2014

Reactivity Ratio Controlled Polycondensation as a Route to Synthesize Functional Poly(arylene Ether)s

Godfred Boakye

Wright State University

Follow this and additional works at: https://corescholar.libraries.wright.edu/etd_all

Part of the Chemistry Commons

Repository Citation
Boakye, Godfred, "Reactivity Ratio Controlled Polycondensation as a Route to Synthesize Functional Poly(arylene Ether)s" (2014).
Browse all Theses and Dissertations. 1260.
https://corescholar.libraries.wright.edu/etd_all/1260
REACTIVITY RATIO CONTROLLED POLYCONDENSATION AS A ROUTE TO SYNTHESIZE FUNCTIONAL POLY(ARYLENE ETHER)S

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

By:

GODFRED BOAKYE

B.S. Kwame Nkrumah University of Science and Technology, 2011

2014

Wright State University
WRIGHT STATE UNIVERSITY

GRADUATE SCHOOL

December 17, 2014

I HEREBY RECOMMEND THAT THE THESIS PREPARED UNDER MY SUPERVISION BY Godfred Boakye ENTITLED Reactivity Ratio Controlled Polycondensation As a Route to Synthesize Functional Poly(Arylene Ether) BE ACCEPTED IN PARTIAL FULFILLMENT OF THE REQUIREMENTS FOR THE DEGREE OF Master of Science.

________________________________________
Eric Fossum, Ph. D.
Thesis Advisor

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

Committee on Final Examination

________________________________________
Eric Fossum, Ph. D.

________________________________________
Kenneth Turnbull, Ph. D

________________________________________
William Feld, Ph. D

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

Boakye, Godfred. M.S., Department of Chemistry, Wright State University, 2014. Reactivity Ratio Controlled Polycondensation As a Route to Synthesize Functional Poly(Arylene Ether)s

Two monomers, 4’,3,5-trifluorodiphenylsulfone, 1, and 4’,3,5-trifluorobenzophenone, 2, have been investigated for their potential use as special BB’B”type monomers to synthesize functionalized, linear PAEs via a process called reactivity ratio controlled polycondensation (RRCP). A model study with monomer 1 resulted in a mixture of unreacted starting material, two mono-substitution products (para- and meta-F substitution) and a significant amount of di-substitution products as evidenced by the GC/MS and $^{13}$C DEPT-90 NMR spectroscopy. Conversely, subjecting monomer 2 to similar conditions, using 3-aminophenol (3f) as the nucleophile, afforded monosubstitution exclusively. A series of functionalized, linear PAEs polymers were prepared by reaction of compound 2 with selected phenols to generate functional B2 type monomers in situ, followed by reaction with Bisphenol-A to afford the corresponding linear poly(arylene ether)s. Molecular weight analysis of the polymers showed relatively high molecular weights with broad molecular weight distributions. The polymerization process was accompanied by the formation cyclic oligomers, which could not be removed via re-precipitation. Thermal analysis of the polymers indicated relatively high thermal stability, under a nitrogen atmosphere, with 5 % weight loss temperatures ranging from 380 °C to 459 °C. All the polymers were completely amorphous displaying only glass transition temperatures ranging from 108 °C to 136 °C.
# TABLE OF CONTENT

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

1.1 Poly(arylene ether)s, **PAE** .......................................................................................... 2

   1.1.1 Poly(phenylene oxide)s, **PPO** ............................................................................. 4

   1.1.2 Poly(arylene ether sulfone)s, **PAES** ................................................................. 5

   1.1.3 Poly(aryl ether ketone)s, **PAEK** ........................................................................... 12

1.2 Synthesis of Poly(arylene ether ketone)s ..................................................................... 14

   1.2.1 Polycondensation Nucleophilic Aromatic Substitution (**NAS**) ....................... 14

1.3 Modification Chemistry ................................................................................................. 18

1.4 Functionalization of Poly(arylene ether)s ..................................................................... 20

   1.4.1 “Pre” - Modification Chemistry ........................................................................... 22

   1.4.2 “Post” - Modification Chemistry ........................................................................ 23

1.5 B₃ Monomers as a Route to Functional **PAES** and **PAEK** ..................................... 26

1.6 Current Project ............................................................................................................. 27

2. EXPERIMENTAL ............................................................................................................ 30

2.1 Materials ..................................................................................................................... 30

2.2 Instrumentation .......................................................................................................... 30

2.3 “Pre” - Functionalization of Compound 1 with 4 - tert - Butylphenol (3d) via
   “One-Pot” Approach ..................................................................................................... 31

2.4 Synthesis of 4’, 3, 5-trifluorobenzophenone, **2** .................................................... 32
2.5 “Pre”- Functionalization of Compound 2 with 3-Aminophenol (3f) As a Model Study.......................................................................................................................................... 33

2.6 General Procedure for the “Pre”- Functionalization of Compound 2 via a “One-Pot”, Two-step Approach .................................................................................................................................. 33

2.7 Random Co-polymerization of “Pre”- Functionalized Compound 2 with 3-methylphenol (3b) and 4,4’-difluorobenzophenone via a “One-Pot” Two-step Approach .................................................................................................................................. 35

3. RESULTS AND DISCUSSION ........................................................................................................ 37

3.1 Monomer Synthesis and Properties .................................................................................... 37

3.2 “Pre” - Functionalization of Compound 1 with 4-tert-Butylphenol (3d) via “One-Pot” Approach .................................................................................................................................... 39

3.3 Synthesis of 4’, 3, 5-Trifluorobenzophenone, 2, by Friedel-Crafts Acylation........ 43

3.4 “Pre”- Functionalization of Compound 2 with 3-Aminophenol (3f) As a Model Study ........................................................................................................................................... 46

3.5 Synthesis of a Series of “Pre”-Functionalized PAEKs via “One-Pot” Approach... 48

3.6 Random Co-polymerization of “Pre”-Functionalized Compound 2 with 3-methylphenol (3b) and 4,4’-difluorobenzophenone via “One-Pot” Two-Step Approach .................................................................................................................................. 50

3.7 Characterization and Thermal Properties of Polymers .................................................. 53

4. CONCLUSION .................................................................................................................................. 60

5. PROPOSED FUTURE WORK. .................................................................................................. 61
6. REFERENCES

62
LIST OF FIGURES

Figure 1. Generic representation of poly(arylene ether) backbone structure .......................... 1

Figure 2. General structures, trade names, and thermal properties of some commercial PAEs................................................................. 3

Figure 3. Some commercially available PAES. ........................................................................ 6

Figure 4. Some major PAEKs with $T_g$ and $T_m$ values 29-32. .................................................. 13

Figure 5. Routes to “Pre” and “Post” chemistry of PAES and PAEK ........................................... 21

Figure 6. Reactivity of the three aryl-fluorides in 4’,3,5-trifluorodiphenylsulfone, 1 and 4’,3,5-trifluorobenzophenone, 2. ................................................................. 27

Figure 7. B₃ monomers for the synthesis of “pre”-functionalized PAES and PAEK ..... 38

Figure 8. Overlay of the 75.5 MHz $^{13}$C DEPT 90 NMR (DMSO-$d_6$) spectra of compound 1 (a) and the products from the reaction shown in Scheme 18 (b). ......................... 41

Figure 9. 300 MHz $^1$H NMR (CDCl₃) spectrum of compound 2. ............................................. 44

Figure 10. 75.5 MHz $^{13}$C NMR (CDCl₃) spectrum of compound 2. ........................................ 45

Figure 11. Overlay of 75.5 MHz $^{13}$C DEPT 90 NMR (DMSO-$d_6$) spectra for monomer 2 and 2f. ................................................................................................................................. 47

Figure 12. Overlay of the 75.5 MHz $^{13}$C DEPT 90 NMR (CDCl₃) spectra of monomer, 2, mono-substituted monomer, 2d and homopolymer, 4d. .................................................. 49

Figure 13. Overlay of the 75.5 MHz $^{13}$C DEPT 90 NMR (CDCl₃) spectra of homopolymer 4b and copolymer 5b. ................................................................. 52

Figure 14. SEC (RI signal) traces of crude and re-precipitated polymers, 4b and 4d ..... 53

Figure 15. TGA traces of Polymers 4a-f and 5b under N₂ atmosphere at a heating rate of 10 °C/min. ..................................................................................................................... 55
Figure 16. Degradation profile of the homopolymer, 4f under N\textsubscript{2} atmosphere at a heating rate of 10 °C/min. ................................................................................................................................. 56

Figure 17. Structural representation of Homo-polymers, 4a-f............................................. 57

Figure 18. DSC traces of polymers, 4a-f and 5b in nitrogen at a heating rate of 10 °C/min. ........................................................................................................................................... 59
LIST OF SCHEMES

Scheme 1. Oxidative coupling of 2,6-dimethylphenol to form poly(phenylene oxide), PPO. ......................................................................................................................................................... 4

Scheme 2. Synthesis of poly(arylene ether sulfones by NAS. ........................................ 7

Scheme 3. Typical NAS mechanism. ................................................................. 8

Scheme 4. Synthesis of poly(arylene ether sulfone)s by NAS. ..................... 10

Scheme 5. Synthesis of PAES via NAS polycondensation reaction with a weak base. .. 11

Scheme 6. Synthesis of PAES by meta-activated NAS polycondensation reaction. .... 12

Scheme 7. Synthesis of poly(ether ether ketone) via NAS. .................................. 15

Scheme 8. Synthesis of poly(ether ketone) via NAS. ........................................... 16

Scheme 9. Synthesis of poly(ether ether ketone) via NAS in the presence of CsF. ...... 17

Scheme 10. Synthesis of meta-PAEKs via NAS. ................................................ 18

Scheme 11. Modification chemistry utilizing “Pre” and “Post” functionalization. .... 19

Scheme 12. Amino-functionalized poly(arylene ether ketone) via “Pre”- modification approach. ................................................................................................................................. 23

Scheme 13. “Post” modification of PAEK via “post” sulfonation route. ................. 24


Scheme 15. Polymerization reaction by an NAS A₂ + BB’B” approach. ............... 26

Scheme 16. Reactivity differences in BB’B” monomers utilized for the synthesis of functional PAES and PAEK. ......................................................................................................................... 28

Scheme 17. “Pre”-functionalization of PAES and PAEK using BB’B” monomers via a “One-Pot” two-step approach. ............................................................................................................. 29
Scheme 18. Synthetic procedure for “pre”-functionalized compound 1 with 3d............ 39

Scheme 19. Synthesis of 4’, 3, 5-trifluorobenzophenone, 2 via Friedel-Craft Acylation. 43

Scheme 20. Synthetic procedure for the “pre”-functionalization of 2 with 3f................. 46

Scheme 21. Synthesis of “pre”-functionalized PAEKs via “one-pot” two-step approach. ................................................................. 48

Scheme 22. Synthesis of random copolymer, 5b via “one-pot” two-step approach via NAS. .................................................................................................................................................................. 51
LIST OF TABLES

Table 1. $^{19}$F, $^{13}$C NMR chemical shifts (ppm) and Activation Energies (kcal/mol) of the electrophilic sites of compound 1 and 2. 54 ................................................................. 38

Table 2. GC/MS Summary of Pre-functionalization of compound 1 with 3d. ............... 40

Table 3. SEC Characterization of Homopolymers, 4a-f and Copolymer, 5d with Percent Yields. ............................................................................................................................... 54

Table 4. Thermal Analysis ($T_g$, $T_d$(5%) under N$_2$ Data for Polymers 4a-f, and 5b. .... 58
ACKNOWLEDGEMENT

First of all, I would like to thank the Almighty God for His love, grace and mercy on my life. I would like to express my sincere gratitude to my advisor, Dr. Eric Fossum for his guidance, support and kindness over the past two years and some months. The opportunities he has provided have shaped my career path and personally build my confidence. I am very thankful of my committee members, Dr. William Feld and Dr. Kenneth Turnbull for their contributions and suggestions towards this thesis. I would also like to thank the past and present members of the Fossum research group, especially Marina, Kara, Abraham, Jesse, Jessica, Bobby Jo and Giovanni as well as the faculty and staff members of the Wright State University Department of Chemistry.
DEDICATION

I would like to dedicate this thesis to my dad, Christopher Yiadom Boakye for his continuous support and love towards me after my mom passed away some twenty-four years ago. I would like to particularly thank my two wonderful sisters Felicia Boakye and Cecilia Nyarko, for being there for me throughout my college years, you guys are awesome and to anyone who has affected my life one way or the other.
1. INTRODUCTION

Poly(arylene ether)s, PAEs, are a class of high performance engineering thermoplastics which have been widely explored due to desirable physical properties such as high glass transition temperature, good thermal stability, high mechanical performance, low dielectric constant and excellent resistance to hydrolysis and oxidation.\textsuperscript{1-4}

A generalized structure of poly(arylene ether)s can be illustrated as in Figure 1.

![Generic representation of poly(arylene ether) backbone structure.\textsuperscript{5}](image)

**Figure 1.** Generic representation of poly(arylene ether) backbone structure.\textsuperscript{5}

The ability of these materials to exhibit an excellent combination of physical, chemical and mechanical properties makes them essential in a variety of industrial applications such as coatings, adhesives, composites, molded components, toughening agents and ultra-filtration membranes.\textsuperscript{6}

However, the ability to use conventional PAEs as thin films and coating materials becomes difficult due to their poor solubility, which also makes polymerization conditions difficult.\textsuperscript{4} As a result, a great deal of effort has been focused on introducing some functionality to PAEs in order to improve and/or maintain their excellent properties for specific applications.
1.1 Poly(arylene ether)s, PAE

Poly(arylene ether)s consist of aryl groups covalently linked by ether bonds in the polymer backbone. Several PAEs are commercially available, and the simplest one is poly(2,6-dimethyl-1,4-phenylene oxide), generally referred to as PPO, which is prepared exclusively by oxidative coupling. Apart from PPO, poly(arylene ether sulfone)s, PAES, and poly(arylene ether ketone)s, PAEKs, are the two most widely utilized engineering thermoplastic materials currently receiving much attention. PAES and PAEKs are synthesized by nucleophilic displacement of activated aromatic di-halides in polar solvents by alkali metal phenolates or Friedel –Crafts processes. General structures, trade names and thermal properties for some PAEs are illustrated in Figure 2.6
PAES and PPO are completely amorphous materials, which require only moderate molding temperatures, while PAEKs are semi-crystalline materials which require higher molding temperatures. As a result both PPO and PAES show only glass transition temperatures, T_g, however, PAEKs show both glass transition temperatures and melting temperatures, T_m as shown in Figure 2 above. In addition, the completely amorphous PAES and PPO materials have relatively poor solvent resistance, but the semi-crystalline PAEKs systems display excellent solvent stability.

**Figure 2.** General structures, trade names, and thermal properties of some commercial PAEs.
1.1.1 Poly (phenylene oxide)s, PPO

The discovery of oxidative polymerization of phenols led to the development of a new family of engineering polymers in the form of poly(phenylene oxide)s. They are basically polyethers with aromatic groups connected by oxygen linkages either at the ortho or para or both positions in the backbone. Poly(phenylene oxide)s have been synthesized in various forms since their discovery in 1916 by Hunter et al and their largest commercial usage is in Noryl (General Electric Co.).

PPOs are synthesized by oxidative coupling of 2,6-disubstituted phenols with hydrogen atoms in the 4-position, by passing oxygen through a vigorously stirred phenol solution containing cuprous chloride catalyst and an amine base.

![Scheme 1. Oxidative coupling of 2,6-dimethylphenol to form poly(phenylene oxide), PPO.](image)

The well-known poly(2,6-dimethyl-1,4-phenylene oxide) is the most common and commercially available form of poly(phenylene oxide) which is referred largely as PPO. PPO is considered to be a high-performance engineering plastic due to its high glass transition temperature ($T_g = 210 \, ^\circ C$), high mechanical strength and excellent hydrolytic stability.

PPO exhibits good dimensional stability in equipment and in parts for fluid handling applications due to the low coefficient of thermal expansion, low uniform mold shrinkage,
low creep under mechanical load, small dimensional changes in aqueous environment, and retention of high tensile and modulus values at elevated temperatures. The polymer shows the lowest water absorption rate of any engineering thermoplastic at both room and elevated temperatures. The rigid structure of the polymer backbone provides PPO with excellent high-temperature physical properties ($T_g = 210 \, ^\circ C$). Owing to these properties, PPO has found applications in a wide range of applications such as the automotive industry, business machine cases, electrical components, and gas separation membranes.

Although PPO exhibits excellent properties, its use has been somewhat restricted over the years due to the high cost of processing the materials.

1.1.2 Poly(arylene ether sulfone)s, PAES

Poly(aryl ether sulfone)s, PAES, are part of a family of amorphous polymers that are useful thermoplastics characterized by excellent mechanical properties, high glass transition temperatures ($T_g$) and good thermo-oxidative stability. Their amorphous character results in poorer chemical resistance as evidenced by solubility in polar aprotic and halogenated solvents. However, they are still used in a wide variety of industrial applications including adhesives, films, membranes and composite matrices. Figure 3 displays examples of some major commercially available PAES material.
Figure 3. Some commercially available PAES.
PAES are characterized by the presence of para-linked aromatic groups connected by ether (-O-), sulfone (-SO₂-) and in some cases alkyl groups as part of the main backbone structure of the polymer. The first commercial PAES was introduced in 1965 by Union Carbide under the trade name UDEL and has a continuous-use temperature of 150 °C and a maximum-use temperature of 170 °C. The polymer was prepared by the nucleophilic polycondensation of 4,4’-dichlorodiphenylsulfone with the alkali salt of Bisphenol-A at moderate temperatures in an aprotic solvent system such as N-methyl-2-pyrrolidinone (NMP), dimethyl acetamide (DMAc), sulfolane or dimethyl sulfoxide (DMSO). (Scheme 2)

![Scheme 2. Synthesis of poly(arylene ether sulfones by NAS.](image)

PAES are generally synthesized by two main methods; Electrophilic aromatic substitution (Friedel-Crafts acylation), EAS and Nucleophilic aromatic substitution, NAS.

Commercially, PAES are synthesized by nucleophilic aromatic substitution, also known as polyetherification, which involves the reaction of a nucleophile and an activated aryl halide in an anhydrous polar aprotic solvent in the presence of a base. The mechanism for this reaction involves two steps: 1) addition of the nucleophile to form a resonance-stabilized carbanion (Meisenheimer complex) and 2) elimination of the leaving group. A typical NAS reaction is shown in Scheme 3.
Scheme 3. Typical NAS mechanism.$^5$

The first step is generally the rate-determining step and is reversible while the second step is normally considered irreversible. As shown above, the nucleophile attacks the carbon atom of the C-X bond, which is further activated by strong electron withdrawing groups such as sulfonyl, phosphoryl or carbonyl, located in the para position. This results in a resonance-stabilized anionic intermediate (Meisenheimer complex) followed by the re-aromatization, with concurrent loss of the leaving group in the second step.

The activating group, most commonly sulfone, ketone, or phosphoryl, present in the aryl halide affects the reaction in two ways. The first one is by decreasing the electron density at the site of the reaction (at the ipso carbon) and secondly by stabilizing the anionic intermediate formed via lowering the energy of the transition state of the reaction.$^{17}$ On the
contrary, the use of electron-donating groups such as amines and methoxy groups tend to decrease the stability of the Meisenheimer intermediate forms, thus hindering substitution.

The reaction rate increases with increasing strength of the nucleophile in the order of $\text{ArS} > \text{RO} > \text{ArO} > \text{OH} > \text{ArNH}_2 > \text{NH}_3 > \text{I} > \text{Br} > \text{Cl} > \text{H}_2\text{O} > \text{ROH}$.\(^{18}\) The reactivity of the halogens was found to be in the order of $\text{F} >> \text{Cl} >> \text{Br} > \text{I}$.\(^{19}\) in spite of the strength of the carbon-fluorine bond. This suggests that the rate-determining step does not involve the departure of the leaving group. Thus the intermediate formed is better stabilized by the highly electronegative fluorine through inductive electron-withdrawing effects.\(^{5}\) The carbon atom attached directly to the fluorine becomes significantly more electrophilic than would be caused by any other halogen and consequently, more susceptible to nucleophilic attack.

The polyetherification reaction is generally carried out in the presence of either aqueous sodium hydroxide (strong base approach) or dry potassium carbonate (weak base approach) in polar aprotic solvents. Both approach undergo similar mechanisms involving first the formation of a diphenolate anion from the reaction of an aromatic bisphenol with a strong or weak base. The generated anion then reacts with an aromatic activated dihalide to produce the diaryl ether linkage. The strong base approach often yields high molecular weight polymers at high temperatures in a short period of time, but it is susceptible to side reactions and solubility problem. The weak base approach has been used successfully to obtain high molecular weight polymers without side reactions and improved solubility of the bisphenolates. The precise amount of weak base used is not extremely crucial to obtain high molecular weight as long as it is present in excess.\(^{16}\)
As depicted in Scheme 4, the polyetherification reactions can be carried out by two different routes, condensation of AA and BB monomers (a) or self-condensation of AB monomers (b).

Scheme 4. Synthesis of poly(arylene ether sulfone)s by NAS.

The first synthesis of PAES utilizing the strong base approach via NAS, was done by R. N. Johnson et al\(^{20}\) in the 1960’s and is shown in Scheme 2 above.

In 1970, Clendening et al\(^{21}\) first studied and revealed the synthesis of PAES with a weak base (K\(_2\)CO\(_3\) and KHCO\(_3\)) via NAS as shown in Scheme 5 below:
Scheme 5. Synthesis of PAES via NAS polycondensation reaction with a weak base.

Note that a majority of PAES are prepared by NAS reactions of para-activated 4,4’-monomers with bisphenolates derived from bisphenols with the activating group residing directly in the polymer backbone. A number of meta-activated 3,5-monomers have also been reported. In these systems the activating groups end up pendent to the polymer backbone. Kaiti et al\textsuperscript{22} first studied meta-activated 3,5-systems notably the 3,5-difluorodiphenyl sulfone systems via NAS. The nucleophilic aromatic substitution took place in the meta-position, relative to the activating group, in this case the sulfone group (Scheme 6).
1.1.3 Poly (aryl ether ketone)s, PAEK

Poly(aryl ether ketone)s such as PEEK, PEK, PEKEKK are linear, semi-crystalline, insoluble, high performance engineering thermoplastics exhibiting a unique combination of physical and thermal stability, chemical and solvent resistance, good mechanical properties over a wide temperature range, good fire resistance and good electrical performance. These properties make PAEKs a class of important advanced materials, which is currently receiving considerable attention for use in aerospace, automobile, nuclear, electronics and other high technology fields. They can be fabricated by conventional techniques such as extrusion and compression molding and can also be applied as matrix resins for high performance reinforced composites.

**Figure 4** displays the structures along with the $T_g$ and $T_m$ values for some of the more common PAEKs. Among these high performance polymers, poly(ether ether ketone) (PEEK) and poly(ether ketone ketone) (PEKK) are the most widely used PAEK
Compared to PAES, which are usually amorphous polymers and subject to solvent attacks, PAEKs are semi-crystalline polymers and resistant to solvent attack. However, their crystallinity and the resulting insolubility in common organic solvents along with very high melting temperatures, generally above 300 °C, makes these polymers difficult to prepare with sufficiently high molecular weight unless extreme reaction conditions are utilized.

**Figure 4.** Some major PAEKs with Tₙ and Tₘ values.¹⁹-³²
Generally, PAEKs are synthesized by one of two routes namely the phenoxide displacement of carbonyl-activated aromatic halides in which a diaryl linkage is formed or by Friedel-crafts electrophilic aromatic polyacylation condensation of aromatic ethers and diaroyl chlorides, in which a diaryl ketone linkage is formed.\textsuperscript{33-34} Similar to PAES, PAEKs can also be prepared by using either an AB monomer or a combination of AA and BB monomers.

1.2 Synthesis of Poly(arylene ether ketone)s

1.2.1 Polycondensation Nucleophilic Aromatic Substitution (NAS)

The NAS polycondensation reaction is one of the most common methods for the synthesis of PAEKs, which is similar to the polyetherification reaction for the synthesis of PAES. The mechanism involves an aryl halide that is activated by a strong electron-withdrawing group, here carbonyl, located at the ortho or para positions, relative to the halide.

Aryl fluorides have been observed to be the most effective of the aryl halides for a number of reasons such as affordability of high-molecular weight polymers.\textsuperscript{5,18,35} Typically, in NAS for PAEKs, potassium carbonate is more often used as a base to prevent side reactions of the alkali metal hydroxides\textsuperscript{36} and dipolar aprotic solvents such as DMSO, DMAc and NMP are utilized.

The first attempt to synthesize PAEKs via NAS was reported by Johnson \textit{et al}\textsuperscript{37} utilizing bisphenolate of hydroquinone and 4,4’-difluorobenzophenone in the presence of NaOH as the base and DMSO as the solvent. High molecular weight polymers were not obtained by this method due to premature crystallization and insolubility of the polymers in DMSO. The observed melting temperature of the polymer was 350 °C with a glass
transition temperature of 160 °C.\textsuperscript{10,38} Owing to these problems, Attwood et al,\textsuperscript{38} and Rose\textsuperscript{39} changed the solvent to diphenyl sulfone and used the weak base Na\textsubscript{2}CO\textsubscript{3} (Scheme 7). The polymerization was carried out near the melting point of the polymer to ensure solubility and high molecular weight PEEK was obtained.

**Scheme 7.** Synthesis of poly(ether ether ketone) via NAS.

Imperial Chemical Industries, ICI, first filed a patent in 1978 to commercialize PEEK under the trade name VICTREX using this method and obtained the patent in 1982. In order to obtain high molecular weight polymers, a careful optimization of reaction conditions is required, since at high temperatures side reactions such as ether exchange and cleavage become significantly pronounced.\textsuperscript{57}

The kinds of monomers that can produce high molecular weight polymers with this method are the expensive difluoro monomers. For carbonyl activated dihalides the less reactive dichloro monomers have failed to produce high molecular weight polymers, partly due to side reactions such as single electron transfer.\textsuperscript{40} The expensive difluoro monomers make the synthesis of PAEKs via NAS less friendly industrially. As a result the need for a lower cost route to PAEKs via NAS has been investigated over the years. The first activated non-fluoro monomer via NAS was reported by Fukawa \textit{et al},\textsuperscript{41} who successfully prepared high molecular weight PEK with inherent
viscosity of 1.15 dL/g using 4,4’-dichlorobenzophenone as shown in Scheme 8. The polymerization reaction was carried out in diphenyl sulfone at high temperatures (2 hours at 280 °C, 1 hour at 300°C, and then 1 hour at 320 °C) in the presence of Na₂CO₃ and SiO₂/CuCl₂ catalyst. The silicon dioxide was removed by washing the product with 4 % aqueous NaOH solution at 60 °C. They proposed that the intermediate formed in this reaction between the 4,4’-dichlorobenzophenone and the silanol on the surface of the silica was a silyl ether.

Scheme 8. Synthesis of poly(ether ketone) via NAS.

The use of fluorides as promoting agents has also been reported to successfully polymerize dichloro monomers with bisphenols to achieve high molecular weight polymers. What the fluoride ion does is to promote the displacement of the chloride site to form a more reactive fluoride site, which then reacts with the phenoxide anion to form high molecular weight polymers. It has been reported that adding 5-10 % of a phase transfer catalyst, such as N-alkyl-4-(dialkylamino)pyridium chloride, significantly increase the nucleophilicity and solubility of the phenoxide anion. This leads to a tremendous reduction
of the reaction time (about 5-fold) to achieve the same molecular weight compared to the un-catalyzed reaction.\textsuperscript{43}

In another study Kricheldorf \textit{et al}\textsuperscript{44} reported using trimethylsilylated phenols to react with activated difluoro monomers such as difluorobenzophenone in the presence of a catalytic amount of CsF to prepare poly(ether ketone)s (\textbf{Scheme 9}). The polymers were prepared in the melt without any solvent.

![Scheme 9. Synthesis of poly(ether ether ketone) via NAS in the presence of CsF.](image)

Recently, carbonyl groups located \textit{meta} to the dihalides have been found to sufficiently activate these dihalides towards NAS to allow the synthesis of PEEK analogues. van Beek and Fossum\textsuperscript{45} reported the synthesis of poly(arylene ether)s with pendant benzoyl groups via NAS. The polymerization involved reaction of 3,5-difluorobenzophenone with a variety of bisphenols in the presence of K\textsubscript{2}CO\textsubscript{3} and NMP/toluene at 185 °C to achieve high molecular weight amorphous polymers (\textbf{Scheme 10})
The polymers displayed glass transition temperatures ranging from 111-133 °C, but showed excellent thermal stability with 5 % weight loss temperatures in the range of 488 °C to 494 °C under nitrogen atmosphere and from 438 °C to 482 °C under air atmosphere.

1.3 Modification Chemistry

The modification of polymer systems, without significantly altering their physical and other properties, has attracted much attention over the years. This has been done by introducing functionalities onto the polymer chain as future sites for cross-linking or grafting of side chains with desired characteristics, without changing the polymer backbone. The functional groups can be introduced prior to (“pre”) or after polymerization is completed (“post”). Both routes have been used to modify polymers as they both serve to introduce functional groups onto the polymer backbone to enhance their properties and also act as access points to further modification chemistries. As shown in Scheme 11, the
“pre”- functionalization approach involves introduction of the desired functional group into the polymer at the monomer stage whilst the “post”-functionalization approach involves introduction of the desired functional group at the polymer stage.

Scheme 11. Modification chemistry utilizing “Pre” and “Post” functionalization.

Each of these methods has its own advantages and disadvantages. For example, the “pre”- functionalization approach involves multistep synthetic procedures, which might lead to undesired side reactions that can interfere with the polymerization process and kinetics. There is also the possibility of an offset of stoichiometry, which might result in low molecular weight polymers. The “post”- polymerization approach is the most widely used method as it overcomes the problems associated with the functional monomer approach. However it faces some problems such as the insufficient installation of
1.4 Functionalization of Poly(arylene ether)s, PAEs

Functional groups can be introduced to PAE systems prior to or after polymerization to extend the range of potential application of these high performance materials. A wide range of functional groups have been incorporated into PAE systems via both routes including: sulfonic acids, aldehydes, amines, alcohols, amides, ketones, and phosphoric acids. Most of the functionalizations were done on para-activated PAE systems, where the functional groups are directly incorporated onto the polymer backbone.

The introduction of functionality to monomers prior to polymerization is increasingly being explored in PAE synthesis. This is strongly evident in polymers that undergo polycondensation reactions as this strategy precisely controls the amount and location of functional groups along the polymer backbone. The criteria for introducing functionalities during the monomer stage require the functional groups to be able to survive the polymerization process. As a result, not all functional groups can be introduced at the monomer stage, some preferably at the polymerization stage.
**Figure 5.** Routes to “Pre” and “Post” chemistry of PAES and PAEK.

The post modification approach is the most common method used to introduce some functionality onto the polymer backbone. Here, the functional groups are either located on electron poor rings with anionic reactions or on electron rich rings with electrophilic chemistry (Figure 5).\(^{46}\) This approach overcomes the limited number of functional monomers that can survive the polymerization conditions,\(^{16}\) but results in substantial changes in the polymer backbone. This might lead to significant changes in the thermal and mechanical properties of these materials.
The recent development of *meta*-activated PAE systems\(^{22,45,51-53}\) has provided polymer chemists with a powerful tool to introduce functional groups to PAE systems without significantly altering the polymer backbone as a result of either “pre”- or “post”-modification chemistry. In these systems the functional groups are located pendent to the polymer backbone, which provides easy access for further modification without significantly disrupting the backbone structure. Thus the ideal situation would be synthesizing a functionalized monomer system that can easily allow “pre”- and “post”-modification.\(^{46}\)

### 1.4.1 “Pre”-Modification Chemistry

Parthiban *et al*,\(^{49}\) utilized pre-modification chemistry to synthesize two isomeric amino-functionalized poly (arylene ether ketone)s from activated difluoro monomers, namely 2-amino-1,4-bis-(4-chlorobenzoyl)benzene and 5-amino-1,3-bis-(4-fluorobenzoyl)benzene with bisphenol-A as the nucleophilic reaction partner (*Scheme* 12). The functionalized polymers showed higher glass transition temperatures and were more thermally stable compared with non-aminated polymers based on 1,4-bis-(4-chlorobenzoyl)benzene or 1,3-bis-(4-fluorobenzoyl)benzene with Bisphenol-A. The advantage of the amino groups is their potential transformation into various functionalities that can allow careful tuning of the thermal and mechanical properties of PAEKs.

1.4.2 “Post” - Modification Chemistry

Liu et al.\textsuperscript{47} in 2007 reported the sulfonation reactions of a series of PEEKs with various phenyl substituents such as phenyl, methylphenyl, trifluoromethylphenyl, and phenoxyphenyl via post sulfonation route under mild reaction conditions (Scheme 13). PEKs with phenyl and 3-methylphenyl pendent groups exhibited controlled sulfonation sites with a single substituted sulfonic acid per repeat unit, leading to sulfonated polymers with well-defined structures normally achieved by a pre-functionalization route. A series of both homo- and copolymers based on phenyl and 3-methylphenyl groups were prepared by controlling the length of unsulfonated segments. The polymers showed excellent mechanical properties, good thermal and oxidative stability, lower methanol permeability compared to Nafion-117 and good dimensional stability in hot water, which makes them...
promising proton exchange membrane materials for proton exchange membrane fuel cells and direct methanol fuel cells.

**Scheme 13.** “Post” modification of PAEK via “post” sulfonation route.
A recent study describing a hybrid “pre”/”post” approach was performed by Tatli et al.\textsuperscript{51} utilizing meta-activated NAS polycondensation reactions of 3,5-difluoro aromatic monomers. These monomers provide an alternative and powerful platform for the introduction of functional groups into PAE systems compared to the analogue 4,4’-difluoro aromatic monomers. The polycondensation reaction involved reaction of a new aryl difluoride monomer, 3,5-difluoro-1-((3-iodophenyl)sulfonyl)benzene and bisphenol-A in the presence of K\textsubscript{2}CO\textsubscript{3} and NMP. The resulting iodo functionalized PAES were then modified via two cross-coupling reactions, Suzuki-Miyaura and Heck as illustrated in Scheme 14. The polymers exhibited moderate thermal stability above 400 °C in air and nitrogen with glass transition temperatures ranging from 131 °C to 165 °C.

\textbf{Scheme 14.} Post Modification of meta-activated PAE system, Iodo conversion via Suzuki-Miyaura and Heck cross-coupling reactions.
1.5 B₃ Monomers as a Route to Functional PAES and PAEK

A BB’B” monomer is a type of B₃ monomer that has unequal reactivity of the B functional groups. This type of monomer can be used to synthesize linear and hyperbranched polymers by utilizing the differences in reactivity of the B functionalities. At lower temperature conditions both B and B’ groups can react with an A₂ monomer resulting in a linear polymer, while at higher temperature conditions, the lowest reactivity group, B’’ can react resulting in branched polymers.

In 2009, Raghavapuram⁵⁴ investigated two BB’B’’ monomers, 4’, 3, 5-trifluorodiphenylsulfone and 4’, 3, 5-trifluorobenzophenone, both of which were designed to undergo NAS reactions to synthesize hyperbranched poly(arylene ether)s via an A₂ + BB’B’’ approach (Scheme 15).

![Scheme 15. Polymerization reaction by an NAS A₂ + BB’B’’ approach.](image)

The polymers obtained were soluble, with increased glass transition temperatures and thermal stabilities as the degree of branching (DB) increased. The T₉ ranged from 126 °C
to 177 °C, while the 5 % weight loss temperatures also ranged from 372 °C to 514 °C under N₂ and from 229 °C to 510 °C under air atmosphere.

1.6 Current Project

The current project is based on previous investigations dealing with the synthesis of hyper-branched poly(arylene ether)s from A₂ + B₃ systems. During the study it was observed that the aryl-fluoride moieties in the B₃ monomers (Figure 6) showed considerable differences in reactivity as illustrated in Scheme 16. The para-fluorine was considerably more reactive than the meta-fluorines, which are of equivalent reactivity after substitution at the para-position. Upon substitution of one of the meta-fluorines, the other one becomes significantly less reactive.⁵⁴ These differences in reactivity can be exploited to introduce some functional groups and prepare the corresponding PAE via a “one-pot” procedure.

Figure 6. Reactivity of the three aryl-fluorides in 4’,3,5-trifluorodiphenylsulfone, 1 and 4’,3,5-trifluorobenzophenone, 2.
Scheme 16. Reactivity differences in BB’B” monomers utilized for the synthesis of functional PAES and PAEK.

As illustrated in Scheme 17, the method that will be utilized is termed Reactivity Ratio Controlled Polycondensation (RRCP). This method will be used to prepare “pre”-functionalized PAES and PEEK analogues via a “one-pot” procedure. In the first step, compounds 1 and 2 (Figure 6) will be reacted separately with a nucleophile (e.g. phenoxide) at a relatively low temperature where only $k_1$ is operative. Upon reaching nearly quantitative conversion, Bisphenol-A will be added and the reaction temperature will be increased to allow the displacement of the remaining meta-activated fluorines. To the best of our knowledge this approach to synthesize functionalized PAES and PEEKs, via “one-pot” using BB’B” monomers, has yet not been studied. The physical properties, such as solubility, polydispersity, thermal stability and glass transition temperature, $T_g$ of the resulting linear polymers with pendant phenoxy functional groups will be investigated.
2. EXPERIMENTAL

2.1 Materials

All reactions were carried out under a nitrogen atmosphere. Reagent-grade anhydrous potassium carbonate powder (K$_2$CO$_3$) and calcium chloride (CaCl$_2$) were dried at 130 °C in an oven before use. 4', 3, 5-trifluorodiphenylsulfone (1) was synthesized according to a literature procedure.$^{54}$ Anhydrous aluminium chloride (AlCl$_3$), 4-tert-butyl phenol, 3-aminophenol, 3-methylphenol, 4-methoxyphenol and 4,4'-difluorobenzophenone were purchased from Sigma Aldrich Chemical Co. and used as received. Bisphenol-A was purchased from Sigma Aldrich Chemical Co., recrystallized from toluene and dried under vacuum prior to use. $N$-Methylpyrrolidinone (NMP) was purchased from Sigma Aldrich Chemical Co., dried and distilled over CaH$_2$ under nitrogen prior to use. Phenol was purchased from Sigma Aldrich Chemical Co. and distilled under vacuum prior to use. 4-Bromophenol was purchased from Sigma Aldrich Chemical Co., recrystallized from hexanes and dried under vacuum prior to use. Fluorobenzene and 3, 5-difluorobenzoyl chloride were purchased from Oakwood Products and used as received.

2.2 Instrumentation

GC/MS analyses were carried out using a Hewlett-Packard (HP) 6890 Series GC with auto injection and a HP 5973 Mass Selective Detector/Quadrupole system.

$^{1}$H and $^{13}$C NMR spectra were acquired using an AVANCE 300 MHz instrument operating at 300, and 75.5 MHz, respectively. Samples were dissolved in appropriate deuterated solvents (DMSO-$d_6$ or CDCl$_3$), at a concentration of (~30 mg / 0.6 mL).
Size Exclusion Chromatography (SEC) analysis was performed using a system consisting of a Viscotek Model 270 Dual Detector (viscometer and light scattering) and a Viscotek Model VE3580 refractive index detector. Two Polymer Laboratories 5 μm PL gel Mixed C columns (heated to 35 ºC) were used with tetrahydrofuran/5% (v/v) acetic acid as the eluent and a GPCMax VE-2001 with pump operating at 1.0 mL/minute. Weight average molecular weights, Mw, was determined via light scattering signal while the dispersity was determined via the refractive index (RI) signal. Calibration was done using polystyrene standards.

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

Melting points were determined on a MEL-TEMP apparatus and are uncorrected. Elemental analyses were obtained from Midwest Microlabs, Inc., Indianapolis, IN.

2.3. “Pre” - Functionalization of Compound 1 with 4 - tert - Butylphenol (3d) via “One-Pot” Approach

Into a 25 mL round-bottomed (RB) flask, equipped with a stir bar, condenser and a nitrogen gas inlet were placed 0.302 g (1.11 mmol) of 4’, 3, 5-trifluorodiphenylsulfone (1), 0.167 g (1.11 mmol) of 4-t-butyl phenol (3d), 1.75 mL of N-methyl-2-pyrrolidone (NMP) and 0.239 g (1.73 mmol) of K2CO3. The reaction mixture was stirred at 45 °C for 10 days at which point GC/MS and NMR spectroscopy indicated quantitative conversion to the desired mono-substituted product with traces of unreacted starting materials and di-substituted products. At this point the reaction was stopped, cooled to room temperature, precipitated from acidified distilled water and extracted three times with chloroform (45
mL). The organic layers were combined, dried over MgSO4 and evaporated to dryness via the rotary evaporator followed by drying in vacuo to obtain 0.2145 g (48 %) of a sticky white solid. \textbf{\textsuperscript{13}C-Dept 90 NMR} (75.5 MHz, DMSO-\textit{d6}, δ): 109.7 (t), 111.4 (dd), 117.9 (s), 120.3 (s), 127.5 (s), 131.0 (s).

\textbf{2.4 Synthesis of 4', 3, 5-trifluorobenzophenone, 2}

In a 100 mL RB flask, equipped with an addition funnel, condenser, a stir bar, a nitrogen gas inlet and a CaCl2 drying tube were placed 9.10 g (68.0 mmol) of AlCl3 and 25 mL of fluorobenzene. 3,5-difluorobenzoylchloride (6.50 mL, 55.0 mmol) was measured under a nitrogen blanket and added to the addition funnel containing 28 mL of fluorobenzene. The resulting mixture was added to the flask, drop wise, over 1 hour at room temperature and maintained with stirring for 24 hours. The reaction mixture was poured into an excess of acidified deionized water (300 mL) and extracted into chloroform (150 mL). The organic layer was washed three times with DI water, dried over MgSO4 and evaporated to dryness via the rotary evaporator followed by drying in vacuo to obtain 11.82 g (91 %) of an off-white solid. The crude product was recrystallized from ethanol and then from ethanol/water to afford 8.02 g (62 %) of white needle-like crystals with a melting point of 65-67 °C. \textbf{\textsuperscript{1}H-NMR} (300 MHz, CDCl3, δ): 7.10 (tt, \textit{J} = 8.5, 2.4 Hz, 1H), 7.21-7.29 (m, 2H), 7.30- 7.38 (m, 2H), 7.87- 7.93 (m, 2H). \textbf{\textsuperscript{13}C NMR} (75.5 MHz, CDCl3, δ): 107.7 (t), 112.7 (dd), 115.8 (d), 132.6 (d), 132.6 (d), 140.4 (t), 162.7 (dd), 165.8 (d), 192.4 (t).
**Elemental Analysis:** Calc. Anal. For C_{13}H_{7}F_{3}O: C, 66.1; H, 2.99; Found: C, 66.03; H, 2.87.

2.5 “Pre”-Functionalization of Compound 2 with 3-Aminophenol (3f) As a Model Study.

Into a 25 mL RB flask, equipped with a stir bar, condenser and a nitrogen gas inlet were placed 0.352 g (1.50 mmol) of 4’, 3, 5-trifluorobenzophenone (2), 0.163 g (1.50 mmol) of 3-aminophenol (3f), 2.50 mL of N-methyl-2-pyrrolidone (NMP) and 0.307 g (2.20 mmol) of K_{2}CO_{3}. The reaction was carried out at 90 °C for 24 hours, after which an aliquot of the reaction mixture analyzed by GC/MS showed about 15% conversion to the desired product. The temperature of the reaction mixture was raised to 110 °C and continuously monitored using GC/MS until quantitative conversion to the desired mono-substituted product. The reaction was stopped, cooled to room temperature, precipitated from distilled water and extracted into chloroform. The chloroform layer was dried over MgSO_{4} and evaporated to dryness via the rotary evaporator followed by drying in vacuo to obtain 0.145 g (30 %) of a dark brown solid. ^{13}\text{C-dept 90 NMR} (75.5 MHz, DMSO-\text{d}_{6}, \delta): 105.5 (s), 107.2 (s), 108.1 (t), 111.0 (s), 112.9 (dd), 117.4 (s), 130.7 (s), 132.9 (s).

2.6 General Procedure for the “Pre”-Functionalization of Compound 2 via a “One-Pot”, Two-step Approach

A typical “pre”-functionalization of compound 2 via a “one-pot” approach will be described using phenol (3a).

**Step 1:** In a 10 mL RB flask, equipped with a stir bar, condenser and a nitrogen gas inlet, were placed 0.236 g (1.00 mmol) of 4’, 3, 5-trifluorobenzophenone (2), 0.097 g (1.03
mmol) of phenol (3a), 1.6 mL of N-methylpyrrolidone (NMP) and 0.207 g (1.50 mmol) of potassium carbonate (K₂CO₃). The reaction flask was immersed in a preheated oil bath and stirred vigorously at 110 °C until complete conversion to the desired mono-substituted product was achieved as evidenced by GC/MS analysis.

**Step 2:** Into the same reaction flask were added 0.228 g (1.00 mmol) of Bisphenol-A, and 0.415 g (3.00 mmol) of K₂CO₃. The reaction temperature was raised to 185 °C and maintained for 24 hours. The reaction was cooled to room temperature, precipitated from acidified distilled water and isolated by vacuum filtration to afford 0.443 g (89%) of a beige colored solid. The solid was dissolved in THF, precipitated from water and re-precipitated from chloroform into hexane: isopropanol mixture (50:50), filtered, and dried to afford 0.349 g (70 %) of 4a as a beige solid. **¹H NMR** (300 MHz, CDCl₃, δ): 1.68 (s, 6H); 6.88-7.40 (b, 18H); 7.79-7.82 (b, 2H) **¹³C NMR** (75.5 MHz, CDCl₃, δ): 31.0, 42.3, 112.0, 113.9, 117.0, 118.9, 119.7, 120.2, 128.3, 130.1, 131.3, 132.5, 140.5, 146.3, 154.0, 155.4, 158.8, 161.9, 194.0

4b (78 %). **¹H NMR** (300 MHz, CDCl₃, δ): 1.67 (s, 6H); 2.35 (s, 3H); 6.87-7.28 (b, 17); 7.79-7.81 (b, 2H) **¹³C NMR** (75.5 MHz, CDCl₃, δ): 21.4, 31.0, 42.3, 112.1, 113.8, 117.0, 117.2, 118.9, 120.8, 125.5, 128.3, 129.7, 131.2, 132.5, 140.1, 140.5, 146.3, 154.0, 155.7, 158.8, 162.0, 194.0

4c (80 %). **¹H NMR** (300 MHz, CDCl₃, δ): 1.68 (s, 6H); 3.82 (s, 3H); 6.81-7.28 (b, 17H); 7.77-7.79 (b, 2H) **¹³C NMR** (75.5 MHz, CDCl₃, δ): 31.0, 42.3, 55.6, 112.1, 113.8, 115.1, 116.2, 118.8, 121.7, 128.3, 130.7, 132.5, 140.4, 146.3, 148.4, 154.0, 156.7, 158.7, 162.8, 194.0
4d (74 %). $^1$H NMR (300 MHz, CDCl$_3$, δ): 1.34 (s, 9H); 1.68 (s, 6H); 6.87-7.42 (b, 17H); 7.78-7.80 (b, 2H) $^{13}$C NMR (75.5 MHz, CDCl$_3$, δ): 31.1, 31.5, 34.4, 42.3, 112.1, 113.8, 116.8, 118.9, 119.8, 126.9, 128.3, 131.0, 132.5, 140.4, 146.3, 147.7, 152.8, 154.1, 158.7, 162.3, 194.0

4e (76 %). $^1$H NMR (300 MHz, CDCl$_3$, δ): 1.68 (s, 6H); 6.85-7.50 (b, 17H); 7.79-7.82 (b, 2H) $^{13}$C NMR (75.5 MHz, CDCl$_3$, δ): 31.0, 42.3, 112.0, 113.8, 116.9, 117.0, 118.9, 119.7, 128.3, 131.0, 132.5, 133.0, 140.7, 146.6, 154.0, 158.0, 159.0, 162.1, 194.0

4f (75 %). $^1$H NMR (300 MHz, CDCl$_3$, δ): 1.67 (s, 6H); 3.77 (s, 2H); 6.36-7.28 (b, 17H); 7.78-7.80 (b, 2H) $^{13}$C NMR (75.5 MHz, CDCl$_3$, δ): 31.0, 42.3, 106.7, 109.9, 111.4, 112.1, 113.8, 117.1, 118.9, 128.3, 130.6, 131.1, 132.4, 140.4, 146.3, 148.3, 154.0, 156.4, 158.7, 161.9, 194.1

2.7 Random Co-polymerization of “Pre”-Functionalized Compound 2 with 3-methylphenol (3b) and 4,4'-difluorobenzophenone via a “One-Pot” Two-step Approach

A co-polymerization reaction was done by using a 50:50 mole ratio of “pre”-functionalized compound 2 with 3b and 4,4'-difluorobenzophenone as the co-monomer. The copolymer synthesis was carried out using the same procedure used for the homopolymerization reactions.

**Step 1:** In a 10 mL RB flask, equipped with a stir bar, condenser and a nitrogen gas inlet, were placed 0.300 g (1.27 mmol) of 4’, 3, 5-trifluorobenzophenone (2), 0.141 g (1.31 mmol) of 3-methylphenol (3b), 2.0 mL of N-methylpyrrolidone (NMP) and 0.267 g (1.93 mmol) of potassium carbonate (K$_2$CO$_3$). The reaction flask was immersed in a preheated...
oil bath and stirred vigorously at 110 °C until complete conversion to the desired mono-
substituted product was achieved as determined via GC/MS analysis.

**Step 2:** Into the same reaction flask were added 0.580 g (2.54 mmol) of bisphenol-A, 0.277
 g (1.27 mmol) of 4,4’-difluorobenzophenone and 1.058 g (7.66 mmol) of K₂CO₃. The
reaction temperature was raised to 185 °C and maintained for 24 hours. The reaction was
cooled to room temperature, precipitated from acidified distilled water and isolated by
vacuum filtration to afford 1.03 g (85 %) of a light brown solid. The solid was dissolved in
2.0 mL of 5 % acetic acid in THF, precipitated from water and reverse precipitated from
THF into hexane: isopropanol mixture (50:50), filtered, and dried to afford 0.873 g (72 %)
of 5b as a light-brown solid. ¹H NMR (300 MHz, CDCl₃, δ): 1.68-1.74 (b, 6H); 2.35-2.38
(b, 1.5H); 6.77-7.83 (b, 17.5) ¹³C NMR (75.5 MHz, CDCl₃, δ): 21.4, 31.0, 42.3, 112.1,
113.9, 117.0, 117.2, 118.9, 119.2, 120.9, 125.5, 128.3, 129.8, 131.1, 132.2, 132.5, 140.3,
140.4, 146.3, 146.7, 153.5, 154.0, 155.3, 158.7, 161.4, 162.1, 194.1, 194.3
3. RESULTS AND DISCUSSION

3.1 Monomer Synthesis and Properties.

The main goal of this project was to utilize the differences in reactivity of the three unique aryl fluoride positions in 4’, 3, 5 - trifluorodiphenyl sulfone, 1, and 4’, 3, 5, - trifluoro benzophenone, 2, to synthesize functional linear PAES and PAEKs via a “one-pot” procedure (Figure 7). The reactivity of the fluorines in these monomers has been probed by 13C and 19F NMR spectroscopy and kinetic studies have also been performed on them. These monomers are examples of B3 monomers, which have been used previously to synthesize hyper-branched polymers.54 The data given in Table 1 confirm that the para-F is more reactive than the meta-fluorines, which means that at lower temperatures the para-F is the first to undergo reaction. At higher temperatures one of the meta-F reacts with subsequent reduction in the reactivity of the other meta-F. By raising the temperature the reactivity of the other meta-F could be enhanced.54 Utilizing these differences in reactivity, completely linear polymers could be synthesized by first converting the para-F to a desired functional group and subjecting the 3, 5-difluoro ring (upper ring) to a typical NAS polycondensation reaction.
Figure 7. B₃ monomers for the synthesis of “pre”-functionalized PAES and PAEK.

The kinetic data also support the fact that the para-F of compound 1 is more reactive than the para-F of compound 2, which means less energy is required to displace the para-F in compound 1 than in compound 2 as shown in Table 1. This makes compounds 1 and 2 potential candidates to synthesize functional linear PAES and PAEKs via both “pre-” and “post-” functionalization approach in “one-pot”. This is what we called Reactivity Ratio Controlled Polycondensation (RRCP) reaction.

Table 1. ¹⁹F, ¹³C NMR chemical shifts (ppm) and Activation Energies (kcal/mol) of the electrophilic sites of compound 1 and 2.⁵⁴

<table>
<thead>
<tr>
<th>Compound</th>
<th>¹⁹F Chemical Shifts</th>
<th>¹³C Chemical Shifts</th>
<th>Activation Energy</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>para-F</td>
<td>meta-F</td>
<td>para-C-F</td>
</tr>
<tr>
<td>1</td>
<td>-104.6</td>
<td>-106.3</td>
<td>166.1</td>
</tr>
<tr>
<td>2</td>
<td>-106.3</td>
<td>109.3</td>
<td>166.2</td>
</tr>
</tbody>
</table>
3.2 “Pre” - Functionalization of Compound 1 with 4 - tert - Butylphenol (3d) via “One-Pot” Approach

With this purpose in mind the next step was to explore the feasibility of “pre”-functionalization of compound 1 via the “one-pot” process. An NAS reaction involving compound 1 and 4-tert-butyphenol (3d) was carried out using K₂CO₃ in NMP as the reaction solvent at 45 °C for 10 days (Scheme 18). The progress of the reaction was monitored by GC/MS and the results are shown in Table 2.

After 4 days of reaction time, a 1:1 mole equivalent of compound 1 with 3d provided a mixture of 2.95 % of 3d, 11.05 % 1, 83.56 % of 1dₓ, and 2.44 % 1dᵧ, which indicates that the para-F is more reactive.

Scheme 18. Synthetic procedure for “pre”-functionalized compound 1 with 3d.
Table 2. GC/MS Summary of Pre-functionalization of compound 1 with 3d.

<table>
<thead>
<tr>
<th>Time (Days)</th>
<th>% 1</th>
<th>% 1d_x</th>
<th>% 1d_y</th>
<th>% 1d_z</th>
</tr>
</thead>
<tbody>
<tr>
<td>4</td>
<td>11.05</td>
<td>83.56</td>
<td>2.44</td>
<td>-</td>
</tr>
<tr>
<td>6</td>
<td>3.83</td>
<td>94.30</td>
<td>1.34</td>
<td>-</td>
</tr>
<tr>
<td>7</td>
<td>3.62</td>
<td>93.53</td>
<td>1.70</td>
<td>1.15</td>
</tr>
<tr>
<td>10</td>
<td>3.05</td>
<td>93.25</td>
<td>2.00</td>
<td>1.70</td>
</tr>
</tbody>
</table>

As shown in Scheme 18 and Table 2, two kinds of mono-substitution occurred, i.e, para-substitution (1d_x) and the meta-substitution (1d_y). The meta-substitution tended to decrease as the reaction progressed with a subsequent increase in the formation of di-substitution (1d_z). After 10 days the reaction was stopped and the contents of the reaction flask were analyzed with $^{13}$C DEPT 90 NMR spectroscopy. An overlay of the spectra of monomer 1 and the products from the reaction flask are shown in Figure 8.
Figure 8. Overlay of the 75.5 MHz $^{13}$C DEPT 90 NMR (DMSO-$d_6$) spectra of compound 1 (a) and the products from the reaction shown in Scheme 18 (b).

The carbon spectrum ($^{13}$C DEPT 90 NMR) of the product from the reaction shown in Scheme 18 shows six major signals representing 6 different CH groups. All the signals arising from the monomer 1 are present in the spectrum of the product with the emergence of two new distinct signals at 117.9 ppm and 127.5 ppm, representing the carbons labeled e and f, respectively. These signals clearly indicate that the major substitution occurred at the $para$-F. Carbon a appears as a triplet at 109.7 ppm in both spectra and carbon b appears at 111.4 ppm as a doublet of doublets in both spectra. Carbons c and d, which appear as doublets at 131.7 ppm and 117.5 ppm in monomer 1 collapsed into singlets at 131.0 ppm and 120.3 ppm, respectively. The remaining signals in the spectrum of the product from the reaction arise from the unreacted monomer 1, $meta$-F substitution, 1dy and di-substitution at both the $para$-F and $meta$-F, 1dz.
The reason for the inability to achieve exclusive mono-substitution at the \textit{para}-position can be explained by the activation energy difference between the \textit{para}- and \textit{meta}-positions. As shown in Table 1, the kinetic data on compound 1 suggest that the energy required to substitute the \textit{para}-F is about 17.5 kcal/mol, while 21.4 kcal/mol was required to substitute one of the \textit{meta}-F’s. Since the energy difference between the \textit{para}-F and \textit{meta}-F is not large enough (~3.9 kcal/mol), an attempt to achieve exclusive mono-substitution in this system is highly unlikely.

The inability to achieve exclusive mono-substitution with compound 1 makes it difficult to synthesized pre-functionalized PAES via a “one-pot” approach since any unreacted starting material will result in significant crosslinking and gelation. In addition, the presence of appreciable amounts of di-substitution would lead to lower molecular weight polymers. As such, our efforts turned to another B$_3$-type monomer, 4’, 3, 5,-trifluorobenzophenone, 2.
3.3 Synthesis of 4’, 3, 5-Trifluorobenzophenone, 2, by Friedel-Crafts Acylation

The general procedure for Friedel-Crafts acylation outlined by Olah in 1973 was followed to synthesize compound 2.\textsuperscript{55-56} The monomer was prepared by the reaction of 3,5-difluorobenzoyl chloride with fluorobenzene in the presence of a slight excess of aluminum chloride (Scheme 19). After 24 hours of reaction time, an aliquot of the reaction mixture was analyzed using GC/MS and the results showed complete conversion to the desired product, 4’, 3, 5-trifluorobenzophenone, 2.

\begin{center}
\begin{tikzpicture}
\node (A) at (0,0) {\includegraphics[width=0.5\textwidth]{scheme19.png}};
\end{tikzpicture}
\end{center}

\textbf{Scheme 19}. Synthesis of 4’, 3, 5-trifluorobenzophenone, 2 via Friedel-Craft Acylation.

After work-up, which involved pouring the reaction mixture into acidified distilled water and ice, extraction into chloroform and evaporation to dryness via the rotary evaporator, followed by drying in \textit{vacuo}, 11.8 g (91\%) of an off-white solid was obtained. The crude product was subjected to recrystallization (twice) using ethanol and ethanol/water to obtain 8.02 g (62\%) of 2 as white needle-like crystals with a melting point of 65-67 °C.
The structure of compound 2 was confirmed by $^1$H and $^{13}$C CPD NMR spectroscopy, GC/MS and elemental analysis. The $^1$H and $^{13}$C NMR spectra of compound 2 are illustrated in Figure 9 and Figure 10, respectively. The $^1$H NMR spectrum of compound 2 displays four unique signals. The most up-field signal, “a” appears as a triplet of triplets due to coupling with two ortho-F’s with equal coupling constants ($^3J_{C-F} = 8.50$ Hz) and two meta-H’s with equal coupling constants ($^4J_{H-H} = 2.40$ Hz). The signals, “b” and “d” all appear as complex series of partially over-lapping second-order multiplets between 7.21 – 7.38 ppm. The signal “c” appears also as complex multiplet between 7.87 – 7.93 ppm.

![Diagram of compound 2]

Figure 9. 300 MHz $^1$H NMR (CDCl$_3$) spectrum of compound 2.

The $^{13}$C NMR spectrum of compound 2 shows nine unique signals with some splitting in some of the signals, due to coupling with the fluorine atoms (Figure 10). The signal, “a” at 107.7 ppm appears as a triplet due to coupling with two ortho-F atoms ($^2J_{C-F} = 25.3$ Hz). Carbons b, at 162.7 ppm ($^1J_{C-F} = 252$ Hz, $^3J_{C-F} = 11.9$) and carbon c, at 112.7 ppm ($^2J_{C-F} = 26.1$ Hz, $^4J_{C-F} = 8.84$ Hz) both appear as a doublet of doublets due to coupling with two non-equivalent fluorine atoms. Carbon d, at 140.4 ppm ($^3J_{C-F} = 7.73$ Hz) appears
as a triplet due to coupling with two equivalent fluorine atoms at the *meta*-position of the upper phenyl ring. The carbonyl carbon \( e \), at 192.4 ppm \( (J_{C\text{-}F} = 2.34 \text{ Hz}) \) appears as a triplet due to coupling with the two *meta*-F atoms on the upper phenyl ring. Carbons \( f \) and \( g \) overlap at 132.6 ppm \( (J_{C\text{-}F} = 3.19 \text{ Hz} \) and \( J_{C\text{-}F} = 9.33 \text{ Hz} \) respectively) and both appear as a doublet with the quartenary carbon \( f \) signal (lower intensity) sandwiched between carbon \( g \) signal. Carbon \( h \) and \( i \) both appear as doublets at 115.8 ppm \( (J_{C\text{-}F} = 22.11 \text{ Hz}) \) and 165.8 ppm \( (J_{C\text{-}F} = 255.53 \text{ Hz}) \) respectively.

Figure 10. 75.5 MHz \(^{13}\text{C}\) NMR (CDCl\(_3\)) spectrum of compound 2.
3.4 “Pre”-Functionalization of Compound 2 with 3-Aminophenol (3f) As a Model Study.

Since exclusively mono-substituted product could not be achieved with compound 1 our attention turned to compound 2. First, compound 2 was reacted with 1 equivalent of 3-aminophenol (3f) under typical NAS reaction conditions, using K₂CO₃ and NMP at 110 °C as shown in Scheme 20. The progress of the reaction was monitored by both GC/MS and ¹³C DEPT 90 NMR spectroscopy.

Scheme 20. Synthetic procedure for the “pre”-functionalization of 2 with 3f.

After 5 days nearly quantitative conversion was observed via analysis of an aliquot via GC/MS. ¹³C DEPT 90 NMR spectroscopy was used to confirm the results obtained from the GC/MS. As shown in Figure 11, there are 4 new CH signals arising from 3f together with the 4 CH signals from the monomer 2. Carbons a, b, c, and d in the DEPT 90 ¹³C NMR spectrum of the monomer, 2 appear as multiplets due to splitting with the meta-F and para-F. Upon displacement of the para-F, the signals for carbons c and d collapsed into singlets. Carbons a and b at 108.1 ppm and 112.9 ppm, respectively, in the
monomer unit remained multiplets in the product due to coupling with the fluorines. This shows that only the *para*-F was substituted during the reaction. The new CH signals e, f, h, and g all appear as singlets at 105.5 ppm, 107.2 ppm, 111.0 ppm, and 130.7 ppm respectively confirming the incorporation of 3f.

**Figure 11.** Overlay of 75.5 MHz $^{13}$C DEPT 90 NMR (DMSO-$d_6$) spectra for monomer 2 and 2f.
3.5 Synthesis of a Series of “Pre”-Functionalized PAEKs via “One-Pot” Approach

Since the para-mono-substituted product was obtained exclusively by using compound 2, a series of “pre”-functionalized PAEKs was investigated using a range of phenols (Scheme 21). The two-step procedure involved the reaction of 2 with 1.03 equivalents of the selected phenol (3a-f) at 110 °C until quantitative conversion (according to the GC/MS) was achieved. In the second step a molar equivalent of Bisphenol-A and the required amount of K₂CO₃ were added to convert the new, functional B₂-type monomer into the corresponding PAEK. The temperature for the second step was increased to 185 °C to ensure high conversion of the meta-fluorine displacements and afford high molecular weight materials after a 24 hour reaction time.


The polymers were precipitated from slightly acidified (pH ~ 5 - 6) distilled water, isolated via vacuum filtration and dried. The polymers showed excellent solubility in tetrahydrofuran (THF), chloroform, dichloromethane (DCM) and N-methyl-2-pyrrolidone.
(NMP), but were insoluble in dimethylsulfoxide (DMSO), methanol (MeOH), ethanol (EtOH), and isopropanol (IPA). The structures of all the polymers were confirmed by $^1$H and $^{13}$C NMR spectroscopy after re-precipitation from chloroform into isopropanol:hexane mixture (50:50) to remove any low molecular weight materials. A $^{13}$C DEPT 90 NMR overlay of monomer, 2, mono-substituted monomer, 2d and homopolymer, 4d is shown in Figure 12 and confirms that the polycondensation reaction led to the targeted functionalized linear PAEK polymer. Polymers 4a-4f showed similar results, thus confirming their structure.

Figure 12. Overlay of the 75.5 MHz $^{13}$C DEPT 90 NMR (CDCl$_3$) spectra of monomer, 2, mono-substituted monomer, 2d and homopolymer, 4d.
As shown in Figure 12 the monomer, 2 shows four unique CH signals at 107.2 ppm, 112.2 ppm, 115.4 ppm and 132.2 ppm respectively. The mono-substituted monomer, 2d shows six unique CH signals indicating the incorporation of the functional group at the para-position of monomer, 2 with the signals at e and d in 2 collapsing into singlet in 2d. The new peaks e and f appear as singlets as shown above. The small signals that appear in the spectrum of 2d correspond to the disubstituted product as a result of the excess 3d used.

With the addition of Bisphenol-A to the mono-functional monomer, 2d, two new sets of peaks arise at 118.9 ppm and 128.3 ppm respectively. The signals a and b, which appear as triplet and doublet of doublets at 107.2 ppm and 112.2 ppm, respectively in the monomer and the mono-functional monomer all appear as singlets at 111.2 ppm and 113.8 ppm respectively in the polymer indicating quantitative displacement of the meta-fluorines. The other smaller signals in the spectrum of 4d might be due to cyclics species or oligomers which are common in meta-activated systems. The re-precipitating solvent used (isopropanol:hexane mixture) was not effective enough to remove these cyclics and oligomers.

3.6 Random Co-polymerization of “Pre”-Functionalized Compound 2 with 3-methylphenol (3b) and 4,4’-difluorobenzophenone via “One-Pot” Two-Step Approach

After successful pre-functionalization of compound 2 via the “one-pot” two-step approach, the next step was to synthesize a copolymer via the “one-pot” two-step method. A functional monomer 2b, was prepared in the same way as described above. Upon quantitative conversion (according to GC/MS), 4,4’-difluorobenzophenone, Bisphenol-A and the required amount of K₂CO₃ were added to the reaction flask (Scheme 22). The temperature of the second reaction step was increased to 185 °C for 24 hours reaction time.
to ensure complete displacement of the meta-fluorines in 2b and para-fluorines in 4,4’-difluorobenzophenone.

Scheme 22. Synthesis of random copolymer, 5b via “one-pot” two-step approach via NAS.

The polymer obtained was precipitated from water, isolated by vacuum filtration and dried. The structure of the copolymer was confirmed by both $^1$H and $^{13}$C NMR spectra after re-precipitating from chloroform into isopropanol:hexane mixture (50:50) and drying in vacuo. An overlay of the $^{13}$C DEPT-90 NMR spectra of polymer 4b and copolymer 5b is shown in Figure 13.
Figure 13. Overlay of the 75.5 MHz $^{13}$C DEPT 90 NMR (CDCl$_3$) spectra of homopolymer 4b and copolymer 5b.

The peaks present in the $^{13}$C DEPT-90 NMR spectrum of the homopolymer 4b all appear in the copolymer 5b as expected with additional sets of peaks arising from the now incorporated non-functionalized 4,4’-difluorobenzophenone monomer. The new peaks k and l appear at 117.2 ppm and 132.2 ppm respectively, with the peak at k overlapping with peaks d and e. The peak i arising from the bisphenol-A at 118.9 ppm in the homopolymer 4b appears at 118.9 ppm and 119.2 ppm in the copolymer 5b due to the different magnetic environment arising from being adjacent to the two different type of monomers incorporated (Figure 13).
3.7 Characterization and Thermal Properties of Polymers

Polymers obtained from meta-activated difluoro aromatics have been shown to possess some amount of cyclic oligomers.\textsuperscript{22,45,51-53} In order to confirm the presence of any cyclics, the crude polymers were analyzed by SEC; some typical traces are shown in Figure 14. The SEC traces showed some amount of cyclic oligomeric species present in the polymer. All the polymers were concentrated in chloroform and re-precipitated from isopropanol:hexane mixture (50:50). As shown in Figure 14, the re-precipitating solvents were not effective in removing all the cyclic oligomers. All the homopolymers showed broad molecular weight distribution compared to the copolymer as can be inferred from their polydispersity (PDI) values displayed in Table 3.

![Figure 14](image_url)

**Figure 14.** SEC (RI signal) traces of crude and re-precipitated polymers, 4b and 4d.
SEC analysis was used to obtain the weight average molecular weight, $M_w$, and poly-dispersity index, PDI, values for all the polymers using 5% acetic acid in THF as the eluent solvent. The results, as listed in Table 3, indicated fairly high molecular weight polymers ranging from 18,700 Da for 4e to 69,000 Da for 4a. The poly-dispersion values were obtained by conventional calibration using Polystyrene standards and ranged from 2.8 for 5b to 10.5 for 4a. The homopolymer 4a exhibited a high molecular weight of 69,000 Da and high PDI value of 10.5. The homopolymer 4e showed a rather low molecular weight of 18,700 Da and high PDI value of 7.5. The other homopolymers 4b, 4c, 4d, and 4f showed similar $M_w$ with relatively similar PDI values except 4c. The copolymer, 5b showed a narrow distribution with a lower PDI value compared to the homopolymers. The rather high PDI values of the homopolymers suggest the inefficiency of the re-precipitating solvent in removing cyclic oligomeric species present in the polymer as confirmed by their GPC traces illustrated in Figure 14.

Table 3. SEC Characterization of Homopolymers, 4a-f and Copolymer, 5d with Percent Yields.

<table>
<thead>
<tr>
<th>Polymer</th>
<th>% Yield</th>
<th>$M_w$ (g/mol)</th>
<th>PDI</th>
</tr>
</thead>
<tbody>
<tr>
<td>4a</td>
<td>70</td>
<td>69,000</td>
<td>10.5</td>
</tr>
<tr>
<td>4b</td>
<td>78</td>
<td>44,000</td>
<td>5.1</td>
</tr>
<tr>
<td>4c</td>
<td>80</td>
<td>45,800</td>
<td>9.1</td>
</tr>
<tr>
<td>4d</td>
<td>74</td>
<td>47,000</td>
<td>5.6</td>
</tr>
<tr>
<td>4e</td>
<td>76</td>
<td>18,700</td>
<td>7.5</td>
</tr>
<tr>
<td>4f</td>
<td>75</td>
<td>39,300</td>
<td>5.0</td>
</tr>
<tr>
<td>5b</td>
<td>72</td>
<td>25,200</td>
<td>2.8</td>
</tr>
</tbody>
</table>
The thermal properties of all homopolymers, 4a-f, as well as the copolymer, 5b were evaluated using thermo-gravimetric analysis (TGA) and differential scanning calorimetry (DSC). TGA was used to determine the degradation temperature at which 5 % weight loss (Td5%) occurred under a nitrogen atmosphere. All the polymers showed a relatively high thermal stability under nitrogen. The thermo-gram for all polymers under nitrogen atmosphere are shown in Figure 15.

Figure 15. TGA traces of Polymers 4a-f and 5b under N₂ atmosphere at a heating rate of 10 °C/min.

Under nitrogen atmosphere all the polymers were fairly stable up to 300 °C with similar degradation step, which can be attributed presumably to both the side chain and the polymer backbone degradation. The homopolymer, 4a showed the highest decomposition temperature of 459 °C whilst the homopolymer, 4c showed the lowest degradation temperature of 380 °C. As shown in Figure 15 and Figure 16, all the polymers showed a
slight weight loss (about 1.8-5.6%) starting around 300 °C, which may be due to cyclic oligomers which could not be removed after re-precipitation. The TGA thermo-gram for homopolymer, 4f under N₂ is shown in Figure 16 and clearly shows one distinct step. All the other homopolymers including the copolymer showed similar degradation profiles.

Figure 16. Degradation profile of the homopolymer, 4f under N₂ atmosphere at a heating rate of 10 °C/min.

The glass transition temperatures of the polymers were obtained using DSC and the corresponding traces are shown in Figure 18. The DSC traces show that the polymers synthesized were completely amorphous (only glass transition temperatures observed) with no other thermal transitions, such as melting point or crystallization temperatures. Since T_g is a measure of the ease of motions in the polymer backbone via rotations around sigma bonds, higher glass transition temperatures can be attributed to polymers with less segmental motion and less free volume for those motions to occur.
As shown in Table 4 and Figure 18, the polymers exhibited T_g values in the tight range of 108 °C to 136 °C. Although the functional groups introduced are not very much different in molecular weight, some of them have polar side groups like 4c and 4f whilst others like 4a, 4b, 4d, and 4e do not (Figure 17). The homopolymer 4b exhibited the lowest T_g, which can be attributed to increased free volume with the methyl group located in the meta-position whilst the homopolymer 4f exhibited the highest T_g, which is as a result of intermolecular attractions and also having polar side groups. The homopolymer 4e exhibited a rather low T_g value of 113 °C, which could be due to its lower molecular weight compared with the other homopolymers.
Table 4. Thermal Analysis (T_g, T_d(5%) under N_2) Data for Polymers 4a-f, and 5b.

<table>
<thead>
<tr>
<th>Polymer</th>
<th>T_g (°C)</th>
<th>T_d(5%) N_2 (°C)</th>
</tr>
</thead>
<tbody>
<tr>
<td>4a</td>
<td>122</td>
<td>459</td>
</tr>
<tr>
<td>4b</td>
<td>108</td>
<td>398</td>
</tr>
<tr>
<td>4c</td>
<td>112</td>
<td>380</td>
</tr>
<tr>
<td>4d</td>
<td>127</td>
<td>400</td>
</tr>
<tr>
<td>4e</td>
<td>113</td>
<td>456</td>
</tr>
<tr>
<td>4f</td>
<td>136</td>
<td>457</td>
</tr>
<tr>
<td>5b</td>
<td>112</td>
<td>448</td>
</tr>
</tbody>
</table>

In a study done by van Beek and Fossum\textsuperscript{45} in 2009, using 3, 5-difluorobenzophenone with an equivalent molar amount of Bisphenol-A, a T_g value of 119 °C with T_d(5%) under nitrogen of 494 °C was observed. These results compare well with the recent investigation as having a functional group on the pendant group does significantly affect the polymer property which can be tailored to meet specific application.
Figure 18. DSC traces of polymers, 4a-f and 5b in nitrogen at a heating rate of 10 °C/min.
4. CONCLUSION

Two monomers, 4’,3-5-trifluorodiphenylsulfone, 1, and 4’,3,5-trifluorobenzophenone, 2, have been investigated for their potential use as special BB’B’’ type monomers to synthesize functionalized, linear PAEs. A model reaction was carried out using compound 1 and, as evidenced by the GC/MS and $^{13}$C DEPT 90 NMR spectroscopy, exclusive mono-substitution was not achieved even after longer reaction times. This makes monomer 1 not suitable for achieving linear functionalized PAES as any unreacted monomer could lead to crosslinking and gelation. As a result, monomer 2 was subjected to similar model reaction conditions using 3f as the functional nucleophile. Exclusive mono-substitution was achieved as evidenced by their GC/MS and $^{13}$C DEPT 90 NMR spectroscopy.

A series of linear functionalized PAEK polymers were synthesized using compound 2 and various phenols via a “one-pot” two-step approach in a typical NAS reaction. The polymers obtained showed excellent solubility in common organic solvents such as NMP, DCM, chloroform and THF, but showed insolubility in DMSO, methanol, ethanol, and isopropanol. The molecular weight and PDI values of the polymers were analyzed with SEC. The polymers exhibited relatively high molecular weight ranging from 18,700 Da for 4e to 69,000 Da for 4a with high PDI values in between 2.8 for 5b to 10.5 for 4a, arising from their broad molecular weight distribution and inability to remove any cyclic oligomeric species after re-precipitation. Thermal analysis on the polymers showed relatively high stability in nitrogen atmosphere with $T_{d(5\%)}$ ranging from 380 °C to 459 °C. All the polymers were amorphous showing only glass transition temperature $T_g$ ranging from 108 °C to 136 °C.
5. PROPOSED FUTURE WORK.

Compound 1 can be re-investigated for the synthesis of functional, linear PAES via “one-pot” two-step approach by varying the reaction conditions until exclusive mono-substitution is achieved.

A series of linear functional PAEK has been synthesized, but there is still the need to improve the reaction conditions to achieve mono-substitution in a relatively short reaction time.

A series of copolymers can also be studied with various ratios of co-monomers to understand the effect on the molecular weight distribution which seems to be broad no matter the group attached at the para-position of monomer 2.

Thermal studies under air atmosphere should be performed as well as re-investigate the polymerization conditions to achieve higher molecular weight, functional PAEKs.
6. REFERENCES


