Modifiable Poly(arylene ether)s and Hyperbranched Poly(esters)

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Modifiable Poly(arylene ether)s and Hyperbranched Poly(esters).

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

Master of Science

By

BRIAN SCOTT WERRY
B.S., Wright State University, 2005

2007
Wright State University
I HEREBY RECOMMEND THAT THE THESIS PREPARED UNDER MY SUPERVISION BY Brian Werry ENTITLED Modifiable Poly(arylene ether)s and Hyperbranched Poly(esters) BE ACCEPTED IN PARTIAL FULFILLMENT OF THE REQUIREMENTS FOR THE DEGREE OF Master of Science.

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Werry, Brian S. M.S., Department of Chemistry, Wright State University, 2007. Modifiable Poly(arylene ether)s and Hyperbranched Poly(esters).

Two different polymer systems have been studied in regards to their potential for functionalization to introduce new characteristics to the polymer. The first polymer system is a poly(arylene ether) with a truly pendant sulfone group from the monomer 3,5-difluorodiphenylsulfone. The work entails incorporating a bromine moiety onto the monomer for the versatile ability to bring in functional groups prior to or post the polymerization. The introduction of bromine onto the pendant ring had the best results from electrophilic bromine addition using N-bromosuccinimide in a mixture of sulfuric acid and acetic acid (80:20) yielding 76% of the desired material. Incorporation of the bromine moiety did not interfere with the nucleophilic aromatic substitution reaction utilized in the polymerization and modification was shown to proceed smoothly both prior and post polymerization. The second project involved the study and production of a poly(ester) hyperbranched system from glycerol and fumaric acid. These hyperbranched polymers were prepared using an A$_2$ + B$_3$ approach in a bulk synthesis. The study involves varying the molar ratio of A$_2$ to B$_3$ and temperature to control the polymerization and avoid gelation while pushing the polymerization to larger molecular weights. The two monomers bring the characteristic of biocompatibility with them into the polymer. In addition, the fumaric acid monomer unit brings an alkene bond available for modification. Average molecular weights achieved were around 5,000 daltons. Obtained PDI values were as low as 4.6, and DB values ranged from 0.26 to 0.38. Analysis on new compounds and polymers was done by NMR spectroscopy, GC/MS, and size exclusion chromatography where applicable.
Table of Contents

I. Introduction .....................................................................................................................1
   Polymers and Composite Materials .........................................................................1
   Modification of Polymers .....................................................................................4
   Overview of This Project ...................................................................................11
   References ........................................................................................................12

II. Monomer Synthesis for Polymer Modification of Poly(arylene ether)s .......................13
   Functionalizing Polymers ..................................................................................13
   Pre and Post Modification a Versatile Approach to Modification .......................13
   Experimental ..................................................................................................19
      Synthesis of 3’-Bromo 3,5-difluorodiphenyl sulfone .....................................19
      Bromination Using NBS in Sulfuric Acid .................................................20
      Bromination Using NBW in DMF ............................................................20
      Bromination Using SMBI in Sulfuric Acid .............................................20
      Bromination Using NBS in Chloroform ...............................................20
      Bromination using Br₂ in Sulfuric acid ................................................21
      Bromination using NBS in Sulfuric acid and Acetic Acid ....................21
      Bromination using NBS in Acetic Acid ...................................................21
      Polymerization with 3’-Bromo 3,5-difluorodiphenyl sulfone ............22
      Suzuki Modification of 3’-Bromo 3,5-difluorodiphenyl sulfone ............22
      Azide Modification of Brominated Polymer ....................................23
   Results and Discussion ....................................................................................25
   Conclusion .....................................................................................................39
   References .....................................................................................................40

III. Bulk Polymerization Studies With Fumaric Acid and Glycerol ................................41
   Hyperbranched Polymers A₂ + B₃ and AB₂ Approach ....................................41
   Experimental ..................................................................................................45
      Typical Polymerization Procedure .......................................................45
      Polymerization With Valeric Acid as Capping Agent ............................46
      Procedure for Model Branching Study ................................................47
   Results and Discussion ..................................................................................48
      1 to 1 Ratio Glycerol to Fumaric Acid at 150°C ..................................48
      1 to 1 Ratio Glycerol to Fumaric Acid at 130°C ..................................50
      1.03 to 1 Ratio Glycerol to Fumaric Acid at 150°C ...............................53
      1.05 to 1 Ratio Glycerol to Fumaric Acid at 150°C ...............................56
      1 to 1 to 1 Glycerol, Fumaric Acid, and Valeric Acid at 150°C ........56
      Degree of Branching .............................................................................57
      Model Synthesis .....................................................................................59
   Conclusion .....................................................................................................66
   References .....................................................................................................67
List of Figures

I. Introduction:

Figure 1. Polymer and monomer structure example...........................................................1

Figure 2. Example of types of structural polymers.............................................................2

II. Monomer Synthesis for Polymer Modification of Poly(arylene ether)s

Figure 1. Gas chromatograph of crude bromination reaction ........................................28

Figure 2. Mass spectrum from 7.08 minute peak from Figure 1 ........................................28

Figure 3. Mass spectrum from 8.63 minute peak from Figure 1 ........................................28

Figure 4. Mass spectrum from 8.75 minute peak from Figure 1 ........................................29

Figure 5. Mass spectrum from 8.80 minute peak from Figure 1 ........................................29

Figure 6. Mass spectrum from 8.99 minute peak from Figure 1 ........................................29

Figure 7. Mass spectrum from 10.13 minute peak from Figure 1 ......................................30

Figure 8. Mass spectrum from 10.24 minute peak from Figure 1 ......................................30

Figure 9. Mass spectrum from 10.36 minute peak from Figure 1 ......................................30

Figure 10. Mass spectrum from 10.49 minute peak from Figure 1 ....................................31

Figure 11. Gas chromatograph of purified brominated material ......................................31

Figure 12. Labeled H$^1$ spectra for 3’-bromophenyl-3,5-difluorophenylsulfone ..............32

Figure 13. Labeled C$^{13}$ spectra for 3’-bromophenyl-3,5-difluorophenylsulfone ..............32

Figure 14. Gas chromatograph of purified Suzuki coupling product .............................33

Figure 15. Mass spectrum from 21.48 minute peak from Figure 14 ...............................34

Figure 16. Labeled H$^1$ peaks for 3’-(p-methoxyphenyl)phenyl-3,5-
difluorophenylsulfone ....................................................................................................34
List of Figures (Continued)

Figure 17. Labeled C\textsuperscript{13} spectra for 3’-(\textit{p}-methoxyphenyl)phenyl-3,5-difluorophenylsulfone .................................................................35

Figure 18. Labeled C\textsuperscript{13} spectra for 3’ bromo poly(aryl ether sulfone) ....................................37

Figure 19. Labeled C\textsuperscript{13} spectra for azido poly(aryl ether sulfone)............................37

Figure 20. Overlay of monomer to polymer then modified polymer..........................38

Figure 21. Infared spectrum of bromo poly(aryl ether sulfone)........................................38

Figure 22. Infared spectrum of azido poly(aryl ether sulfone)..........................................39

III. Bulk Polymerization Studies With Fumaric Acid and Glycerol

Figure 1. SEC trace overlay of 1 to 1 ratio polymerization at 150°C .........................49

Figure 2. Plot of polymer size growth vs. time for 1 to 1 ratio polymerization at 150°C ............................................................................................................50

Figure 3. Plot of polymer PDI vs. time for 1 to 1 ratio polymerization at 150°C .....................................................................................................................50

Figure 4. SEC trace overlay of 1 to 1 ratio polymerization at 130°C .........................51

Figure 5. \(M_w\) vs. time for 1 to 1 ratio polymerization at 130°C.................................52

Figure 6. PDI vs. time for 1 to 1 ratio polymerization at 130°C...............................52

Figure 7. SEC trace overlay of 1.03 to 1 ratio polymerization at 150°C .................54

Figure 8. \(M_w\) vs. time for 1.03 to 1 ratio polymerization at 150°C..........................54

Figure 9. PDI vs. time for 1.03 to 1 ratio polymerization at 150°C..........................55

Figure 10. SEC trace overlay 1 to 1 to 1 ratio B\textsubscript{3} to \textit{A}_2 to valeric acid polymerization at 150°C ...........................................................................57
List of Figures (Continued)

Figure 11. C\textsuperscript{13} DEPT 135 overlay of model study .............................................................62

Figure 12. C\textsuperscript{13} DEPT 135 overlay of 1:1 B\textsubscript{3} to A\textsubscript{2} at 150\textdegree C .............................................63

Figure 13. C\textsuperscript{13} DEPT 135 overlay 1 to 1 to 1 ratio B\textsubscript{3} to A\textsubscript{2} to valeric acid polymerization at 150\textdegree C ....................................................................................64
List of Schemes

I. Introduction

Scheme 1. Generic examples of polymer modification methods ........................................5

Scheme 2. H. Ritter et al. modified monomer polymerization ........................................7

Scheme 3. G. Ahmetli et al. modification of polystyrene polymers ..................................8

Scheme 4. Hay et al. modification scheme of poly(arylene ether sulfone)s ....................10

Scheme 5. Z. Li et al. polymer functionalization after activation of pendant group .......10

II. Monomer Synthesis for Polymer Modification of Poly(arylene ether)s

Scheme 1. Grignard synthesis of 3,5-difluorodiphenylsulfone ......................................14

Scheme 2. Scheme of prior or post polymer modification ..............................................15

Scheme 3. Flow scheme of possible routes to adding functionality to a polymer

through the use of a brominated monomer ......................................................................16

Scheme 4. Grignard synthesis for introduction of bromine moiety ...............................17

Scheme 5. Nucelophilic aromatic substitution with bromine ........................................18

Scheme 6. Possible products from nucleophilic aromatic substitution ..........................26

Scheme 7. Modification prior to polymerization using Suzuki coupling .....................33

Scheme 8. Polymerization of 3’-bromophenyl-3,5-difluorophenylsulfone

with bisphenol A .............................................................................................................36

Scheme 9. Post modification of polymer by azide substitution .....................................36

III. Bulk Polymerization Studies With Fumaric Acid and Glycerol

Scheme 1. Polymerization scheme for glycerol and fumaric acid .............................44
List of Schemes (Continued)

**Scheme 2.** Polymerization with valeric acid as capping agent........................................56

**Scheme 3.** Reaction sequence of glycerol in model study .................................................59
List of Tables

I. Introduction

Table 1. Examples of polymers and properties .................................................................3

II. Monomer Synthesis for Polymer Modification of Poly(arylene ether)s

Table 1. Results of brominating methods of 3,5-difluoro-diphenyl sulfone ..................25

III. Bulk Polymerization Studies With Fumaric Acid and Glycerol

Table 1. SEC analysis results 1 to 1 ratio B₃ to A₂ polymerization at 150°C ..............49

Table 2. SEC analysis results 1 to 1 ratio B₃ to A₂ polymerization at 130°C ...............51

Table 3. SEC analysis results 1.03 to 1 ratio B₃ to A₂ polymerization at 150°C ..........53

Table 4. SEC analysis results 1.05 to 1 ratio B₃ to A₂ polymerization at 150°C ..........56

Table 5. SEC analysis results 1 to 1 to 1 ratio B₃ to A₂ polymerization at 150°C with valeric acid capping agent .............................................................57

Table 6. C¹³ NMR spectral glycerol branching unit assignments of secondary carbon .58

Table 7. SEC results for individual polymerizations and degree of branching ..........65
Acknowledgements

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I. INTRODUCTION

Over the years, the chemistry of polymers and monomers has received considerable attention and produced a variety of polymers and materials which can be found in almost every aspect of life. A polymer is a molecule comprised of smaller molecules, called monomers, which are connected, typically via covalent bonds, to form the repeating units that build the larger molecule. Poly(styrene), for example, is the polymer made from styrene units.

![Polymer and monomer structure example](image)

**Figure 1.** Polymer and monomer structure example.

Polymers make up a majority of the “structural” world and can be found in something as simple as a plastic spoon to extremely complex biological systems. Some well-known examples of polymers include rubber, cellulose, DNA, and Styrofoam.

The physical and chemical differences among the various classes of polymers are determined, primarily, by the intermolecular forces between polymer molecules and intramolecular forces within individual polymer molecules. Influencing these properties
are the shape, size, and functional groups present within (backbone) and on (pendant) the polymer. The shape of the polymer has a significant influence in the physical characteristics of the polymer. Dendritic polymers are perfectly branched polymers showing low viscosities and a large number of end groups. Hyperbranched polymers lack the perfect branching of dendritic polymers, but display properties between the dendritic and linear class. Linear polymers are more likely to entangle and therefore have higher viscosities than the branched analogues. The level of entanglement plays a role in the viscosity and strength of the polymer network. These structural attributes of polymers strictly influence the physical properties of the polymer and influence characteristics such as viscosity, solubility, tensile strength, density, etc.

![Linear](image1)

![Hyperbranched](image2)

![Dendritic](image3)

**Figure 2.** Example of types of structural polymers.

Chemical properties, however, are governed by the functional groups present within and attached to the polymer. Incorporation of functional groups onto polymer systems will be the focus of this discussion. There are really two roles that functional groups can
play in a polymer. They can be a part of the polymer backbone giving rise to the polymer’s structural characteristics and affecting the physical properties as well as having some influence on its chemical properties. The functional groups in the backbone are often used to identify many classes of polymers such as poly(aliphatic)s, poly(ester)s, poly(sulfone)s, poly(ether)s, poly(aryl ether)s, poly(ketone)s. The possibilities are essentially limitless due to the vast number of different functional groups and the ability to combine and mix the assortment of groups together; for example, poly(aryl ether ketone)s. Table 1 lists some classes of polymers with an example and description of the pertinent properties displayed by the polymer family.

**Table 1.** Examples of polymers and properties.[11]

<table>
<thead>
<tr>
<th>Type</th>
<th>Example</th>
<th>Characteristic Properties</th>
</tr>
</thead>
<tbody>
<tr>
<td>Poly(ether)s</td>
<td>Poly(ethyleneglycol)</td>
<td>Soluble in many solvents</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Liquid or low melting solids</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Used in many molded products</td>
</tr>
<tr>
<td>Poly(aliphatic)s</td>
<td>Poly(ethylene)</td>
<td>Good chemical resistance</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Excellent chemical resistance</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Used in many molded products</td>
</tr>
<tr>
<td>Poly(sulfone)s</td>
<td>Udel® polysulfone</td>
<td>High impact polymers</td>
</tr>
<tr>
<td></td>
<td></td>
<td>High temp. resistant</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Chemical stability</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Rigid</td>
</tr>
<tr>
<td>Poly(ester)s</td>
<td>Poly(ethylene terephthalate)</td>
<td>Good processability</td>
</tr>
<tr>
<td></td>
<td></td>
<td>High strength</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Good gas and liquid barrier</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Rigid</td>
</tr>
<tr>
<td>Poly(amide)s</td>
<td>Nylon6-6</td>
<td>Flexibility</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Abrasion resistance</td>
</tr>
<tr>
<td></td>
<td></td>
<td>High Impact strength</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Resistant to organic solvents</td>
</tr>
</tbody>
</table>
The other role is a functional group that is pendant to the polymer backbone. Pendant groups can influence the polymer properties through intermolecular forces, act as some kind of active site in a system i.e., catalyst, increase or decrease solubility in solvents, and bring a whole assortment of new characteristics to the original polymer.

The ability to add functional groups on to polymers, referred to as polymer modification, is not a new concept. Polymer modification makes up a majority of the polymer research field and actually precedes the actual study and understanding of polymers. Natural polymers have been, years before their discovery, modified to provide new useful materials. Charles Goodyear, in 1839, discovered that heating natural rubber with sulfur created a new strong and resistant material. The rubber was being cross-linked, forming a network of the polymers that made the natural polymer more resistant. In 1865 cellulose was reacted with acetic acid, acetic anhydride, and sulfuric acid to produce a new modified polymer to be used as a fiber in the fabric industry. Both of these early developments in polymer technology were empirical because of a lack of knowledge about polymer science. Advancement in the understanding and development of polymers and its science has been rapid since the 1930’s. A vast number of synthetic polymers have since been developed and are available for modification.

Polymer functionalization centers around imparting new properties (e.g. chemical, biophysical, biocompatibility, permeability, physicochemical, photonic, and electronic) to materials for uses in inorganics and organics as catalysts and supports; medicine; optoelectronics; biomaterials; paints; varnishes; building materials; photographic materials; lubricants and fuel additives. In principle, any chemistry that has been applied to small molecules can be applied to polymers in order to functionalize them.
There are essentially only two methods available to incorporate functional groups pendant to the backbone. The first method involves incorporation of the desired functional group during the synthesis of the polymer through polymerization and copolymerization of monomers containing the desired functional group. The second approach involves direct modification on the already formed polymer chain. Each of the two approaches has its own advantages and disadvantages, and one approach may be ideal for a particular system when the other would be totally impractical.

**Scheme 1.** Idealized generic examples of polymer modification methods.

- **Polymerization with Functional Group**
  - \( \text{monomer} \quad \text{FG} \quad \text{polymerization} \)

- **Co-polymerization with Functional Group**
  - \( \text{monomer} + \text{monomer} \quad \text{FG} \quad \text{polymerization} \)

- **Direct Functionalization on polymer**
  - \( \text{functionalization} \)
Much of polymer research goes into developing these new monomer derivatives to form functional polymers.\textsuperscript{[2][3][4]} By building the functionality into the monomer, the functional group is built into the system as the polymer grows. The advantage of this approach is the potential to control the amount, gradient, and location of where the functional groups are located within the polymer. However, if the functional group on a modified monomer directly interacts with the system by inductive and/or mesomeric effects there can be interference in the reactivity and cause a change in the efficiency of the polymerization. Also, if the functional group reacts in an undesired way during the polymerization process, you can lose the original functionality desired from the functional group, and/or interfere with the polymerization either by quenching it or possibly cross-linking the system.

An example of a functionalized monomer is the synthesis of a carboxylic acid derivative of bisphenol A, 1, to polymerize with 4,4′-difluorobenzophenone, 3, to study the property changes from the unmodified version as reported by H. Ritter et al. (Scheme 2).\textsuperscript{[5]} Along with the polymer possessing acidic properties, the glass transition temperature, $T_g$, increased substantially (158°C to 187°C). This is due to the additional sites for hydrogen bonding that the pendant functional groups bring to the polymer.
Modification of polymers by direct chemical modification to the polymer makes it possible to create new classes of polymers that cannot be prepared by monomer modification owing to a functional group’s instability or interference with the desired polymer synthesis reaction. Direct modification of polymers, however, does have disadvantages that must be considered before a polymer can be functionalized by this method including: 1) the functionalization reaction should be carried out under mild conditions so as not to harm or degrade the polymer, 2) any reactions used must be clean and selective, because every undesirable group formed becomes a part of the polymer.
chain, 3) the modified polymers rarely have every repeat unit functionalized, so the
distribution is most often not uniform, and 4) reactions involving polymers have quite
different characteristics and reactivity from the analogous small molecule and might
require changes to the reaction designed for small molecules.

An example of direct modification can be seen in research reported by Gulnare
Ahmetli et al.[6] where post modification was done on polystyrene, 5, to study the
changes in thermal properties (Scheme 3). Polystyrene was modified with maleic
anhydride, 6, and acetic anhydride, 8. The modified polymers 7 and 10 exhibited a better
stability against thermal degradation than the unmodified polystyrene. Modification with
epichlorohydrin, 11, followed by dehydrochlorination produced an epoxy polystryene,
13, for the possibility of further modification or cross-linking.

**Scheme 3.** G. Ahmetli et al. modification of polystyrene polymers.
A more versatile approach, which is attracting considerable attention, is the preparation of a monomer containing a moiety that is inert to and does not interfere with the polymerization process, but undergoes facile and selective conversion to a variety of functional groups before or after incorporation into the polymer. The ability to add functionality to the monomer prior to polymerization or to the polymer after its synthesis, at the active moiety, is what gives this method its versatility. A. S. Hay et al. [7] utilized this method to add functionality to poly(arylene ether sulfone)s. The work utilizes the \(N\)-phenylimide pendant group on the \textit{bis}-phenolic monomer, 3,8-bis(4-hydroxyphenyl)-\(N\)-phenyl-1,2-naphthalimide, as a site for functionalization by transimidization (Scheme 4). Another interesting project comes from M. D. Guiver et al. [8] who prepared a bisphenol monomer with grafting capability. The monomer has a pendant sulfide group that can be oxidized to the corresponding sulfone group that activates the fluorine atom in the \textit{para} position for further \textit{S}_{\text{N}}\text{Ar} reactions (Scheme 5).
Scheme 4. Hay et al. pre and post modification scheme of poly(arylene ether sulfone)s.

The R-pendants are able to be attached before or after polymerization by transimidization.

Scheme 5. Z. Li et al. polymer functionalization after activation of pendant group.
Herein two projects undertaken with the purpose of preparing readily modifiable polymers are discussed. Each project will be presented as its own chapter. Chapter two is a project entailing the synthesis of a sulfone monomer with a bromine moiety that does not interfere with the polymerization process and offers the ability to add functionality to a poly(arylene ether) either prior to or post polymerization. Chapter three describes an \( A_2 + B_3 \) hyperbranching polyesterification study with glycerol and fumaric acid which are two low cost, biologically compatible materials. This project starts with a thorough study on the hyperbranched polymer growth of these two with regards to branching structure, molecular weight, and polydispersity index. The project’s conclusion will be the ability to modify the hyperbranched polymer at its available modification sites, hydroxyl or carboxylic acid groups, and then its ability to be used for specific applications such as drug delivery or low VOC epoxy resin systems.
References


II. MONOMER SYNTHESIS FOR POLYMER MODIFICATION OF POLY(ARYLENE ETHER)S

An important aspect of polymer chemistry is the ability for polymeric materials to possess complex properties and specific functionality. The functional groups can be introduced at the monomer synthesis stage or via chemical modification on preformed polymers. Each of these methods has its associated advantages and disadvantages. A significant complication that arises when incorporating the functional groups prior to the polymerization reaction is the possibility of interference with the polymerization process resulting in undesired side reactions. Modification, via a polymer analogous reaction, is a potential solution to functional group interference. However, post polymeric modifications often require multiple steps and severe reaction conditions that may jeopardize the integrity of the polymer backbone. An alternative approach that allows more versatility would be to prepare a monomer containing a moiety that allows facile and mild conversion to a variety of functional groups either at the monomer or polymer stage.

For this study, it was sought to add this versatile ability to add specific functionality to the already well known and widely applied poly(arylene ethers)s. Poly(arylene ether)s have gained significant attention due to their favorable combination of properties such as thermo-oxidative stability, solvent resistance, electrical performance, flame resistance, and retention of physical properties at elevated temperatures[1]. Poly(arylene ether)s are
typically prepared via the nucleophilic aromatic substitution of activated aromatic fluorides or chlorides with bis-phenolates derived from the corresponding bisphenols. We have recently reported the synthesis of 3,5-difluorodiphenylsulfone, 3, (Scheme 1) via a nucleophilic substitution reaction of 3,5-difluorophenylmagnesium bromide, 2, with benzenesulfonyl chloride, 1. The resulting difluoro monomer can then be used as the electrophilic component in nucleophilic aromatic substitution, NAS, polycondensation reactions with a variety of bisphenols. Because the activation is provided by the phenyl sulfonyl group, located in the meta position to both electrophilic sites, the resulting poly(arylene ether)s possess the phenyl sulfonyl group as a truly pendant moiety. It is worth mentioning that, in contrast to a typical poly(arylene ether sulfone) in which the activating sulfonyl group is present in the backbone, the material possessing the sulfone as a pendant group leaves the polymer as a poly(arylene ether) with a structure similar to poly(phenylene oxide), but with a readily modifiable side group.

Scheme 1

Introduction of an aryl bromide on the pendant ring, prior to the polymerization reaction would afford a versatile platform for both pre- and post polymerization modification chemistry. Scheme 2 shows the two possible routes to add functionality to poly(arylene ether)s using the brominated material. The top path shows modification of
the monomer before polymerization and the bottom path shows modification on the polymer, both paths utilizing the aryl bromide site. The resulting aryl bromide is not likely to interfere with the NAS reaction utilized to prepare the polymers. In addition, the chemistry of aryl bromides is very rich and should provide efficient means to a diverse set of functional groups.

**Scheme 2**

![Scheme 2 Diagram](#)

Possible functional group pendants that are then available through the brominated material are shown in **Scheme 3**. Coupling reactions of aryl halides such as Suzuki\(^3\), Sonogashira\(^4\) and Grignard offer a wide range of alkyl and aryl substitution options. A metal halogen exchange reaction affords the possibility to introduce a carboxylic acid pendant group or other functionality via reaction with a variety of electrophiles. The Heck reaction works well with aryl bromides and offers the option of introducing substituted alkenes onto the polymer\(^5\). The ability to substitute the halide for an azide
group or terminal acetylene opens up another cascade of possibilities with “click” chemistry. [6]

Scheme 3

Introduction of the desired bromo moiety was previously attempted by a fellow group member using the same nucleophilic substitution reaction utilized for the synthesis of 3, but using 4-bromobenzenesulfonyl chloride, 4, and 3,5-difluorophenylmagnesium bromide, 2, to afford 5, (Scheme 4). However, this approach proved to be inefficient for two reasons. First, the starting material is quite expensive, relative to benzenesulfonyl chloride. Second, metal halide exchange of the desired product, 5, with excess Grignard
reagent, resulted in the formation of 3,5-Difluorodiphenylsulfone, 3, which proved difficult to separate from the desired product.

Scheme 4

Therefore, an approach involving the subsequent addition of a bromine moiety to 3 (Scheme 5) should provide the flexibility to introduce a variety of functional groups, both prior to the polymerization reaction, or after its use to prepare a poly(arylene ether). It should be noted that introduction of the bromide after the poly(arylene ether) has been formed is difficult as the electrophilic aromatic substitution would most likely occur at the electron rich bisphenol segment.

There are a variety of methods to introduce a bromine atom onto the aryl ring of these monomers. Presented here are our efforts to provide a flexible route to functionalized poly(arylene ether)s via aryl bromide chemistry. This approach utilizes the phenylsulfone pendant monomer and offers versatility in modification through either prior or post-polymerization functionalization. The possibilities discussed here are relatively inexpensive and offer good yields without sacrificing ease of synthesis.
Experimental

Materials. Sodium monobromo isocyanuric acid, SMBI, was obtained from TCI. All other reagents and solvents were received from Aldrich and used without further purification. 3,5-difluorodiphenyl sulfone, 3, was prepared according to a literature procedure.[2]

Instrumentation. $^1$H and $^{13}$C NMR spectra were obtained using a Bruker Avance 300 MHz instrument operating at 300 and 75.5 MHz respectively. $^{19}$F NMR spectra were acquired using a Bruker Avance 400 MHz instrument operating at 376.5 MHz with 10% CFCl$_3$ as an external standard, and the instrument set relative to the lock signal. Reaction progress was followed by removing aliquots and analysis using a Hewlett Packard 6890 series GC system and Hewlett Packard 5973 mass selective detector.

Synthesis of 3’-Bromo 3,5-difluorodiphenyl sulfone, 6.

In a 250 mL round bottom flask was placed 5.044 g (19.84 mmol) of 3 dissolved in 100 mL of an 80:20 sulfuric acid: acetic acid solution. The reaction mixture was cooled by an acetone/ice bath (-15°C) at which point 3.708 g (20.83 mmol) of N-bromosuccinimide, NBS, was added and the resulting solution was left to stir for 24 hours. Initial analysis by GC-MS showed that 76.33% of the desired mono-brominated material, 6, was formed. Work up included precipitation of products from water and recrystallization from a mixture of ethanol, chloroform and toluene at a ratio of 80:10:10 to obtain 3.327 g of 6 as white flakey crystals (50.34%) with a mp of 132-133°C. $^1$H NMR (CDCl$_3$, δ): 7.04 (tt, 1H, ArCH), 7.44 (t, 1H, ArCH), 7.48 (dtd, 2H, ArCH), 7.75 (dt, 1H, ArCH), 7.88 (dt, 1H, ArCH), 8.07 (t, 1H, ArCH). $^{13}$C NMR (CDCl$_3$, δ): 109.3 (t,ArCH), 111.4 (d,ArCH), 123.6 (ArCBr), 126.5 (ArCH), 130.7 (ArCH), 131.1 (ArCH),
137.0 (ArCH), 142.1 (ArCS), 144.2 (ArCS), 162.9 (dd, ArCF). $^1$H NMR (DMSO, δ) - 106.2 (ArF). MS (EI): [M$^+$] m/z calcd for C$_{12}$H$_7$F$_2$O$_2$SBr, 333.93; found 334. Calcd Anal. for C$_{12}$H$_7$F$_2$O$_2$SBr: Calcd.: C, 43.26; H, 2.12. Found: C, 43.12; H, 2.19.

**Bromination of 3,5-Difluorodiphenyl sulfone using NBS in Sulfuric acid**

In a 25 mL round bottomed flask, were placed 0.715 g (2.81 mmol) of 3 and 14 mL of concentrated sulfuric acid. Then 0.526 g (2.95 mmol) of N-bromosuccinimide was added and the resulting mixture was left to stir for 4 hours at room temperature. Analysis by GC/MS shows that 63.14% of 6 was formed.

**Bromination of 3,5-Difluorodiphenyl sulfone using NBS in DMF**

In a 25 mL round bottom flask, 0.074 g (0.291 mmol) of 3 was added and dissolved in 3 mL of dimethylformamide. Then 0.057 g (0.321 mmol) of N-bromosuccinimide was added and left to stir for 24 hours at room temperature. Analysis by GC-MS showed no product formed. The temperature was increased to 135˚C and left to stir for another 24 hours. Analysis by GC-MS showed no product being formed.

**Bromination of 3,5-Difluorodiphenyl sulfone using SMBI in Sulfuric acid**

To a 50 mL round bottom flask, 0.111 g (0.437 mmol) of 3 was added followed by 5 mL of sulfuric acid. Then 0.140 g (0.612 mmol) of sodium monobromoisocyanuric acid, dissolved in another 5 mL of sulfuric acid, was added dropwise. The reaction was cooled with an acetone/ice bath. A GC-MS sample taken 2 hours into the reaction showed 55.78% of 6 was formed.

**Bromination of 3,5-Difluorodiphenyl sulfone using NBS in Chloroform**

To a 50 mL round bottom flask, 0.097 g (0.383 mmol) of 3 was dissolved into 5 mL of chloroform. Then 0.102 g (0.574 mmol) of N-bromosuccinimide was added to the
solution followed by addition of 0.5 mL of methanesulfonic acid. The reaction was run at room temperature. A sample taken after 48 hours showed by GC-MS analysis that 76.52% of 6 had been produced. Work up included quenching the reaction with water (10 mL) and extraction by dichloromethane (3 x 10 mL). The combined extracts were washed with 5% NaOH (5 mL) and then with water (2 x 10 mL), dried over MgSO₄, and the solvent removed under reduced pressure.

**Bromination of 3,5-Difluorodiphenyl sulfone using Br₂ in Sulfuric acid**

In a 25 mL round bottom flask, 0.105 g (0.334 mmol) of 3 was added and dissolved in 2 mL of sulfuric acid. Then 1.067 g (6.680 mmol) of bromine was added and left to stir for 24 hours at room temperature. Analysis by GC-MS showed no product formation. The temperature was raised to 170°C and left to stir for 6 hours before analysis by GC/MS showed 48.42% of 6 had formed.

**Bromination of 3,5-Difluorodiphenyl sulfone using NBS in Sulfuric acid and Acetic Acid**

In a 250 mL round bottom flask, 5.044 g (19.84 mmol) of 3 was added and dissolved in 100 mL of an 80% sulfuric acid : acetic acid solution. Then 3.708 g (20.83 mmol) of N-bromosuccinimide was added and left to stir for 24 hours while being cooled by an acetone/ice bath. Analysis by GC-MS showed 76.33% of the desired compound 6 was formed.

**Bromination of 3,5-Difluorodiphenyl sulfone using NBS in Acetic Acid**

In a 10 mL round bottom flask, 0.030 g (0.118 mmol) of 3 was added and dissolved in 2 mL of acetic acid. Then 0.022 g (0.124 mmol) of N-bromosuccinimide was added and left to stir for 48 hours at room temperature. Analysis by GC-MS showed no product formation.
formation. The temperature was raised to 110°C and left to stir for 6 hours before analysis by GC/MS showed no product formation.

**Polymerization Procedure with 6 to yield 13**

In a 50 mL round bottomed flask equipped with a stir bar, Dean Stark trap, condenser, and gas adapter were placed 0.546 g (1.64 mmol) of 3’-bromophenyl-3,5-difluorophenyl sulfone, 6, 0.374 g (1.64 mmol) of bisphenol A, 0.340 g (1.5 equiv) of K₂CO₃, 5 mL of NMP, and 5 mL of toluene. The Dean Stark trap was filled with toluene, and the mixture was heated to 165 °C for 4 hours of azeotropic drying to ensure complete dryness. The toluene was removed, and the reaction temperature was raised to 185 °C for an additional 16 h, at which point the mixture was cooled to room temperature and slowly poured into 150 mL of vigorously stirred distilled water to precipitate the polymer as a brown solid (0.8039 g, 94 %). The solid was then redissolved in THF, and reprecipitated from 150 mL of vigorously stirred methanol and dried in vacuo to afford 0.7188 g (84%) of 13 as an off-white fibrous powder. ¹H NMR (CDCl₃, δ): 6.74, 6.78, 6.80, 6.90, 6.93, 7.12, 7.18, 7.19, 7.20, 7.21, 7.22, 7.25, 7.26, 7.31, 7.32, 7.34, 7.44, 7.46, 7.47, 7.53, 7.56, 7.66, 7.69, 7.76, 7.78, 7.83, 7.86, 8.02. ¹³C NMR (CDCl₃, δ): 31.0 (CCH₃), 42.4 (C), 110.9 (ArCH), 112.5 (ArCH), 119.2 (ArCH), 123.3 (ArCBr), 126.2 (ArCH), 128.5 (ArCH), 130.5 (ArCH), 130.8 (ArCH), 136.5 (ArCH), 143.0 (ArCS), 143.2 (ArCS), 146.9 (ArCC), 153.2 (ArCO), 159.6 (ArCO). IR (NaCl) 3691, 3154, 2970, 2253, 1588, 1502, 1438, 1319, 1292, 1217, 1174, 1154, 1132, 1097, 1004, 710, 836, 678, 610.

**Suzuki modification of Monomer 6 to afford 3’-(p-Methoxyphenyl)-3,5-difluorodiphenyl sulfone, 11**
A method similar to that first reported by Novak et al. was utilized for the Pd(OAc)$_2$ catalyzed reaction.$^7$ A 25 mL Schlenk flask was charged with 0.1138 g (0.3416 mmol) of 3'-bromophenyl 3,5-difluorophenyl sulfone, 6, 0.062 g (0.409 mmol) of 4-methoxyphenyl boronic acid, and 3 mL of reagent grade acetone. In a separate Schlenk flask were placed 0.115 g (0.836 mmol) of Potassium carbonate, 0.002 g (0.003 mmol) of Palladium(II) acetate (dissolved in 1 mL of acetone), and 3 mL of distilled water. The contents of both Schlenk flasks were subjected to three freeze-pump-thaw cycles, back-filled with nitrogen, and then combined. The reaction mixture was heated to 70°C for 12 hours followed by the addition of an additional 10% of the boronic acid and heating for an additional 6 hours. The layers were separated and the organic layer was diluted with toluene, washed with brine and dried over MgSO$_4$. Removal of the solvent under reduced pressure followed by purification by column chromatography (Dichloromethane:Hexanes=4:1) afforded 11 (109.5 mg, 89%). $^1$H NMR (CDCl$_3$, $\delta$): 3.86 (s, 3H, OCH), 6.99 (tt, 1H, ArCH), 7.01 (dd, 2H, ArCH), 7.51 (dtd, 2H, ArCH), 7.53 (dd, 2H, ArCH) 7.58 (t, 1H, ArCH), 7.78 (dt, 1H, ArCH), 7.85 (dt, 1H, ArCH), 8.10 (t, 1H, ArCH). $^{13}$C NMR (CDCl$_3$, $\delta$): 55.5 (OCH$_3$), 108.9 (t, ArCH), 111.3 (d, ArCH), 114.6 (ArCH), 125.9 (ArCH), 126.0 (ArCH), 128.4 (ArCH), 130.1 (ArCH), 131.3 (ArCC), 132.1 (ArCH), 140.8 (ArCC), 142.7 (ArCS), 145.2 (ArCS), 160.2 (ArCO), 162.9 (dd, ArCF). MS (EI): [M$^+$]/m/z calcd for C$_{19}$H$_{14}$F$_2$O$_3$S, 360.06; found 360.

**Azide modification of Brominated Polymer**

In a 50 mL round bottomed flask equipped with a stir bar, condenser, and gas adapter were placed 0.221 g of polymer 13 (0.424 mmol of polymeric units), 0.055 g (0.848 mmol) of sodium azide, 0.004 g (0.021 mmol) of sodium ascorbate, 0.008 g (0.042
mmol) of copper(I) iodide, 0.006 g (0.063 mmol) of N,N,N’-trimethylethylenediamine, and 8 mL of NMP:H₂O (47:3) as solvent. The contents were left to react at reflux temperature for 24 hours. The mixture was then cooled and slowly poured into 25 mL of vigorously stirred ethanol to precipitate the polymer as a white solid. The ethanol was then decanted off and dried in vacuo to afford 14. \(^1\)H NMR (CDCl₃, δ): 1.57 (s), 1.69 (s), 1.57 (b), 1.90 (m), 2.17 (t), 2.50 (s), 2.69 (s), 3.31 (m), 5.67 (b), 6.70 (b), 6.79 (b), 6.95 (b), 7.07 (b), 7.16 (b), 7.19 (b), 7.53 (b), 7.86 (b). \(^{13}\)C NMR (CDCl₃, δ): 17.68, 28.22, 29.59, 30.69, 30.99, 42.38, 49.44, 110.99, 112.19, 119.10, 119.58, 127.72, 128.43, 129.35, 130.19, 133.49, 146.80, 153.34, 159.42, 175.09. IR (NaCl) 3465, 2250, 2123, 1680, 1502, 1217, 1057, 820, 758, 621 cm⁻¹.
**Results and Discussion**

In order to find the most efficient route to 3’-bromo-3,5-difluorodiphenyl sulfone, 6, several brominating methods were explored and are listed in **Table 1**. A reaction scheme showing the possible product outcomes is shown in **Scheme 6**. Unlike the Grignard synthesis, the addition of the bromine moiety by electrophilic aromatic substitution should place the bromine *meta* to the sulfone on the unsubstituted ring. This is the most favored site due to it being the most electron rich position on the structure. However, other sites on the molecule also have the potential to be substituted. The *para*-position between the two fluorine groups is slightly activated to act as a site for electrophilic bromination. Even after bromination at this position the *meta* positions on the unsubstituted ring are still available for substitution which results in a di-brominated species. Another possible product that can form is the species in which bromination occurs at both *meta*-sites. Even being brominated once at one of the meta-sites is not enough to deactivate the other *meta* site from electrophilic bromination. The resulting products of these competing reactions are observed in all of the product mixtures. The mildest brominating conditions were therefore attempted first, due to the fact there are multiple sites available for bromination of 3 which, as stated above, would lead to the formation of a number of undesired compounds.

**Table 1.** Results of various brominating conditions on 3,5-difluoro-diphenyl sulfone, 3.

<table>
<thead>
<tr>
<th>Reagent</th>
<th>Solvent</th>
<th>Acid</th>
<th>Temp.</th>
<th>Starting Material</th>
<th>Mono&lt;sup&gt;+&lt;/sup&gt; Brominated</th>
<th>Mono&lt;sup&gt;–&lt;/sup&gt; Brominated</th>
<th>Di Brominated</th>
</tr>
</thead>
<tbody>
<tr>
<td>6</td>
<td>NBS(1.1) Dimethylformamide</td>
<td>Acetic acid</td>
<td>135°C</td>
<td>100%</td>
<td>100%</td>
<td></td>
<td></td>
</tr>
<tr>
<td>6</td>
<td>NBS(1.05)</td>
<td>Acetic acid</td>
<td>110°C</td>
<td>100%</td>
<td>100%</td>
<td></td>
<td></td>
</tr>
<tr>
<td>6</td>
<td>Br2</td>
<td>Sulfuric acid</td>
<td>170°C</td>
<td>42.06%</td>
<td>48.42%</td>
<td>3.62%</td>
<td>5.90%</td>
</tr>
<tr>
<td>6</td>
<td>NBS(1.05)</td>
<td>Sulfuric acid</td>
<td>Sulfuric acid</td>
<td>Rm Temp</td>
<td>18.10%</td>
<td>66.70%</td>
<td>&lt;1.0%</td>
</tr>
<tr>
<td>6</td>
<td>SMBI(1.4)</td>
<td>Sulfuric acid</td>
<td>Sulfuric acid</td>
<td>-15°C</td>
<td>14.50%</td>
<td>55.80%</td>
<td>3.40%</td>
</tr>
<tr>
<td>6</td>
<td>NBS(1.5)&lt;sup&gt;2&lt;/sup&gt;</td>
<td>Chloroform</td>
<td>MSA (20 eq)</td>
<td>Rm Temp</td>
<td>2.90%</td>
<td>76.50%</td>
<td>&lt;1.0%</td>
</tr>
<tr>
<td>6</td>
<td>NBS(1.5)&lt;sup&gt;2&lt;/sup&gt;</td>
<td>Chloroform</td>
<td>MSA (2.5 eq)</td>
<td>Rm Temp</td>
<td>34.70%</td>
<td>55.70%</td>
<td>&lt;1.0%</td>
</tr>
<tr>
<td>6</td>
<td>NBS(1.05)</td>
<td>Acetic acid</td>
<td>Sulfuric acid</td>
<td>-15°C</td>
<td>12.02%</td>
<td>76.33%</td>
<td>&lt;1.0%</td>
</tr>
</tbody>
</table>

<sup>(1)</sup> Desired mono-brominated monomer.  <sup>(2)</sup> Undesired mono-brominated monomer.  <sup>(3)</sup> 22 hours reaction time.  <sup>(4)</sup> 20 hours reaction time.  
<sup>(5)</sup> 72 hours reaction time.  <sup>(6)</sup> 240 hours reaction time.
Initial work using Br\textsubscript{2} in sulfuric acid proved unsuccessful unless forcing conditions were used. With the high temperature needed and bromine’s tendency to vaporize, a high pressure reactor would be required to utilize this method. Also, considering that the selectivity for single bromination of the compound was poor, this method was not pursued any further. It has been previously reported that dimethyl formamide worked as a solvent/catalyst for electrophilic bromine transfer using NBS,\textsuperscript{[8]} thus bromination using this method was attempted on 3. Unfortunately, even when heated to 135°C the ring is too electron deficient for this method to proceed. Using acetic acid as the acid catalyst, and solvent, with NBS also produced no brominated product even when the reaction was heated to 116°C.

Switching to sulfuric acid as the acid catalyst and solvent afforded brominated products with NBS or sodium monobromoisoncyanuric acid (SMBI). SMBI is a relatively new brominating agent that has been shown to offer more selectivity than NBS in electrophilic bromination of aryl compounds.\textsuperscript{[9]} However, SMBI did not offer such a benefit for 3, rather producing a range of the mono and di-brominated isomers. In the
hope of utilizing concentration affects to bring the selectivity more towards the desirable products, the compound was dissolved in chloroform and methane sulfonic acid was used as the catalyst while using NBS as the brominating agent. The results show this to have better yields and selectivity for the desired mono-brominated compound than sulfuric acid. However, the excess amount of acid required goes against the idea of efficiency.

Sulfuric acid gave similar results to the chloroform and methane sulfonic acid and offered an efficient means of preparation. Utilizing acetic acid’s ability to dissolve the materials, but not being strong enough react them, mixtures of sulfuric acid and acetic acid were used to tone down the strength down of solvent mixture as well as allow for cooler temperatures to be used. A mixture of 80% sulfuric acid to acetic acid had the best results in terms of yield and synthetic feasibility giving rise to 76.3% yield of the desired mono-brominated material. Ratios with lower percentages of sulfuric acid presented problems with solubility of the starting materials.

GC/MS analysis was done on the crude material (Figure 1). It showed a [M⁺] m/z of 254 at 7.08 minutes (Figure 2), this was labeled compound 3 which has a calculated mass of 254.02. The major peak at 8.63 minutes (Figure 3) gave a [M⁺] m/z of 334. This was determined to be a mono brominated compound, which has a calculated mass of 333.15, and showed a peak split because of the bromo isomers. This peak was also considered compound 6 because of it being the most favored mono brominated product due to electronics and later confirmed by NMR spectroscopy. Peaks at 8.75 (Figure 4), 8.80 (Figure 5), and 8.99 (Figure 6) minutes also showed a [M⁺] m/z of 334 representing other isomers of the mono brominated compound. Peaks at 10.13 (Figure 7), 10.24 (Figure 8), 10.36 (Figure 9), and 10.49 (Figure 10) minutes gave [M⁺] m/z of 412 and
had a triplet of peaks because of the bromo isomers. These were considered the di brominated compounds of 3 which have a calculated mass of 412.04.

**Figure 1.** Gas chromatograph of crude product from the synthesis of 6.

**Figure 2.** Mass spectrum from 7.08 minute peak from Figure 1.

**Figure 3.** Mass spectrum from 8.63 minute peak from Figure 1.
Figure 4. Mass spectrum from 8.75 minute peak from Figure 1.

Figure 5. Mass spectrum from 8.80 minute peak from Figure 1.

Figure 6. Mass spectrum from 8.99 minute peak from Figure 1.
Figure 7. Mass spectrum from 10.13 minute peak from Figure 1.

Figure 8. Mass spectrum from 10.24 minute peak from Figure 1.

Figure 9. Mass spectrum from 10.36 minute peak from Figure 1.
Work up of the sulfuric acid, acetic acid and NBS reaction is relatively simple with little or no loss of material. The product is precipitated out of the reaction mixture by adding it directly to a stirring solution of water. After collecting the precipitated material, by filtration, purification is achieved by a recrystallization from a mixture of ethanol:chloroform:toluene in a ratio of 80:10:10. Analysis using GC/MS (Figure 11) NMR spectroscopy (Figure 12) (Figure 13) and elemental analysis shows the final product to be the desired compound, analytically pure and in reasonable yield. The method offers a cost efficient means of producing 6 with acceptable yields.
Figure 12. 300 MHz $^1$H NMR spectrum (CHCl$_3$) for 6.

Figure 13. 75.5MHz $^{13}$C NMR spectrum (CDCl$_3$) for 6.
With the desired mono-brominated monomer in hand, example modification reactions were carried out to demonstrate the versatility that the bromine moiety provides. Scheme 7 depicts an example of “prior to” polymerization modification. A Suzuki coupling reaction using 4-methoxyphenyl boronic acid was used to functionalize the sulfone monomer. The reaction proceeded smoothly to produce 11. Analysis using GC/MS (Figure 14)(Figure 15) and NMR spectroscopy (Figure 16) (Figure 17) showed the final product to be the desired compound. The newly modified monomer, now able for polymerization, is just one of many potentially available through this method.

Scheme 7

![Scheme 7 Diagram]

Figure 14. Gas chromatograph of Suzuki coupling product 11.
Figure 15. Mass spectrum from 21.48 minute peak from Figure 14.

Figure 16. 300 MHz $^1$H NMR spectrum (CDCl$_3$) aromatic region for 11. (-OCH$_3$ @ 3.87 ppm)
To explore the ability to run “post” modifications, 6 was first polymerized following literature procedures for previous polymerization reactions of 3 (Scheme 8). The polymer, 13, of 6 and bisphenol A, showed a weight average molecular weight, $M_w$, of 250,000 Daltons with a PDI of 7.70, similar to polymers of 3 and bisphenol A. The resulting polymer was then subjected to conditions for azide substitution at the bromine moiety[10] (Scheme 9) to show proof of concept for direct post-polymerization modification. Carbon-13 NMR analysis showed a conversion from the bromo poly(aryl ether sulfone) (Figure 18) to the azido poly(aryl ether sulfone) (Figure 19). Figure 20 demonstrates this with the carbon-13 overlay of monomer, bromo polymer, and modified azido polymer. The $^{13}\text{C}$ peak for the aryl carbon bromine bond, 123.3 ppm, disappears in the azido modified polymer carbon-13 scan but the presence of the carbon azide bond has
not been identified. Using infrared spectrometry the presence of the azide is confirmed in the polymer. Figure 21 and 22 show the infrared analysis with a new peak forming for the modified polymer at 2123 cm\(^{-1}\) which is in range of the reported signal for aryl azides C-N stretch.\(^{[11]}\)

**Scheme 8**

\[
\begin{align*}
\text{F} & \quad \text{O} \\
\text{F} & \quad \text{O} \\
\text{Br} & \quad \text{Br} \\
\end{align*}
\]

\[\text{SO}_3\] \quad \text{K}_2\text{CO}_3 \quad \text{NMP} \quad \text{Toluene} \quad \text{C} \quad \text{CH}_3 \\
\text{HO} \quad \text{OH} \\
\text{S} \quad \text{O} \quad \text{O} \\
\text{F} \\
\text{Br} \\
\text{Br}
\]

**Scheme 9**

\[
\begin{align*}
\text{F} & \quad \text{O} \\
\text{F} & \quad \text{O} \\
\text{N}_3 & \quad \text{H} \\
\end{align*}
\]

\[\text{K}_2\text{CO}_3 \quad \text{N,N,N'}-\text{trimethylethlenediamine} \quad \text{NMP}:\text{H}_2\text{O} (47:1) \]

\[
\begin{align*}
\text{Br} & \quad \text{Br} \\
\text{S} \quad \text{O} \quad \text{O} \\
\text{F} \\
\text{N}_3
\end{align*}
\]
Figure 18. 75.5MHz $^{13}$C NMR spectrum (CDCl$_3$) for 13.

Figure 19. 75.5MHz $^{13}$C NMR spectrum (CDCl$_3$) for 14.
Figure 20. Overlay of monomer 6, bromo-polymer 13, and azido-polymer 14.

Figure 21. Infrared spectrum of 13.
Conclusions

Having the ability to add functionality to a polymer “prior to” or “post” polymerization allows for a versatile approach to prepare a wide variety of poly(arylene ether)s. Addition of a bromine substituent onto this monomer gives the desired versatility without interfering with the polymerization reaction. Sulfuric acid and acetic acid showed the best balance between yield and efficiency as solvents and catalyst for the bromination reaction using NBS.
References


III. BULK POLYMERIZATION STUDIES WITH FUMARIC ACID AND GLYCEROL

While dendritic polymers \cite{1,2,3} offer a unique set of characteristics due to their molecular architecture, producing them can be tedious. Hyperbranched polymers \cite{4,5,6,7}, which share many of the unique characteristics possessed by dendrimers including: 1) low intrinsic viscosity, 2) excellent solubility characteristics, and 3) a large number of end groups, are an alternative to perfectly monodisperse dendrimers. Hyperbranched polymers, while sharing a three-dimensional architecture like that of dendrimers, can be prepared by one-pot, one step polymerization reactions, unlike dendrimer preparation which often requires multiple protection and de-protection steps. However, hyperbranched polymers are not mono disperse like dendritic systems and often exhibit quite broad molecular weight distributions. Numerous synthetic routes to hyperbranched polymers are available, but this discussion will focus mainly on the $A_2 + B_3$ method.

Recently $A_2 + B_3$ monomers \cite{8,9,10} have received more attention for the production of hyperbranched polymers, whereas $AB_2$ \cite{11,12,13} monomers were originally the focus. It was Flory who first proposed the use of $A_2 + B_3$ monomer systems for the preparation of hyperbranched polymers.\cite{11} This shift in focus is due to the fact that $AB_2$ monomers are often difficult to prepare because of the inherent limitation that only compatible functional groups can be present on the same monomer unit. By contrast $A_2$ and $B_3$ monomers are typically easy to prepare and are often commercially available. The
disadvantage with $A_2 + B_3$ polymerizations is the inevitable gelation of the system whereas it is statistically impossible to reach gelation using $AB_2$ systems.\textsuperscript{[11]} Flory predicted the $AB_x$ monomer polymerizations never would reach a critical gelation point from his statistical calculations (Equation 1). Using a coefficient that represents the probability that the chain ends in a branching unit, $f$. This coefficient was termed the branching coefficient, $\alpha$, and if $\alpha(f-1)\geq1$ gelation occurs. The branching coefficient is related to the conversion of functional groups A ($p_a$) and B ($p_b$).

$$\alpha = (p_b) = (p_a)/(f-1) \leq 1/(f-1) \quad \text{Equation 1}$$

The critical value for $\alpha$ at which gelation occurs can be found with $\alpha_c = 1/(f-1)$. In an $AB_x$ system, the maximum possible conversion of A groups is equal to 1. Therefore, $\alpha$ never reaches $\alpha_c$ and gelation does not occur. However, in an $A_2 + B_3$, system after incorporation of a specified number of A groups, the system will unavoidably reach a gelation point. Flory first predicted this and it was later shown by Jikei.\textsuperscript{[14][15]} Flory’s equation, known as the Flory-Stockmayer model (Equation 2), predicts when the extent of the reaction, $p$, exceeds the critical conversion value $p_c$.

$$p_c = 1/[(x_a-1)(x_b-1)]^{1/2} \quad \text{Equation 2}$$

The values of $x_a$ and $x_b$ are the monomer’s functionality, so $x_a = 2$ and $x_b = 3$ for an $A_2 + B_3$ system at a monomer molar ratio of 1:1. Using the equation, this system, of A:B at 1:1.5, would give a $p_c$ of 0.71, so after conversion of 71% of the A functional groups into the hyperbranched polymer the system would reach gelation. The concentration of monomers, methods of addition, and side reactions such as cyclization as well as monofunctional capping agents are used to prolong the polymerization beyond the critical conversion in order to form larger polymer sizes.
Hyperbranched polyesters can be prepared by means of a condensation reaction using either the AB$_2$ or A$_2$ + B$_3$ methods. Polyesters have a wide variety of uses in the industry as fibers, films, filters, and casting materials. They have good mechanical properties and are extremely heat resistant. Bernd Bruchmann and Jean-Francois Stumbe have reported the use of two readily available materials, adipic acid and glycerol, to build hyperbranched polyesters.$^{[16]}$ Their work was published during the course of this research and was a useful reference. For this research, glycerol and fumaric acid were chosen based on the criteria set to build a biocompatible hyperbranched polymer. With the two monomers both already being biologically friendly, a poly(ester) of the two units should prove to be a beneficial polymer in the biological field. Fumaric acid also brings more advantages; 1) its rigid structure should give rise to higher molecular weights in the hyperbranched polymers due to less intramolecular cyclization and 2) the potential to add functionality to the hyperbranched polymer through the alkene sites.

In this work, we wish to present results from the polyesterification of the B$_3$ monomer, glycerol, 1, and A$_2$ monomer, fumaric acid, 2, under solvent free conditions (Scheme 1). This particular system has a number of promising features including: 1) “solvent free” polymerization conditions, 2) relatively low cost reagents, 3) biocompatibility of the final polymer, and 4) the possibility for modification at the alkene sites provided by the fumaric acid component. In addition, the carboxylic acid and alcohol end groups can be readily modified in order to tune the solubility and physical properties of these materials.$^{[17][18][19]}$
Scheme 1

\[ \text{Linear 1,3 Glycerol} \quad + \quad \text{Terminal 2,3 Glycerol} \quad \xrightarrow{p-TSA} \quad \text{Dendritic Glycerol} \]

\[ \text{Terminal 1,3 Glycerol} \quad + \quad \text{Linear 1,2 Glycerol} \quad \xrightarrow{p-TSA} \quad \text{Terminal Fumaric Acid} \]
Experimental

Materials.

Glycerol, fumaric acid, valeric acid, dicyclohexylcarbodiimide, 4-dimethylaminopyridine, p-toluenesulfonic acid, p-TSA (Aldrich), and ethyl hydrogen fumarate (Lancaster) were used as received.

Instrumentation.

$^1$H and $^{13}$C NMR spectra were obtained using a Bruker Avance 300 MHz instrument operating at 300 and 75.5 MHz respectively. Samples were dissolved in DMSO-$d_6$. SEC analysis was performed using a Viscotek Model 300 TDA system equipped with a refractive index detector operating at 70°C. Polymer Laboratories 5 μm PL gel mixed C columns were used with NMP (with 0.5% LiBr) as the eluent and a Thermoseparation Model P1000 pump operating at 0.8 mL/minute. Molecular weights are reported relative to polystyrene standards.

Typical Polymerization Procedure for Glycerol and Fumaric acid.

To a 50 mL round bottomed flask equipped with a magnetic stirrer and a nitrogen gas inlet, were added 8.444 g (91.77 mmol) of 1 and 10.651 g (89.09 mmol) of 2. The mixture was heated to 150°C while stirring followed by addition of 0.051 g (0.27 mmol) of p-TSA as a condensation catalyst. Dry nitrogen gas was then allowed to flow through the reaction vessel. Aliquots were then removed at intervals for SEC and NMR spectroscopic analysis. Variations on this procedure included reaction temperature, monomer ratio, and reaction time as outlined in Table 1. $^1$H NMR (DMSO, $\delta$): 2.51 (t, 1.00H), 3.35 (m, 7.03H), 3.71 (b, 17.71H), 4.05 (m, 3.54H), 4.20 (m, 3.35H), 6.62 (s, 0.46H), 6.66 (b, 0.06H), 6.67 (b, 0.04H), 6.69 (b, 0.07H), 6.72 (dd, 0.82H), 6.78 (bd,
Polymerization of Glycerol and Fumaric Acid with Valeric Acid as a Capping Agent.

To a 250 mL round bottomed flask equipped with a magnetic stirrer, condenser, and a nitrogen gas inlet were added 8.176 g (88.85 mmol) of 1, 10.315 g (88.85 mmol) of 2, and 9.074 g (88.85 mmol) of 3. It should be noted the mixture of glycerol and fumaric acid never became miscible with the liquid layer of valeric acid. The vessel was heated to 150°C while stirring followed by addition of 0.051 g (0.26 mmol) of p-TSA as a condensation catalyst. Dry nitrogen gas was then allowed to flow through the reaction vessel. Initially for 210 minutes the polymerization was run with a condenser to prevent the loss of 3. Aliquots were then removed at half-hour intervals for SEC and NMR analysis. $^1$H NMR (DMSO, δ): 0.86 (m), 1.29 (m), 1.51 (m), 2.20 (m), 2.31 (m), 2.53 (s), 3.40 (m), 3.62 (bm), 4.20 (bm), 5.36 (b), 6.65 (s), 6.78 (b). $^{13}$C NMR (DMSO, δ): 13.38, 13.43, 13.49, 21.47, 21.52, 21.62, 26.38, 26.43, 26.48, 26.53, 32.93, 33.05, 33.24, 33.27, 37.24, 38.82, 39.27, 39.56, 39.86, 40.11, 59.27, 59.36, 59.47, 59.59, 59.74, 61.48, 61.65, 61.69, 61.96, 62.22, 62.37, 62.58, 62.85, 63.00, 63.30, 63.50, 64.49, 64.65, 65.21, 65.38, 65.64, 65.77, 65.87, 65.97, 66.09, 66.54, 66.67, 68.27, 68.46, 68.66, 69.05, 69.24, 69.90, 70.11, 71.53, 73.25, 131.81, 132.29, 132.45, 132.57, 132.68, 132.99, 133.18, 133.45, 133.51, 133.68, 133.89, 134.54, 134.76, 134.80, 134.95, 135.10, 135.15, 135.33.
**Procedure for Model Branching Study**

To a 100 mL round bottomed flask equipped with a magnetic stirrer were added 0.683 g (7.429 mmol) of 1, 50 ml of dichloromethane, 0.214 g (1.485 mmol) of monoethyl fumarate, 0.181 g (1.485 mmol) of dimethylaminopyridine, and 0.306 g (1.485 mmol) of dicyclohexylcarbodiimide. The glycerol had poor solubility in the dichloromethane but went in as the reaction proceeded. The reaction was run at room temperature for 24 hour at which time an aliquot was taken for $^{13}$C NMR analysis. This procedure was repeated by adding one half of an equivalent, in relation to glycerol, of monoethyl fumarate, dimethylaminopyridine, and dicyclohexylcarbodiimide each time with a sample being taken after 24 hours for $^{13}$C analysis. This was repeated until the total equivalents added were equal to 3. $^1$H NMR (DMSO, $\delta$): 1.13 (m), 1.26 (t), 1.48 (b), 1.62 (b), 1.73 (b), 2.02 (bd), 2.30 (b), 2.52 (b), 2.72 (s), 2.88 (s), 2.95 (s), 3.02 (s), 3.18 (s) 3.23 (s), 3.45 (m), 3.64 (d), 3.75 (d), 4.07 (m), 4.21 (m), 4.50 (m), 4.94 (m), 5.18 (m), 5.46 (m), 7.82 (b), 8.11 (d), 8.32 (d), 8.43 (m), 8.97 (b). $^{13}$C NMR (DMSO, $\delta$): 13.79, 13.87, 13.95, 24.44, 24.80, 24.86, 25.31, 25.37, 28.66, 28.87, 29.48, 30.84, 33.31, 34.44, 37.39, 38.46, 38.49, 39.47, 39.71, 39.97, 47.48, 50.54, 52.43, 54.16, 59.27, 60.09, 60.17, 61.03, 61.08, 62.50, 62.81, 63.35, 65.80, 65.84, 66.77, 68.26, 69.14, 69.84, 73.28, 77.11, 106.15, 106.46, 106.58, 106.96, 107.11, 108.19, 125.08, 132.36, 132.53, 132.84, 133.12, 133.15, 133.40, 133.55, 133.75, 133.98, 141.51, 142.07, 142.49, 144.95, 148.65, 149.07, 153.90.
Results and Discussion

The one step polyesterification reactions of 1 and 2 were carried out with varying temperature and monomer ratios while dry N₂ flowed over the reaction in order to pull off the water by-product formed during the reaction. The initial polyesterification with a 1 to 1 ratio of monomers 1 and 2 was performed at a temperature of 150°C. Individual samples were taken throughout the polymerization reaction in order to follow the molecular weight growth of the hyperbranched polymer. Size exclusion chromatography, SEC, was run on these samples and showed that the two monomers do indeed react to form a polymer system (Table 1) (Figure 1). A sample taken at 80 minutes displayed a weight average molecular weight, $M_w$, around 1,100 g/mol with a polydispersity index, PDI, of 1.3. This relates to, on average, every polymer chain is made up of 10 units, this could equate to 5 fumaric acid units and 5 glycerol units. At the time of this sample withdrawal, the polymerization appeared to be gel free with the sample being completely soluble in N-methylpyrrolidone, NMP. A sample taken at 260 minutes showed a $M_w$ of 3,100 g/mol, corresponding to approximately 30 units, with a PDI of 2.8. The sample at this time had increased in viscosity, possibly a sign of the polymer system being more linear than dendritic or becoming somewhat cross-linked. Also, the sample still appeared gel free with good solubility in NMP. The following sample taken at 320 minutes started to show a large increase in viscosity, becoming gummy like. The presence of partially insoluble material also started to become apparent when trying to dissolve the samples in NMP. These are signs that the system was starting to crosslink and gel. In Figure 2 is shown a plot of polymer size versus time and it depicts a sharp, exponential-like increase in size, which might be explained by the crosslinking of individual hyperbranched
molecules or a dramatic increase in molecular weight. The change in PDI of the polymer is then also plotted versus time in Figure 3.

**Table 1.** SEC analysis results for 1:1 Molar Ratio (B$_3$:A$_2$) Polymerization at 150°C.

<table>
<thead>
<tr>
<th>Time</th>
<th>Mw (g/mol)</th>
<th>PDI</th>
</tr>
</thead>
<tbody>
<tr>
<td>80 min</td>
<td>1,095</td>
<td>1.34</td>
</tr>
<tr>
<td>260 min</td>
<td>3,131</td>
<td>2.85</td>
</tr>
<tr>
<td>320 min</td>
<td>4,736</td>
<td>3.28</td>
</tr>
</tbody>
</table>

**Figure 1.** SEC trace overlay for 1:1 Molar Ratio (B$_3$:A$_2$) Polymerization at 150°C.
In order to study the temperature and kinetic effects on the growth of the polymer, a polymerization was carried out at a temperature of 130°C using a ratio of 1 to 1 of compounds 1 and 2. It was anticipated that the lower temperature would also help to limit any side reactions such as ether bond formation. Table 2 shows the Mw’s and
PDI’s of the polymer samples while Figures 4, 5 and 6 display the SEC traces, the growth of size verse time, and PDI verse time plots of the samples.

**Table 2.** SEC analysis results for (1:1) Molar Ratio (B$_3$:A$_2$) Polymerization at 130°C.

<table>
<thead>
<tr>
<th>Time</th>
<th>Mw (g/mol)</th>
<th>PDI</th>
</tr>
</thead>
<tbody>
<tr>
<td>360 min</td>
<td>1,867</td>
<td>1.65</td>
</tr>
<tr>
<td>400 min</td>
<td>2,293</td>
<td>2.00</td>
</tr>
<tr>
<td>430 min</td>
<td>2,401</td>
<td>1.89</td>
</tr>
</tbody>
</table>

**Figure 4.** SEC trace overlay for (1:1) Molar Ratio (B$_3$:A$_2$) Polymerization at 130°C.
Figure 5. Plot of polymer size growth vs. time for (1:1) Molar Ratio (B₃:A₂) Polymerization at 130°C.

Figure 6. Plot of polymer PDI vs. time for (1:1) Molar Ratio (B₃:A₂) Polymerization at 130°C.

Obviously the $M_w$ values grew much slower than the polymerization run at 150°C. It took over twice as long for the polymerization to reach sizes equivalent to those from the
150°C polymerization reaction. The PDI, however, never went higher than 2 and gelation was not observed during the time frame in which the polymerization was being run. The growth and PDI from this polymerization seem odd with the size of the polymer seeming to level out and there being a decrease in PDI value in the 430 minute sample. The polymerization should be re-run to see if this trend is reproducible. What these results do show, and is to be expected, is that the polymerization proceeds at a slower rate which offers more control in sizes and delaying gelation of the system. At this lower temperature the tendency for formation of ether bonds may be decreased significantly which would also decrease the chance of crosslinking.

A study on the ratio of monomers was also done. As it is known that the probability for gelation of a system is higher for \( A_2 + B_3 \) polymerizations as the ratio of functional groups approaches unity. Therefore, a number of polymerization reactions were performed in order to monitor the effect that monomer ratio had on this system. Staying at a temperature of 150°C the molar ratio of glycerol was increased by 0.03 giving a ratio of 1.03 to 1 of glycerol to fumaric acid. In Table 3 are shown the sizes and PDI’s for the samples taken throughout the polymerization. Figures 7, 8 and 9 show the SEC traces, a plot of polymer growth to time, and a plot of polymer PDI to time, respectively.

Table 3. SEC analysis results of (1.03:1) Molar Ratio (B₃:A₂) Polymerization at 150°C.

<table>
<thead>
<tr>
<th>Time</th>
<th>Mw (g/mol)</th>
<th>PDI</th>
</tr>
</thead>
<tbody>
<tr>
<td>80 min</td>
<td>951</td>
<td>1.17</td>
</tr>
<tr>
<td>360 min</td>
<td>1,993</td>
<td>1.78</td>
</tr>
<tr>
<td>420 min</td>
<td>5,453</td>
<td>4.46</td>
</tr>
<tr>
<td>445 min</td>
<td>5,448</td>
<td>3.61</td>
</tr>
</tbody>
</table>
Figure 7. SEC spectrum overlay of (1.03:1) Molar Ratio (B₃:A₂) Polymerization at 150°C.

Figure 8. Plot of polymer size growth vs. time of (1.03:1) Molar Ratio (B₃:A₂) Polymerization at 150°C.
The increase in concentration of glycerol further takes the functional group ratio away from unity causing the polymerization to slow and take longer to reach the gel point. The maximum molecular weight that can be achieved, before the system hits its gel point, appears to be near a weight average molecular weight of 5,500 g/mol. The last three samples taken had insoluble material when dissolved into NMP for SEC analysis. Crosslinking of the system appears to happen just before 400 minutes for this method. The last data plot for the PDI of this polymerization drops significantly. This can be due to more of the system crosslinking leaving a smaller range of polymers that are soluble in the NMP so that the only polymer sizes detected are those able to go in.

From this the ability to delay crosslinking and achieve smaller polymer sizes, by increasing the difference in concentration of B to A functional groups available, is possible. Another similar polymerization was done with a change in monomer ratio.
Glycerol’s concentration was increased more to give a ratio compared to fumaric acid of 1.05 to 1. The temperature of the polymerization was kept at 150°C and smaller molecular weights were seen (Table 4) when compared to the 1.03 to 1 ratio polymerization.

Table 4. SEC analysis results.

<table>
<thead>
<tr>
<th>Time</th>
<th>Mw (g/mol)</th>
<th>PDI</th>
</tr>
</thead>
<tbody>
<tr>
<td>80 min</td>
<td>1,043</td>
<td>1.25</td>
</tr>
<tr>
<td>360 min</td>
<td>1,227</td>
<td>1.44</td>
</tr>
</tbody>
</table>

A polymerization was run similar to the 1 to 1 polymerization at 150°C but with an end capping agent present to cap functional groups and slow polymer growth and delay crosslinking (Scheme 2). Valeric acid, 3, was chosen as the capping agent. This capping agent also enhances the solubility of the polymer within organic solvents by increasing the hydrophobicity. An immediate problem was discovered, which was that the liquid valeric acid was not miscible in the glycerol solution. Two layers were evident during the entire polymerization reaction.

Scheme 2

However, the polymerization was prolonged and never appeared to approach a gel point through the visual clue that the sample was completely soluble. The interface of the two layers must have provided sufficient contact to cap sites on the growing polymer. Table
5 shows the $M_w$ and PDI of samples taken at various reaction times. Figure 10 shows an overlay of the SEC traces of samples taken at various time intervals.

Table 5. SEC analysis results for polymerization with capping agent.

<table>
<thead>
<tr>
<th>Time</th>
<th>$M_w$ (g/mol)</th>
<th>PDI</th>
</tr>
</thead>
<tbody>
<tr>
<td>60 min</td>
<td>378</td>
<td>1.25</td>
</tr>
<tr>
<td>240 min</td>
<td>724</td>
<td>1.68</td>
</tr>
<tr>
<td>420 min</td>
<td>1,904</td>
<td>2.45</td>
</tr>
<tr>
<td>540 min</td>
<td>4,435</td>
<td>2.79</td>
</tr>
<tr>
<td>600 min</td>
<td>7,520</td>
<td>3.66</td>
</tr>
</tbody>
</table>

Figure 10. SEC trace overlay for polymerization with capping agent.

Degree of Branching

An important aspect of hyperbranched polymers is the average branching structure possessed by the systems. Typically, the degree of branching, DB, is determined by finding the number of terminal, linear and dendritic fragments in the polymer. Often,
NMR spectroscopy is used to count the number of the individual species with the assignments being based on model compounds with similar structures. For the current system, the glycerol unit provides an adequate $^{13}$C NMR spectroscopic handle to determine the number and types of repeat units present in these poly(ester)s.

Proton NMR spectra on this system were not defined enough to identify these units which is the preferable method for calculating the degree of branching. The glycerol CH protons would need to be distinguished in order to identify linear, branching, and terminal groups. However, the proton signals are already tightly bunched and, after polymerization, become indistinguishable overlapping peaks, therefore, Carbon-13 NMR spectroscopy was utilized.

Other researchers have done similar work with glycerol as the B$_3$ component and used carbon NMR spectroscopy to determine the DB values. Unfortunately, there is an issue with discrepancies of signal assignment between the different studies. B. Bruchmann et al.$^{[16]}$ refers to R. Gross et al.$^{[21]}$ for carbon NMR assignments of the terminal, linear, and dendritic units. However, even in the same NMR solvent the assignments don’t match. The $^{13}$C NMR assignments by B. Bruchmann and R. Gross are compared in Table 6. In addition, neither author gives any reasoning behind their assignments. Therefore, a thorough study to identify and assign the possible glycerol hyperbranched units in confidence was undertaken.

Table 6. $^{13}$C NMR spectral assignments of the secondary carbon atoms in the glycerol branching unit (data taken from references 16 and 21) of hyperbranched polyesters.

<table>
<thead>
<tr>
<th>Assignments by</th>
<th>Terminal 1,3</th>
<th>Terminal 1,2</th>
<th>Linear 1,3</th>
<th>Linear 1,2</th>
<th>Dendritic</th>
</tr>
</thead>
<tbody>
<tr>
<td>B. Bruchmann</td>
<td>75.5</td>
<td>72.1</td>
<td>66.3</td>
<td>69.4</td>
<td>68.9</td>
</tr>
<tr>
<td>R. Gross</td>
<td>75.5</td>
<td>69.8</td>
<td>67.5</td>
<td>72.1</td>
<td>68.8</td>
</tr>
</tbody>
</table>
Because synthesizing each individual unit as a model compound proved to be a daunting task, a different approach was taken. By taking a mono protected \( \text{A}_2 \) monomer, monoethyl fumarate (MEF), and slowly adding it, in portions, to glycerol, \(^{13}\text{C} \) NMR spectroscopy was used to follow the signals as the glycerol was converted from terminal, to dendritic units (Scheme 3). Due to its simplicity the secondary carbon in the glycerol units was chosen to follow the types of glycerol units formed. Reaction with the primary hydroxyl groups in glycerol is favored due to steric considerations and the fact that there are two primary alcohols for every secondary alcohol unit. Thus, at the lower concentrations of MEF, the samples will consist of primarily the 1,2 terminal glycerol unit with minor amounts of the 1,3 terminal glycerol unit. As more of the MEF is added the 1,2 and 1,3 linear glycerol units grow in and the 1,3 linear unit is expected to dominate. As the ratio approaches 3 equivalents the only unit growing in, as the rest decrease, will be the dendritic glycerol unit.

Scheme 3
Because it allowed ease and certainty in the identification of the CH, secondary carbon, in glycerol $^{13}$C DEPT 135 NMR spectroscopy was used to follow the conversion of glycerol units. Figure 11 depicts an overlay of the spectra gathered at each equivalent addition of MEF. The shift for the glycerol peak is located at 72.51 ppm, which was confirmed from a NMR spectrum of just glycerol in CDCl$_3$. Two easily distinguishable peaks, when deciphering the $^{13}$C NMR spectra overlay, of the equivalent additions of MEF are the 1,2 terminal unit peak at 69.09 ppm because it is the first peak to show up at low concentrations of MEF, and the dendritic unit peak at 69.82 ppm because it is the last peak to form after all the equivalents of MEF have been added. The peak at 77.05 ppm can be attributed to the 1,3 terminal unit, because it begins to show up around one equivalent and then reduces in size as the equivalents of MEF approach two. Left to assign are the 73.23 ppm and 68.21 ppm peaks to the two linear units. The most favorable of the two linear units is the 1,3 linear unit. It was assigned the most predominate of the two remaining peaks, 68.21 ppm. The remaining peak is left at 73.23 ppm, which reduces in size quicker than the peak at 68.21 ppm. This is a characteristic of the 1,2 linear model unit, because of its available primary hydroxyl group as compared to the 1,3 linear model unit's available secondary hydroxyl group.

In an actual polymerization the growth scheme acts differently. Unlike the model study none of the glycerol units will disappear. As dendritic units are formed it causes an increase in terminal units. An overlay of NMR spectra of three samples taken from a polymerization, 1 to 1 glycerol to fumaric acid at 150°C, at different times is shown in Figure 12. The NMR chemical shifts don’t match the model study and this has been attributed to the presence of water in the polymer samples. However, the growth of
peaks does follow the same pattern and the shifts appear to be in the same relative order. Identified now, $^{13}$C DEPT 135 NMR spectroscopy can be used to find the degree of branching of the built polymers.

The $^{13}$C NMR spectra of the polymerization with end capping agent valeric acid showed more peaks than were identified by the model growth study. Most of the peaks can be attributed to new terminal, linear and dendritic units because of the valeric acid causing a different shift than fumaric acid when bound to the glycerol. However, the shifts of the new peaks are within the ranges of the previously identified units. Identifying the peaks will take another model study so no degree of branching calculation was done on the polymerization with capping agent. An overlay of $^{13}$C NMR spectra of the products, at different times, from the polymerization reaction with valeric acid is shown in Figure 13.
Figure 11. 75.5 MHz $^{13}$C DEPT 135 overlay of model study.
Figure 12. 75.5 MHz $^{13}$C DEPT 135 overly of 1:1 of B$_3$ to A$_2$ at 150°C.
Figure 13. $^{13}$C DEPT 135 overlay of 1:1:1 1, 2 and 3 at 150°C.
Using carbon NMR, a tentative assignment of secondary glycerol carbon peaks, and equation 3 [22], a degree of branching, DB, was calculated for the larger molecular weight polymers. (Table 7) Equation 1 is used in this case because it is better suited for smaller sized polymers.

\[
DB = \frac{(2D)}{(2D + L)}
\]

Equation 3

The value of D is equivalent to the number of dendritic units and L equivalent to the number amount of linear units in the polymer.

Table 7. SEC results and degree of branching data for individual polymerizations reactions.

<table>
<thead>
<tr>
<th>Ratio*</th>
<th>Temp.</th>
<th>Time</th>
<th>Mw</th>
<th>PDI</th>
<th>DB</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.05:1</td>
<td>150°C</td>
<td>80min</td>
<td>1,043</td>
<td>1.255</td>
<td>-</td>
</tr>
<tr>
<td></td>
<td></td>
<td>360min</td>
<td>3,081</td>
<td>2.511</td>
<td>0.26</td>
</tr>
<tr>
<td>1.0:1.0</td>
<td>150°C</td>
<td>80min</td>
<td>1,095</td>
<td>1.339</td>
<td>-</td>
</tr>
<tr>
<td></td>
<td></td>
<td>260min</td>
<td>3,131</td>
<td>2.853</td>
<td>-</td>
</tr>
<tr>
<td></td>
<td></td>
<td>320min</td>
<td>4,736</td>
<td>3.284</td>
<td>0.38</td>
</tr>
<tr>
<td>1.0:1.0</td>
<td>130°C</td>
<td>360min</td>
<td>1,867</td>
<td>1.648</td>
<td>-</td>
</tr>
<tr>
<td></td>
<td></td>
<td>400min</td>
<td>2,293</td>
<td>1.995</td>
<td>-</td>
</tr>
<tr>
<td></td>
<td></td>
<td>430min</td>
<td>2,401</td>
<td>1.878</td>
<td>0.30</td>
</tr>
</tbody>
</table>

The degrees of branching for the three polymerization reactions agree with the molecular weight results where larger differences in ratio and lower temperatures resulted in lower degrees of polymerization and slower polymerizations, respectively.

It should be noted that the polymerization of 1 and 2, in bulk, acts as a slow addition polymerization with slow addition of the $A_2$ monomer. Initially, 2 did not dissolve
completely into 1 and slowly dissolved as the polymerization proceeds. The amount of surface area of 2 present then affects how much is available for the reaction and, thus, gives the polymerization a slow addition characteristic. This explains why, initially, in the polymerization there is little branching and it is not until later on that branching begins to be observed.

Conclusions

The polymerization of glycerol and fumaric acid does exhibit $A_2$ and $B_3$ characteristics in the formation of a hyperbranched polymer. The ability to control the degree of polymerization and branching during the polymer build by modifying variables, such as temperature, monomer ratio, and available surface area, makes this system a possibility for the preparation of functionalized, branched polyesters for uses such as epoxy resin systems and biocompatible polymers. Future work includes modification studies of the polymers such as incorporating epoxy units at the alkene sites for further functionalization or functionalizing the terminal hydroxyl and carboxylic acid end groups.
References


