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Functionalized, Semicrystalline Poly(Ether Ketone)s via in situ Modification Chemistry

Raghavendhar Reddy Kotha
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Functionalized, Semicrystalline Poly(Ether Ketone)s via \textit{in situ} modification chemistry

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

Master of Science

By

RAGHAVENDHAR REDDY KOTHA

B.Sc., Osmania University, 2004

2010

Wright State University
I HEREBY RECOMMEND THAT THE THESIS PREPARED UNDER MY SUPERVISION BY Raghavendhar Reddy Kotha ENTITLED Functionalized, Semicrystalline Poly(Ether Ketone)s via in situ modification chemistry BE ACCEPTED IN PARTIAL FULFILMENT OF THE REQUIREMENTS FOR THE DEGREE OF Master of Science.

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ABSTRACT

Kotha, Raghavendhar Reddy. M.S., Department of Chemistry, Wright State University, 2010. Functionalized, Semicrystalline Poly(Ether Ketone)s via in situ modification chemistry.

AB₃ monomer (3,4,5-Trifluoro-4’-hydroxybenzophenone) was used for polymerizations in order to mimic the combination of AB and AB₂ monomers, and which has potential to facilitate concurrent polymerization and functionalization. ‘Pre’ and ‘post’ polymerization functionalization of the PEK system was done using phenol, 4-bromophenol, and 3/4-aminophenol. The solubility of the functionalized polymers was increased; and the crystallinity was decreased significantly compared to the corresponding unfunctionalized homopolymer. The polymers were characterized by ¹H and ¹³C NMR spectroscopy, Gel Permeation Chromatography (GPC), Thermogravimetric Analysis (TGA), and Differential Scanning Calorimetry (DSC). DSC results showed that the crystallinity of the polymer was tuned by the amount of functionalizing agent used. The homopolymer was highly crystalline and the crystallinity decreased as the amount of the functionalizing agent increased. When greater than 50 mol % of the functionalizing agent was utilized, the materials became completely amorphous.
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INTRODUCTION

Having a wide range of applications from commodity plastic materials to highly specialized medical devices, polymer chemistry is a great field, especially since polymers are relatively easy to process, generally inexpensive, and capable of being tailored to a particular structure-property relationship. In particular, poly(arylene ether)s (PAEs) are well known high-performance engineering thermoplastics which have a wide range of applications in the aerospace, automobile, electrical, and electronics industries.

Linear polymers

Linear polymers are well known for their high performance and valuable mechanical properties. Particularly, linear aromatic polymers are well known for their applications as coatings, structural resins, and polymer films, which are very useful in the aerospace and electronics industries. A linear polymer does not have any branching or cross-linking, except the pendant groups associated with the monomer. The long chains in linear polymers are held together by covalent bonds. The great mechanical properties of linear polymers can be explained by the presence of chain entanglements. On the other hand, chain entanglements make linear polymers highly viscous, which can cause difficulties in processing.

Aromatic polyimides, and PAEs are well known examples for this class of materials. However, PAEs are often preferred over polyimides because they are more easily processed due to the flexible ether and ketone groups in the polymer backbone.

Dendrimers

Dendrimers are highly branched and monodisperse macromolecules. They are symmetrical, three dimensional polymers, which are distinguished by a unique tree-like
branching design and dense spherical geometry in solution. In general, dendrimers are made up of a central core, branching units, and terminal functional groups. Because of this unique type of architecture, dendrimers possess encapsulating properties. Dendrimers also have many useful properties such as great solubility, low viscosity, and large number of modifiable end groups available. A large number of dendrimers have been investigated for use as carriers in drug delivery, and gene therapy.

Apart from having a wide range of applications, dendrimers, however have poor mechanical properties, which can be explained by the absence of chain entanglements. Additionally the use of dendrimers is limited by the fact that dendrimer synthesis involves a multi-step approach.

Dendrimers were developed in the 1980's. There are two main approaches for dendrimer synthesis, the divergent and convergent methods. The divergent method is a technique in which a dendrimer grows from a multifunctional core outwards in a stepwise fashion. This is done by repetitive addition of monomer units. However, the divergent synthesis has its own limitations such as difficulties in purification of the final product, lengthy multistep synthesis, and incomplete reaction of the end groups, which leads to structural defects. The convergent method has been developed to overcome the deficiencies of the divergent method. In this method, construction of dendrons is done from the outside toward the central core. Purification in this method is easier due to only a small number of reactions that occur at each step. Hence the structural defects in final products are negligible. On the other hand, this approach has some limitations in terms of steric hindrance when dendrons couple to the multifunctional core unit. Because the synthesis of dendrimers involves multi-step approaches, and a number of intermediate purification steps, their use is limited.
Hyperbranched Polymers

The drawbacks of the dendrimers, like limited use for large-scale industrial applications and the expense of making dendrimers by complex multistep synthesis, can be avoided using hyperbranched polymers, since most of the applications of the polymers do not require structural perfection. There are a couple reasons to consider hyperbranched polymers as substitutes for dendrimers, including the ease of making branched polymers via a single-step synthesis, having more or less similar properties to dendrimers, such as high solubility and low viscosity, and they can be economically promising products for large-scale industrial applications.

Many of the applications of hyperbranched polymers are based on a large number of functional groups in the molecule and the absence of chain entanglements. Tuning the properties like reactivity, solubility, and mechanical properties can be done by the modification of the functional groups in the polymer.

In order to obtain a balance between mechanical properties and processability, variation of the degree of branching can be employed. Figure 1 compares the mechanical properties and branching. Since linear polymers have great chain entanglements, they possess great mechanical properties, such as hardness, tensile strength, and compressive strength, etc., however, it can be very difficult to process them, because they are highly viscous. On the other hand, dendrimers are completely branched, which is also not ideal. Polymers having an intermediate architecture, compared to linear polymers and dendrimers, would be the ideal condition, and hyperbranched polymers fill this void. Hence, the properties of the hyperbranched polymers lie in between linear polymers and dendrimers.
Figure 1: Relationship between branching and mechanical properties for linear, hyperbranched and dendritic polymers.

Degree of Branching

As shown in Scheme 1, hyperbranched polymers contain three different kinds of units, i.e, linear, dendritic and terminal groups. The degree of branching, DB, can be estimated by an equation which was introduced by Frechet et al.,\textsuperscript{11} where D stands for the dendritic, T represents the terminal, and L is the number of linear segments, respectively.\textsuperscript{11}

\[
\text{DB \%} = \frac{(D+T)}{(D+T+L)} \times 100. \quad \text{Equation 1.}
\]

The DB for a dendrimer is 1, since it is completely branched, and the DB for a linear polymer is 0, since there is not any branching. Hyperbranched polymers have a DB in between 0-1, since they have both linear and dendritic units.
**Scheme 1**: Generic synthesis of a hyperbranched polymer

**Figure 2**: Relationship between intrinsic viscosity ($\eta$) and molecular weight (MW) of linear, hyperbranched, and dendritic polymers.

Log $\eta$ vs Log MW
**Figure 2** shows that linear polymers usually have high viscosity and dendrimers (perfectly branched polymers) have low viscosities. Hyperbranched polymers lie in between linear polymers and dendrimers. In the case of linear polymers, the viscosity increases as the MW increases until it reaches a critical point of entanglement ($M_c$). Once it reaches $M_c$, the viscosity increases rapidly as the MW increases. In contrast to linear polymers, the viscosity of dendrimers rises to a maximum, and later decreases as the MW increases, whereas the viscosity of the hyperbranched polymers is often directly proportional to their MWs. 7

There are various approaches to synthesize hyperbranched polymers, like $AB_m$, $A_2+B_3$, and $AB'B'$, etc. **Scheme 2** depicts some of the common synthetic approaches for hyperbranched polymers.

**Scheme 2**: Schematic representation of various synthetic approaches for hyperbranched polymers. 7
**AB\(_2\)** Approach

This is the most common and classical approach of all for hyperbranched polymer synthesis in step.\(^{20}\) The approach was initially used by Kim and Webster\(^ {12}\) to synthesize hyperbranched poly(phenylene)s. In this case A and B are different functional groups, in such a way that the functionality A can react only with the functionality B of another molecule, or vice versa.\(^ {7, 10}\) Examples of AB\(_2\) type monomers are shown in **Figure 3**. Though this is the most predominant approach, AB\(_2\) monomer systems have one major drawback, which is lack of control over the degree of branching of the polymer.\(^ {7}\)

![AB\(_2\) Monomer](image)

\(X = \text{CO, SO}_2\)

**Figure 3.** Two examples of AB\(_2\) monomers designed to undergo nucleophilic aromatic substitution.

**ABB’ Approach**

In this approach A, B, and B’ have different reactivities, so that the functionality A can react with only B/B’ of the other monomer unit or vice versa. In this case, usually linear polymer is obtained at lower temperatures, and branching is increased as the temperature increases.\(^ {7}\) Jikei \textit{et al} explored the ABB’ approach via the use of 4-(2, 4-diaminophenoxy) benzoic acid (Figure 4) as a monomer in the synthesis of poly (amide)s.\(^ {13}\)
Figure 4: An example of an ABB’ monomer used to prepare branched polyamides

A₂ + B₃ Approach

This approach simulates the AB₂ approach, but utilizes monomers that are commercially available or relatively easy to prepare. At the initial stage of the polymerization A reacts with one of the B’s and forms an AB₂ monomer. Examples of A₂ and B₃ monomers are shown in Figure 5. The major drawback of the AB₂ approach, which is lack of control of the degree of branching, can be circumvented by this approach. However, the A₂ + B₃ approach has a critical drawback in that it often leads to cross linking, which causes gelation.

Figure 5: An example of an A₂ and B₃ type monomers.

AB₃ Approach

Synthesis of hyperbranched polymers has also been done using an ABB’B’’ type monomer, which is shown in the Figure 6 below. This kind of monomer can be used to synthesize branched poly (aryl ether sulphone)s, PAES.
Figure 6: Example of an AB₃ type monomer

Polyarylene ethers (PAEs)

In recent years PAE’s have become one of the most significant classes of high performance engineering plastics. These materials are well known for their excellent physical properties such as high thermal and oxidative stability, chemical resistance, and toughness. PAE’s can be used as castable matrix resins, membrane materials, and as insulating materials in the microelectronics industry. The structures of some of the common PAE systems are shown in Figure 7. There is an assumption to explain the great thermal and mechanical properties of the PAE’s, that the aromatic portion in the PAE’s, is the reason for their thermal stability, and these polymers are easily processed because of ether linkages.
PAE Synthesis

PAE’s are generally synthesized by a poly condensation method, such as nucleophilic, or electrophilic aromatic substitution reactions, as well as by oxidative coupling of phenol derivatives.¹⁵, ²¹, ³⁴

Scheme 3: Representative scheme for the synthesis of PEEK via Nucleophilic Aromatic Substitution (SNAr).
Specifically, aromatic poly (ether ketone)s are synthesized using two different approaches; Aromatic electrophilic substitution (Friedel-Craft’s acylation) and Nucleophilic Aromatic Substitution (NAS). Scheme 3 depicts the NAS approach to synthesize PEEK. 22, 23

Poly Ether Ketones (PEK’s)

Semicrystalline aromatic poly(ether ketone)s, PEK’s, are widely used as high-performance engineering thermoplastics and they have great industrial importance due to their excellent physical, mechanical and chemical properties. Because of their thermal, oxidative and chemical stability, they are widely used as a matrix resin for advanced composite materials in the aircraft and automobile industries.24, 25 Figure 8 depicts the structures of PEEK and PEK.

Figure 8: Two of the poly (ether ketone) s having industrial importance. 22

Due to the consecutive ether linkages, PEEK is more flexible and retains its melt processibility compared to PEK, which usually possesses a higher melting point.22 However, these materials have a limitations like preparation and processing, due to their crystalline nature.4 High molecular weight poly (ether ketone)s are difficult to synthesize, characterize and process, since they are poorly soluble in most of the common organic solvents. Polymers need to be soluble in organic solvents in order to perform NMR spectroscopy and GPC analyses, essential information to help understand the structure-property relationship of the polymers at the molecular level. 4, 24
Some approaches have been developed in order to overcome the ‘solubility’ issue. One of them is to make blends or perform copolymerization of PEEK with other polymers like poly(ether sulfone)s. Since poly(ether sulfone)s are amorphous thermoplastics and they have great oxidative stability, heat, steam resistance, higher Tₜ’s and good solubility, and these polymers could potentially improve the solubility of PEK/PEEKs.¹

**Functionalization of Aromatic Poly(Ether Ketone)s:**

Modification of the polymers is a second approach to overcome the solubility issue. Enhancement of the solubility of PEEKs by sulfonating the polymers by dissolving in conc. H₂SO₄ was reported.²⁴ However, this method worked only for PEEK, not for PEK, and PEKK, due to the de-activating carbonyl group present on each ring. The Howard group²⁴ was able to derivatize PEEK and PEK reversibly by dithioketalization of the carbonyl groups with 1,2-ethanediol or 1,3-propanedithiol. The chemistry involved in this approach involves a routine method of protection of carbonyl groups.²⁴

Though, as mentioned above, there are a few approaches available to modify poly(ether ketone)s to make them semicrystalline, soluble PEEK’s with greater thermal properties, the most attention has been paid to functionalization of the polymers over the past few years.²⁶,²⁷,²⁸,²⁹,³⁰ The functionalization process is not only the solution for the ‘solubility’ issue, it can also bring more functional groups into the polymer, hence, further modification of the polymers also can be achieved in order to improve the physical, chemical and mechanical properties of the polymer.

The functionalization of the polymers can be achieved in two ways.²⁶,³⁰ One can do polymerization of functionalized monomers or by post-chemical modification of the obtained polymers. **Schemes 4 and 5**, below, help to explain this concept.
Scheme 4: Polymerization of functionalized monomer.

Scheme 5: Post-modification of pre-made polymers.
**Fluorinated Polymers**

Due to the fact that fluorine-containing polymers have shown great improvement in chemical, thermal and photochemical stability of the materials, considerable attention has been devoted to the synthesis of such species. The additional stability of these polymers can be explained by the highly stable C-F bond. Fluorine containing polymers have interesting properties, including low dielectric constants, flame resistance, very low water absorption, increased solubility and significantly higher glass transition temperatures, relative to their nonfluorinated analogues.

Teflon is the best example to describe the properties like excellent chemical and environmental resistance of fluorinated polymers compared to those of hydrocarbon polymers. Fluorinated aromatic PAE’s containing hexafluoroisopropylidene (HXIP) units have shown improvements in solubility, flame resistance, and glass transition temperatures, with concurrent decreases in crystallinity, and dielectric constant.

**Nucleophilic Aromatic Substitution**

Nucleophilic aromatic substitution (NAS) is one of the most common pathways to synthesize most of the available polymers like PAE, PEK/PEEK, etc. NAS is a reaction in which a nucleophile substitutes a leaving group on an aromatic ring. The mechanism involved in NAS reactions is shown in Scheme 6. In the first, rate determining, step a nucleophile attacks the *ipso* carbon, which has an electropositive nature because of strong electron withdrawing groups like carbonyl, or sulfonyl groups. This leads to the formation of an activated complex (anionic intermediate) that is also known as a Meisenheimer complex. Having strong withdrawing groups at the ortho/para positions can facilitate the reaction. These withdrawing groups stabilize the Meisenheimer complex by both inductive and resonance effects.
Computational tools are useful to assess the ability of the electron-withdrawing group to reduce the electron density at the *ipso* position to the leaving atom (like halides, particularly F in polymer chemistry). In addition to computational methods like RHF (Hartee-Fock molecular orbital calculations), and DFT (Density Functional Theory), $^1$H, $^{13}$C, and $^{19}$F NMR shift values also allow assessment of the reactivity of the electrophilic sites.

**Scheme 6:** General mechanism of Nucleophilic Aromatic Substitution.

The second step is the loss of the halide group, which reforms the aromatic ring. Better leaving groups like halides (F’, Cl’, Br’) facilitate the reaction. Earlier studies also reported that strong electron withdrawing groups at the *meta* position could also facilitate the NAS reaction. The effect of the strength of the electron withdrawing group, located at the meta-position, on the ability of a monomer to undergo NAS reaction was reported by Fossum *et al.* who found that sufficiently strong electron withdrawing groups could also facilitate NAS reactions from the *meta* positions. Two of the monomers having the *meta* activating groups, which are used in PAE synthesis are shown in Figure 9. In such cases, the inductive effect is the only factor that facilitates the reaction.
Figure 9: Aromatic fluoride monomers with electron withdrawing groups at meta position.

CURRENT PROJECT

The main goal of the current project is to synthesize semicrystalline, functionalized PEK's in order to overcome the current issues with PEK class polymers, (i.e., solubility) as well as to improve their processability, thermal, and mechanical properties. An important additional goal of the current project is to develop an efficient methodology based on the reactivity differences between meta and para aromatic fluorides to synthesize the functionalized PEKs via an in situ method (one pot synthesis of functionalized PEK polymers).

An AB3 monomer was designed, synthesized and subsequently used for polymerizations in order to mimic the combination of AB and AB2 monomers, which should facilitate polymerization and functionalization at one time.

Figure 10: AB3 type monomer designed for concurrent polymerization and functionalization.
2. Experimental

The approach that has been used is very similar to that the approaches followed by Shravanthi, R. et al., and Amanda Ike et al. All reactions were carried out under a nitrogen atmosphere and syringes were used for all transfers, as required. The solvents, 2-N-Methylpyrrolidinone, NMP, and Dimethyl sulfoxide, DMSO, were dried over CaH₂, followed by distillation under a nitrogen atmosphere prior to use. The base used in the Nucleophilic Aromatic Substitution (NAS) reactions was Potassium Carbonate (K₂CO₃), which was dried in an oven at 130 - 140 °C. 4-methylphenol (4-Cresol) was recrystallized from hexanes. Phenol was distilled under nitrogen. 3,4,5-Trifluorobenzoic acid was purchased from Oakwood Products; Anisole, Phenol, 4-Cresol, 4-Bromophenol, 3-Aminophenol, and 4-Aminophenol were purchased from Sigma- Aldrich Co.

Instrumentation

The approach that has been used is very similar to that the approaches followed by Shravanthi, R. et al., and Amanda Ike et al. The GC/MS instrument used was a HP 6890 Series GC with auto injection, and a PH5973 mass selective detector/quadrapole system. BRUKER AVANCE 300 MHz instrument which was operated at 300 and 75.5 MHz respectively, was used to acquire ¹H and ¹³C NMR spectra. DMSO-d₆ or CDCl₃ were used as a solvent as required, to dissolve the samples. BRUKER AVANCE 400 MHz instrument, which was operated at 376.5 MHz using 10 % CFCl₃ as an external standard with the instrument set relative to the lock signal, was used to acquire the ¹⁹F NMR spectra. Samples were dissolved in DMSO-d₆. Gel Permeation Chromatography, GPC analysis has been performed using a Viscotek Model 300 TDA system equipped with refractive index, viscosity, and light scattering detectors operating at 70°C. Polymer laboratories 5μM PL gel columns (guard column, and two mixed D columns) have been
used. NMP (with 0.5 % LiBr) was used as the eluent and a thermoseparation model P1000 pump operating at 0.8 mL/min. Molecular weights of the polymers were calculated from the RI signal and are reported relative to polystyrene standards. DSC analyses were done under nitrogen, and TGA analyses were done both in nitrogen as well as air atmosphere. TA instruments Q 200 DSC and Q 500 TGA were used respectively, at a heating rate of 10⁰C/min. Melting points were determined using a Mel-Temp instrument and are uncorrected.

**Synthesis of 3,4,5-Trifluoro-4'-methoxybenzophenone, 1.**

In a 250 ml round-bottomed flask equipped with a stir bar, condenser, and gas adapter, were placed 10.0 g (56.8 mmol) of 3,4,5-trifluorobenzoic acid, 24 mL (4 eq.; 227 mmol) of Anisole, and Eaton’s reagent (15.5 g of P₂O₅ in 100 mL of MSA, 1:9 ratio). The reaction flask was then immersed in an oil bath and heated to 75 °C for 75 minutes at which point the solution was cooled to room temperature and slowly poured into 500 mL of vigorously stirred distilled water. The layers were separated and the aqueous layer was extracted 3 times with ~ 200mL of chloroform. The resulting organic layers were combined and washed with DI-water, dilute HCl solution, 5 % sodium bicarbonate solution, and DI-water. The organic layer was then dried over magnesium sulfate and concentrated via a rotary evaporator to obtain the crude product as a brown solid. The crude product was recrystallized from 70 % ethanol/water to afford 10.2 g. (67.5 %) of white crystals with a melting point 100-101°C. Elem. Anal. Calcd. for C₁₄H₉F₃O₂: C, 63.16 %; H, 3.41 %; Found: C, 63.22 %; H, 3.31 %. ¹H-NMR (DMSO-d₆, δ): 3.87 (s, 3 H); 7.08-7.11 (d, 2 H); 7.76-7.8 (d, 2 H); 13C-NMR (DMSO-d₆, δ): 55.6 (s, 1 C); 128(s, 2 C); 134.1 (s, 2 C); 132.4 (s, 1 C); 191 (s, 1 C); 139.5 (s, 1 C); 114-114.26 (s, 2 C); 151.5-151.7 (dd, 2 C), 148.3-148.4 (dd, 2 C); 19F-NMR (DMSO-d₆, δ): -134.77 (d, 2 F); -157.2 (t, 1 F)
Synthesis of 3,4,5-Trifluoro-4'-hydroxybenzophenone, 2.

In a 250 ml round-bottomed flask equipped with a stir bar, condenser, and gas adapter, were placed 10.0 g (37.6 mmol) of 1, 130 mL of glacial acetic acid, and 70 mL of 48 % HBr. The reaction flask was then immersed in an oil bath and heated to reflux for 48 hours. Then the solution was cooled to room temperature and poured dropwise, using a separatory funnel into 1000 mL of distilled water. The resulting solids were collected by vacuum filtration. The solid was redissolved in ether, washed with DI-water, saturated Sodium bicarbonate solution, and DI-water. The ether solution was dried over magnesium sulfate, filtered, and concentrated via rotary evaporator to obtain the crude product as a brown solid. The crude product was then recrystallized from ethanol/water to afford 6.9 g (73 %) of 2 as white crystals with a melting point of 160 - 161 °C. Elem. Anal. Calcd. for C13H7F3O2 : C, 61.91 %; H, 2.80 %. Found: C, 61.95 %; H, 2.71 %. 1H-NMR (DMSO-d6, δ): 10.58 (s (broad), 1 H); 6.90-6.93 (d, 2 H); 7.68-7.71 (d, 2 H); 7.57-7.62 (t, 2 H); 13C-NMR (DMSO-d6, δ): 55.6 (s, 1 C); 162.6 (s, 1 C); 115.4 (s, 2 C); 132.7 (s, 2 C); 126.6 (s, 1 C); 190.7 (s, 1 C); 134.3-134.5 (dd, 1 C); 113.8-114.1 (dd, 2 C); 151.5-151.7 (dd, 2 C), 148.2-148.4 (dd, 2 C); 142.5-142.9 (t, 1 C), 139.1-139.5 (t, 1 C); 19F-NMR (DMSO-d6, δ): -134.63 (d, 2 F); -157.2 (t, 1 F).

Model Reactions for monosubstituted monomer:

Model reactions were carried out at different temperatures (80, 120, 140, 160, and 200 °C), in either NMP or DMSO. The reactions were continued for 4 (at 200 °C) up to 24 hours (at 80 °C).

General Procedure model reactions

In a 25 mL RB flask equipped with a stir bar, condenser, and gas adapter, were placed 0.1 g (0.37 mmol) of 3,4,5-trifluoro-4'-methoxybenzophenone, 0.04 g (0.37 mmol) of 4p-cresol, 0.08 g (1.5 equiv) of K2CO3, and 1.14 mL of NMP. The reaction flask was immersed in an oil bath and
heating was started (140 °C). The reaction was monitored by taking aliquots, throughout the reaction period, which were analyzed using GC/MS. The remaining solution was precipitated from DI-water and extracted using ether. The ether solution was then separated, and washed with DI-water, saturated sodium bicarbonate, and DI-water. The ether solution was then dried over magnesium sulfate, and volume was reduced via rotary evaporation to afford 0.12 g (90 %) as a white solid. Variations of the reaction conditions are noted in Table 1.

The NMR data reported below is for the model reaction that was carried out at 140 °C.

1H-NMR (DMSO-d$_6$, δ): 3.90 (s, 3 H); 6.97-7.00 (d, 2 H); 7.80-7.84 (d, 2 H); 7.42-7.45 (dd, 2 H); 6.87- 6.9 (d, 2 H); 7.12- 7.13 (d, 2 H); 2.31 (s, 3H); 13C-NMR (DMSO-d$_6$, δ): 55.6 (s, 1 C); 163.7 (s, 1 C); 115.1 (s, 2 C); 133 (s, 2 C); 130.15 (s, 1 C); 192 (t, 1 C); 135.3 (s, 1 C); 114-114.3 (m, 2 C); 157 (dd, 2 C); 157.4 (dd, 2 C); 134.7- 135.0 (t, 1 C); 155.4 (s, 1 C); 115.4 (s, 2 C); 129.0 (s, 2 H); 132.4 (s, 1 C); 20.6 (s, 1 C); 19F-NMR (DMSO-d$_6$, δ): -126.5 (s, 2 F).

Polymerization Reactions

General procedure for Homo-polymers

In a 25 mL RB flask equipped with a stir bar, condenser, and gas adapter, were placed 0.5 g (2 mmol) of 3,4,5-trifluoro-4'-hydroxybenzophenone 2, 0.4 g (1.5 equiv) of K$_2$CO$_3$, and 6 mL of NMP. The flask was immersed in an oil bath and heated to 180 °C for 16 hours. The reaction mixture was then cooled to room temperature, precipitated from isopropanol/ water solution and a few drops of conc. HCl were added to the solvent mixture. The polymer was redissolved in NMP and precipitated a second time using the same solvent mixture. The resulting solid was isolated via filtration to afford 0.41 g (89 %) of an off-white solid, after vacuum drying.

Variations of the reaction conditions are noted in Table 2.
General procedures for synthesis of functionalized polymers

Procedure for the Pre-Functionalizationed polymerization using 4-bromophenol as functionalizing agent

In a 25 mL RB flask equipped with stir bar, condenser, and gas adapter, were placed 0.3g (1.2 mmol) of 3,4,5-trifluoro-4’-hydroxybenzophenone, 0.021 g (0.12 mmol) of 4-bromophenol (10 mole %), 0.27 g (1.5 equiv) of K$_2$CO$_3$, and 2.4 mL of NMP. The flask was immersed in an oil bath, and heated to 80 °C for 4 hours at which point the temperature was raised to 150 °C for 12 more hours. The reaction mixture was then cooled to room temperature, and slowly added to a vigorously stirred isopropanol / water solution containing a few drops of conc. HCl. Reprecipitation was also done using the same solvent mixture. The resulting solid was isolated via filtration, followed by vacuum drying to afford 0.274 g (93 %) of a brown solid. Variations of the reaction conditions are noted in Table 4.

Procedure for the Post-Functionalizationed polymerization using 4-bromophenol as functionalizing agent

In a 25 mL RB flask equipped with a stir bar, condenser, and gas adapter, were placed 0.3 g (1.2 mmol) of 3,4,5-trifluoro-4’-hydroxybenzophenone, 0.27 g (1.5 equiv) of K$_2$CO$_3$, and 2.4 mL of NMP. The flask was immersed in an oil bath and heated at 150 °C for 12 hours, at which point 0.021 g (0.12 mmol) of 4-bromophenol (10 mole %) was added to the reaction mixture. The reaction was further heated for 4 hours at 150 °C. The reaction mixture was then cooled to room temperature, and slowly added to an isopropanol/ water solution containing a few drops of conc. HCl. Reprecipitation was also done using the same solvent mixture. Filtration was done to obtain the resulting solid, which was dried under vacuum to afford 0.256 g (87 %) of a brown solid.
3. Results and Discussion

The main purpose of this project was to synthesize semicrystalline, functionalized poly(ether ketone)s via a “one-pot” in situ modification approach. PEK based materials have received a lot of attention in recent years because of their unique properties and the ability to tailor their physical properties by introducing functional groups, in a straightforward manner, would provide a significant contribution to the field. In order to achieve the main goal, a specific kind of monomer was used, designed in such a way that it could facilitate concurrent polymerization and functionalization. Thus, the concept of utilizing an AB$_3$ monomer was used, because it could mimic the combination of AB and AB$_2$ monomers as shown in the scheme 7.

The AB$_3$ monomer also provides an avenue to tailor the branching in PEK via reaction temperature modulation, especially if the reactivity of each of the B functional groups is considerably different.

![Scheme 7: Schematic representation of AB$_3$ monomer.](image)

Initial work on this project was to verify whether branched polymer was synthesized using this monomer, since Ike et al reported that the sulfone analogue afforded branched polymers at higher temperatures compared to a more linear polymer when prepared at lower
temperatures. 14 Hence, one could envision that branching might also occur with the $\text{AB}_3$ ketone system.

![AB3 Sulfone monomer](image1)

![AB3 Ketone monomer](image2)

**Figure 11.** $\text{AB}_3$ type sulfone and ketone monomers.

**Synthesis of protected monomer 1 & monomer 2**

The syntheses of 3,4,5-trifluoro-4′-methoxybenzophenone, 1, and 3,4,5-trifluoro-4′-hydroxybenzophenone, 2, are summarized in **Scheme 8**. Reaction of 3,4,5-trifluorobenzoic acid with anisole in the presence of an excess of Eaton’s reagent lead to the formation of protected monomer 1 in 67.5 % yield. Deprotection of the phenol group was achieved by reaction with HBr in acetic acid. The desired monomer 2 was purified by recrystallization to afford a white crystalline material in 73 % yield. Confirmation of both structures was provided by GC/MS, NMR spectroscopy, and elemental analysis.

![Scheme 8](image3)

**Scheme 8:** Synthesis of $\text{AB}_3$ monomer.
The $^1$H-NMR and $^{19}$F-NMR spectra of the monomers are shown in Figures 12 and 13. Molecules 1 and 2 display 4 different peaks in their $^1$H NMR spectra, since they have four unique protons. For the protected monomer 1, a peak is present at 3.8 ppm, which indicates the presence of the methoxy group (i.e., the phenol group is protected) whereas in the case of monomer 2 no such peak was observed for the latter, but a peak at 10.5 ppm was observed, which clearly indicates a phenolic proton. Both 1 and 2 showed a unique peak at about 7.6 ppm as a multiplet due to the proton adjacent to the fluorine atoms. This particular proton has coupling with the fluorine atoms, hence it appears as multiplet rather than a singlet. Both 1 and 2 also showed a water peak in DMSO-$d_6$ at 3.3-3.4 ppm, which is labelled as peak 1 in Figure 12.

The $^{19}$F-NMR spectra indicate that the meta positions are more electrophilic and, thus, more reactive for nucleophilic aromatic substitution, NAS, than is the para position. This observation contradicts the basic knowledge about the NAS, that electron withdrawing groups at the para position, facilitate the NAS, since nucleophilic attack should occur at the para position and lead to a more stable intermediate Meisenheimer complex. However, in the case of nucleophilic attack at the meta position, it doesn’t lead to the formation of a stable Meisenheimer complex. Hence, even though the $^{19}$F-NMR data indicates that the meta positions, relative to the carbonyl, are more electrophilic, one can expect nucleophilic substitution may occur at the para position rather than at the meta position.
Figure 12: $^1$H NMR spectra of protected and deprotected AB$_3$ monomers.

Figure 13: $^{19}$F- NMR of protected and deprotected AB$_3$ monomer.
Model reactions

The reactivity of the electrophilic sites was estimated based on the model reactions. Protected monomer 1 was used for model reactions as illustrated in Scheme 9. Model reactions were carried out either in NMP or DMSO solvent, with 1 equivalent of 1, 1 equivalent of p-cresol, and K₂CO₃ serving as the base to deprotonate the phenol group. The progress of the reactions was monitored by removing aliquots and analyzing them using GC/MS. The final samples were further analyzed by ¹H, ¹³C, and ¹⁹F NMR spectroscopy.

Scheme 9. Schematic representation of model reactions.
The $^{13}$C-NMR spectra indicate only mono-substitution occurred, irrespective of the reaction temperature, and other reaction conditions. If any di (or) tri substitution had occurred, more peaks for $p$-cresol groups would have been observed, as well as having different chemical shifts.
shifts for the resultant product. One would also have a different chemical shift for a new type of C-F.

Figure 15: $^{19}$F-NMR spectra of protected monomer and model reactions carried out at 140 and 200 °C.

The $^{19}$F-NMR spectra display only a single peak for the model reaction products; indicating that the fluorines in 3 are symmetrical. The GC/MS data confirmed this as only one product was observed, indicating that only one fluorine atom was substituted during the reaction. Analysis of the model reactions indicate that only mono substitution occurred in the AB$_3$ ketone system, confirmed by both GC/MS and NMR data. However, this observation does not correlate
with the observation from its sulfone analogue, where significant disubstituted product was formed and branching was achieved. In the case of the sulfone, the observed branching may be explained by the considerably higher overall reactivity of the electrophilic sites due to the presence of the strongly withdrawing sulfone group compared to the somewhat weaker electron withdrawing ketone group present in 1.

Reactivity comparison

![Diagram showing comparison of AB₃ sulfone and AB₃ ketone monomers](image)

**Figure 16**: Comparison of AB₃ sulfone and AB₃ ketone monomers

Some information regarding the relative reactivity of the electrophilic sites in 2, compared to those in the corresponding sulfone analogue, can be gleaned from their respective $^{19}$F-NMR data. The AB₃ sulfone has 2 peaks, at -131.5 ppm (meta F) and -153.5 ppm (para F), whereas the AB₃ ketone monomer has 2 peaks, at -134.6 ppm (meta F) and -157.2 ppm (para F). More downfield $^{19}$F NMR chemical shifts are indicative of more reactive electrophilic sites. The meta fluorine atom peak in the sulfone structure is 3 ppm downfield, relative to the meta fluorine atom signal in the ketone structure, indicating that the sulfone is much more reactive than its ketone analogue. The $^{19}$F NMR data for the model reaction products provide further evidence to conclude that the sulfone monomer is highly reactive compared to the ketone analogue. The $^{19}$F-NMR spectrum of the mono-substituted sulfone has one peak present at -123 ppm (meta F),
whereas its ketone analogue shows a single peak at -126.5 ppm, about 3.5 ppm upfield. That is the reason why the ketone might not react further to get branching, however, further diagnosis has to be done ith the AB₃ monomer to know its absolute reactivity, and whether di-substitution is possible.

**Polymerization of monomer 2**

The polymerization of the AB₃ monomer is shown in **Scheme 10**. The polymerization is a typical nucleophilic aromatic substitution polycondensation process, and was carried out at different temperatures ranging from 150 °C, to 189 °C in either NMP or DMSO solvent. At least 1.5 equiv of K₂CO₃ were used for 1 equiv. of monomer 2 in order to make sure all phenol groups were deprotonated to the corresponding phenoxide, which obviously acts as the nucleophile for substitution of the fluorine(s).

![Scheme 10: Schematic representation for homo-polymerization reactions.](image)

The polymerizations were monitored by removing aliquots and analyzing them using GPC. The polymers were purified by an initial precipitation and subsequent re-precipitation from isopropanol /water solution. The polymers were dried under vacuum for 12 hours, using a drying pistol, to remove residual NMP, isopropanol and water. The characterization data for the homopolymers are summarized in **Table 1**.
Since the homopolymers were poorly soluble in organic solvents, analysis of their molecular structure by NMR spectroscopy was not possible. Furthermore, the molecular weight (MW)s, obtained using GPC, do not represent the whole polymer sample, rather, only the polymers which were soluble in NMP. Proper instruments were used in order to get thermal analysis, TGA and DSC data. The TGA overlay in Figure 17 shows that the homopolymers have high T_d values, which indicate they are highly thermally stable. Decomposition temperatures, T_d (5 %)'s of the homopolymers were in the range of 421- 485 °C, while T_d (10 %)'s were in the range of 477 - 538 °C. Figure 18 gives a view of the DSC overlay of homopolymers. The glass transition temperatures, T_g's, of the homopolymers were in the range of 155 – 183 °C, and the melt temperatures T_m’s were in the range of 316 -340 °C, while the reported T_g and T_m values for non-

<table>
<thead>
<tr>
<th>Polymerization</th>
<th>Conditions</th>
<th>% Of yield</th>
<th>M_n (Da)</th>
<th>PDI</th>
<th>TGA (in °C)</th>
<th>DSC (in °C)</th>
</tr>
</thead>
<tbody>
<tr>
<td>A</td>
<td>NMP; 150 °C; 12 hrs</td>
<td>81</td>
<td>5700</td>
<td>2.45</td>
<td>453</td>
<td>477</td>
</tr>
<tr>
<td>B</td>
<td>NMP; 180 °C; 16 hrs</td>
<td>89</td>
<td>4700</td>
<td>2.2</td>
<td>478</td>
<td>533</td>
</tr>
<tr>
<td>C</td>
<td>DMSO; 180 °C; 16 hrs</td>
<td>92</td>
<td>4500</td>
<td>2.1</td>
<td>421</td>
<td>510</td>
</tr>
<tr>
<td>D</td>
<td>DMSO; 189 °C; 16 hrs</td>
<td>87</td>
<td>4000</td>
<td>1.6</td>
<td>485</td>
<td>538</td>
</tr>
</tbody>
</table>
fluorinated PEK are 154 °C and 366 °C, respectively. However a $T_m$ was not observed for polymer A.

**Figure 17:** TGA overlay of homopolymers. A: 150 °C in NMP; B: 180 °C in NMP; C: 180 °C in DMSO; D: 189 °C in DMSO.
Figure 18: DSC overlay of homopolymers. A: 150 °C in NMP; B: 180 °C in NMP; C: 180 °C in DMSO; D: 189 °C in DMSO.

The DSC overlay in Figure 18 depicts that all of the homopolymers, except A, are semicrystalline and $T_g$, $T_c$, and $T_m$ of the polymers were tuned by reaction conditions. In the case of polymer A, no $T_m$ was observed, which at a first glance might indicate a completely amorphous sample, however, a more likely explanation is that polymer A is highly crystalline. At the lower reaction temperatures (in this case, 150 °C) the nucleophilic substitution might be highly selective, in which case, the nucleophile reacts at only the *para* position of monomer 2 resulting in a completely linear and highly symmetrical polymer.
Initially, only B, C, and D polymers, shown in Table 1, were synthesized. Since the homopolymers were poorly soluble in organic solvents further analysis of the obtained polymers was not possible. Hence, an attempt was made to monitor the reaction every hour using GPC, so that it might be able to understand the progress of the polymerization. The results are tabulated in Table 2. The data indicate that, with few exceptions, the peak molecular weight ($M_p$) values increased as the reaction proceeded. It is reminded that GPC can only determine the molecular weights of the polymeric species that are soluble in the eluent (in this case, NMP).

Table 2: GPC Data for the Homopolymerization of AB$_3$ monomer at 150 °C in NMP.

<table>
<thead>
<tr>
<th>No. of hours</th>
<th>$M_n$ (in Daltons)</th>
<th>$M_p$ (in daltons)</th>
<th>PDI</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>2900</td>
<td>2500</td>
<td>1.6</td>
</tr>
<tr>
<td>2</td>
<td>7600</td>
<td>6000</td>
<td>1.28</td>
</tr>
<tr>
<td>3</td>
<td>7800</td>
<td>6600</td>
<td>1.34</td>
</tr>
<tr>
<td>4</td>
<td>7500</td>
<td>6500</td>
<td>1.26</td>
</tr>
<tr>
<td>5</td>
<td>7600</td>
<td>7000</td>
<td>1.5</td>
</tr>
<tr>
<td>6</td>
<td>4400</td>
<td>7500</td>
<td>1.46</td>
</tr>
<tr>
<td>7</td>
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<td>7000</td>
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</tr>
<tr>
<td>8</td>
<td>4700</td>
<td>7500</td>
<td>2.26</td>
</tr>
<tr>
<td>9</td>
<td>5000</td>
<td>7900</td>
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</tr>
<tr>
<td>10</td>
<td>5200</td>
<td>7900</td>
<td>2.16</td>
</tr>
<tr>
<td>11</td>
<td>4800</td>
<td>10000</td>
<td>2.11</td>
</tr>
<tr>
<td>12</td>
<td>5700</td>
<td>9100</td>
<td>2.45</td>
</tr>
</tbody>
</table>
Pre and Post functionalization of PEK:

In order to overcome the solubility issues as well to introduce new functional groups on the PEKs, attempts at functionalization were carried out. Two different approaches were utilized, pre, and post functionalization of the PEK polymers. In the first case, a functional group was added to monomer and the reaction was started at lower temperatures, in order to make sure that only functionalization of the monomer was achieved. Once the functionalized monomer was obtained, the reaction temperature was raised so that polymerization process could be facilitated. This method takes advantage of the significant reactivity difference between the para and meta electrophilic sites.

Scheme 11. Schematic representation of Pre-functionalized polymerizations of PEK.

R = C₆H₆, 4-Br-C₆H₄, 3-NH₂-C₆H₄, and 4-NH₂-C₆H₄
Scheme 11 depicts the reaction involved in the formation of the pre-functionalized monomers, and their subsequent polymerization. The functionalizing agents that were incorporated into the polymers included phenol, 4-bromophenol, 3-aminophenol, and 4-aminophenol. The above reactants were chosen because the functional groups could greatly facilitate further modification of the PEKs.

The second approach, which is post-modification of the polymers, was done using the same functional groups as mentioned above. In this case, polymerization of monomer 2 was done for 12 hours, at which point the functionalizing agent was added to the reaction mixture and heating was continued for 4-6 more hours. The schematic representation of the post functionalization for PEK is shown in Scheme 12.

![Scheme 11](image)

**Scheme 11.** Schematic representation of the post-functionalized polymerization reactions.

R = C₆H₅, 4-Br-C₆H₄, 3-NH₂-C₆H₄, and 4-NH₂-C₆H₄

**Scheme 12.** Schematic representation of the post-functionalized polymerization reactions.
Phenol functionalized polymerizations

Phenol was used as a functionalizing agent for both ‘pre’ and ‘post modifications. Mole %’s of 10, 25, 50, 75, and 100 % were used for the pre-functionalization approach. All these reactions were done with a second reaction temperature of 170 °C and NMP was used as the solvent. However, only 10 mole % was used for post modification, since ‘post’ modification carries the risk of polymer degradation.

Table 3: Data for Phenol-functionalized polymers.

<table>
<thead>
<tr>
<th>Type</th>
<th>Polymer</th>
<th>M_{n} (Da)</th>
<th>% of yield</th>
<th>PDI</th>
<th>TGA (in °C)</th>
<th>DSC (in °C)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>T_{5%}</td>
<td>T_{10%}</td>
</tr>
<tr>
<td>PRE</td>
<td>10%</td>
<td>5100</td>
<td>92</td>
<td>2.44</td>
<td>454</td>
<td>520</td>
</tr>
<tr>
<td></td>
<td>25%</td>
<td>4700</td>
<td>91</td>
<td>2.0</td>
<td>418</td>
<td>468</td>
</tr>
<tr>
<td></td>
<td>50%</td>
<td>4580</td>
<td>86</td>
<td>1.97</td>
<td>364</td>
<td>405</td>
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<tr>
<td></td>
<td>75%</td>
<td>3700</td>
<td>81</td>
<td>1.73</td>
<td>349</td>
<td>390</td>
</tr>
<tr>
<td></td>
<td>100%</td>
<td>3300</td>
<td>87</td>
<td>1.7</td>
<td>346</td>
<td>385</td>
</tr>
<tr>
<td>POST</td>
<td>10%</td>
<td>4700</td>
<td>91</td>
<td>2.3</td>
<td>420</td>
<td>487</td>
</tr>
</tbody>
</table>

The polymerization reactions were monitored by taking aliquots for analysis with GPC. The final polymers were purified by precipitating twice from isopropanol/water solution. The polymers were then dried under vacuum for 12 hours using a drying pistol, to make sure that the polymers were completely free of residual solvents. The solubility of the functionalized polymers was increased significantly as the amount of the functionalizing agent was increased.
In order to analyze the structure and property relationships, characterization of the polymers was done by NMR spectroscopy. The molecular weights obtained using GPC are summarized in Table 3. The molecular weights of the polymers decreased as the % of the functionalizing agent was increased, perhaps because the functional groups, like phenol, at the para position, forced the polymer to adopt a more compact conformation in solution. Alternatively, since the reactivity of the “pre” functionalized monomer should be lower than the unfunctionalized monomer, the lower molecular weight might also simply be a result of a slower reaction.

Figure 19 displays a TGA overlay of the phenol-functionalized polymers and the data is tabulated in Table 3. The \( T_d \) data from Table 3 indicate that the 50 or higher mole % functionalized polymers are not thermally stable. The decomposition temperatures, \( T_d (5\%)*'s \) of the phenol-functionalized polymers were in the range of 346 - 454 °C while the \( T_d (10\%) \) values were in the range of 385 - 520 °C. Figure 20 gives a view of the DSC overlay of Phenol-functionalized polymers. The \( T_g \) values of the phenol-functionalized polymers were in the range of 105 – 162 °C, while the \( T_m \) values were in the range of 314 - 326 °C.
Figure 19: TGA overlay of Phenol-functionalized polymers. A: 10 mole % (Pre); B: 10 mole % (Post); C: 50 mol % (Pre); D: 75 mol % (Pre); E: 100 mol % (Pre).

Figure 20: DSC overlay of Phenol-pre functionalized polymers.
**Figure 20** depicts how the crystallinity of the PEK was tuned using different mole %’s of phenol as functional agent. The 10 % pre-functionalized polymer was highly crystalline compared to all other polymers shown in the **Figure 20**. The crystallinity of the polymers decreased as the amount of the phenol incorporated in to the polymer increased.

**Figure 21**: $^{19}$F- NMR spectra of phenol functionalized polymers.

Since, the solubility of the functionalized polymers was significantly increased, compared to homopolymers, $^{19}$F-NMR spectroscopic analysis of the phenol-functionalized polymers was now possible. **Figure 21** displays an overlay of $^{19}$F-NMR spectra for the 50, 75, and 100 mol % phenol functionalized polymers.
Scheme 13: Assumptions to rationalize the phenol-functionalized polymerizations.

If the polymerization proceeded according to the earlier predictions, (i.e., only monosubstitution occurs and branching is not expected) only two peaks (1 and 3 in Figure 21) should be observed in the above figure, since the polymer should be obtained by the dimer A shown in Scheme 12 below. It is because A is more nucleophilic compared to monomer 2 hence, the polymerization proceeds in a linear fashion, by reaction of A with monomer 2. However, Figure
clearly demonstrates that there are two more peaks gradually increasing as the amount of the phenol is increased, which brings a couple of questions to mind.

One of these questions might be answered by the contents of Scheme 13. Thus, once \( A \), an \( \text{AB}_4 \) type dimer is formed, there are two other electrophilic sites also available for nucleophilic aromatic substitution, which might be the direction in which the polymerization takes place, and that might be the reason for getting two extra peaks. However, additional information is required before coming to a firm conclusion.

**4-Bromophenol functionalized polymerizations**

Since the solubility of the phenol-functionalized polymers was significantly increased compared to homopolymers, as well the crystallinity being tuned by the level of functionalization, further functionalizations of PEK was encouraged. As such, 4-bromophenol was used as the functionalizing agent for both ‘pre’ and ‘post’ modifications. The stoichiometry was varied from 10 to 50 mole % for the ‘pre’ functionalization approach. Post modifications were also done using the same mole %’s of 4-bromophenol, in order to verify whether any degradation occurred as the amount of functionalizing agent was increased.

The polymerization reactions were monitored by removing aliquots which were analyzed by GPC and the molecular weight and all other characterization data are tabulated in Table 4. The final polymers were purified using the same methods as described earlier. The solubility of the 4-bromophenol functionalized polymers was increased significantly as the amount of the functionalizing agent was increased.

It is readily apparent that the molecular weights of the polymers were decreased as the % of the functionalizing agent was increased. Figure 22 displays the TGA overlay of the 4-bromophenol-functionalized polymers. Decomposition temperatures, \( T_d \) (5 %)’s, of the 4-bromophenol-
Functionalized polymers were in the range of 360 - 470 °C, while \( T_d \) (10 %) s were in the range of 404 - 531 °C. Figure 23 gives a view of the DSC overlay of 4-bromophenol-functionalized polymers. The \( T_g \) values of the bromophenol-functionalized polymers were in the range of 129 – 152 °C, and \( T_m \) values were in the range of 312 - 330 °C. Table 4 illustrates that as the amount of 4-bromophenol added was increased the thermal stability of the polymer decreased, which was also observed with the phenol-functionalized polymers. The data indicate that incorporation of 10 and 25 mole % of the functional groups might be the favorable condition in order to achieve thermally stable, semicrystalline polymers having functional groups.

Table 4: Data for 4-bromophenol functionalized polymerizations.

<table>
<thead>
<tr>
<th>Type</th>
<th>Polymer</th>
<th>% of yield</th>
<th>( M_n ) (Da)</th>
<th>PDI</th>
<th>TGA (in °C)</th>
<th>DSC (in °C)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>( T_d ) 5%</td>
<td>( T_d ) 10%</td>
</tr>
<tr>
<td>PRE</td>
<td>10%</td>
<td>93</td>
<td>5000</td>
<td>2.35</td>
<td>450</td>
<td>520</td>
</tr>
<tr>
<td></td>
<td>25%</td>
<td>91</td>
<td>4460</td>
<td>1.9</td>
<td>440</td>
<td>504</td>
</tr>
<tr>
<td></td>
<td>50%</td>
<td>87</td>
<td>3700</td>
<td>2.7</td>
<td>355</td>
<td>410</td>
</tr>
<tr>
<td>POST</td>
<td>10%</td>
<td>90</td>
<td>4500</td>
<td>2.1</td>
<td>470</td>
<td>531</td>
</tr>
<tr>
<td></td>
<td>25%</td>
<td>83</td>
<td>1800</td>
<td>1.7</td>
<td>390</td>
<td>457</td>
</tr>
<tr>
<td></td>
<td>50%</td>
<td>81</td>
<td>1500</td>
<td>2.1</td>
<td>360</td>
<td>404</td>
</tr>
</tbody>
</table>
The DSC data for the 4-bromophenol-pre-functionalized PEKs are shown in Figure 23. In this case also, the crystallinity was tuned by changing the amount of functionalized group added. The crystallinity was decreased from the 10% functionalized polymer to the 25 % one. This crystallinity difference is even higher when the 25 % functionalized polymer is compared with 50 % functionalized one. The 50 mole % functionalized polymer almost lost its crystallinity and became essentially amorphous.
Figure 23: DSC overlay of 4-bromophenol-pre functionalized polymers.

3/4-Aminophenol functionalized polymerizations

Since it was observed that only the 10 and 25 mol % functionalizations afforded semicrystalline materials, subsequent modification with 3-Aminophenol, and 4-Aminophenol were carried out at these same levels. However, since some evidence of chain degradation was observed at higher % post modifications, only 10 mole % post modifications were done. The 3 and 4-aminophenol functionalized polymerization reactions were monitored by removing aliquots for analysis with GPC and the molecular weight results are listed in Table 5. The polymers were purified using the same methods as earlier.

The solubility of the 3, and 4-aminophenol functionalized polymers was increased significantly as the amount of the functionalizing agent increased similar to the earlier cases. It can be observed from the Table 5 that, the molecular weights of the polymers were slightly increased in the case of pre-functionalized polymers. Intermolecular forces, like hydrogen bonding, might be the reason for higher MWs, and better solubility. However, in the case of post
functionalized polymers, the MWs were decreased. Polymer degradation during the modification process might be the reason for the lower MWs.

Table 5: Data for 3/4-Aminophenol functionalized polymerizations.

<table>
<thead>
<tr>
<th>Functional group</th>
<th>Type</th>
<th>Polymer</th>
<th>% of yield</th>
<th>$M_n$ (Da)</th>
<th>PDI</th>
<th>TGA (in °C)</th>
<th>DSC (in °C)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>$T_d$ 5%</td>
<td>$T_d$ 10%</td>
</tr>
<tr>
<td>3-Aminophenol</td>
<td>PRE</td>
<td>10%</td>
<td>91</td>
<td>4700</td>
<td>2.2</td>
<td>492</td>
<td>535</td>
</tr>
<tr>
<td></td>
<td></td>
<td>25%</td>
<td>88</td>
<td>5700</td>
<td>1.8</td>
<td>495</td>
<td>536</td>
</tr>
<tr>
<td></td>
<td>POST</td>
<td>10%</td>
<td>90</td>
<td>3200</td>
<td>1.9</td>
<td>482</td>
<td>532</td>
</tr>
<tr>
<td></td>
<td>PRE</td>
<td>10%</td>
<td>92</td>
<td>5100</td>
<td>2.8</td>
<td>487</td>
<td>537</td>
</tr>
<tr>
<td>4-Aminophenol</td>
<td>POST</td>
<td>10%</td>
<td>91</td>
<td>3000</td>
<td>5.1</td>
<td>437</td>
<td>515</td>
</tr>
</tbody>
</table>

Further analysis of the polymers was done by NMR spectroscopy and thermal methods. Figure 24 has shown the TGA overlay of 3/4-aminophenol-functionalized polymers. The decomposition temperatures, $T_d$ (5 %)’s of the phenol-functionalized polymers were in the range of 437- 500 °C, while $T_d$ (10 %)’s were in the range of 515 - 543 °C. Figure 25 gives a view of the DSC overlay of the 3/4 – aminophenol-functionalized polymers. The $T_g$’s of the phenol-functionalized polymers were in the range of 165 – 174 °C, while the $T_m$ values were in the range of 315 -329 °C.
**Figure 24.** TGA overlay of 3 / 4-Aminophenol-pre functionalized polymers. A: 3-Aminophenol-10 mole % (Pre); B: 3-Aminophenol- 25 mole % (Pre); C: 3-Aminophenol- 10 mole % (Post); D: 4-Aminophenol- 10 mole % (Pre); E: 4-Aminophenol- 25 mole % (Pre); F: 4-Aminophenol- 10 mole % (Post).

**Table 5** and Figure 24 depict the thermal stability of the polymers and indicate that the 10 and 25 % functionalized polymers are more thermally stable compared to both the phenol and 4-bromophenol analogues. The presence of strong intermolecular forces might be the reason for the higher thermal stability of these polymers.
**Figure 25**: DSC overlay of 3/4-aminophenol-pre functionalized polymers. A: 3-Aminophenol-10 mole % (Pre); B: 3-Aminophenol-25 mole % (Pre); C: 4-Aminophenol-10 mole % (Pre); D: 4-Aminophenol-25 mole % (Pre).

The DSC traces for the 3/4-aminophenol-pre-functionalized PEKs, are shown in the **Figure 25**. In this case, the crystallinity was decreased substantially from the 10% functionalized polymer to the 25% one. However, the 3/4-aminophenol-functionalized polymers are a bit less crystalline, compared to their phenol and 4-bromophenol analogues. At each level of modification the aminophenol functionalized materials possessed a somewhat higher $T_g$ value than either phenol or bromophenol systems. The presence of hydrogen bonding in the aminophenol functionalized polymers might be the reason for higher $T_g$ values. However, if that is the case, the 25% functionalized polymer should have a higher $T_g$ value compared to their 10% analogue and this is not the behavior observed. The reason for this might be that the higher % functionalized polymers are most likely to favor a cyclization process, same as in the case of phenol-
functionalized polymers, hence $T_g$ values might decreased slightly as the amount of functional group added increased.

In order to further study and compare the thermal properties of the obtained polymers, further TGA and DSC analyses were also done. **Figures 26 and 27** illustrate the comparison of 10 % functionalized polymers with the homopolymers. **Figure 26** is the DSC overlay of 10 % pre-functionalized polymers comparison with homopolymer. **Figure 27** is the DSC overlay of 10 % pre-functionalized polymers comparison with homopolymer. Both the data from the tables along with **Figures 26 and 27** confirm that the crystallinity of the polymers was tuned by the amount of the functional group added.

![DSC overlay of 10 %-pre functionalized polymers comparison with homopolymer. A: homo; B: 4-aminophenol; C: 3-aminophenol; D-4-bromophenol; and E: phenol functionalized polymers.](image)

**Figure 26**: DSC overlay of 10 %-pre functionalized polymers comparison with homopolymer. A: homo; B: 4-aminophenol; C: 3-aminophenol; D-4-bromophenol; and E: phenol functionalized polymers.
Figures 26 and 27 show that the homopolymer, at least the sample prepared at 150 °C, doesn’t possess an observable $T_c$ or $T_m$, which indicates that it may be highly crystalline. However, in the case of the functionalized polymers, the crystallinity was decreased significantly.

![DSC overlay of 10% post functionalized polymers comparison with homopolymer.](image)

Figure 27: DSC overlay of 10% post functionalized polymers comparison with homopolymer. A: homo; B: 4-aminophenol; C: 3-aminophenol; D: 4-bromophenol;

As a continuation of the DSC analysis, the 25% functionalized polymers were also compared to get an idea regarding the extent to which crystallinity was decreased as the amount of the functional group increased. Based on Figure 28 and the data from the tables, it is observed that the 25% functionalized polymers are semi-crystalline in nature as well. However, the 3/4-aminophenol polymers might have little lower crystallinity compared to their phenol and 4-bromophenol analogues.
Figure 28. DSC overlay of 25 % pre-functionalized polymers. A: phenol; B: 4-bromophenol; C: 3-aminophenol; D: 4-aminophenol.

TGA in air atmosphere

TGA analysis for the 10% pre-functionalized polymers, as well as the homopolymer, was done under air atmosphere in order to estimate the thermal stability of the polymers in real world conditions. Usually, the polymers are thermally less stable in air compared to nitrogen atmosphere. It might be because the polymers decompose faster in the presence of oxygen in the air. There is thermal stability and then there is thermooxidative stability. Nitrogen tends to remove the oxidative part. Table 6 shows the TGA values of the 10% pre-functionalized polymers, and homopolymer, in an air atmosphere. The data shows that the decomposition temperatures in air are significantly lower compared to the ones in determined in a N\textsubscript{2} atmosphere.
Table 6: TGA analyses (in air) of 10 % pre-functionalized polymers in comparison with homopolymer.

<table>
<thead>
<tr>
<th>Functional group</th>
<th>TGA (in °C) (AIR)</th>
<th>TGA (in °C) (N₂)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>T_d (5 %)</td>
<td>T_d (10 %)</td>
</tr>
<tr>
<td>Homopolymer</td>
<td>450</td>
<td>485</td>
</tr>
<tr>
<td>Phenol</td>
<td>403</td>
<td>484</td>
</tr>
<tr>
<td>4-Bromophenol</td>
<td>457</td>
<td>508</td>
</tr>
<tr>
<td>3-Aminophenol</td>
<td>456</td>
<td>491</td>
</tr>
<tr>
<td>4-Aminophenol</td>
<td>454</td>
<td>492</td>
</tr>
</tbody>
</table>

Figure 29. TGA analyses (in air) of 10 % pre-functionalized polymers in comparison with homopolymer.

Figure 29 explains the lower decomposition temperatures for the polymers in air. In N₂ atmosphere, polymers are highly stable and they didn’t even lose 50 % of the polymer at 600 °C.
However, in air, ~100 % of the polymer was decomposed at 600°C, which is clear evidence that polymers are not as thermally stable when compared to N₂ data.

**Conclusions**

Semicrystalline, functionalized PEKs were synthesized via an *in situ* modification approach. The homo polymerization reactions might be selective at lower temperatures and, as result, a highly crystalline polymer might have been obtained, while at higher reaction temperatures, semicrystalline homo polymers were achieved. However, all of the homopolymers have poor solubility in organic solvents. Functionalization of PEKs was done successfully via both “pre”, and “post” modification approaches. The molecular weights of the functionalized polymers, except in the case of aminophenol functionalized polymers, were decreased as the amount of the functional group added, concurrently, significant increases in polymer solubility were achieved. The use of DSC analysis allowed a determination of the crystallinity of the polymers obtained. All of the 10 and 25 mole % functionalized polymers were semicrystalline, while the 50 mole % functionalized polymers were minimally crystalline. At levels higher than 50 %, the functionalized polymers were completely amorphous.

**Future Work**

Since semicrystalline homopolymers were achieved at higher temperatures, functionalizations of the polymers need to be done under the same conditions, in both NMP and DMSO solvent, in order to increase the solubility of the homopolymers and tune the crystallinity with a minimal amount of the functionalizing agent. Functionalizations of polymers should also be done at lower temperatures in highly polar solvents like DMSO, in order to verify the trend of tuning the crystallinity and solubility.
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