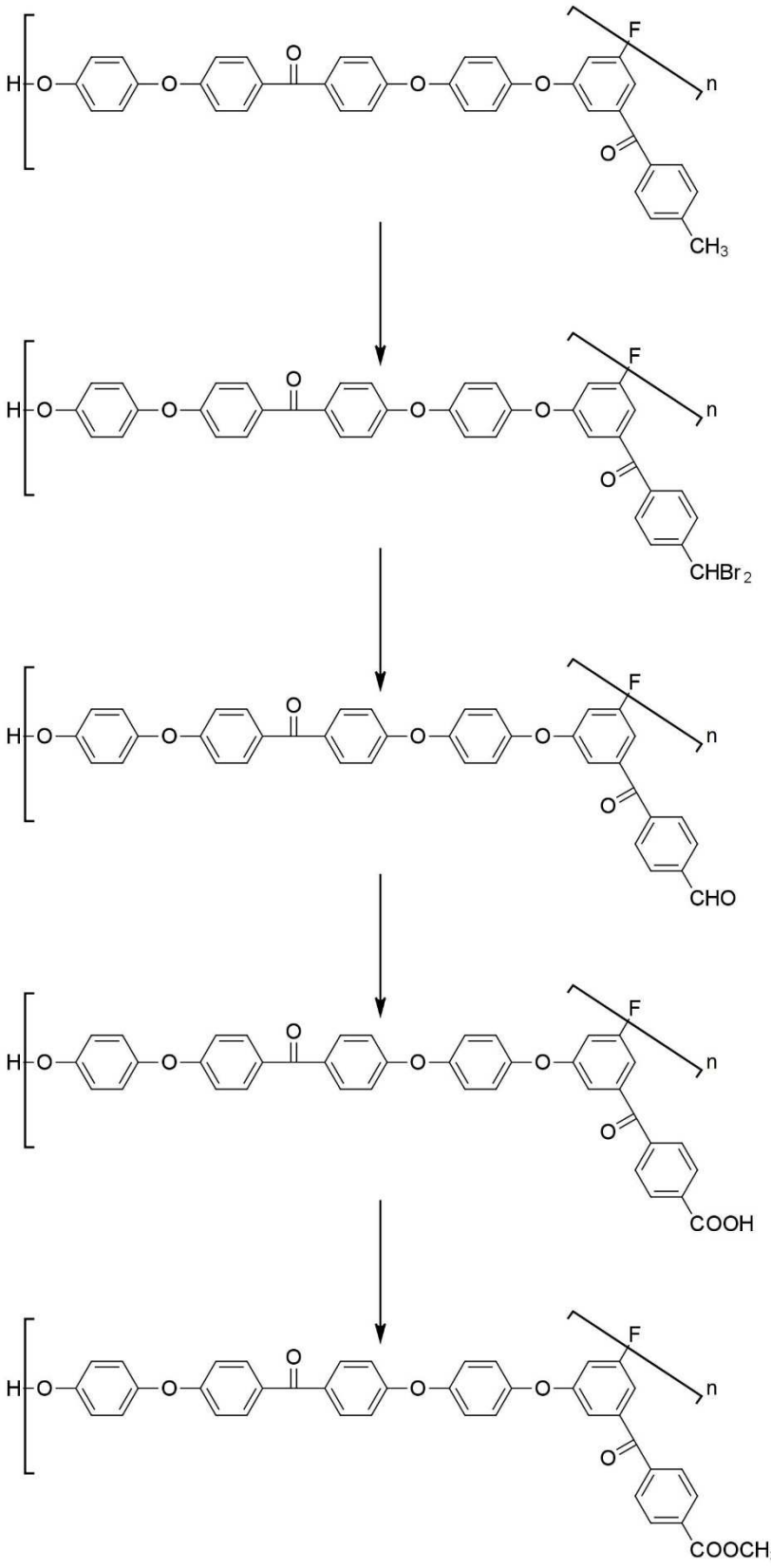
The 3,5-difluoro aromatics will undergo NAS, which will allow for the preparation of **PAEs**. To avoid synthetic challenges, and to achieve varying ratios of functionalized ***m*-PEEK** to **PEEK**, an oligomeric bisphenol is synthesized from **2** with a slight modification from the published work by Hwang *et al*.[20] The 4,4'-bis(4-hydroxyphenoxy)benzophenone (**4**) is polymerized with various functionalized 3,5-difluoro monomers and varying ratios of **2** to explore the thermal and physical properties.

The general polymerization (**Scheme 17**) for molar variations utilizes published work by Fortney and Fossum.[19]



Scheme 17. Synthesis of P_y-X-*m*-P_z Copolymers (X: Pendant Functional Group)

After polymerization, preformed polymer modifications provide the possibility of additional functional groups. The procedure by Wang *et al*. describes the conversion of a methyl substituent to additional functional groups on the preformed polymer (**MePEEK**).[17] **Scheme 18** shows the possible conversions of **P_{50}-*Alt-methyl-m*-P_{50} copolymer**.



Scheme 18. Possible Modification of **P_{50}-*Alt-methyl-m*-P_{50} copolymer**

EXPERIMENTAL

Chemicals and Instrumentation

The monomer reactions were conducted with a nitrogen or argon purge, while polycondensation reactions were performed with a nitrogen sweep. Most solvents and reagents were purchased from Sigma Aldrich Chemical Company (Aldrich). The anhydrous potassium carbonate (K_2CO_3) from Aldrich was dried at 130 °C before use. *N*-Bromosuccinimide (NBS) from Aldrich was recrystallized in water, and vacuum dried prior to use. Thionyl chloride ($SOCl_2$) was used immediately after distillation and transferred, via cannula, to nitrogen-purged vessels. *N*-methylpyrrolidinone (NMP) was dried over and distilled from calcium hydride (CaH_2) prior to use. All boronic acid derivatives, palladium catalyst, and 4-*tert*-butylphenol were used as received from Aldrich. *N*-iodosuccinimide (NIS) at 98% purity was used as received from Acros Organics. 3, 5-Difluorobenzoic acid, 4,4'-difluorobenzophenone, and hydroquinone were purchased from Oakwood Products at ≥99%. The 4,4'-difluorobenzophenone was recrystallized from ethanol prior to use. Benzene, fluoro-, chloro-, bromo-, and iodobenzene were used without further purification as received from Aldrich. Hydrobromic acid (HBr) was 48 wt. % in water ≥ 99.99% from Aldrich. 4-Methoxyphenol (MEHQ) was *ReagentPlus*®, ≥99% from Aldrich and recrystallized from ethanol. All other acids, denatured ethanol, methylene chloride, and isopropanol were used as received from Pharmco-Aaper. ACS-certified toluene, acetone, sodium bicarbonate, aluminum chloride ($AlCl_3$) and magnesium sulfate ($MgSO_4$) were used as

received from Fischer Scientific, except toluene, which was dried with sodium metal, and freshly distilled prior to use. Lastly the deuterated solvents, such as acetone-d_6, dimethylsulfoxide (DMSO-d_6), and chloroform-*d* ($CDCl_3$) were purchased from Aldrich and transferred under nitrogen via syringe.

Nuclear Magnetic Resonance (NMR) ^1H and ^{13}C NMR spectra were obtained using a Bruker Avance 300 MHz spectrometer, operating at 300 and 75.5 MHz, respectively. Samples were dissolved in deuterated solvents at concentrations of 50-80 mg / 0.7 mL. A Mel-Temp instrument was utilized to determine melting points, which are uncorrected. The Gas-Chromatographic-Mass Spectrometric (GC-MS) data were obtained with a Hewlett-Packard (HP) 6890 Series with a HP 5973 Mass Selective Detector/Quadrupole system, and the flow rate was 1 mL / min, with helium as the carrier gas to a HP-5MS capillary column. Differential Scanning Calorimetry (DSC) and Thermal Gravimetric Analysis (TGA) data were performed on TA Instruments DSC Q200 and TGA Q500, respectively. The instruments had a heating ramp of 10 °C per minute, and were conducted under nitrogen and air, as needed.

3,5-Difluorobenzophenone, DFK, 1

Prior to acylations, 3,5-difluorobenzoic acid was reacted with freshly distilled thionyl chloride and catalytic amounts of DMF(2 drops). After two hours at 55 °C, the excess thionyl chloride was distilled between 75 and 77 °C. The acid halide was then fractionally distilled at 174 °C, and recovery was generally around 75%. To a 50 mL round bottom flask, equipped with a gas inlet, addition funnel, condenser, and drying tube, were added 3.01 g (22.6 mmol) of $AlCl_3$. A mixture of 3.62 g (20.5 mmol) 3,5-difluorobenzoyl chloride and 8.01 g (102.5 mmol) benzene was added dropwise to the

$AlCl_3$. The reaction mixture was stirred for 4 hours, before heating to 75 °C. After 16 hours the reaction mixture was quenched by pouring into acidic ice water, followed by addition of 300 mL of chloroform, and transferring to a separatory funnel. The layers were separated and the organic layer was washed with 5 wt. % bicarbonate, distilled water, and then dried with $MgSO_4$ and the solvents were removed, via rotary evaporation, leaving an off-white solid. The crude material was recrystallized from aqueous ethanol to afford (3.00 g, 67 %) of a crystalline white solid with a m.p. 58-59 °C (lit.[21] m.p. 57-58 °C); ^{1}H NMR (300 MHz, $CDCl_3$, δ) 7.04 (tt, 1H, J = 8.4, 2.4 Hz), 7.31 (m, 2H), 7.51 (m, 2H), 7.63 (tt, 1H, J = 7.5, 1.2 Hz), 7.78 (m, 2H).

(3,5-Difluorophenyl)(4-methylphenyl)methanone, 7

The procedure described for preparation of **1** was used with toluene instead of benzene for synthesis of **7**. After the addition of all reagents, the reaction mixture was stirred for 4 hours at 25 °C. The reaction was quenched with water, diluted with additional toluene (350 mL), and transferred to a separatory funnel. The organic layer was washed with 5 wt. % bicarbonate, distilled water, dried with $MgSO_4$ and evaporated to leave a beige solid. The solid was recrystallized from aqueous ethanol to afford a crystalline white solid (91%): ^{1}H NMR (300 MHz, $CDCl_3$, δ) 2.36 (s, 3H, CH_3), 6.93 (tt, 1H, J = 8.7, 2.1 Hz, ArCH), 7.20 (m, 4H, ArCH), 7.62 (d, 2H, J = 8.1 Hz, ArCH), ^{13}C NMR (75 MHz, $CDCl_3$, ppm) 21.66, 107.37 (t, J = 24.75 Hz), 112.77 (dd, J = 25.5, 9.0 Hz), 129.62, 130.20, 133.72, 140.97 (t, J = 7.5 Hz), 144.12, 162.75 (dd, J = 249.75, 12 Hz), 193.57 (t, J = 2.6 Hz).

3,4,5-Trifluorobenzophenone, 8

The compound 3,4,5-trifluorobenzophenone (**8**) was synthesized following a previously published procedure by Raghavapuram.[22] The NMR parameters and physical constants were consistent with those reported in the literature (lit.[23] m. p. 66 °C; found 66 – 68 °C).

(3,5-Difluorophenyl)(4-chlorophenyl)methanone, 9

The procedure described for preparation of **1** was used with chlorobenzene instead of benzene for synthesis of **9**. After the addition of all reagents, the reaction mixture was stirred for 4 hours at 25 °C. The reaction was quenched with acidic water, diluted with methylene chloride (200 mL), and transferred to a separatory funnel. The organic layer was washed with 5 wt. % sodium bicarbonate, distilled water, dried over $MgSO_4$ and evaporated to yield a light yellow solid. The solid was recrystallized from aqueous ethanol to afford a crystalline white solid (95%): found m.p. 75-77°C.

(3,5-Difluorophenyl)(4-bromophenyl)methanone, 3

A 50 mL round bottom flask, equipped with an addition funnel, condenser, and gas inlet, was charged with 5.62 g (42.2 mmol) of $AlCl_3$. A mixture of 6.77 g (38.3 mmol) of 3,5-difluorobenzoyl chloride and 6.02 g (38.3 mmol) of bromobenzene was added dropwise to the $AlCl_3$. During the addition the reaction mixture was kept below 10 °C, and was allowed to warm to 25 °C over four hours. The reaction mixture was quenched with acidic H_2O, diluted with 300 mL of methylene chloride, and transferred to a separatory funnel. The organic layer was washed with distilled H_2O, dried over $MgSO_4$ and evaporated to leave a light orange solid. The solid was recrystallized from aqueous ethanol. The crude material was recrystallized from aqueous ethanol to afford a

crystalline white solid (10.0 g, 88 %): m.p. 85-86 °C, ^{1}H NMR (300 MHz, $CDCl_3$, δ) 7.05 (tt, 1H, J = 8.7, 2.4 Hz, ArCH), 7.27 (m, 2H, ArCH), 7.66 (s, 4H), DEPT90 NMR (75 MHz, $CDCl_3$, ppm) 107.94 (t, J = 25.5 Hz), 112.81 (dd, J = 25.5, 9.0 Hz), 131.39, 131.94. ^{13}C NMR (75 MHz, $CDCl_3$, ppm) 107.93 (t, J = 25.5 Hz), 112.79 (dd, J = 25.5 Hz, 9.0 Hz), 128.37, 131.38, 131.93, 135.10, 140.10 (t, J = 7.6 Hz), 162.75 (dd, J = 249.75, 12 Hz), 192.76 (t, J = 2.43 Hz).

(3,5-Difluorophenyl)(4-iodophenyl)methanone, 10

The procedure described for preparation of **3** was used with iodobenzene instead of bromobenzene for synthesis of **10**. After the addition of all reagents, the reaction mixture was stirred for 8 hours at 0 °C. The reaction was quenched with water, diluted with methylene chloride (300 mL), and transferred to a separatory funnel. The organic layer was washed with 5 wt. % bicarbonate, distilled water, dried with $MgSO_4$ and evaporated off to present a light purple solid. The solid was recrystallized from aqueous ethanol to afford a crystalline white solid (17%): ^{1}H NMR (300 MHz, $CDCl_3$, δ) 7.05 (tt, 1H, J = 8.4, 2.4 Hz, ArCH), 7.27 (m, 3H, ArCH), 7.66 (s, 3H, ArCH), ^{13}C NMR (75 MHz, $CDCl_3$, ppm) 107.96 (t, J = 25.5 Hz), 112.81 (dd, J = 25.5, 9.0 Hz), 128.39, 131.39, 131.95, 135.11, 140.10 (d, J = 7.5 Hz), 162.75 (dd, J = 249.75, 12 Hz), 192.81.

General Procedure for Suzuki Coupling

(3,5-Difluorophenyl)[p-(2-naphthyl)phenyl]methanone, 17

The phosphine-free Suzuki Miyaura coupling was slightly modified from a procedure reported by Wallow *et al*.[12] Initially, a 10 molar % stock solution was made with 0.0378 g (0.168 mmol) of palladium acetate, $Pd(OAc)_2$, and 10 mL of acetone. To a 25 mL Schlenk flask, equipped with a stir bar, were added 2.0 mL of palladium stock

solution, potassium carbonate (1.14 g, 8.26 mmol) and 9.0 mL of distilled water for a concentration of 0.9176 M. A second Schlenk flask, equipped with a stir bar, was charged with **3** (1.00 g, 3.37 mmol), 2-naphthylboronic acid (0.681 g, 3.96 mmol), and 9.0 mL of acetone, for a concentration of 0.37 M. Both Schlenk flasks were purged with nitrogen followed by three freeze-pump-thaw cycles, and then back filled with nitrogen prior to a cannula transfer to combine the catalyst with the reactants. The reaction mixture was heated to 60 °C for four hours at which point an aliquot was removed for GC/MS analysis, which showed complete conversion. The reaction mixture was then poured into distilled water, and a crude off-white precipitate was isolated by filtration. The solid was recrystallized from aqueous ethanol to afford a crystalline white solid (1.08 g, 93%) with a m.p. of 149-150 °C, ^{1}H NMR (300 MHz, $CDCl_3$, δ) 7.05 (tt, 1H, J = 8.7, 2.4 Hz, ArCH), 7.36 (m, 2H, ArCH), 7.53 (m, 2H, ArCH), 7.76 (dd, 1 H, J = 8.5, 1.9 Hz, ArCH), 7.88 (m, 7H, ArCH), 8.10 (m, 1H, ArCH), ^{13}C NMR (75 MHz, $CDCl_3$, ppm) 107.65 (t, J = 24.75 Hz), 112.88 (dd, J = 25.5, 9.0 Hz), 125.12, 126.52, 126.61, 126.64, 127.46, 127.72, 128.39, 128.82, 130.71, 133.12, 133.58, 135.04, 136.97, 140.79 (t, J = 7.5 Hz), 145.90, 162.75 (dd, J = 249.75, 12 Hz), 193.45.

(4-Biphenylyl)(3,5-difluorophenyl)methanone, 16

The procedure described for preparation of **17** was used with phenylboronic acid instead of 2-naphthylboronic acid for synthesis of **16**. After combination of all reagents, the reaction mixture was stirred for 4 hours at 60 °C. An additional 10% of phenylboronic acid was added, and the reaction continued for 8 hours more. The reaction contents were then poured into distilled water, and crude off-white product was isolated by filtration. The crude material was recrystallized from isopropanol to afford a

crystalline white solid (94%): m.p. 134-135 °C, ^{1}H NMR (300 MHz, $CDCl_3$, δ) 7.05 (tt, 1H, J = 8.4, 2.4 Hz, ArCH), 7.45 (m, 5H, ArCH), 7.66 (m, 2H, ArCH), 7.72 (m, 2H, ArCH), 7.88 (m, 2H, ArCH), ^{13}C NMR (75 MHz, $CDCl_3$, ppm) 107.63 (t, J = 25.0 Hz), 112.86 (dd, J = 25.5, 9.0 Hz), 127.23, 127.32, 128.40, 129.03, 130.63, 135.01, 139.71, 140.78 (t, J = 7.87 Hz), 146.00, 162.75 (dd, J = 249.75, 12 Hz), 193.46.

1-[4'-(3,5-Difluorobenzoyl)-4-biphenylyl]-1-ethanone, 18

The procedure described for preparation of **17** was used with 4-acetylphenylboronic acid instead of 2-naphthylboronic acid for synthesis of **18**. After combination of all reagents, the reaction mixture was stirred for 4 hours at 60 °C. An additional 10% of 4-acetylphenylboronic acid was added, and the reaction continued for 8 hours more. The reaction contents were then poured into distilled water, and crude off-white product was isolated by filtration. The crude material was recrystallized from isopropanol to afford a crystalline white solid (92%): m.p. 159-160 °C, ^{1}H NMR (300 MHz, $CDCl_3$, δ) 2.66 (s, 3H, CH_3), 7.06 (tt, 1H, J = 8.4, 2.4 Hz, ArCH), 7.35 (m, 2H, ArCH), 7.76 (m, 4H, ArCH), 7.90 (m, 2H, ArCH), 8.08 (m, 2H, ArCH), ^{13}C NMR (75 MHz, $CDCl_3$, ppm) 26.66, 107.80 (t, J = 25.12 Hz), 112.87 (dd, J = 25.5, 9.0 Hz), 127.42, 127.49, 129.06, 130.66, 135.85, 136.75, 140.46 (d, J = 7.5 Hz), 144.12, 144.51, 162.75 (dd, J = 249.75, 12 Hz), 193.30, 197.48.

General Model Reaction for Pre Functionalized Monomers

In a 20 mL flask, equipped with stir bar, condenser, and gas inlet, were placed, 100 mg (0.337 mmol) of **3**, 1.00 g (0.673 mmol) of *t*-butyl phenol, 140 mg (1.010 mmol) of K_2CO_3, and 0.5 mL of NMP. The reaction mixture was heated at 170°C for four

hours, at which point an aliquot was removed and analyzed by GC-MS, showing the desired product was not formed.

4,4'-Bis(*p*-hydroxyphenoxy)benzophenone, 4

The compound 4,4'-bis(*p*-hydroxyphenoxy)benzophenone (**4)** was synthesized following a previously published procedure by Hwang *et al*.[20] Found m.p. 220-222 °C, ^{1}H NMR (300MHz, DMSO-d_6, δ) 6.83 (d, 4H, J = 8.7 Hz, ArCH), 6.96 (d, 4H, J = 2.7 Hz), 6.99 (d, 4H, J = 2.7 Hz), 7.70 (d, 4H, J = 8.7 Hz, ArCH), 9.53 (s, 1H, OH), ^{13}C NMR (75MHz, DMSO-d_6, ppm) 115.81, 116.43, 121.70, 131.01, 131.98, 146.44, 154.58, 162.05, 193.07.

Poly(ether ether ketone), PEEK

PEEK was prepared following a procedure published by Rose *et al*.[8]

General Polycondensation Procedure

P_{50}-*Alt-phenyl-m*-P_{50} copolymer

In a 10 mL round bottom flask, equipped with a condenser, gas inlet, and mechanical stir bar, were placed 0.5635 g (4.077 mmol) K_2CO_3, 0.4000 g (1.359 mmol) 3,5-difluoro-4'-phenylbenzophenone, and 0.5415 g (1.359 mmol) bis-[4-(4-hydroxy-phenoxy)-phenyl]-methanone. A concentration of 0.65 mol/L was used by the addition of 2.1 mL NMP. The reaction mixture was stirred and heated to 185˚C for 34 hours. The reaction mixture was precipitated in distilled water to afford an off-white solid. The solid was dissolved in 20mL of chloroform precipitated in methanol, and then ethanol. The off-white solid was vacuum dried at 110 ˚C to obtain 0.682 g of polymer. ^{13}C NMR (75 MHz, $CDCl_3$, δ) 111.66, 111.76, 113.72, 113.87, 117.00, 120.97, 121.13, 121.65, 127.03, 127.26, 128.35, 129.00, 130.71, 132.26, 132.35, 135.45, 139.71, 139.75, 140.49,

145.72, 151.86, 151.91, 152.10, 152.31, 152.49, 158.90, 158.97, 159.02, 161.40, 194.05, 194.73.

P_{50}-*Alt-methyl-m*-P_{50} copolymer

^{13}C NMR (75 MHz, $CDCl_3$, δ) 21.69, 111.52, 111.63, 116.95, 117.03, 120.91, 121.12, 121.69, 129.10, 130.29, 132.28, 134.12, 140.68, 143.86, 151.81, 152.08, 152.29, 152.54, 158.80, 158.91, 161.47, 175.07, 194.09, 194.86.

P_{50}-*Alt-naphthyl-m*-P_{50} copolymer

^{13}C NMR (75 MHz, $CDCl_3$, δ) 110.64, 112.73, 115.96, 119.97, 120.11, 120.64, 124.07, 125.42, 125.58, 126.25, 126.68, 127.33, 127.76, 129.76, 131.24, 131.31, 132.03, 132.52, 134.46, 135.95, 135.99, 139.50, 144.61, 150.89, 151.07, 151.31, 151.47, 157.90, 158.01, 160.37, 193.01, 193.71.

RESULTS AND DISCUSSION

3,5-Difluorobenzophenone, DFK, 1

The base compound, **1**, was first synthesized by a few general routes (*vide infra*). Friedel-Crafts acylation provided the highest yield with lowest number of byproducts. Synthesis by Grignard produced multiple side reactions with only 15-20% product yield. Further discussion of the syntheses will be presented in a later section that describes other monomers formed by the general route (**Scheme 21**). The structure of DFK (**1**) was confirmed by a melting point of 58-60 °C, and its ^{1}H NMR spectrum (**Figure 4)**.

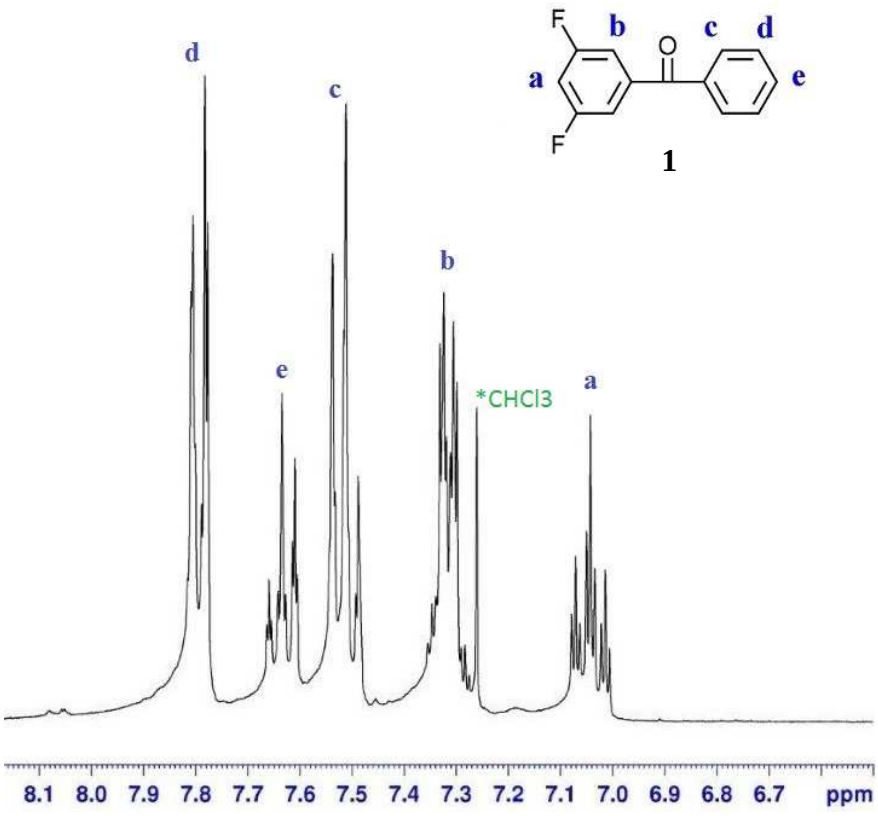
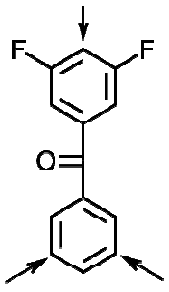


Figure 4. Expanded 300 MHz ^{1}H NMR spectrum ($CDCl_3$) of **1**

The expanded ^{1}H NMR shows absorption of the protons (8H) on the aromatic rings, and the most distinguishing feature is the proton **a** between the C-F groups as a triplet of triplets at 7.04 ppm (J = 8.4, 2.4 Hz). The other protons (5H**) b,c,d** resulted in multiplets. Proton **e** (1H) also results in a triplet of triplets at 7.63 ppm (J = 7.5, 2.1 Hz). With pure **1** in hand, further reactions were carried out to prepare functionalized monomers for subsequent conversion to functionalized polymer systems via the "pre" approach.

Electrophilic Aromatic Substitution of 3,5-Difluorobenzophenone (1)

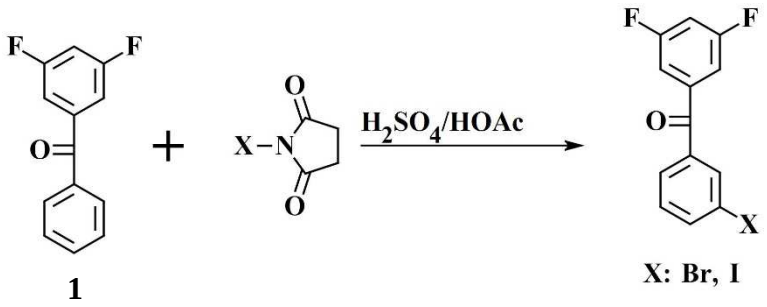
The ideal position for "pre" functionalization would be *meta* to the carbonyl with a group that could survive polymerization. A viable substituent would be a halogen (Br or I) or a nitro group, which would be reduced to an amine prior to polymerization. Attachment of these substituents could be achieved with EAS. Electrophilic aromatic substitutions of the base compound may occur at two different positions. **Figure 5** shows the most electron rich location on the structure at the carbon between the two fluorines, as measured by ^{13}C NMR (108 ppm). The *meta* position on the adjoining benzene ring, while less electron rich, as measured by ^{13}C NMR (131 ppm), is not sterically hindered, and the most likely location of mono substitution. The intermediate formed when the EAS occurs between the two fluorine atoms has a resonance form in which the (+) charge is adjacent to the carbonyl, whereas, the intermediate formed on the lower ring does not.



1

Figure 5. Base compound (**1**) and most likely substitution locations

As previously discussed, the bromination reaction is a typical electrophilic aromatic substitution. Due to unexpected results of multiple substitutions, the reaction conditions were adjusted in favor of the monosubstituted analogs, but **Scheme 19** shows the general route. The reactions were monitored by GC-MS, and indicated an assortment of products. Varying reaction conditions were explored to reduce the reaction rate of substitution, and to achieve a majority of mono substituted product.



1

Scheme 19. General Halogenation Reaction of **1**

Multiple attachments were occurring during the reaction, where GC-MS results showed the formation of a mixture of unreacted, mono, di, and tri substituted **1**. **Figure 6** shows the presence of isomers, and also suggested the substitution was not selective.

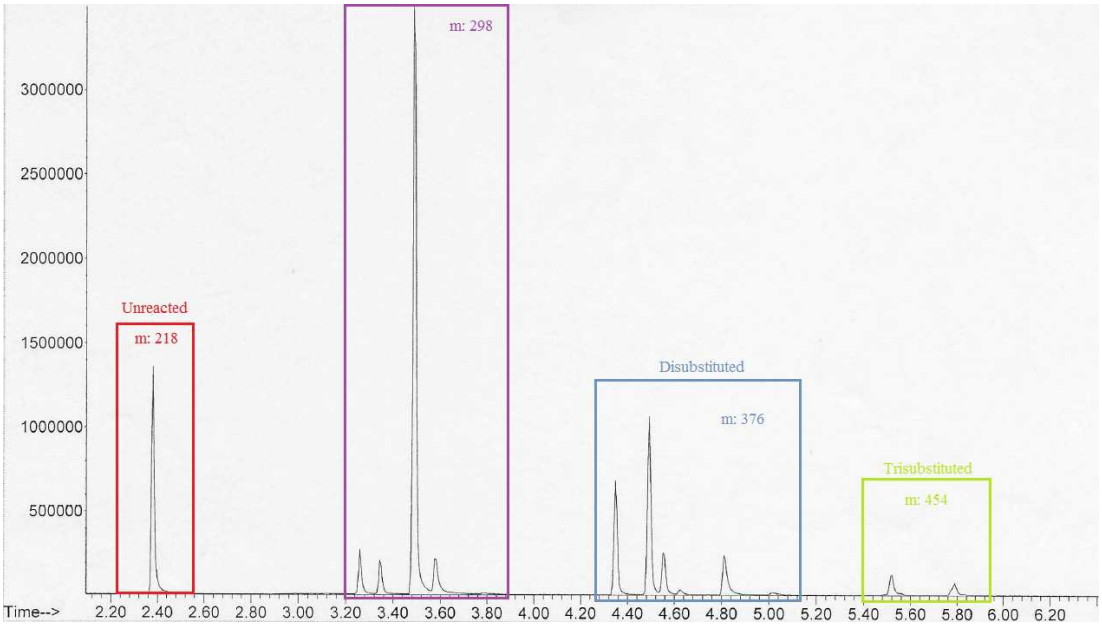


Figure 6. GC Chromatogram Bromination

In **Figure 6**, the monosubstituted in the **purple** box was the majority product with four isomers. The bromination was occurring at the *ortho* and *para* positions on both rings, which suggests the reaction conditions may have been too aggressive. The reactions varied with isomer formation, but some reactions had five isomers for a single bromine attachment. The chromatogram shows the analysis of an aliquot removed during the reaction of **1** with a 10% excess of *N*-bromosuccinimide (NBS), and a ratio of 80:20 sulfuric acid to acetic acid after 24 h. The reaction conditions of the presented chromatogram along with reaction variations are found in **Table 2**.

Table 2. Reactions Conditions for Mono Substitution of **1**

Reactant	H_2SO_4 : HOAc	Desired Product (%)	Selectivity (%) Unreacted:Mono:Di:Tri	t (hrs)	Temp. (□)	Isomer Formation of Desired Product (%)
NBS	80:20	37.4	24.9: 37.4: 10.8: 1.9	24	60	9.3 [a]
NBS	20:80	54.3	12.2: 54.3: 10.3: 0	24	25	20.9
NBS	0:100	50.9	5.1: 50.9: 7.0: 0	72	60	20.3
NBS	10:90	36.8	32.8: 36.8: 5.9: 0	72	60	23.0
NBS	50:50	33.7	55.0: 33.7: 0.9: 0	1	0	10.4 [b]
NBS	50:50	42.4	24.5: 42.4: 7.1: 0	2	0	18.9 [b]
NBS	50:50	45.2	19.6: 45.2: 8.5: 0.8	3	0	17.9 [b]
NBS	50:50	44.0	20.5: 44.0: 8.0: 0.8	48	25	19.0 [b]
SMBI	100:0	22.8	40.8: 22.8: 15.3: 11.8	2	25	7.7
NIS	100:0	25.1	34.7: 25.1: 24.6: 5.5	18	25	6.0
NIS	50:50	37.8	17.7: 37.8: 12.7: 0	22	25	31.3
HNO_3	100:0	24.9	41.7: 24.9: 18.0: 0	24	0	9.7
HNO_3	100:0	0	0: 0: 82.2: 0	24	0	17.8 [c,d]

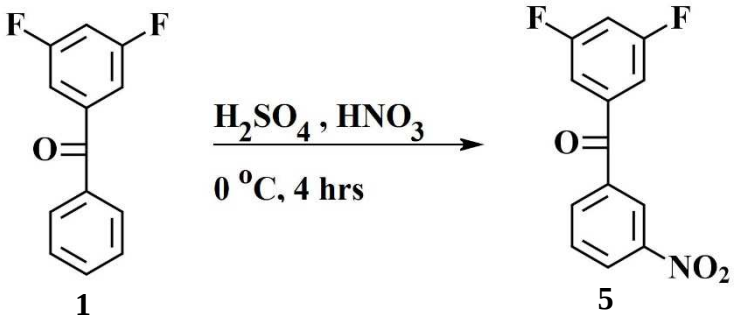
[a] Initial reaction used a 10% excess of NBS, and all proceeding halogenations reduced the excess to 5%. [b] Same reaction monitored over time. [c] The reaction used double the initial amount of Nitric Acid. [d] Reaction yielded only di substituted isomer.

Temperature variations did not appear to alter the formation of undesired products. After initial exploration, the temperature was fixed at 0°C for the addition of reactants followed by a gradual warming to 25°C for the remaining reaction. Limiting the reaction time resulted in unsubstituted starting material in the reaction mixture. The ratio of sulfuric to acetic acid had the greatest impact on the outcome. Reduction in sulfuric acid extended the product formation time. While higher concentrations of sulfuric acid resulted in the lower mono substituted isomers, and greater quantities of di and tri substituted material. Sodium monobromoisocyanurate (SMBI) was used as an alternative brominating agent, but its use provided no advantage to NBS for mono

substitution. Similar results were noticed with the iodination. A slight excess (5%) of *N*-iodosuccinimide (NIS) was used with conditions similar to bromination (**Table 2)**. Optimal conditions for bromination and iodination were not achieved.

(3,5-Difluorophenyl)(*m*-nitrophenyl)methanone, 5

The placement of a nitro group for post functionalization (or pre as the amino group) was also explored. Typical conditions with nitric and sulfuric acid were utilized to substitute a nitro group onto the base compound. The general reaction conditions are shown by **Scheme 20**.



1 **5**

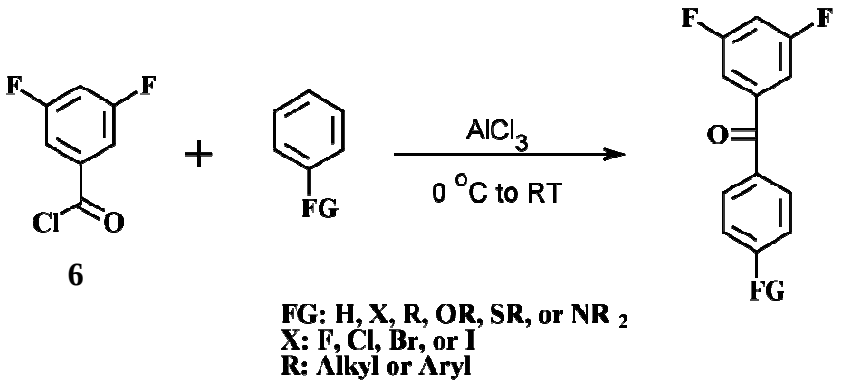
Scheme 20. General Nitration Reaction of **1**

The last two entries in **Table 2** show the results and variation in reactions. The disubstituted product was insoluble in common organic solvents, which made further characterization difficult. In general with EAS, the results showed a lack of selectivity, and ease of substitution. The formation of multiple products made the isolation of the desired product cumbersome. Another approach with the monomer synthesis containing a "post" functionalizable group was investigated.

Synthesis of DFK (1) with Pendant Functional Groups

The synthetic objective for all monomers was to develop a process, which provided a high yielding product, ease of synthesis, and minimal purification. With the consideration to the objective, Friedel-Crafts acylation was utilized with 3, 5-

difluorobenzoyl chloride **6**, benzene, and a Lewis acid catalyst (**Scheme 21**). The base monomer **1** was obtained after the reaction was quenched with water. The crude product was purified by two recrystallizations in ethanol and water. The process afforded a 67% yield of the desired material with a purity of 99.2% (GC). A similar synthetic route was employed for the monomers with pendant functional groups, at the *para* position rather than *meta* to the carbonyl.



Scheme 21. General Acylation for **1** and Other Monomers

(3,5-Difluorophenyl)(4-methylphenyl)methanone, 7

The 4'-methyl-3,5-difluorobenzophenone (**7**) was synthesized with 3,5-difluorobenzoyl chloride, aluminum chloride, and an excess of toluene, and was quenched with water after 4 hours. The solution was water washed, and recrystallized from ethanol and water, after removal of the toluene, to afford a 91 % yield of analytically pure **7** as white crystals. The structure of the monomer was verified with ^{1}H and ^{13}C NMR, and GC-MS analyses. **Figure 7** and **8** shows the ^{1}H and ^{13}C NMR spectra.

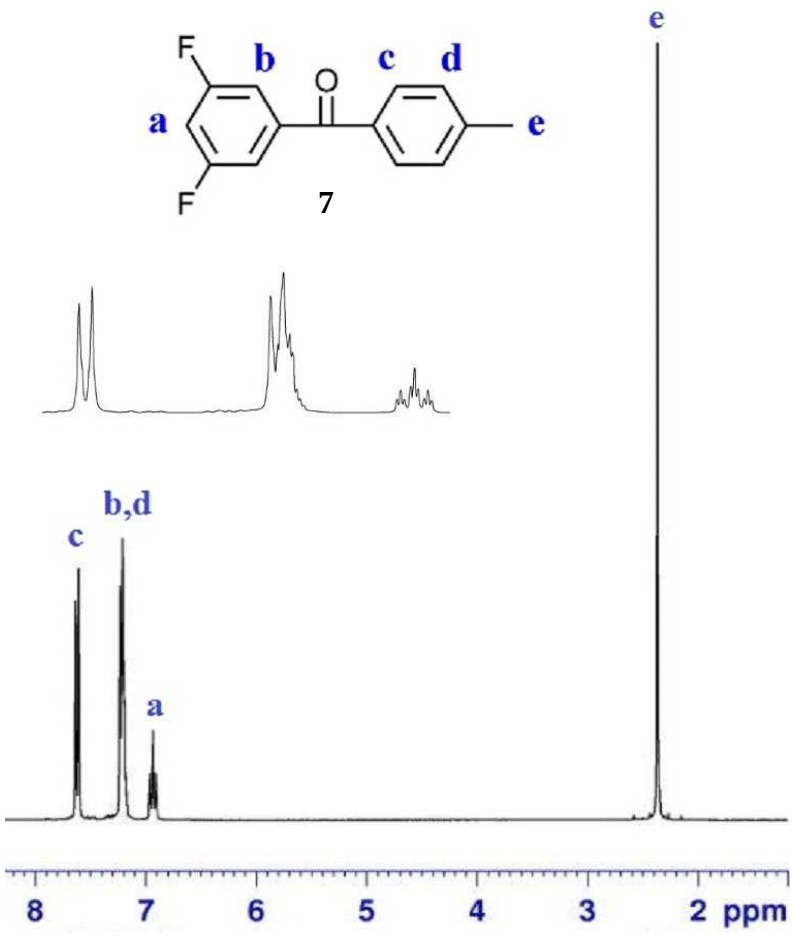


Figure 7. Expanded 300 MHz ^{1}H NMR spectrum ($CDCl_3$) of **7**

Due to fluorine coupling, splitting is observed most notably with proton **a** between the fluorines, which results in a triplet of triplets at 6.93 ppm (J = 8.7, 2.1 Hz). Aromatic protons **b** (2H) between the carbonyl and fluorine overlaps with the protons (2H) **d** beside the pendant methyl group, which appears as a multiplet at 7.20 ppm. The remaining aromatic protons (2H) **c** adjacent to the carbonyl appears as a doublet at 7.62 ppm (J = 8.1 Hz). Finally, the protons **e** (3H) of the pendant methyl group are observed as a singlet at 2.36 ppm.

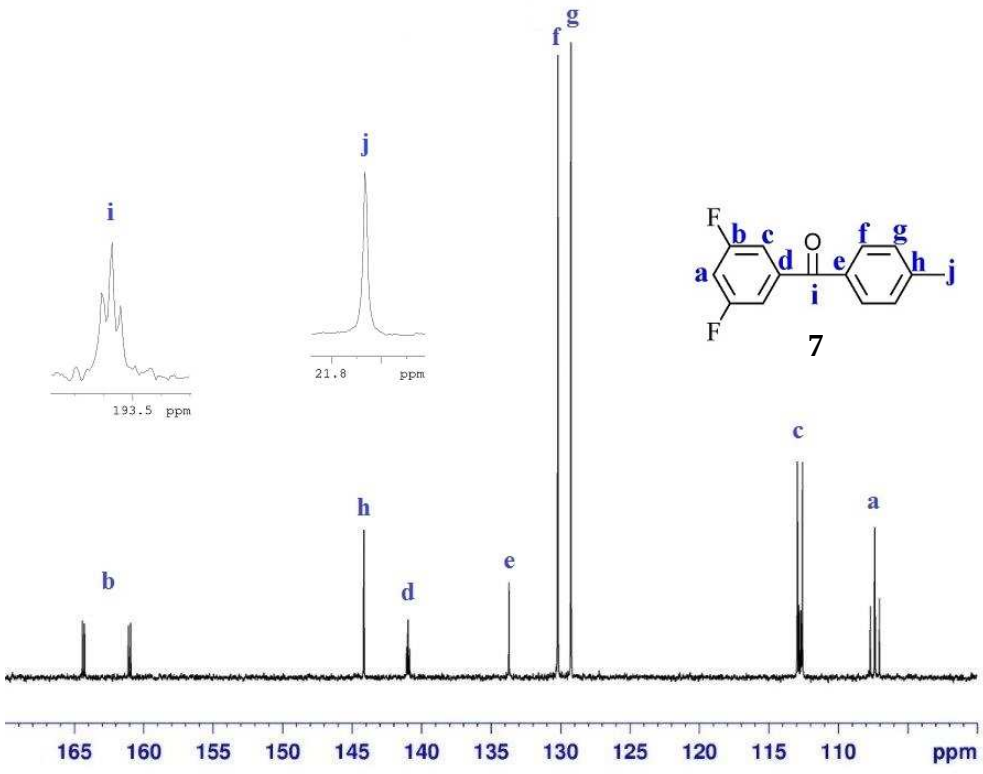


Figure 8. Expanded 75 MHz ^{13}C NMR spectrum ($CDCl_3$) of **7**

In the ^{13}C NMR spectrum (**Figure 8**), all of the signals for carbons **e**, **f**, **g**, and **h** on the phenyl ring, as well as the methyl group **j**, appear as singlets observed at 133.7, 130.2, 129.6, 144.1, and 21.7 ppm, respectively. The remaining carbon atoms, located on the fluorinated ring, all display fluorine coupling. The carbon labeled **a**, between the fluorine atoms, gives rise to a triplet at 107.4 ppm (J = 24.8 Hz). The aromatic C-F, **b**, appears as a doublet of doublets at 162.8 ppm (J = 249.8, 12 Hz). A doublet of doublets is shown at 112.8 ppm (J = 25.5, 9.0 Hz) for carbon **c**. Both the carbonyl **i** and the carbon **d** meta to the C-F appear as triplets with the carbonyl **i** at 193.6 ppm (J = 2.6 Hz) and carbon **d** at 141.0 ppm (J = 7.5 Hz).

4'-Bromo-3,5-difluorobenzophenone, 3

The first monomer synthesized with a pendant functional group was **3**, which was synthesized with either 3,5-difluorobenzoyl chloride or 3,5-difluorobenzoic acid. From the benzoic acid, polyphosphonic acid was used as the catalyst and solvent with phosphorus pentoxide and 5% excess bromobenzene. The reaction required heating to 135 °C for 4 days to reach product formation > 70%. The reaction was quenched with ice water and extracted with dichloromethane (DCM). Residual acid was removed with 5% bicarbonate washes followed by water washes, and then the solvent was removed to recrystallize the product with ethanol**.** Purified product was obtained in a 54% yield with a melting point of 87-89 °C.

For all the acylation reactions, synthesis began with the conversion of the acid to acid chloride with freshly distilled thionyl chloride and catalytic quantity of *N*,*N*-dimethylformamide (DMF). The solution was heated for 2 hours at 55 °C before fractional distillation. Excess thionyl chloride was removed at 73 to 77 °C and the 3,5-difluorobenzoyl chloride was distilled at 173 °C. The yield varied from 64 to 79% and was dependent on fraction quantity and the amount of material remaining in the flask. The purified liquid was kept under nitrogen in sealed containers and transferred by cannula as required.

Primary synthesis of **3** and other variations were made as shown in **Scheme 21** for the reaction of bromobenzene with 3,5-difluorobenzoyl chloride and aluminum chloride. The reactants were present in equimolar amounts and no solvent was used. An excess of bromobenzene resulted in the increase of byproducts, which included the formation of **1**,

dibromobenzene, and tribromobenzene, as observed with GC-MS analysis. With equimolar reactants, the reaction was conducted under argon and the reactants were charged to the aluminum chloride. The solution was stirred until a thick purple paste formed before the reaction was quenched with acidic ice water. The same purification as previously discussed was performed to yield 78 to 93% of a white solid, which melted at 85-86 °C. The monomer structure was verified with ^{1}H and ^{13}C NMR spectroscopy, GC-MS, and elemental analysis. **Figure 9** and **10** show the ^{1}H and ^{13}C NMR spectra.

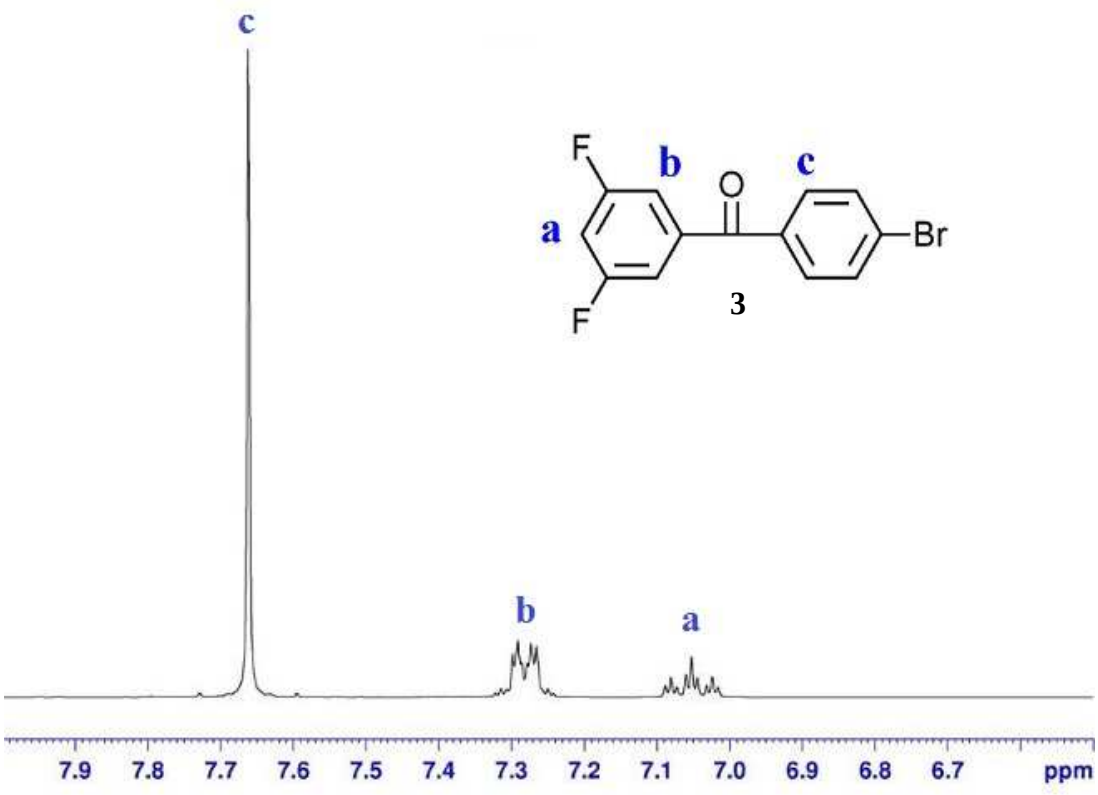


Figure 9. Expanded 300MHz ^{1}H NMR spectrum ($CDCl_3$) of **3**

In the expanded ^{1}H NMR spectrum (**Figure 9**) of **3**, the protons (4H) **c** *ortho* and *meta* to the bromine absorption appears as a singlet at 7.66 ppm with peak integration confirming four protons. A multiplet absorption corresponding to the aromatic proton

(2H) **b** on the fluorinated ring is observed at 7.27 ppm. The remaining aromatic proton **a** between the two C-F groups is shown as a triplet of triplets at 7.05 ppm (J = 8.7, 2.4 Hz).

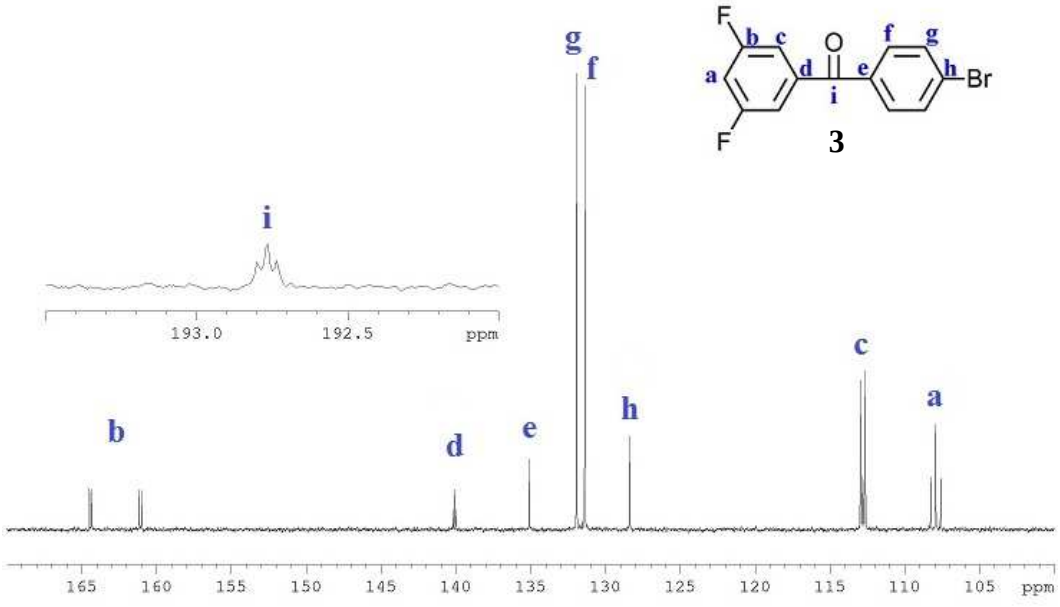
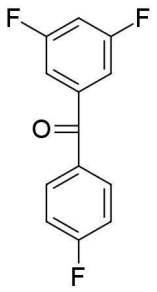


Figure 10. Expanded 75 MHz ^{13}C NMR spectrum ($CDCl_3$) of **3**

In the expanded ^{13}C NMR spectrum (**Figure 10**), carbons located closely to the fluorine atoms display signal splitting from fluorine coupling. The carbon **a** *ortho* to both fluorinated carbons resulted in a triplet at 107.9 ppm (J = 25.5 Hz), and the aromatic C-F **b** is observed as a doublet of doublets at 162.8 ppm (J = 249.8, 12 Hz). A doublet of doublets is shown at 112.8 ppm (J = 25.5, 9.0 Hz) for carbon **c**. Both the carbonyl **i** and the carbon **d** *meta* to the C-F appear as triplets with the carbonyl **i** at 192.8 ppm (J = 2.4 Hz) and carbon **d** at 140.1 ppm (J = 7.6 Hz). All remaining carbons **e**, **f**, **g**, and **h** on the phenyl ring with the bromo group appear as singlets at 135.1, 131.4, 131.9, and 128.4 ppm respectively.

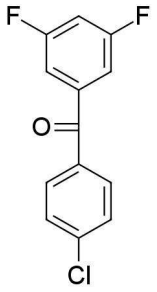
Halogenated DFK (1) Derivatives

To further explore the dehalogenation phenomenon during the synthesis of **3**, via the Friedel-Crafts acylation process, a series of halogenated **1** systems was investigated. An increased formation of **1** was observed with excess bromobenzene, so other pendant halogens were synthesized to explore dehalogenation occurring during the acylation.



8

Previously, 4',3-5-trifluorobenzohenone **8** was made and the reaction was completed with five equivalents of fluorobenzene to the acid halide.[22] Dehalogenation of **8** to **1** was not observed, but 10% of 2',3,5-trifluorobenzophenone was detected by GC-MS. The reaction results correlated to previous research, which also showed ~10% *ortho* isomer formation.[22]



9

The synthetic method was then utilized to make 4'-chloro-3,5-difluorobenzohenone **9** with the same ratio of chlorobenzene to acid halide (5:1).[12] After four hours, the reaction was complete with the formation of < 3% *ortho* isomer and 97%

9 (GC-MS). The synthesis results suggested that the chloro group did not displace as easily as the bromo group, but an iodo group may be even more susceptible to dehalogenation.

The synthesis of 4'-iodo-3,5-difluorobenzophenone **10** was carried out with equimolar amounts of reactants, and purification was identical to that for **3**. Typically, the yield of **10** was under 50% with concurrent formation of **1** and diiodobenzene, as confirmed by GC-MS. The presence of the desired material was confirmed by GC-MS, however, during sodium bicarbonate washes some of the iodo groups were removed resulting in the formation of **1**. After recrystallization from aqueous ethanol, the product structure was confirmed by ^{1}H and ^{13}C NMR, but in only 90 % purity as approximately 10 % **1** was also present.

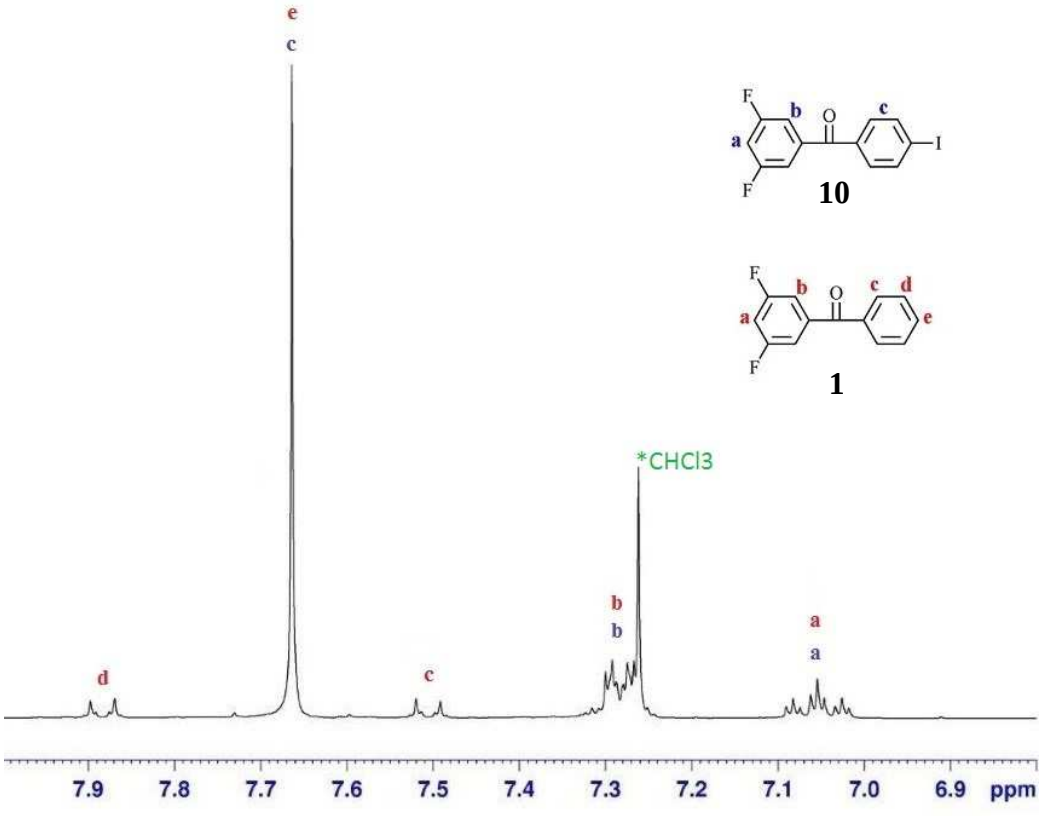
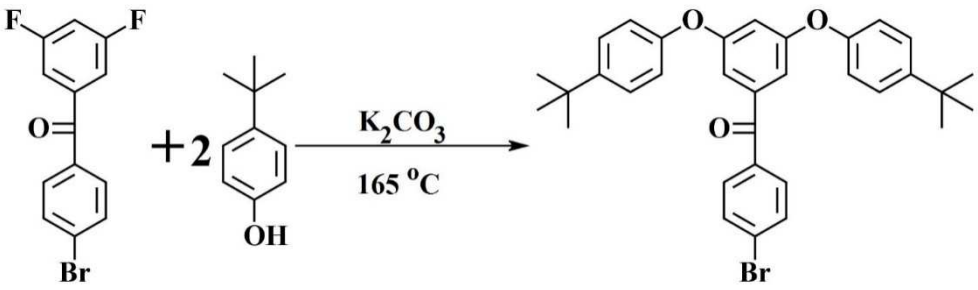


Figure 11. Expanded 300MHz ^{1}H NMR spectrum ($CDCl_3$) of **10** with **1** impurity

The expanded ^{1}H NMR is similar to **3**, and the protons (4H) **c** *ortho* and *meta* to the bromine absorption appears as a singlet at 7.66 ppm. A multiplet absorption corresponding to the aromatic proton (2H) **b** on the fluorinated ring is observed at 7.27 ppm. The remaining aromatic proton **a** between the two C-F groups is shown as a triplet of triplets at 7.05 ppm (J = 8.7, 2.4 Hz). The protons of the impurity overlap some of the signals, bur the protons **c**, **d** on the phenyl ring without fluorines *ortho* and *meta* to the carbonyl appear as multiplets at 7.51 and 7.88 ppm respectively. **Figure 5** of the expanded proton NMR of **1** is in agreement with the additional proton signals identified in **Figure 11**. Also the integration concurred with % area for the impurity to product ratio previously observed by GC-MS.

Polymerization Feasibility Study

With successful introduction of a halogen group to **1,** a model reaction similar to polymerization conditions was conducted with **3** and later with **9**. The model reaction was used to determine if the pendent halogen would survive the polymerization conditions. The monomers were heated to 165 °C with potassium carbonate and 4-*tert*-butylphenol **11**. The expected product of the model reaction is shown, with **3**, in **Scheme 22**.

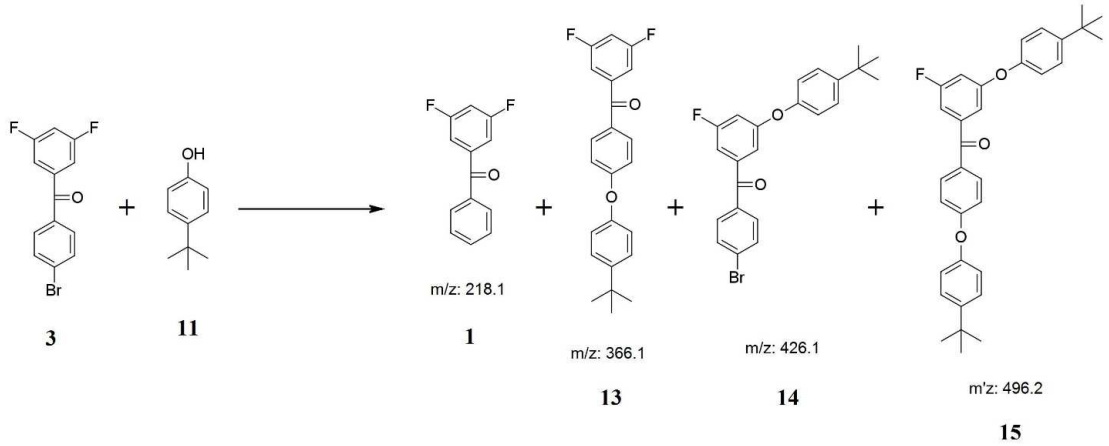


3 **11** **12**

Scheme 22. Model Reaction with **3**

Initial reaction with two equivalents of **11** did not result in difluoro displacement to form **12**. Unfortunately, based on GC-MS, the primary displacement with one equivalent of **11** was at the bromo group in the *para* position for **3**. GC-MS analysis showed that the product was 62% monobromo substituted **13** (m/z) 366, 7% of debrominated monomer **1** (m/z) 218, and 31% monofluoro substituted **14** with one equivalent of **11**. After 12 hours with two equivalents of **11**, 89% of the disubstituted **15** was formed.

Similar results were observed to a lesser extent with **9**. The displacement of the chlorine was at 25% while the fluorine displacement was around 53%. The **9** showed 15% disubstitution with attachments at one fluorine and the *para* chlorine.



Scheme 23. Reaction Outcomes Observed with **3** and **11**

The actual reaction outcome is shown by **Scheme 23** with **3**, and the results were more pronounced with **3**. The primary displacement at the *para* position was between 40 and 60 % by GC-MS, but displacement could possibly be controlled to exclusively attach at the *para* position with lower temperatures. After the initial reaction with **11**, **3** was heated in *N*-Methyl-2-pyrrolidone (NMP**)** at 160 to 180 °C to determine any additional reactions, for which the outcome is shown by **Scheme 23**. The model reactions were

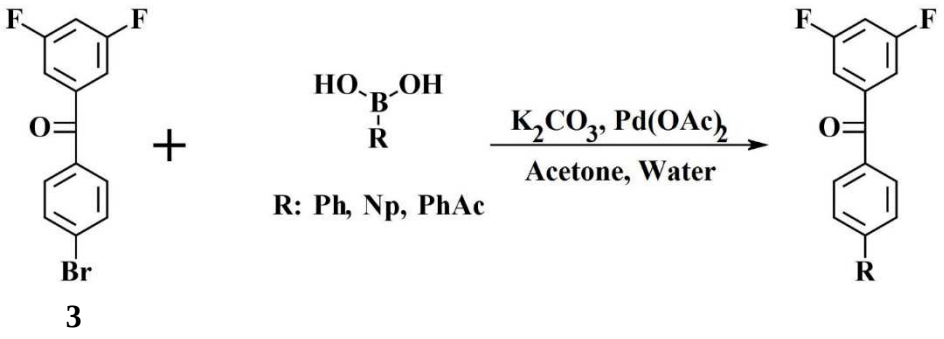
varied by temperature, base and molar equivalent of **11**. Potassium carbonate (K_2CO_3) was replaced with potassium *tert*-butoxide (*t*-BuOK). The reaction variations performed are shown in **Table 3**.

Table 3. Reaction Conditions with Percentage of Product Formation by GC-MS

Reaction Conditions				% of **Identified Compounds** (m/z) by GC-MS			
Molar Equivalent of **11**	t (hrs)	T (°C)	Base	**1** (218.1)	**13** (366.1)	**14** (426.1)	**15** (496.2)
1	24	180	*t*-BuOK	2.2	31.3	45.5	20.6
1	12	180	*t*-BuOK	8.8	37.0	38.9	15.2
1	24	165	K_2CO_3	6.9	30.7	62.4	0
2	12	170	K_2CO_3	0	2.4	8.6	88.9
1	24	160	K_2CO_3	11.6	37.5	47.1	0

Monomer Modification by Suzuki-Miyaura Coupling

For pre modification of **3**, a modified phosphine free Suzuki-Miyaura Coupling reaction was utilized with aromatic boronic acids. Since post modification was not a possibility with the brominated monomer pre functionalization of the monomers was utilized. The general reaction scheme, for modification reactions of the three monomers, is illustrated in **Scheme 24.**



Scheme 24. General Phosphine Free Suzuki-Miyaura Coupling Reaction

Initially, phenyl boronic acid was reacted with **3** in acetone and water. Palladium acetate and potassium carbonate were used to help facilitate the reaction at 60 °C after system degassing. The air-free synthesis was based on previous work by Wallow *et al.*[12] After four hours, the product was extracted from the reaction mixture with toluene, followed by washing with brine and later water washes. The organic layer was removed, via rotary evaporation, and the product was recrystallized from aqueous ethanol to obtain 84% yield of the desired product. The material showed a purity of 99.1% by GC-MS and its structure was also confirmed by ^{1}H and ^{13}C NMR spectroscopic analysis.

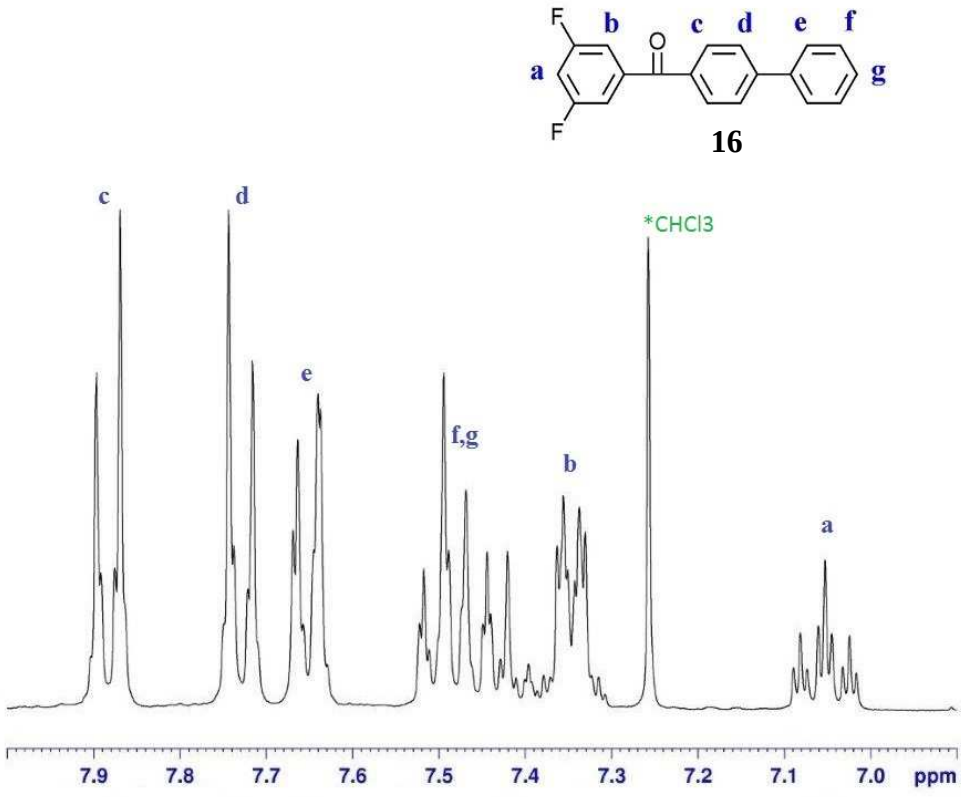


Figure 12. Expanded 300 MHz ^{1}H NMR spectrum ($CDCl_3$) of **16**

The successful incorporation of the phenyl group was very evident in the expanded ^{1}H NMR spectrum (**Figure 12**). The protons (4H) **c** and **d**, which originally

overlapped as a singlet at 7.66 ppm now appear as multiplets at 7.72 and 7.88 ppm respectively. Also the spectrum shows the absorption from the attached phenyl ring protons (5H) as multiplets at 7.45 and 7.66 ppm. The ^{13}C NMR spectrum also confirms the replacement of the bromo group with the phenyl ring.

The expanded ^{13} C NMR was similar to that of the reactant except for the additional carbon absorptions and the carbon shifts for the C atoms adjacent to the point of attachment of the pendent phenyl ring. The phenyl ring gave rise to singlets in the spectrum from carbon atoms **j**, **k**, **l**, and **m**, located at 135.1, 127.3, 129.0, and 128.4 ppm, respectively. The most noticeable change in the spectrum was the absence of the chemical shift for the carbon atom where the bromo group was attached and appearance of the new peak where the phenyl group was incorporated. The carbon **h** absorptions shifted downfield from 128.4 to 139.7 ppm. The other noticeable shift was the carbon **e** adjacent to the carbonyl shifting downfield from 135.1 to 146.0 ppm.

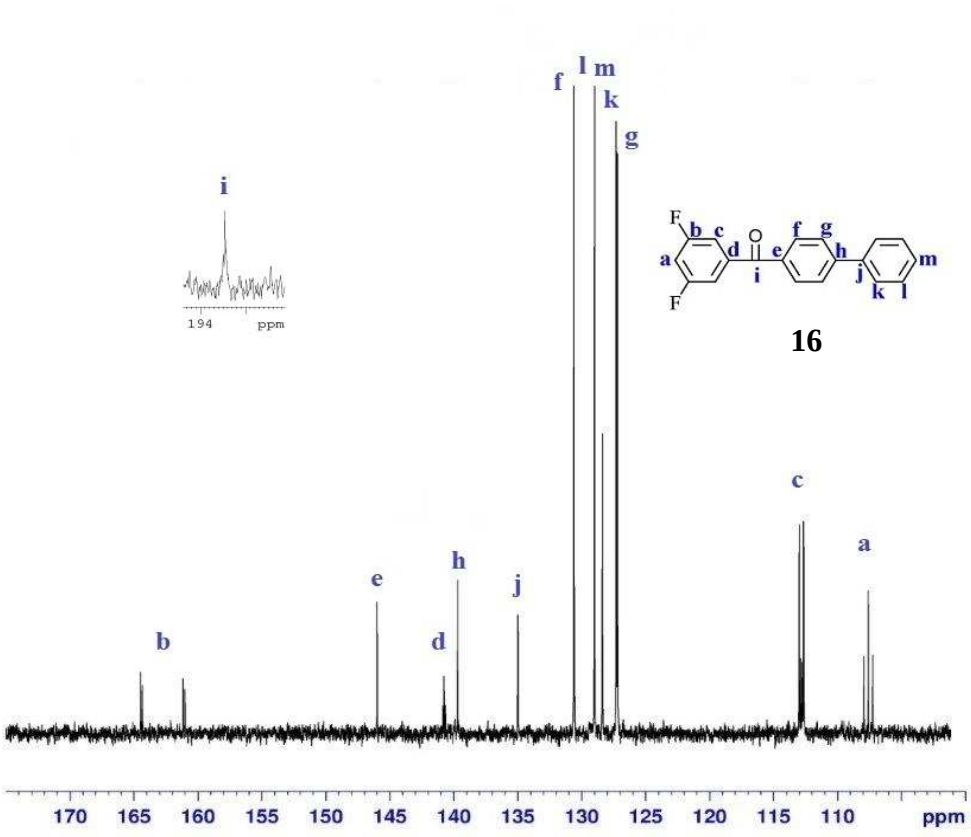


Figure 13. Expanded 75 MHz ^{13}C NMR spectrum ($CDCl_3$) of **16**

(3,5-Difluorophenyl)[*p*-(2-naphthyl)phenyl]methanone, 17

Pre modification of the brominated monomer was also completed with 2-naphthylboronic acid, using conditions identical to those previously discussed. The reaction was monitored for formation of the desired product by GC-MS analysis. After the purification and recrystallization, pure white crystals were obtained at a purity of 99.5% by GC-MS. The melting point was 149-150 °C, and further confirmation of the product was provided by ^{1}H and ^{13}C NMR spectra.

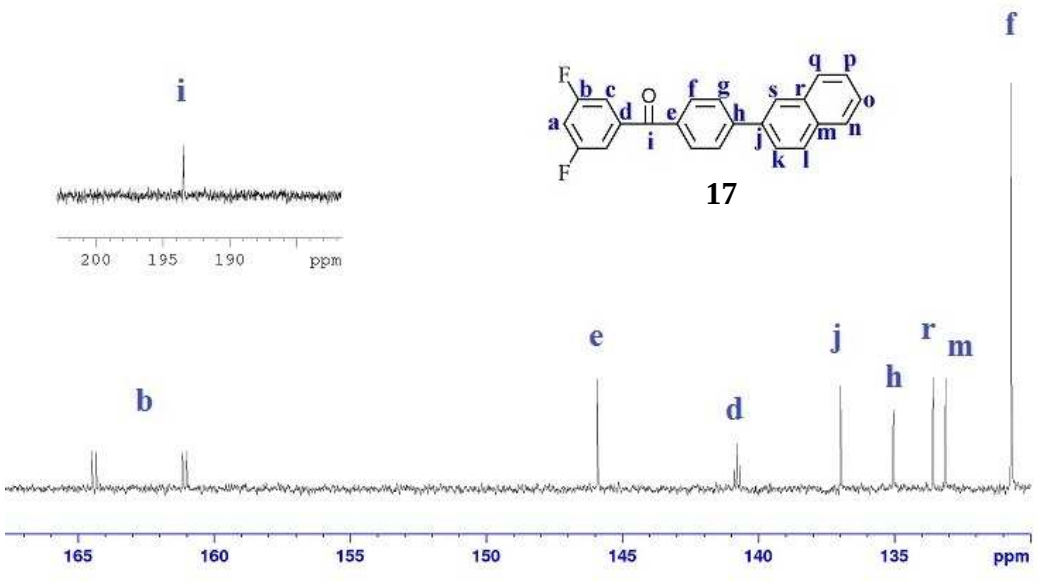


Figure 14. Expanded 75 MHz ^{13}C NMR spectrum ($CDCl_3$) of **17**

The ^{1}H NMR shows several multiplets and was not a definitive confirmation of the formation of **17** in comparison to the ^{13}C NMR. The expanded ^{13}C NMR better illustrates the shifts after attachment as well as the additional carbons present. **Figure 14 and 15** illustrate the carbon absorption of the product. Similar features were present and expected from the base monomer **1**. Other peaks noticed were used to identify and verify the formation of the desired product. Both the carbon **e** beside the carbonyl and the carbon **h** *para* to the carbonyl have shifted significantly to 145.9 and 135.0 ppm. The original absorption prior to reaction was at 128.4 ppm for the brominated carbon **h**, and carbon **e** was at 135.1 ppm.

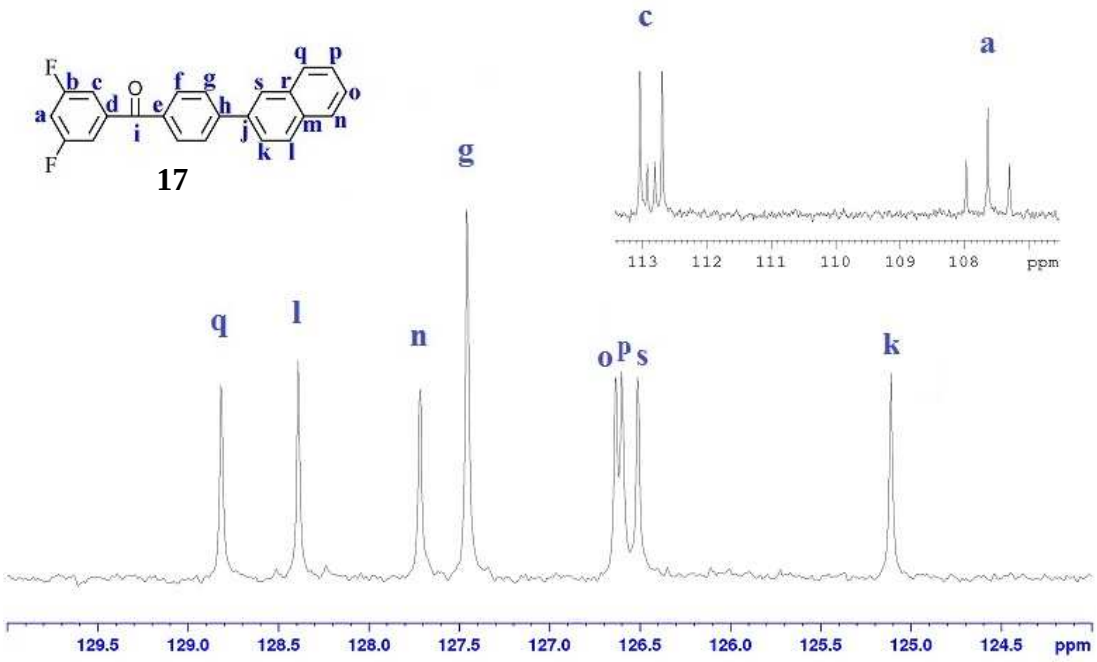


Figure 15. Expanded 75 MHz ^{13}C NMR spectrum ($CDCl_3$) of **17**

Noticeable additions to the spectrum were from the carbons associated with the naphthyl group. All absorptions associated with the naphthyl appear as singlets and were denoted in **Figure FRD# 11a** and **11b**, between 125 and 140 ppm.

1-[4'-(3,5-Difluorobenzoyl)-4-biphenylyl]-1-ethanone, 18

Pre modification of **18** was also completed with 4-acetylphenylboronic acid, using conditions identical to those previously discussed. The reaction was monitored for formation of the desired product by GC-MS analysis, and additional 4-acetylphenylboronic acid (10%) was charged after four hours to advance the reaction to completion. After 12 hours, the crude material was purified and recrystallized from aqueous ethanol to afford pure white crystals at a purity of 99.6% by GC-MS. The melting point was 159-160 °C, and further confirmation of the product was provided by ^{1}H and ^{13}C NMR spectra.

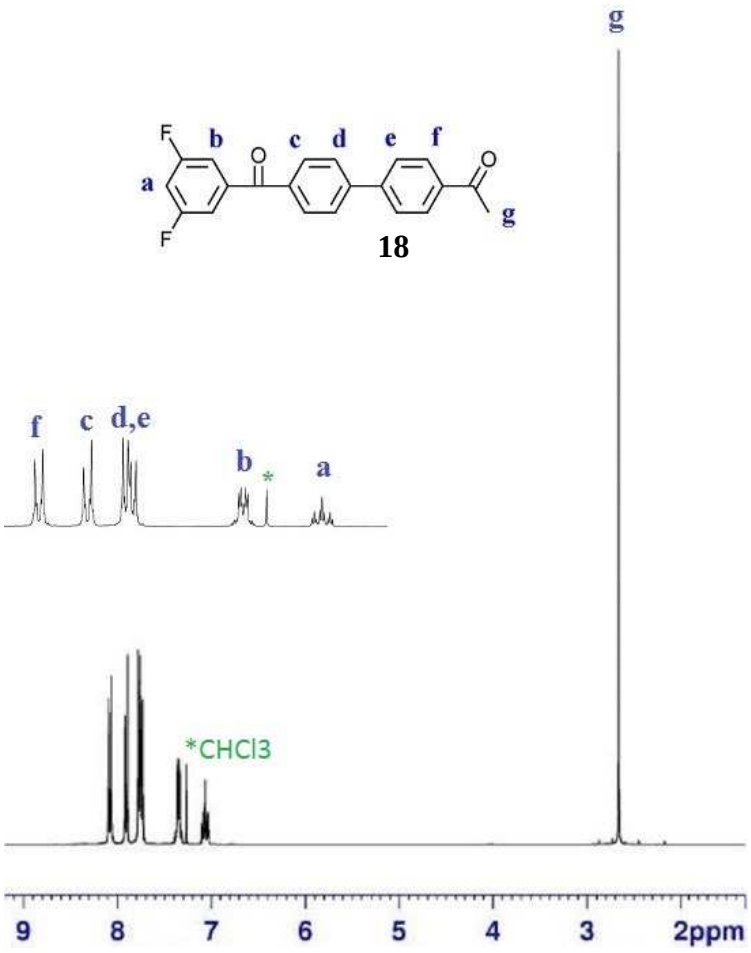


Figure 16. Expanded 300 MHz ^{1}H NMR spectrum ($CDCl_3$) of **18**

The expanded ^{1}H NMR in **Figure 16** shows the replacement of the bromo group on the phenyl ring with the additional protons from the phenyl ring attachment and the protons of the methyl group from the acetyl group. The proton (1H) **a** between the two fluoro groups appears as a triplet of triplets at 7.06 ppm (J = 8.4, 2.4 Hz). The other two protons (2H) **b** on the fluoro phenyl ring appear as a multiplet at 7.35 ppm. The aromatic protons **e, f** of the phenyl acetate appear as two multiplets at 7.76 and 8.08 ppm (4H). The remaining aromatic protons **c**, **d** appear as two multiplets at 7.76 and 7.90 (4H). The methyl protons **g** of the acetyl group appear as a singlet at 2.66 ppm and integrate for 3 hydrogens.

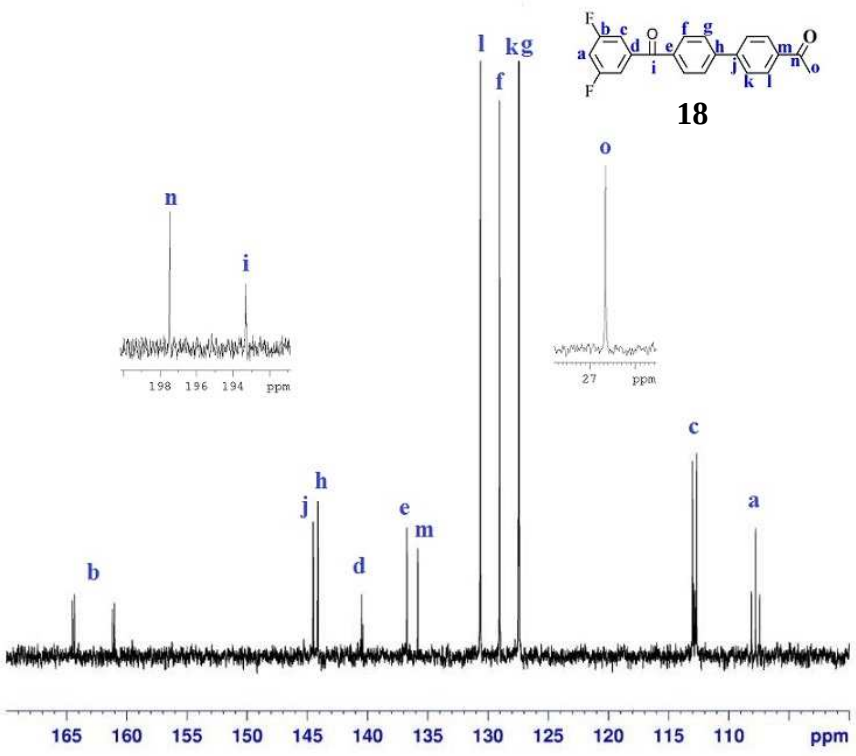
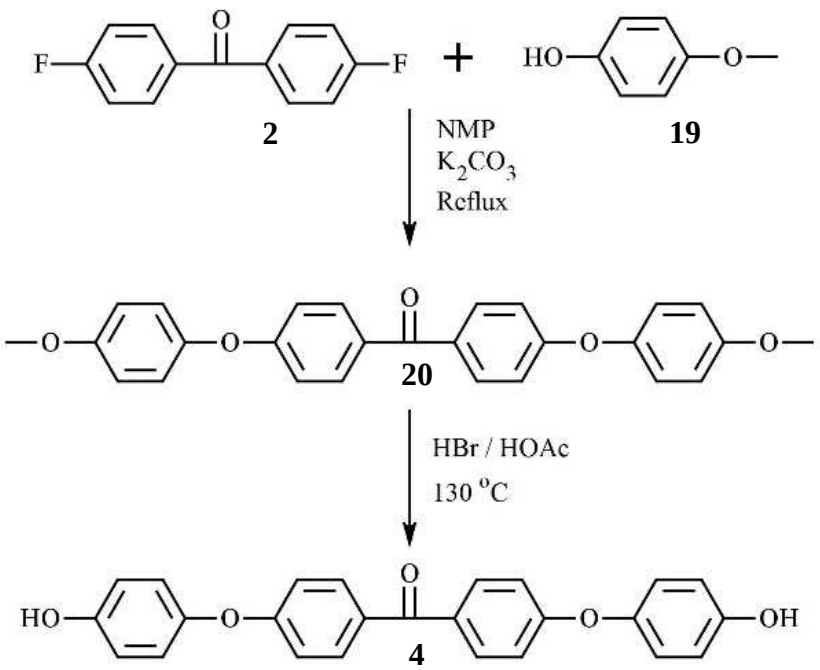


Figure 17. Expanded 75 MHz ^{13}C NMR spectrum ($CDCl_3$) of **18**

The expanded ^{13}C NMR in **Figure 17** shows additional evidence of the acetylphenyl group attachment with the methyl carbon **o** appearing at 26.7 ppm and the carbonyl **n** appearing at 197.5 ppm. The remaining carbons (**j,k,l,m**) of the acetylphenyl group appear at 144.2, 127.9, 130.7 and 135.9 ppm, respectively.

4,4'-Bis-(4-hydroxyphenoxy)benzophenone , 4

To achieve an alternating polymer system of **PEEK**, with the substituted benzophenone isomers, a bisphenol oligomer was prepared with 4,4'-difluorobenzophenone (**2**) as the starting material. A previously reported procedure by Hwang et al., with minor modifications, was utilized for the synthesis of 4,4'-bis-(4-hydroxyphenoxy)benzophenone (**4**) (**Scheme 25**).[20]



Scheme 25. Reaction for 4,4'-bis-(4-hydroxyphenoxy)benzophenone , **4**

Initially, **2** was reacted with *p*-methoxyphenol, in NMP at reflux. The reaction was monitored with GC-MS, and determined to be complete after eight hours. At which point the reaction mixture was poured into water to isolate the product, which was recrystallized from aqueous ethanol. The phenol groups were then deprotected by reaction with hydrogen bromide and glacial acetic acid at 130 °C for 48 hours at which point the solution was cooled and poured into ice water. The product was extracted into methylene chloride and washed with 5% bicarbonate and distilled water. After solvent removal, the crude material was purified by recrystallization from aqueous ethanol to afford a white crystalline solid with a melting point of 220-222 °C. The structure was confirmed by ^{1}H and ^{13}C NMR spectroscopy.

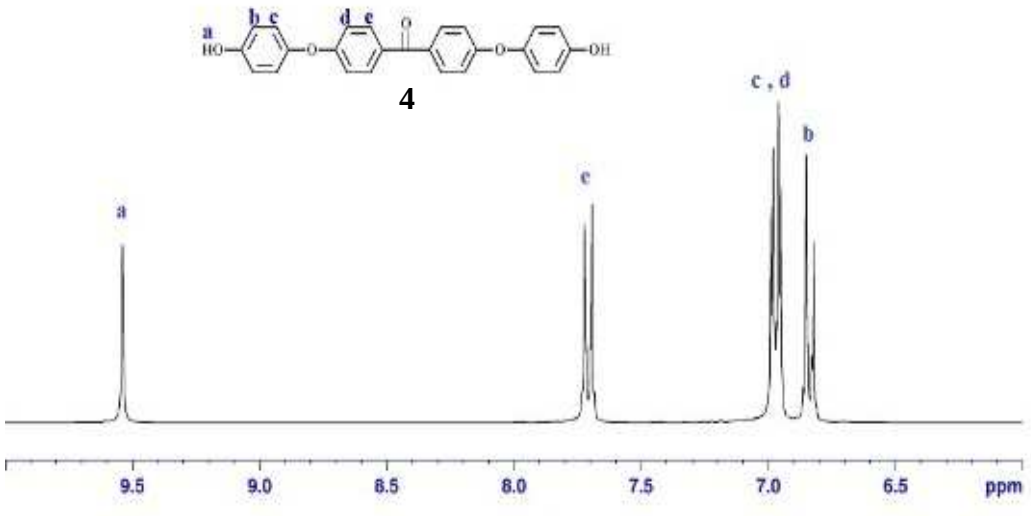


Figure 18. Expanded 300 MHz ^{1}H NMR spectrum (DMSO-d_6) of **4**

The expanded proton NMR (**Figure 18**) of **4** shows the deprotection of the hydroxyl groups with appearance of the absorbance for the hydroxyl protons **a** (2H) at 9.53 ppm as a singlet. The signals for **b** and **e** appear as two doublets at 6.83 ppm (4H, J = 8.7 Hz) and 7.70 ppm (4H, J = 8.7 Hz), respectively. The signals for **c** and **d** appear as two doublets at 6.96 ppm (4H, J = 2.7 Hz) and 6.99 ppm (4H, J = 2.7 Hz), respectively.

The expanded carbon NMR spectrum (**Figure 19**) of **4** shows the carbonyl signal at 193.1 ppm. The aromatic methane signals (**b**,**c**,**f**,**g**) appear at 115.8, 116.4, 121.7, and 132.0 ppm respectively. The quaternary carbon signals (**a**, **d**, **e**, **h**) appear at 162.1, 131.0, 146.4, and 154.6 ppm respectively.

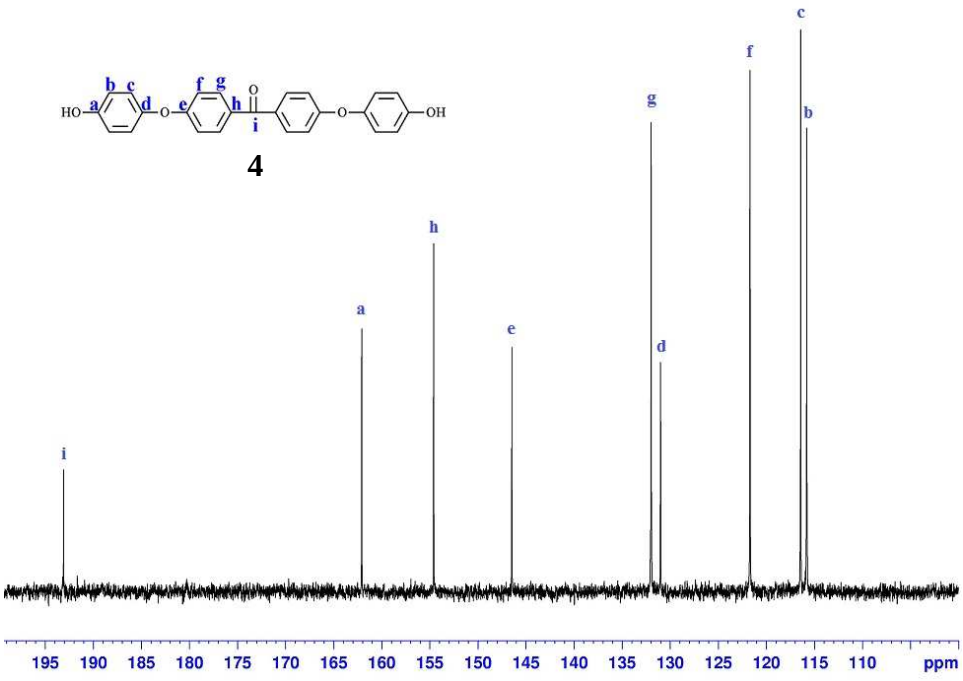


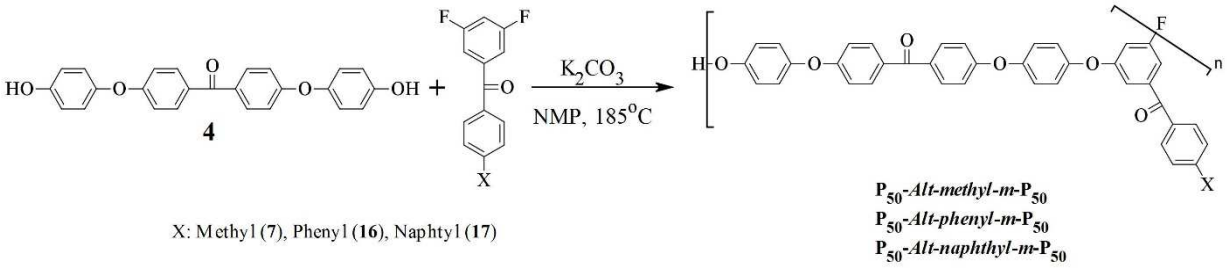
Figure 19. Expanded 75 MHz ^{13}C NMR spectrum (DMSO-d6) of **4**

Synthesis of PEEK

The condensation polymerization to form the aromatic poly(ether ether ketone) **PEEK** reported by Rose and Staniland was reproduced.[8] The polycondensation occurred in the presence of diphenyl sulphone (solvent) with hydroquinone and **2**. The electron withdrawing carbonyl activated the halogen atoms for nucleophilic aromatic substitution (NAS). The aryl dihalide and bisphenol were heated to 180 °C to form a clear solution before the addition of anhydrous potassium carbonate. The mixture was then ramped in temperature and held for 1 hour at 200, 250, 320 °C. The 320 °C polymer solution was then poured on to a metal tray to cool. The solid reaction mixture was milled, and passed through a 500 µm sieve. The light gray powder was successively washed with *N*,*N*-dimethylformamide/water, acetone, water, and acetone/methanol. The polymer was then dried at 140 °C under vacuum for 72 hours. Thermal analysis data were acquired and compared to other polymer derivatives.

General Synthesis for Alternating Copolymer

Alternating copolymers with pendant functional groups utilized the synthetic route discussed by Fortney and Fossum.[19] The successful synthesis of alternating copolymers by NAS was completed with the dialkali metal salt as well as equimolar quantities of **4**, and pendant functionalized diaryl halides. (**Scheme 26**) The reactions were conducted at 185 °C for upwards of 48 hours before precipitations. After reaction the polymers were initially precipitated into water and redisolved in chloroform to precipitate by dropwise addition into ethanol and then repeated in methanol. The off-white powders were dried in vacuo at 110 °C for 24 hours.



Scheme 26. Synthesis of Alternating Functionalized **PEEK** Copolymers

The structures of the polymers were confirmed by ^{1}H and ^{13}C NMR spectroscopy. The ^{13}C NMR (75 MHz) spectra can be found in **Figures 20, 21, 22** for the three copolymers **P_{50}-*Alt-methyl-m*-P_{50}** copolymer, **P_{50}-*Alt-phenyl-m*-P_{50}** copolymer and **P_{50}-*Alt-naphthyl-m*-P_{50}** copolymer.

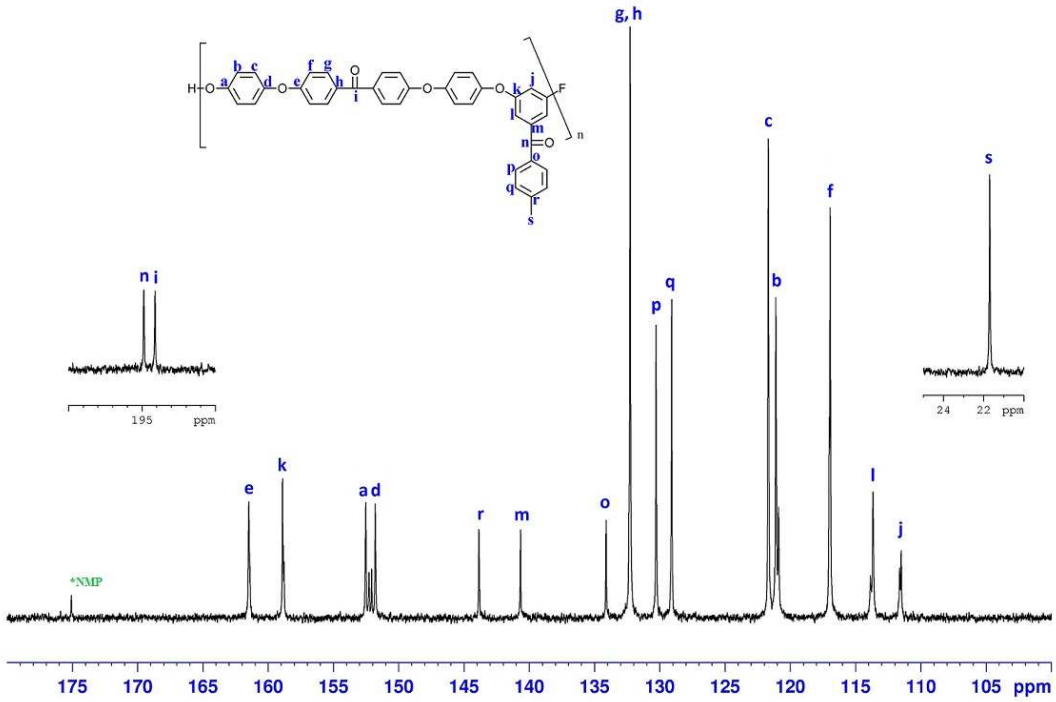


Figure 20. 75 MHz ^{13}C NMR ($CDCl_3$) of **P_{50}-*Alt-methyl-m*-P_{50}** copolymer

Figure 20 shows the carbon NMR spectrum for copolymer **P_{50}-*Alt-methyl-m*-P_{50}** which confirms the addition of the tolyl functional group with the methyl carbon absorbing at 21.6 ppm and the aromatic carbons of the tolyl phenyl absorbing at 129.1 (CH), 130.2 (CH), 134.1 and 143.8 ppm. Two carbonyls signals are observed at 194.0 ppm and 194.7 ppm for the **4** unit and **16** unit, respectively. The four line pattern that is observed between 151.8 ppm and 152.5 ppm is caused by transetherification which was originally reported by Fortney and Fossum where the same pattern was observed in the ^{13}C NMR spectrum of alternating **PEEK**-alt-m-**PEEK** prepared from 4,4'-Bis-(4-hydroxyphenoxy)benzophenone and 3,5-difluorobenzophenone.[19]

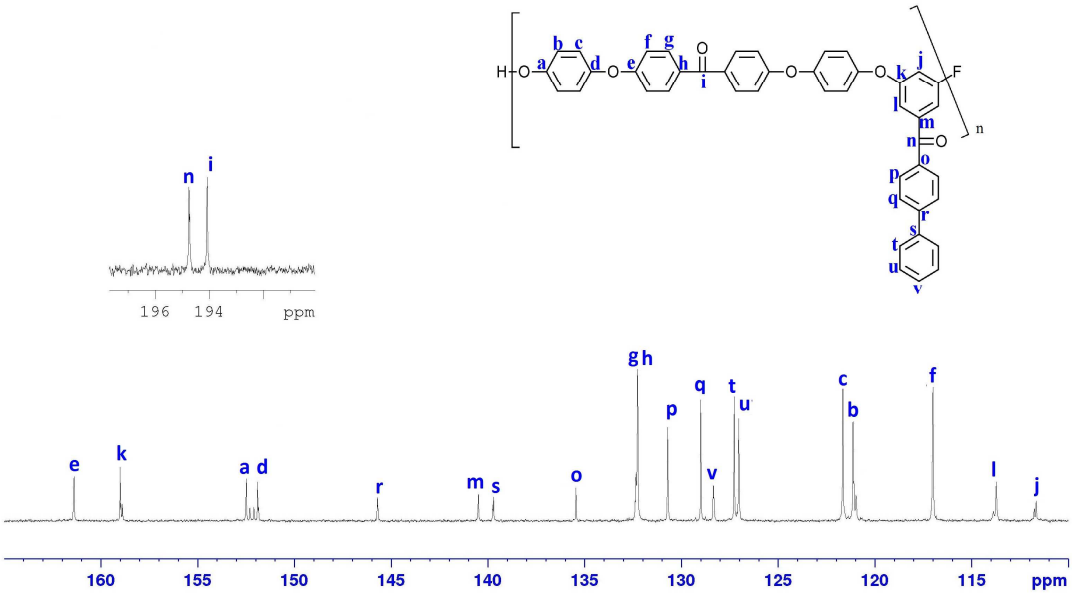


Figure 21. 75 MHz ^{13}C NMR ($CDCl_3$) of **P_{50}-*Alt-phenyl-m*-P_{50}** copolymer

The ^{13}C NMR spectrum of copolymer **P_{50}-*Alt-phenyl-m*-P_{50}** is shown in **Figure 21**. The signals for the aromatic carbons of the biphenyl unit are observed at 127.0 (CH), 127.2 (CH), 128.3 (CH), 129.0 (CH), 130.7 (CH), 135.4, 139.7, and 145.7 ppm.

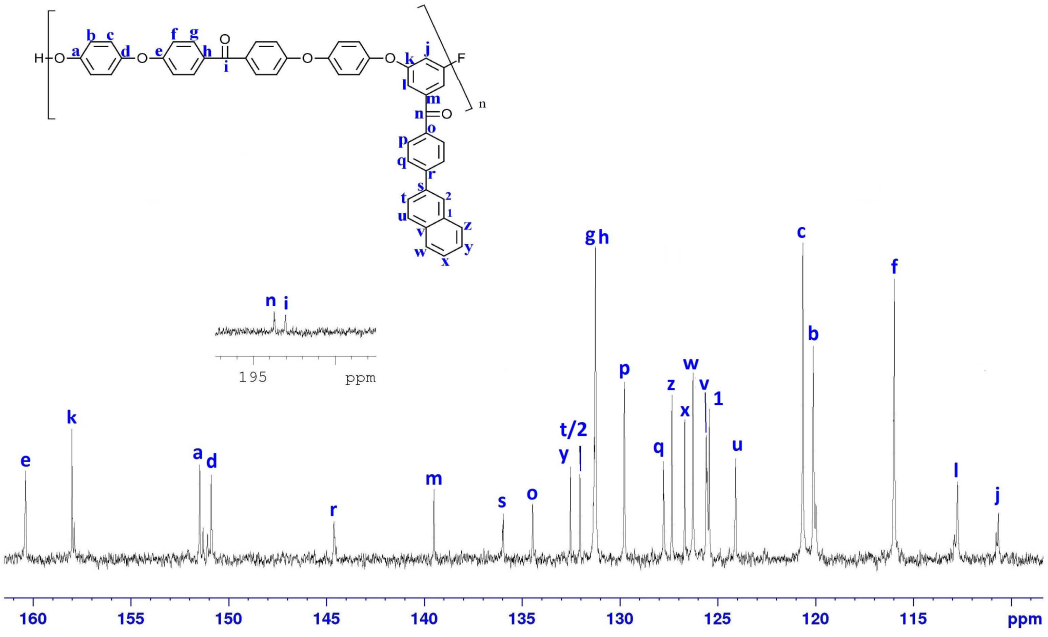
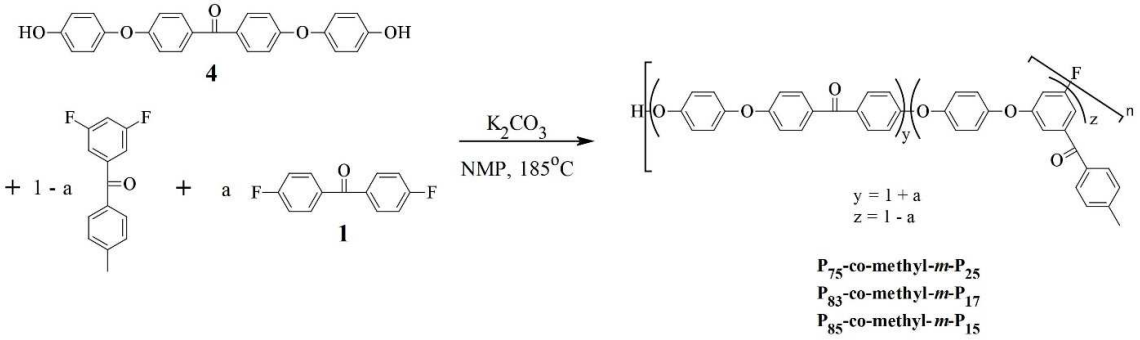


Figure 22. 75 MHz ^{13}C NMR ($CDCl_3$) of **P_{50}-*Alt-naphthyl-m*-P_{50}** copolymer

The structure of copolymer **P$_{50}$-*Alt-naphthyl-m*-P$_{50}$** was confirmed by its ^{13}C NMR spectrum (**Figure 22**). The signals for the aromatic carbons, associated with the naphthyl ring, are observed at 124.0 (CH), 125.4, 125.5, 126.2 (CH), 126.6 (CH), 127.3 (CH)127.7 (CH), 132.0 (CH), 132.5 (CH), and 134.4 ppm.

Methyl Substituted Copolymers

To further study the influence of the percentage of **PEEK** segments, a series of copolymers was synthesized with increasing molar amounts of **PEEK** segments, and decreasing quantities of **7**. The reaction conditions and processing were identical to those previously discussed for the alternating copolymer systems. As such, **P$_{50}$-*Alt-methyl-m*-P$_{50}$** was compared to **P$_{75}$-*co-methyl-m*-P$_{25}$**, **P$_{83}$-*co-methyl-m*-P$_{17}$** and **P$_{85}$-*co-methyl-m*-P$_{15}$** (**Scheme 27**), where **PEEK** segments were increased from 50 % to 75, 83, and 85 %, respectively.



Scheme 27. Synthetic Route for Pendant Methyl Copolymers

The increase in **PEEK** segments increased the viscosity of the reaction mixture. The reduction in backbone deformity decreased the polymer solubility. **P$_{85}$-*co-methyl-m*-P$_{15}$** had low solubility. The impact of the **PEEK** segments affected the polymer solubility and thermal properties.

Table 4. Summary of Polymer Solubility

	NMP	DMSO	DMAc	THF	Chloroform
PEEK	-	-	-	-	-
P_{85}-*co*-*methyl*-*m*-P_{15}	-	-	-	-	-
P_{83}-*co*-*methyl*-*m*-P_{17}	+/-	-	-	-	-
P_{75}-*co*-*methyl*-*m*-P_{25}	+	+/-	+/-	-	-
P_{50}-*Alt*-*methyl*-*m*-P_{50}	+	+	+	+/-	+
P_{50}-*Alt*-*phenyl*-*m*-P_{50}	+	+	+	+	+
P_{50}-*Alt*-*naphthyl*-*m*-P_{50}	+	+	+	+	+

PEEK has been well known for having limited solubility, and in some applications the chemical resistance is ideal. The decrease in **PEEK** segments and the increase of bulkier substituents improves the solubility in common organic solvents. A summarization of the solubility of the polymers is depicted in **Table 4**.

Thermal Analysis

Thermal gravimetric analysis (TGA) and differential scanning calorimetry (DSC) were utilized to determine the thermal properties of the polymer systems. The glass transition temperature (T_g) and the decomposition temperature under nitrogen after 5 % weight loss ($T_{(d\ 5\%,\ N2)}$) were determined and compared in the following figures.

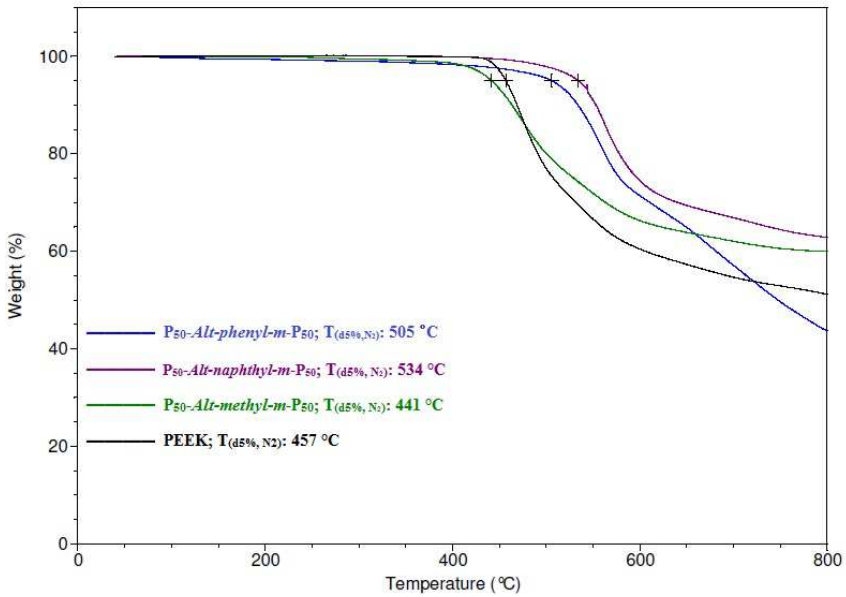


Figure 23. TGA thermograms of **PEEK**, **P_{50}-*Alt*-*methyl*-*m*-P_{50}**, **P_{50}-*Alt*-*phenyl*-*m*-P_{50}**, and **P_{50}-*Alt*-*naphthyll*-*m*-P_{50}** under nitrogen atmosphere

The thermograms of the alternating functionalized polymers (**Figure 23**) are compared to the synthesized **PEEK**. Without multiple step degradations being observed, the thermogram suggests backbone decomposition is occurring, and it is not the loss of pendant functional groups. As the aromaticity decreases from naphthyl to phenyl to methyl, so does the $T_{(d\ 5\%,\ N2)}$ at 534, 505, and 441 °C, respectively. The polymers with phenyl and naphthyl substituents endure higher temperatures; rendering more stable polymers with better heat resistance. **P_{50}-*Alt-methyl-m*-P_{50}** is comparable to **PEEK**.

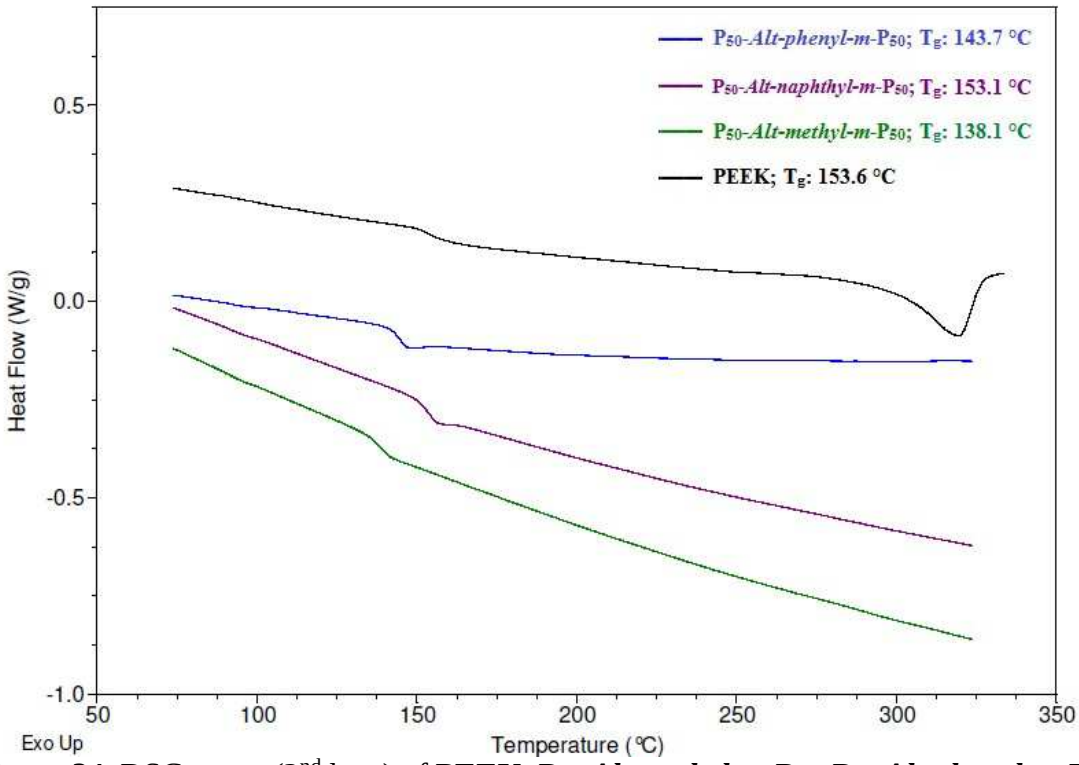


Figure 24. DSC traces (2nd heat) of **PEEK**, **P_{50}-*Alt-methyl-m*-P_{50}**, **P_{50}-*Alt-phenyl-m*-P_{50}**, and **P_{50}-*Alt-naphthyll-m*-P_{50}**

Thermal analysis by DSC indicated that the alternating functionalized polymers were completely amorphous as only glass transition temperatures, T_g, were observed. As the bulky substituent was reduced from naphthyl to phenyl to methyl, the T_g values also decreased with values of 153, 144, and 138 °C, respectively. The increasing T_g values

for **P_{50}-*Alt-phenyl-m*-P_{50}**, and **P_{50}-*Alt-naphthyll-m*-P_{50}** may be a result of the reduction in free volume for the polymer systems. The changes in the polymer system affect sterics, free volume, and intermolecular forces. **PEEK** 'in-house' sample shows a T_g of 154 °C as well as a T_m of 320 °C, and the 2nd heating and cooling traces are depicted in **Figure 25**.

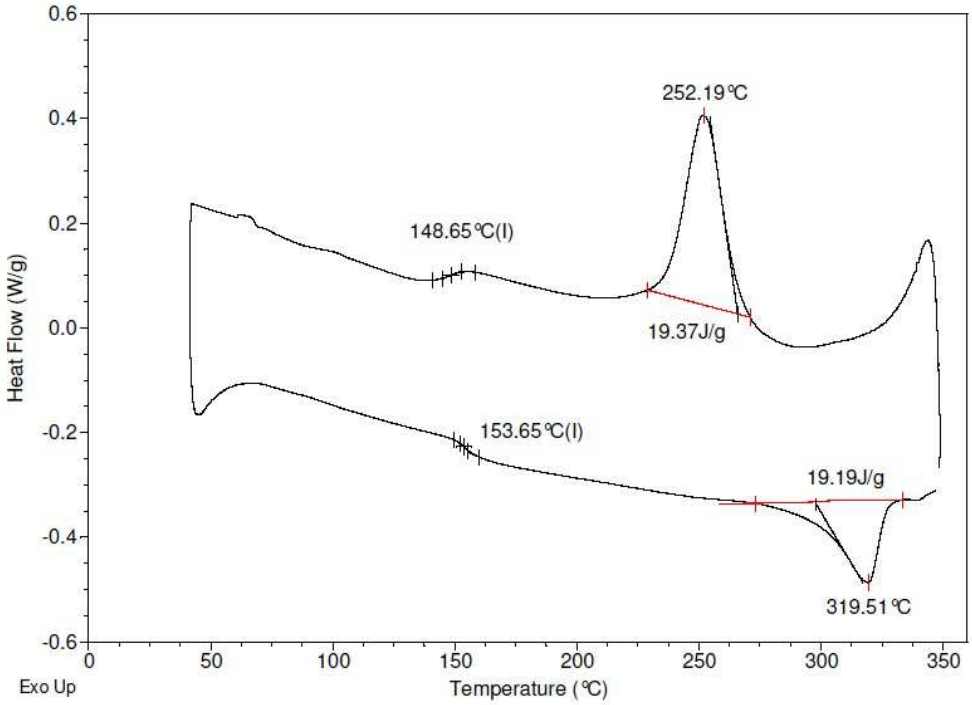


Figure 25. DSC 2nd heating and cooling curve of **PEEK** prepare "in house."

The **PEEK** sample shows similar T_g values on the 2nd heat (154 °C) to cooling (148 °C), which is higher than reported by Victrex at 143 °C. The sample displayed a T_c on cooling at 252 °C, and enthalpy of 19.4 J/g. Similar enthalpy of 19.2 J/g is observed for the T_m at 320 °C, and is lower than reported by Victrex at 343 °C.

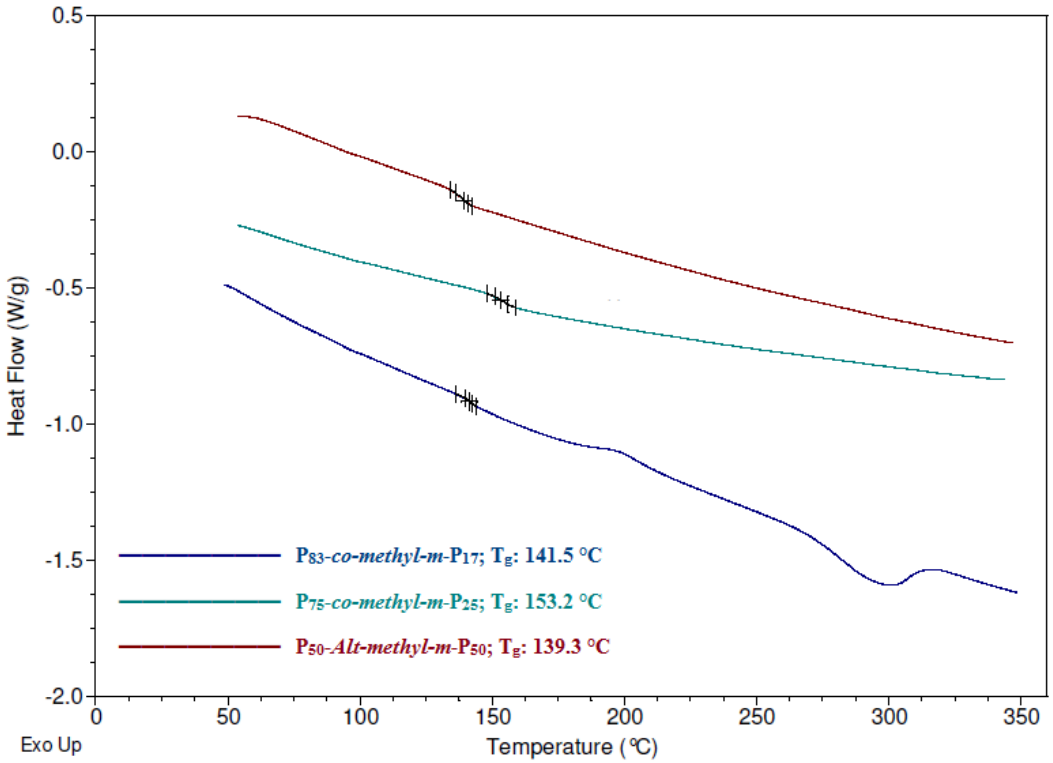


Figure 26. DSC traces (2nd heat) of **P_{50}-*Alt-methyl-m*-P_{50}**, **P_{75}-*co-methyl-m*-P_{25}**, and **P_{83}-*co-methyl-m*-P_{17}**

As expected, the polymers with elevated **PEEK** segments displayed evidence of crystallinity. **P_{75}-*co-methyl-m*-P_{25}** has the highest T_g of 153 °C, and this could be due to the polymer having a higher molecular weight. **P_{83}-*co-methyl-m*-P_{17}** is crystalline, and has a T_g of 142 °C, and comparable to **PEEK**. **Figure 27** depicts the heating and cooling curve of the semi-crystalline, **P_{83}-*co-methyl-m*-P_{17}**.

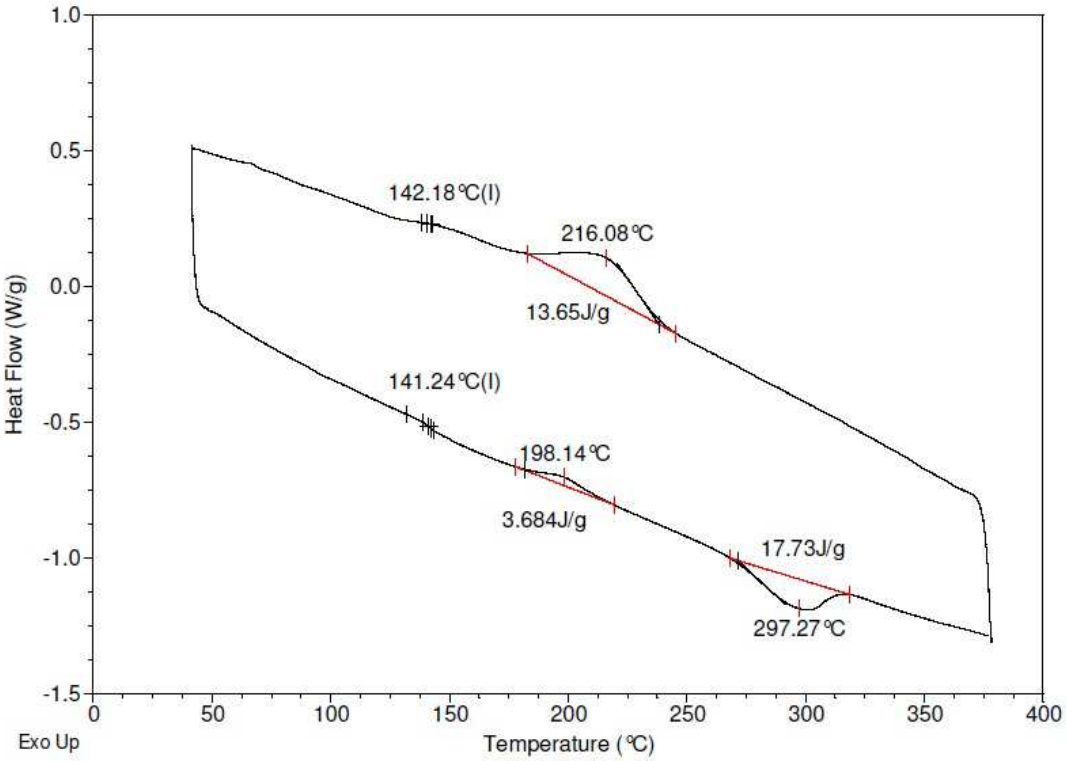


Figure 27. DSC 2nd heating and cooling curve of **P_{83}-*co*-methyl-*m*-P_{17}**

The sample shows similar T_g values on the 2nd heat (141 °C) to cooling (142 °C). The sample displayed a T_c on heating at 198 °C and cooling at 252 °C. The combined enthalpy of the T_c on heating and cooling is 17.3 J/g. A similar enthalpy of 17.7 J/g is observed for the T_m at 297 °C. **Table 5** summarizes the thermal data for all of the polymers reported.

Table 5. Summary of Thermal Analysis for Polymers

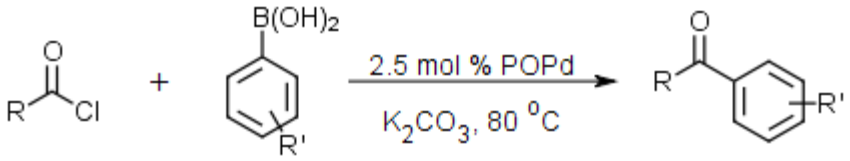
	$T_{(d\ 5\%)}$ (°C)	T_g (°C)	T_c (°C)	ΔH (J/g)	T_m (°C)	ΔH (J/g)	T_c (°C)	ΔH (J/g)
P_{50}-*Alt*-*phenyl*-*m*-P_{50}	505	144	-	-	-	-	-	-
P_{50}-*Alt*-*naphthyll*-*m*-P_{50}	534	153	-	-	-	-	-	-
P_{50}-*Alt*-*methyl*-*m*-P_{50}methyl	441	138	-	-	-	-	-	-
P_{75}-*co*-*methyl*-*m*-P_{25}	-	153	-	-	-	-	-	-
P_{83}-*co*-*methyl*-*m*-P_{17}	-	139	198	3.68	297	17.7	216	13.7
PEEK	457	154	-	-	320	19.2	252	19.4

Conclusion

The isolation of *meta* bromo substituted **1** was not completed due to the unfavorable reaction outcomes. Several monomers were synthesized by Friedel-Crafts Acylation, and an alternative monomer was explored with the bromo group in the *para* position, which was successfully modified prior to polymerization with Suzuki-Miyaura Cross-Coupling reactions. Even though the bromo group on **3** could not survive polymerizations, other monomers were polymerized with various **PEEK** segments. Alternating functionalized **PEEK** copolymers were confirmed and compared to traditional **PEEK** synthesized 'in house'. The copolymers showed greater thermal stability and solubility in common organic solvents. Also semi-crystalline polymers had better solubility than traditional **PEEK**, and also provided a site for further functionalization at the pendant methyl group. All polymers demonstrate the benefits of a structurally modified functional **PEEK**, and should be investigated further.

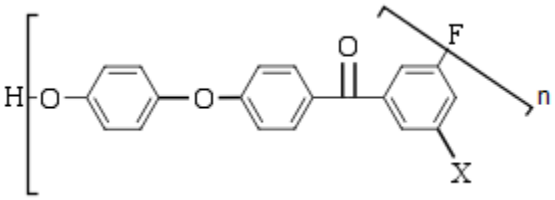
Future Work

In hindsight, monomer synthesis would have been completed with a solvent such as methylene chloride to possibly increase yield and reduce the concentration of reactants, which may also reduce or eliminate formation of by-product **1**. Another possible route for *meta* substituted halogens would have been to try the reaction in a polar solvent such as DMF with NBS and without the aid of strong acids. As previously mentioned milder conditions could help deter di and tri substitution. The *meta* position could have also been added to the system during synthesis, based on work published by Ekoue-Kovi *et al.*[24] (**Scheme 28**)



Scheme 28. Potential Synthetic Route for *meta* Halogen Benzophenone [24]

Even though the *para* position would not survive polymerization, the site could be functionalized prior to polymerization (alkyl, aryl, ether, thioether, tertiary amine) and functionalization could occur with preformed polymers containing some substituents. Additional substituents should be explored, and incorporated during monomer synthesis or monomer modification prior to polymerization.



Based on the model reaction another functionalized polymer isomer could be explored. Further study of 3,5,4'-trihalogens should be completed to determine the reactivity differences between the fluorine, bromine, and iodine at the meta and para locations. The possibility would be to introduce a meta halogen on a structural isomer. The model reaction did suggest the polymerization could occur exclusively at the 3, 4' locations, and could further be promoted by the use of a halogen in the *meta* position, which is less susceptible to NAS, such as bromine or iodine.

Finally, post functionalization conditions should be explored for the methyl substituent to further functionalize the preformed polymer.

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VITA

Rachael Stuck attended Greenview High School and graduated in 2004. She attended Wright State University and received her Bachelor of Science in Chemistry in 2010. She became employed to Heraeus Precious Metals North America Daychem LLC (Vandalia, OH) in 2012 as an R&D Chemist II. While working at Heraeus, she was a co-inventor of a patent (US20160085148A1) of sulfonic acid derivative compounds as photoacid generators (PAGs) in resist applications. In 2017, she received her Master of Science in Chemistry from Wright State University.