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Approaches to the Synthesis of Novel Triptycene Dendrimers and Hyperbranched Poly(phenylene sulfides) and Poly(phenylene sulfones)

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Approaches to the Synthesis of Novel Triptycene Dendrimers and Hyperbranched Poly(phenylene sulfides) and Poly(phenylene sulfones)

By

Alfredo Mellace
This manuscript has been read and accepted by the Graduate Faculty in the
Department of Chemistry and Biochemistry in satisfaction of the dissertation requirement
for the Degree of Doctor of Philosophy.

Date: May 2003

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Seton Hall University
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Abstract

Approaches to the Synthesis of Novel Triptycene Dendrimers and Hyperbranched Poly(phenylene sulfides) and Poly(phenylene sulfones)

By

Alfredo Mellace

Research Mentor: Dr. James E. Hanson

Hyperbranched and dendritic polymers are materials that have generated intense interest over the past decades. New synthetic and analytical methodologies have allowed the preparation of highly branched molecules under controlled conditions and novel properties have been noted for these materials. Although hyperbranched and dendritic molecules are both members of a class of compounds with high degrees of branching originating from some focal point they are nonetheless different in the synthetic methods used to prepare them. Dendrimers are considered perfect branched polymers because they contain uniform structures and molecular weights. In order to achieve such uniformity, multistep syntheses are required that make use of protective and deprotective steps. The major problem with this methodology is that a large amount of starting materials is needed for a relatively small amount of polymer. Hyperbranched polymers on the other hand offer an attractive alternative since they can be prepared in one step. The polymers produced using this methodology are not as uniform as dendrimers but exhibit nearly the same physical properties.
Two directions of research will be reported. The first direction is the synthesis of a triptycene dendrimer via a Diels-Alder precursor, 2-methylanthroate, which is reacted with benzoquinone to form a triptycenequinone adduct. This adduct is then used to generate the monomer and a generation zero triptycene dendron. The attempt to generate G1 triptycene by coupling the generation zero dendron and monomer is also described. All compounds are fully characterized using NMR, IR, MS, and UV.

The second part describes the synthesis of two unsymmetrical hyperbranched polymers. The first polymer, a hyperbranched poly(phenylene sulfide), is generated by reacting 3,4-dichlorobenzenethiol in the presence of a base. Oxidation of the resulting polymer produces the second hyperbranched system, a poly(phenylene sulfone). The polymers were synthesized using either homopolymerizations of the monomer or copolymerization between the monomer and a core former. The hyperbranched poly(phenylene sulfide) exhibits enhanced solubility, a higher glass transition, and comparable thermal stability to linear poly(phenylene sulfide). The hyperbranched poly(phenylene sulfone) is nearly insoluble but has a high thermal stability similar to its linear analogue. Both polymers are characterized using DSC and TGA thermal analysis as well as IR. Hyperbranched poly(phenylene sulfide) is further characterized via the use of NMR, MALDI, EA, QELS, and SEC-LALLS.
Dedication

I would like to dedicate this thesis to those people in my life who have supported me throughout school and especially in the last five years in preparation for one of the most prestigious degrees in one of the most difficult fields of science, Organic Chemistry.

I would like to thank my parents Carlo and Teodolinda Mellace for all their love and encouragement since the first day I ever went to school. They always said whatever you want to do you are able to do and whatever you decide we will always be there for you. This support has made it possible for me to achieve what I have. I would also like to thank them for their understanding of the long days and nights I dedicated to fulfilling the requirements needed for graduation.

I would also like to thank my wife Martina Mellace and my daughter Sophia Mellace who have endured the long days and nights required for me to complete my research and this dissertation. To my wife who always gave me courage with a smile and her love and my little principessa who always made me stronger with her smile and eagerness to spend time with me when I would arrive home. I would also like to thank them for giving me strength through the ups and downs encountered during my time at Seton Hall especially on days when the chemistry did not bring a smile but a frown.
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I would like to thank my mentor Dr. James Hanson for his tutelage and guidance during my time at Seton Hall University. I learned very much from him not only in experimental organic chemistry but also in theoretical organic. I would also like to thank him for introducing me not only to the field of organic chemistry but also to polymers and thereby broadening my horizons in science.

I would like to thank the faculty at the Department of Chemistry and Biochemistry at Seton Hall University for always making me feel comfortable with any questions that I may have had in the respective fields of chemistry.

I would also like to thank my friends in the various groups beginning with my own group on the 4th floor and ending on the 1st floor in Dr. Marzabadi’s group. Special thanks go to Luba, Jack, Lucy, Adela, Cosimo, Jaimee, Jayesh, Nagon, and Pradeep for making my time fun, fulfilling, and interesting at Seton Hall.
"Longa Expositio Machinalis Scientia Particulæ
Elementi est Causa Perturbationis in Existentia"

"Chronic Exposure of Molecular Engineers to the Elements Causes Perturbation in Existence"

Alfredo Mellace September 2002
Chapter 1

Introduction
Macromolecules have been of interest since the beginning of the twentieth century for their unique properties of broad applicability. What are macromolecules? Macromolecules are extremely large molecules that exhibit functions and properties that are not evident or existent in small molecules. Most macromolecules are also polymers. Polymers are high molecular weight constructs that consist of either the same repeating unit or alternating units in their main backbone.\(^1\)

Examples of polymers can be found in biological systems such as DNA and proteins. These biological polymers consist of different arrangements of nucleotides (DNA) or amino acids (proteins) that give functions to various systems in a living organism. There are also other biological polymers such as glycogen which is a polymer made up of repeating carbohydrate units.\(^2\)

In non-biological systems there are many tangible examples of polymers. For example, poly(isoprene) is the polymer with which car, truck, and airplane tires are made. Poly(vinyl chloride) is a material used in making pipes and other plumbing supplies, wire insulation, and many other items. Other polymers can be found in paint, adhesives, glues, soda bottles, and plastics ranging from kitchenware to toys. Also many cosmetics such as creams, shampoos, and soaps are made with polymeric materials.\(^1\) Polymers also play important roles as drug delivery agents.

One way of classifying polymers is based on their topology. There are two major topological classes of polymers: linear and branched. Linear polymers have a linear
backbone that may or may not contain side chain units. One example is poly(ethylene oxide) that is linear with no side chains. Polystyrene is a linear polymer that has benzene rings as its side chains (Figure 1). The aromatic side-chain in polystyrene is important for the properties of the polymer. There are many other linear polymers formed by both addition and condensation methods. Branched polymers include lightly branched polymers, hyperbranched polymers, dendritic polymers, and network polymers. The discussion here will focus on hyperbranched and dendritic polymers. Hyperbranched polymers are a sub-class of branched polymers that are highly branched and have degrees of branching less than 1 (degree of branching will be discussed further below) thus their structure is irregular. Dendrimers are highly branched polymers whose degree of branching is 1 and thus have a regular structure.

Linear polymers are most often constructed by mixing components together and letting them react either by a chain mechanism (radical or ionic) or by a condensation mechanism to produce a linear polymer (Figure 2). Hyperbranched polymers (discussed below) are most often prepared by condensation polymerization of AB₂ monomers, although some examples of chain mechanisms are known (Figure 3). Dendrimers are also highly branched but they are constructed one branch or cascade unit at a time and each intermediate in the polymerization is isolated and purified. This method of polymerization assures that the polymer produced has nearly perfect branching. As will be discussed below there are two methods by which dendrimers can be constructed. Both methods for dendrimer preparation are long, laborious, and sometimes very complex. A consequence of these dendrimer syntheses is that without extremely high yields the throughput is quite poor and many times only a small amount
of the largest polymers can be produced. This is where hyperbranched polymers are advantageous. They are similar to dendrimers in terms of their structure and yet their synthesis can be carried out on a much larger scale with significantly improved throughput.

The interest in dendrimers has at least three sources. First, dendrimers are structurally interesting given the various shapes that they can form and the wide array of monomers that can and have been used. Second, their properties deviate from those of linear polymers. For example, when a dendrimer or hyperbranched polymer grows large enough its intrinsic viscosity declines because it exhibits globular behavior unlike linear polymers (Figure 4). This is because in a linear polymer the various chains can entangle regardless of MW whereas in a high MW dendrimer the chains are too highly branched and cannot entangle. Third, dendrimers can be used to carry out unique functions that are difficult for other structures. For example, crown ethers are known to act as phase transfer catalysts where they enhance the solubility of certain ions in nonpolar organic solvents. An example would be 18-crown-6, which enhances the solubility of potassium salts. Highly branched polymers have been designed to carry out such functions not only for ions or single atoms, but also for molecules. This is similar to active transport of compounds into living cells. Frechet and co-workers have demonstrated that a poly(aryl) ether dendrimer whose surface is modified with carboxylate groups will complex and solubilize compounds that normally do not dissolve in aqueous media. One example of a compound that was trapped inside the dendritic core was 2,3,6,7-tetranitrofluorenone (solubility increased by a factor of 260). This process can be envisioned by what Meijer calls the dendritic box (Figure 5). Other
applications that have been found for dendrimers are drug delivery, radiation therapy, and other techniques for probing biological systems such as labeling in the organs and the blood. Dendrimers can also be used to introduce genetic material into the cell cytoplasm, advantageous over current uses of retro-viruses which have proven to cause infection in the host. Dendrimers can be used to control linear polymerizations. The dendrimer is connected to a polymer chain so that the cavity of the dendrimer shields the reactive end from reacting with other chains. Since the monomer is smaller than the polymer chains, it diffuses through the dendritic surface and into the interior where it can react with the polymer reactive end (Figure 6). Overall the applications of hyperbranched polymers are mostly reserved for classical uses since their irregular structure and high polydispersity restricts them from becoming specialty materials. However, some literature reports are beginning to surface describing them as useful components in specialty materials.
Part II

Dendritic Structures

In 1941 Flory was the first to statistically study polymerizations with monomers possessing AB$_x$ structures where $x \geq 2$. AB$_x$ monomers exist in both hyperbranched and dendritic molecules. He described the probability of a functional unit of one branch coupling another branched unit by the following equation:

$$\alpha = \frac{p}{(x-1)}$$

where $\alpha$ is the branching coefficient describing the probability, $f$ is the number of functional groups of the monomer, and $p$ is the fraction of groups reacted. The relationship holds true as long as there are no intramolecular cyclizations and that both B groups have the same reactivity. Flory further showed that the three dimensional structure of a polymer molecule appeared only after a certain amount of polymerization had occurred.

Years later interest began in molecules for host-guest chemistry and supramolecular chemistry. In the 50-60s, efforts concentrated on crown ethers and cryptands. In the 70s, several research groups began synthesizing and investigating highly flexible compounds to be used as ligands or catalysts. This interest prompted the first "cascade" synthesis of a dendrimer. In 1978 Vogtle and co-workers carried out the this first divergent dendritic synthesis.$^{19,28}$ A divergently grown polymer is constructed by starting from the core and growing the polymer towards the periphery by adding generations. A generation in a divergently grown polymer is defined as a tier of monomers added to the already existing polymer.
The method used for this synthesis was a Michael addition followed by a reduction. The first step produces a small branched system where the two nitrile groups are considered unreactive. After this step the reduction activates the system by producing two nucleophilic amines that are then reacted with the same monomer acrylonitrile. The process can then be repeated as desired: the second addition (second generation molecule) leads to 4 cyano groups, the third addition leads to 8 cyano groups, etc. As can be seen from the Figure 7, Vogtle's cascade synthesis failed to achieve good yields by the second generation. Later in the 1990's, this synthesis was simultaneously improved by Worner, Mulhaupt, Brander-van den Berg and Meijer. One key point in their method is that the product of each addition step is purified to produce a sample where all molecules are identical. This is the common practice in organic synthesis but is not common or traditional practice in polymer synthesis. Polymer syntheses are usually conducted as batch processes, with a product composed of many different molecules with different molecular weights. To describe such a sample, average molecular weights are employed.

The two most commonly used averages are the number average molecular weight \( M_n \) and the weight average molecular weight \( M_w \). These are defined by the following equations:

\[
M_n = \frac{\sum N_i M_i}{\sum N_i}
\]
In these equations \( N_i \) represents the number of molecules or the number of monomers \( i \) of molecular weight \( M_i \).\(^1\) The reason for two average molecular weight equations is that in a sample where many molecular weights are present each contributes differently to the bulk mass of the sample. In the \( M_n \) value, all molecules contribute equally. This is useful for many properties (i.e. osmotic pressure) but overlooks the greater contribution made by the larger components in the sample. For other properties such as viscosity, the \( M_w \) value takes into account the contribution of the larger molecules in the sample that do in fact represent the bulk mass and properties of the sample. In order to determine if the polymer molecules are all the same molecular weight and therefore uniform in size, the ratio of \( M_w/M_n \) is calculated. This ratio is known as the polydispersity and is defined by the following equation:

\[
PD = \frac{M_w}{M_n}
\]

When the ratio is equal to unity the polymer is considered monodisperse where all the molecules have the same molecular weight. The greater the ratio deviates from unity, the greater the molecular weight distribution.

In 1985 Tomalia used another approach to synthesize cascade macromolecules.
He used methyl acrylate in a Michael type addition with ammonia to produce the required core that would then react with ethylene diamine and so forth to produce a PAMAM (polyamidoamine) dendrimer.\textsuperscript{19,21} The same year Newkome reported on branched structures he named arborols (\textbf{Figure 8}).\textsuperscript{22} Tomalia produced the largest divergently grown dendrimer of ten generations.\textsuperscript{19,21}

Frechet in 1990 introduced another approach where a dendrimer would be grown from its periphery in towards a center which gave the structure (also known as a branch) a “wedge” shape.\textsuperscript{19,23} This type of synthetic methodology is known as the convergent approach. Once the wedge (branch or monodendron) is grown to its maximum size (depending on steric effects and chemical efficiency) it can be connected to a polyfunctional core completing a dendrimer. The classical Frechet convergently synthesized dendrimer is the poly(aryl ether) dendrimer shown in \textbf{Figure 9}.\textsuperscript{24} In the same figure is a different approach used to construct a similar dendrimer, which was developed by Hanson.\textsuperscript{25} Both these techniques have produced the largest convergently grown dendrimers to date of six generations. A generation for a convergent system is when a branch is connected to its monomer. The limiting factor in growing very large dendrimers convergently or divergently is known as dense packing. This describes the phenomena that as highly branched molecules increase in generations, their periphery becomes so crowded with end groups that they exceed the available space. Therefore, due to the steric environment the polymer must stop growing.\textsuperscript{10,19}

What are some of the advantages and disadvantages of using either the convergent or divergent approach? The divergent approach suffers from failed couplings of all reactive ends. This makes purification difficult since the impurities produced from the
incomplete couplings are similar in size and structure to the actual desired product. These
imperfections give higher polydispersities. Nevertheless, the divergent approach produces
larger dendritic species. The convergent approach leads to more perfect dendrimers since
there are only two reactive ends and the product and starting materials are different
enough to facilitate purification. Separations become more difficult for higher
generations but the problems are not as severe as in the divergent approach. The
disadvantages with the convergent approach are the requirement for large amounts of
starting material to produce a relatively small amount of final product. The quantity of
the final product is less than that of the divergent approach. In the convergent approach
more functionality and diversity can be introduced throughout the generations of the
dendrimer. Another problem encountered with the convergent approach is low yields in
the higher generations because of stercics.

The next section will briefly show other monomers that can be used
for synthesizing dendrimers. Figure 10 is an example of highly conjugated divergently
grown dendrimer that has an appearance similar to that of graphite.26,27 Figure 10b
illustrates a divergently grown super triptycene compound that introduces three
dimensionality, rigidity, and cavity forming ability.19,28 Figure 11 illustrates a
carbosilane dendrimer where silicon is introduced in the main structure.19,29 In the same
figure is an example of an adamantane dendrimer.19,30,31 This dendrimer introduces
chirality, more flexibility than the super triptycene, and an ester linkage associated with
the points of connectivity. Figure 12 shows an example of poly(benzyl ether) wedge
connected to a fullerene32 and multiple wedges connected to a porphyrin.33 These two
dendrimers can be used to carryout photophysical studies, electron transfer studies,
acetylene) synthesized by Moore (Figure 13). This type of dendrimer is useful in the construction of molecular frameworks.

Given the above structures and their various conformations, a dendrimer could be constructed where various properties from the above dendrimers could be incorporated. The monomer of choice was based on triptycene. Paul Bartlett first synthesized triptycene in six steps in 1942 (Figure 14). The original purpose of synthesizing this compound was to compare the reactivity of the bridgehead carbons and hydrogens to those of the triphenylmethyl system. It was found that the reactivity in the triptycene system was diminished substantially when forming free radicals, carbanions, and in oxidation, all of which produced in return an anthraquinone derivative. Later studies on the acidity of the bridgehead protons in the triptycene system were compared again to the acidity of the methine in the triphenylmethyl system. Again the triphenylmethyl system demonstrated marked difference in reactivity. This is because in the triptycene system the orbitals are orthogonal to the bridge position and the bridge position is fixed. In the triphenylmethyl system the benzene rings can rotate and orient themselves such that conjugation can occur (Figure 15). Triptycene has also been used to study barriers to rotation between triptycenes or groups on the bridge position of the triptycene and adjacent moieties on the triptycene benzene rings (Figure 16). Syntheses of triptycenes have been carried out in various ways such that many isomers have been produced and various functional groups have been placed on the bicyclic skeleton. Various modifications of triptycenes have also been used to detect explosives such as the iptycene derivative synthesized by Swager to detect TNT. The triptycene system has also been used as proof for the formation of benzyne (Figure 17).
Part III

Hyperbranched Polymers

This section will discuss the less than perfect dendritic analogues known as hyperbranched polymers (HYP) a term first used by Kim and Webster. Recent interest has been sparked by the ease of synthesizing of HYPs while maintaining a high degree of chemical and physical similarity to their perfect dendritic analogues. Moreover, HYPs have properties comparable to linear polymers of the same chemical composition, i.e. thermal degradation and mechanical properties, with enhanced solubility. Unlike dendrimers which have a degree of branching (DB) of 1 or 100% and a PD = 1, hyperbranched polymers have DBs ranging between .5-.7 (50%-70%) and PDs greater than one indicating that these polymers are not “perfect.”

The degree of branching for an AB₂ (dendritic or hyperbranched) system can be described by the following equation:

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

where D represents the number of dendritic, T the terminal, and L the linear moieties. The numbers required to calculate the DB can often be obtained by integration of the appropriate peaks in a ¹H NMR spectrum. The above calculation proves to be most useful when dealing with hyperbranched systems since for the most part each variable does have some significance. A dendrimer will lead to a DB of 100% branching since there are no linear units. A linear polymer does not have any significant branching and the number of
terminal groups relative to the linear groups is so small that the DB approaches zero. **Figure 18** illustrates the three different branching units that can be present in a hyperbranched molecule. An important point to understand is that even though a polymer may have 100% degree of branching, its PD may still be greater than one. The reason is that the polymer may contain perfectly dendritic molecules of varying size thus giving a difference in the MW. The $M_w$ will be affected greatly but not the $M_n$. This can complicate structure determination if the different molecular species are very similar. Materials with polydisperse distribution of structures are less useful for structure-function studies or as biomolecule mimics. The improved solubility of hyperbranched polymers like their dendritic counterparts, can be attributed to their reduced crystallinity and increased amorphous structure (less stacking interactions). Polymer topology also controls solubility. Having many functional groups (like a dendrimer) on the surface of a polymer can change its solubility. An example is a polymer having terminal carboxylic acid groups that will then dissolve in aqueous media. This can occur if sufficient acid groups are present in the molecule. Linear molecules tend to be able to stack more easily thus, reducing solubility. Addition of terminal acid groups does not enhance solubility because there are only two terminal groups located at the end of a long carbon chain. In a dendrimer the terminal groups are 50% of the molecule and therefore have a large effect on solubility. In hyperbranched systems the terminal groups are generally 25%-35% of the molecule, nevertheless a similar solubility is achieved (**Figure 19**). This increase in solubility is attributed to the spherical or globular shape that these polymers generally take in solution. Therefore, even though not perfect hyperbranched systems do offer an attractive alternate to both dendrimers and linear polymers.\textsuperscript{42,43,44}
A number of examples will be presented to show the variety of hyperbranched polymers that have been prepared. Based on Flory’s predictions (Figure 20), Kricheldorf in 1982 began the pioneering work to design syntheses to construct hyperbranched polymers. Kricheldorf and others used polyesters as their target compounds since the starting materials were readily available. Kricheldorf’s first synthesis produced the polyester in Figure 21 via a copolymerization of 3-acetoxybenzoic acid and 3,5-bis(acetoxy)benzoic acid or 3-(trimethylsiloxy)benzoyl chloride and 3,5-bis(trimethylsiloxy)benzoyl chloride. The $M_n$ for these polymers was 10,000 D - 29,000 D and 3,300 D - 3,700 D respectively by GPC. Later the synthesis was improved independently by both Frechet and Voit independently who used a homopolymerization process (Figure 22). Frechet used 3,5-bis(trimethylsiloxy)benzoyl chloride while Voit employed 3,5-bis(acetoxy)benzoic acid. They reported getting $M_w$ of 184,000 D and $>800,000$ D respectively by GPC. Both reported that the polymer is amorphous since there was no melting temperature ($T_m$) and achieved high thermal stability with decomposition temperatures ($T_d$) of 560°C and 408°C respectively (somewhat comparable to the linear polymer of 610°C). Frechet and Voit reported PD of 3.8 and 65.7 respectively, a DB of 55%, and a glass transition ($T_g$) of 190°C and 200°C respectively. The linear polymer has a $T_g$ of 145°C. The reasons for the dramatic difference in the glass temperature between the linear and hyperbranched polymers is due to the large number of hydroxyl groups present in the hyperbranched system. These can hydrogen bond and decrease the flexibility of the polymer by increasing its rigidity thus requiring more energy to disorder the polymer from the glass. Solubility of the hyperbranched polymers also increased, not only in organic media (THF) but also in
aqueous base media relative to the linear analogue (as postulated earlier in the introduction). Furthermore, the viscosity of the solution was reported by Voit to decrease giving evidence of the globular shape of the molecule. This example was given in detail to show how hyperbranched polymers are comparable and advantageous over the equally composed linear polymer and simpler to synthesize than the dendritic counterpart.48

The remainder of the examples that will be given presented will be an overview of other polymers that have been made along with their PD, molecular weights, and DB. Another example of a hyperbranched polyester (Figure 23) was given by Feast.49 The reported Mw for this synthetic method using dimethyl 5-(2-hydroxyethoxy) isophthalate was 37,900 D (for the largest polymer by GPC), PD 5.3 and a DB = 50%. Two other examples of self-condensing polymerizations are the hyperbranched polyethers first prepared by Frechet using 5-(bromomethyl)-1,3-dihydroxybenzene as the monomer (Figure 24).50 The Mw reported for these polymers ranged from 22,700 D to 28,500 D by GPC with a PD of 2.01. Frechet also reported a comparison between the hyperbranched and dendritic polyethers giving evidence of their similar solubilities in common organic solvents and similar thermal properties (Tg was 43 °C for the dendritic and 51 °C for the hyperbranched). Both materials had similar Tg to the linear polymer (38 °C), with better solubility as expected. The decomposition rate was the same under nitrogen as it was in air giving a significant weight loss after 400 °C. Miller and Neenan51 also prepared other hyperbranched polyethers using phenoxide monomers that contained two sulfonyl, carbonyl, or tetrafluorophenyl-activated aryl fluoride moieties that are then substitutued during the reaction (Figure 25). They were able to achieve an Mw of 134,000 D by GPC with a PD = 3.78 and solubility in THF, toluene, and chloroform

15
solvents. The thermal stability was higher than any of the other ether polymers with 95% retention of mass at 500 °C under nitrogen.

Another example of hyperbranched polyether formation is by using the clever ring opening approach of Frechet for making polyethers using a hydrogen transfer technique. This method is based on pKa differences between the oxygen of a ring opened epoxide and a phenol proton (Figure 26)\textsuperscript{52}. Here, Frechet reports $M_w$ from 8,000 amu to 74,600 amu by GPC with a PD = 1.3 to 12, respectively.

Feast synthesized hyperbranched analogues of Tomalia's poly(amido)amines (Figure 27),\textsuperscript{53,54} using a melt polymerization (self-condensing polymerization) with N-acryloyl-1,2-diaminoethane hydrochloride as the monomer, which undergoes both a protection/deprotection in situ followed by a Michael addition to form the polymer. Feast reports $M_n$ of 1,500 D - 21,000 D obtained using NMR and MALDI with PD = 1.5-62.4. Furthermore the DB reported are from 65% - 90% which indicates that there are few if any linear units within the polymer thus exhibiting solution dynamics nearly identical to Tomalia's “perfect” dendrimer. The polymer was reported to be stable up to 300 °C, with a $T_g$ that varied with chain length from 18 - 130 °C.

The use of three-dimensional cores (Figure 28) has also been employed by Reichert and Mathias\textsuperscript{55,56} who used tetrakis(4-iodophenyl)adamantane along with 3,5-dibromooaniline under a CO atmosphere with a Pd catalyst to produce adamantane coupled polyaramids. The hyperbranched polyaramids had increased solubility since the aramids independently were insoluble in organic solvents such as N’N-dimethylformamide (DMF), 1-methyl-2-pyrrolidinone (NMP), N’N-dimethylacetamide (DMAc) because of hydrogen bonding and crystallinity. This increase in solubility can
be attributed to the adamantane core and hyperbranched structure disrupting the crystallinity of the molecule. These polyaramids had DB of 20% and were thermally stable up to 450 °C. These hyperbranched polymer, like most other hyperbranched polymers does not have a $T_m$.

The polymers discussed above focused on oxygen and nitrogen heterolinkages in the backbone. The following discussion will include carbon-carbon linked polymers. The first aryl-aryl coupled polymers were introduced by Kim and Webster (Figure 29) who carried out a synthesis with (3,5-dibromophenyl) boronic acid as the monomer in the presence of a Pd catalyst to afford the hyperbranched polyphenylenes (a self-condensing polymerization). They were able to obtain a GPC $M_n$ of 32,000 D, a PD= 1.13, and a DP = 20% - 70%. The reaction was also carried out with 1,3,5,-tribromobenzene as the monomer using activated Mg to generate a Grignard and Ni as a catalyst. This route gave lower MW and higher PD. An important aspect of this polymer is that the terminal ends increase solubility and alter its thermal properties. Another method of producing polyphenylenes is repetitive addition reactions consisting of Diels-Alder reactions followed by CO extrusion (Figure 30). The reported $M_w$ was from 3000 D-107,500 D.

Although selected examples of hyperbranched polymers were discussed above, many other examples of hyperbranched polymers are known in the literature. Some of the self-condensing hyperbranched polymers are: polyurethanes, poly(ethersulfones), poly(etherketones), polycarbonates, poly(phenylacetylene)s, and polycarbosilanes. Some ring-opening hyperbranched polymers are: polyesters, poly(ethylenimine), and polyamines. The main example of addition hyperbranched polymers are the polyphenylenes. Another technique which was not discussed is the
with an initiating group that can be activated by a catalyst such as ZnCl₂ and that will propagate through the double bond (chain growth) and condense at the initiating site with the double bond (step growth) Figure 31.⁶⁷,⁶⁸

A final example is related to the second project included in this dissertation, the synthesis of novel hyperbranched sulfide polymers. The first reported synthesis of a hyperbranched sulfide polymer was by Kakimoto et al.⁶⁹ The synthesis began with 1,3,5-tribromobenzene to produce the monomer. The tribromobenzene was first reacted with sodium phenylthiolate to render 1-bromo-3,5-bis(phenylthio)benzene. This product was then reacted with sodium methanethiolate followed by nitric acid to yield the 1-(methylsulfoxide)-3,5-bis(phenylthio) benzene; the monomer for this hyperbranched polymerization. This adduct was then treated with trifluoromethanesulfonic acid to give a hyperbranched sulfonium polymer. This was heated with pyridine to give the hyperbranched 1,3,5 sulfide isomer (Figure 32). The Mₚ for this polymer and the PD were reported as being 25,700 D and 1.45 respectively. The polymer proved to be soluble in DMF, chloroform, and other common organic solvents whereas the semicrystalline linear polyphenyl sulfide (PPS) is nearly insoluble in most organic solvents. The hyperbranched PPS reported also had a higher Tₛ than the linear PPS; 124 °C vs. 85 °C respectively. There was no Tₘ given as the high degree of branching gave the polymer an amorphous structure.

This next section will discuss methods to control the polymerization and to produce polymers that may have a more defined shape. Another issue that will be discussed is the ability to use monomers with various functional groups, or monomers that can have functionality introduced after polymerization to carry out specific functions.
that can have functionality introduced after polymerization to carry out specific functions. The third and final part will briefly discuss intramolecular cyclizations during the polymerization process.

As mentioned above the simplest way of making hyperbranched polymers is to charge a vessel with AB₂ monomer either with a solvent or neat (melt), add some initiator, and heat until the desired degree of polymerization is reached. The problem with this “one-pot” technique is that the polymers tend to have high polydispersities. To this end there have been many techniques presented to control the growth and polydispersity of the growing polymer.

The first method is the addition of core forming reagents that trap some of the reactive ends of the hyperbranched polymer thus reducing the ability for larger growth. Feast conducted a study using two different core formers: trimethyl 1,3,5-benzenetricarboxylate (a B₃ core) and dimethyl isophthalate (a B₂ core). These were copolymerized with dimethyl 5-(2-hydroxyethoxy)isophthalate to see the effect on the molecular weight and the PD (Figure 33). The conclusion was that there is a marked decrease in the molecular weight (Graph 1) and a difference if a tri-core vs. a di-core is used (Graph 2). Somewhat unexpected was the overall unmarked effect of the cores on the PD (Graph 3). Feast attributes this to the transesterifications that occur during the reaction overshadowing the effect that a core molecule has on the PD. Overall, cores can affect PD by reducing the number of active ends, but if there are secondary processes that are occurring then adding a core may not control the PD. In another report Feast observed that the addition of a core to the reaction increased the DB nearly to unity. Frey et al. reported another method where they used slow monomer addition and core
the monomer over a period of 80h to the core molecules produced lower PD and increased their MW. The DB was increased to 66% relative to the no core bulk polymerization. All MW were obtained using GPC-LALLS and DMF/guanidinium mixture since the terminal hydroxyl groups tended to aggregate. The core molecules, monomers, and the data obtained are in Figure 34. An interesting method was developed by Kakimoto et al.\textsuperscript{71} where the pre-fabrication of perfect dendritic monomers (4 and 6) were compared to the simple analogue (2) via the use of coupling agents (Figure 35). The results were an increase in DB and a decrease in PD.

The variation of functional groups in polymers is known to change thermal properties and solubility. As discussed earlier, the addition of a three-dimensional core to a hyperbranched polymerization will affect both the $T_g$ and solubility of a polymer. Another factor that can affect solubility is the type of functional group located at the surface of the polymer. The following two examples by Voit show how hyperbranched polyesters can be altered to enhance solubility in aqueous alkaline media and how multiple functional groups can be modified to change properties for better SEC separation, characterization, and thermal stability. The first example is with the phenol, trimethylsilyl (TMS), and acetate terminated polyesters (Figure 36).\textsuperscript{47} All these polymers show an enhanced solubility over their linear counterpart in common solvents. This is especially true for the phenol terminated polymers that can be solubilized in basic aqueous media. The $T_g$'s for the three variants are as follows: phenol terminated compounds 200 °C-225 °C, TMS protected compound 185°C, and the acetate compounds 147 °C-160 °C. Temperature ranges are observed because an increase in $T_g$ was observed with increases in MW. Thermogravimetric analysis in nitrogen or air (in line GC/MS)
with increases in MW. Thermogravimetric analysis in nitrogen or air (in line GC/MS) showed decomposition of the TMS protected system at 411 °C (loss of various siloxanes), phenol terminated system at 408 °C (loss of water since the terminal groups in proximity can hydrogen bond), and the acetate terminated compounds at 350 °C (loss of acetic acid). The modification for SEC separation was implemented because highly polar compounds (OH, COOH, NH) tend to stick to the column surface. Therefore, having access to the above polar groups simplifies derivatization both to get greater solubility and aid in characterization. The second example is an acid terminated polyester (Figure 37). The synthesis of the polymer using 5-acetoxyisophthalic acid gave a $T_g$ of 250 °C while the addition of the an ethoxy chain in the backbone (increase in entropy proportional to an increase in the degrees of freedom) caused the $T_g$ to decrease to 150 °C. This is a perfect example where polymer properties can be altered by incorporating various functional groups within the polymer chains.

The final topic that will be discussed is intramolecular cyclizations. Intramolecular cyclizations of hyperbranched polymers during polymerization have been reported both by Feast$^{54}$ and Frechet$^{48,51}$ as a process observed in MALDI-TOF mass spectra. Even though the amount of cyclizations is usually minimal and sometimes does not occur at all, there are specific cases where cyclizations do occur. Primarily, at low monomer concentrations a reactive end may find its tail instead of a monomer and cyclize. Cyclization products have not really been isolated due to their small quantity and their continuous reaction with other components in the reaction mixture. Therefore, Yamamoto et. al.$^{74}$ have devised a bulky catalyst to induce cyclization so that controlled
Hyperbranched polymers have proven to be very attractive alternatives to both linear and dendritic polymers. What applications are there for these materials? Like most of their linear components, hyperbranched polymers can become important in developing a range of materials that can serve as blend components, additives, and coating (paints, lacquers, vanishes etc.) components. Hyperbranched polymers that contained acrylates, vinyl ethers, allyl ethers, epoxide, and hydroxide functional groups were considered for use as thermosets or high functionality cross linkers. Thermosets are highly cross-linked polymers whose polymer chains have lost their ability to flow past one another, therefore they do not melt, or mold very easily. Kim et al. showed that blending their polyphenylene hyperbranched polymer with linear polystyrene reduced the viscosity and shear rates (the rate at which molecular planes flow past each other) relative to polystyrene itself. Hyperbranched polyesters were found to be highly miscible with linear polyesters, polyamides, and polycarbonates presumably through hydrogen bonding. This enables polymer blends to become more effective. Hong et al. found that by mixing aliphatic polyesters with polyethylene created changes in the flow characteristics of the polymer (rheology). Blends of hyperbranched poly(etheramide)s with linear polyamide showed reduction in melt viscosity which can aid in facilitating polymer processing into a useful material.

Hyperbranched polymers have also found uses in fields other than the traditional polymer chemistry. Globular hyperbranched polymers have found use in producing nanoporous materials that are of interest in chromatography and in the production of aerogels and xerogels. Hyperbranched polymers been used in low dielectric constant materials. Hyperbranched poly (aryl ether phenylquinoxaline)s have been used for
aerogels and xerogels. Hyperbranched polymers have been used in low dielectric constant materials. Hyperbranched poly (aryl ether phenylquinoxaline)s have been used for organic-inorganic structure control in the production of microelectronics. Other fields that have benefited by continuous and innovative studies on hyperbranched polymers are nonlinear optics, sensorics, liquid crystal chemistry, molecular imprinting, catalysis, and soluble functional supports.

Given the variety of chemical, physical, and applicable work that has already been conducted on these polymers it is wise to continue to elaborate, ameliorate, innovate and create new systems based on what has already been done. Doing so will open new doors to new applications, perhaps towards the medical sector that for hyperbranched polymers is still considered not applicable due to their irregular shape. This irregularity makes them difficult to study precisely in order to manipulate them into something exact which is needed for biological work. By continuous work and development of synthetic methods it will be possible to one day make the “perfect” hyperbranched molecule for each application.
References


73. Higuchi, M.; Kanazawa, H.; Tsuruta, M.; Yamamoto, K. *Unpublished Results*.


Figure 1. Linear Polymers. a) Poly (ethylene oxide)  b) Polystyrene
Figure 2. Various syntheses of polystyrene. (a) radical (b) anionic (c) cationic (d) condensation \(^{1,5}\)
Figure 3. Representation of a hyperbranched architecture
Figure 4. Schematic plots for the relationship between \( \log M \) and \( \log [\eta] \) macromolecules.\(^{43}\)
Addition of guest

Shell addition

Trapped guests cannot be removed by extractions

Removal of guest

Shell removal

No guests

No guests

Figure 5. Meijer's Dendritic Box.
One end of the polymer chain is attached to the dendrimer.

The bulk of the polymer chain resides in solution.

Monomer molecules are able to diffuse into the cavity of the dendrimer.

The growing tip of the polymer chain resides in the cavity of the dendrimer, shielding it from reaction with a chain or another growing tip.

Figure 6. A dendritic polymer controlling a polymerization.
Figure 7. First dendrimer synthesis using the divergent approach.²⁰
Figure 8. a) Tomalia’s PAMAM dendrimer b) Newkomes arborols
Figure 9. a) Hanson's reversed Frechet method. b) Frechet's original method.
Figure 10. a) Mullen's polyphenylene via consecutive Diels-Alder reactions
b) Hart's iptycene (super triptycene)
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b) Polyaryl ether dendrimer coupled to a porphyrin.33
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Triptycene's name originates from a similarity with an antique book with three leaves on one hinge a.k.a triptych.

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In the triptycene system the orbitals represent a radical or cation where conjugation with the adjacent aromatics is not strong because the aromatic orbitals are locked by the bridge conformation and orthogonal to the bridgehead orbital thus minimizing overlap.

In the triphenylmethy system the aromatics are free to rotate and can overlap thus stabilizing the radical or cation more efficiently.

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Pentiptycene group with polymer backbone.

Benzyne traps anthracene to form triptycene.

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Degree of Branching \((DB) = \frac{D + T}{D + T + L}\)

**Figure 18.** Architecture of hyperbranched polymers from \(AB_2\) monomers.
Figure 19. a) Linear heptamer with one acid functionality and minimal aqueous solubility
   b) A hyperbranched heptamer containing multiple acid groups and much greater solubility.1
Figure 20. Synthetic strategies towards networks and hyperbranched polymers based on the classic branched polycondensation approach of Flory.\textsuperscript{42}
Figure 21. Kricheldorf's method of synthesizing a copolymeric hyperbranched polyester consisting of: a) terminal unit b) dendritic unit and c) linear unit. 91
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Figure 24. Frechet's hyperbranched version of the poly(arylether) dendrimer.\textsuperscript{59}
Figure 25. Miller and Neenan's poly(arylether) dendrimer.\textsuperscript{51}
Figure 26. Frechet's hyperbranched polyester via a clever proton transfer reaction.53
Figure 27. Feast’s hyperbranched PAMAM analog of Tomalia’s PAMAM dendrimer.
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Figure 29. Kim and Webster's hyperbranched polyphenylenes. Terminal groups with non-polar moieties were soluble in ether and lowered T_g.s. Functionalization with Li and CO₂ produced water soluble micelles. 

\[ X = \text{Br, CO}_2\text{H} \]

TMS, methyl
Figure 30. Hyperbranched polyphenylenes via a Diels-Alder reaction followed by CO extrusion.\textsuperscript{58,92}

\[ R = \text{H, CH}_3, \text{C}_6\text{H}_6 \]
Figure 31. An example of a self condensing vinyl polymerization of 3-(1-chloroethyl) styrene.
Figure 32. Hyperbranched poly (phenylene) sulfides produced from poly (sulfonium cation).69
Figure 33. Effect of monomer addition to a hyperbranched polymerization. a) $M_w$ of polymers with core addition over time. b) Effect of core functionality on $M_w$. c) Effect of core addition on polydispersity.
Table 1. Comparison of SEC Data of Linear Polyester P_b50 and Hyperbranched Polyester P_b50, Measured in THF as Well as DMF/GHC; Polymerization Was Carried Out in Bulk without Core Molecule (SEC-LALLS)

<table>
<thead>
<tr>
<th></th>
<th>P_b50 (THF)</th>
<th>P_b50 (DMF/GHC)</th>
<th>P_b00 (THF)</th>
<th>P_b00 (DMF/GHC)</th>
</tr>
</thead>
<tbody>
<tr>
<td>M_\mu</td>
<td>349700</td>
<td>4700</td>
<td>14200</td>
<td>14300</td>
</tr>
<tr>
<td>M_n</td>
<td>65600</td>
<td>3400</td>
<td>6900</td>
<td>7000</td>
</tr>
<tr>
<td>M_\mu/M_n</td>
<td>5.33</td>
<td>1.38</td>
<td>2.06</td>
<td>2.04</td>
</tr>
</tbody>
</table>

Monomers and core molecules used in this study: AB₂ monomer 35BCI, AB commoner 3BCI, and B₃-core molecules TMP, B₃-OH, and B₃-Si.

A

P_b50 = hyperbranched homopolymer of 35BCI (DB = .5)
P_b00 = linear homopolymer of 35BCI (DB = 0)
B = bulk polymerization
SMA = slow monomer addition

Figure 34. Effect of no core/bulk and core/slow monomer addition on degree of branching, polydispersity, and M_w

Table 1 shows the effect of bulk polymerization. Table 2 shows the effect of core molecules along with slow monomer addition. 

Table 2. Experimental Data for Hyperbranched Homopolyester Samples Based on TMP, B₃-OH, and B₃-Si, Respectively, as Core Molecules; Preparation by Slow Monomer Addition

<table>
<thead>
<tr>
<th>sample</th>
<th>m/c</th>
<th>DB</th>
<th>M_w</th>
<th>M_n</th>
<th>PD</th>
</tr>
</thead>
<tbody>
<tr>
<td>T-P SMA(1)</td>
<td>110/1</td>
<td>0.55 ± 0.02</td>
<td>275 300</td>
<td>184 600</td>
<td>1.49</td>
</tr>
<tr>
<td>T-P SMA(2)</td>
<td>220/1</td>
<td>0.63 ± 0.02</td>
<td>136 200</td>
<td>112 700</td>
<td>1.21</td>
</tr>
<tr>
<td>T-P SMA(3)</td>
<td>440/1</td>
<td>0.64 ± 0.02</td>
<td>301 900</td>
<td>277 900</td>
<td>1.05</td>
</tr>
<tr>
<td>T-P SMA(4)</td>
<td>660/1</td>
<td>0.64 ± 0.02</td>
<td>273 100</td>
<td>247 200</td>
<td>1.11</td>
</tr>
<tr>
<td>T-P SMA(5)</td>
<td>880/1</td>
<td>0.64 ± 0.02</td>
<td>117 400</td>
<td>83 900</td>
<td>1.40</td>
</tr>
<tr>
<td>B-P SMA(1)</td>
<td>660/1</td>
<td>0.61 ± 0.02</td>
<td>505 100</td>
<td>323 900</td>
<td>1.42</td>
</tr>
<tr>
<td>B-Si-P SMA(1)</td>
<td>147/1</td>
<td>0.66 ± 0.02</td>
<td>254 200</td>
<td>193 900</td>
<td>1.31</td>
</tr>
</tbody>
</table>

* T = TMP as core molecule, B = B₃-OH as core molecule, BSi = B₃-Si as core molecule. a Monomer/core ratio. d Determined by eq 1 from 1H ¹H NMR spectra. d Main mode of the distribution.
Scheme 1. Synthesis of AB$_x$ ($x = 2, 4, \text{and} 8$) Monomers

Scheme 2. Direct Polycondensation of AB$_x$ ($x = 2, 4, \text{and} 8$) Monomers

Table 1. Synthesis of Hyperbranched Aromatic Polyamides by Direct Polycondensation

<table>
<thead>
<tr>
<th>entry</th>
<th>monomer</th>
<th>condensing agents</th>
<th>equiv to COOH</th>
<th>yield (%)</th>
<th>$\eta_{vis}$ (dL/g)</th>
<th>$M_n$</th>
<th>$M_n/M_w$</th>
<th>DB$^c$</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>2</td>
<td>TPP/Py</td>
<td>1.0</td>
<td>97</td>
<td>0.25</td>
<td>155 000</td>
<td>3.0</td>
<td>0.32</td>
</tr>
<tr>
<td>2</td>
<td>2</td>
<td>TPP/Py</td>
<td>2.0</td>
<td>100$^d$</td>
<td>0.21</td>
<td>139 000</td>
<td>2.7</td>
<td>0.72</td>
</tr>
<tr>
<td>3</td>
<td>4</td>
<td>TPP/Py</td>
<td>1.0</td>
<td>96</td>
<td>0.25</td>
<td>193 000</td>
<td>3.3</td>
<td>0.67</td>
</tr>
<tr>
<td>4</td>
<td>4</td>
<td>TPP/Py</td>
<td>2.0</td>
<td>c</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>5</td>
<td>4</td>
<td>DBOP</td>
<td>1.2</td>
<td>99</td>
<td>0.25</td>
<td>139 000</td>
<td>2.7</td>
<td>0.67</td>
</tr>
<tr>
<td>6</td>
<td>6</td>
<td>TPP/Py</td>
<td>1.0</td>
<td>61</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>7</td>
<td>6</td>
<td>DBOP</td>
<td>1.2</td>
<td>94</td>
<td>0.36</td>
<td>109 000</td>
<td>2.6</td>
<td>0.84</td>
</tr>
</tbody>
</table>

$^a$ Measured at a concentration of 0.5 g/dL in DMF containing 0.01 mol/L of LiBr at 30 °C. $^b$ Determined by GPC based on polystyrene standards. $^d$ Determined by $^1$H NMR. $^e$ Precipitation occurred during the polymerization. $^c$ Gelation occurred during the polymerization.

Figure 35. Effect of monomer multiplicity on degree of branching. Scheme 1-2, synthesis of pre-fabricated dendrons. Table 1 shows the results on the degree of branching.
Figure 36. Voit's hyperbranched polyester with terminal acid functionality to change the physical properties of the polymer. 73
Figure 37. Voit's hyperbranched polyester with terminal hydroxyl, acetate or trimethylsilyl moieties to change the physical properties of the polymer.\textsuperscript{47}
Chapter 2

Synthesis and Characterization of Novel Triptycene Structural Units in the Synthesis of Dendrons
Introduction

Dendrimers have proven themselves to be interesting and increasingly useful, and new compounds are being generated increasing the pool of materials available for study. The synthesis of triptycene dendrimers and their lower generations may be important to explore routes that can be used to produce new compounds or polymers with novel and useful properties. Although triptycene has been known since the 1940’s, the various synthetic routes to triptycene rarely produce good yields. This is particularly evident once the symmetry of the molecule is broken. For example, the Bartlett triptycene shows D_{3h} symmetry. The reason why the symmetry is important is because it allows for crystallinity. Once the symmetry is broken, the crystallinity begins to decrease. Later in the results and discussion it will become evident since the compound is unsymmetrical and purification difficulties were encountered since numerous isomers of one compound were present.

The idea to construct this polymer began with the decision as to which isomer would be used since many are available through the anthracene and anthraquinone routes. Given Bartlett’s synthesis of triptycene, it was envisioned that by construction of an anthracene with a 2-position substitution followed by a Diels-Alder reaction with benzoquinone would give the desired adduct. This synthetic path would yield a 1,4-hydroquinone isomer that would then be coupled to some benzylic group as in the Frechet/Hanson method (discussed in the Introduction) for producing a convergent dendritic polymer. The retro synthetic analyses in Scheme 1 and Scheme 2 show the two routes available to produce the monomer required to synthesize the triptycene
dendrimers. The triptycene dendrimer should have certain synthetic and structural features resembling the Frechet poly(aryl ether) dendrimer. One possible difference between the two dendrimers is that the distance between the reactive site and the nucleophiles is greater. This distance can be interpreted as an internal spacer possibly giving access to higher generations (Figure 1). Other differences between the two polymers are that the triptycene monomer is significantly greater in mass than the Frechet monomer and that spatial arrangement in the main backbone structure may give rise to different restricted conformational properties. Thus, differences in physical, chemical, and thermal properties between the two polymers may be observed. Furthermore, the triptycene dendrimer may offer an alternative to the adamantane monomers (discussed in Chapter 1) since the direction of growth favors a greater spatial arrangement yielding a larger growth. Therefore, in order to prove the hypothesis the synthesis of the triptycene monomer and dendrimer must be performed to prove or disprove these predictions.
Results

Two methods that most readily afford the desired products are available; Method A and Method B. These two methods differ primarily because the two Diels-Alder precursors are isomers of one another and that may affect the [4+2] cycloaddition.\textsuperscript{10,23} The Diels-Alder reaction is affected by electronics. Therefore, using Method A the precursor anthracene and dienophile benzoquinone should afford the theoretically favorable HOMO/LUMO interaction producing the Diels-Alder adduct efficiently. Method B is an alternative route to see if the electron withdrawing ester on the anthracene will affect the Diels-Alder reaction. Method B would be preferred since it shortens the synthesis by two steps.

Method A

The choice of substitution position on the anthracene ring was the 2-position; the most readily available starting material (RASM) was 2-methylanthraquinone. The synthetic route to produce 2-anthrylmethyl acetate is shown in Scheme 3. The synthesis was performed as reported in the literature\textsuperscript{11} except for the acetylation of 2-hydroxymethylanthracene to the desired product.\textsuperscript{12-15}

The synthesis begins with the oxidation of the 2-methylanthraquinone (SM) to anthraquinone-2-carboxylic acid (1) using chromium trioxide in acetic acid. The product was obtained in a 64-70% yield. The melting point agreed with the reported literature value of 291-292 °C and the spectral data agreed as well. The main changes observed in the $^1$H NMR are the disappearance of the methyl peak and a downfield shift of the
aromatic protons to 8 and 8.8 ppm (Spectra 1 & 2). The I.R. spectrum (Spectrum 3) shows that the carbonyl peak of the quinone is still present at 1700 cm\(^{-1}\) and a new carbonyl appears at 1600 cm\(^{-1}\) along with an OH stretch at 3000 cm\(^{-1}\) (hydroxyl of acid). Anthraquinone-2-carboxylic acid is then reduced to anthracene-2-carboxylic acid (2) using ammonium hydroxide, zinc dust, and cupric sulfate. The yield was 70% and the melting point of this compound was 283-284°C, in agreement with the literature value.\(^{11}\) The aromatic region in the \(^1\)H NMR was found between 7.5 and 8.8 ppm (Spectrum 4). The carbonyl peaks at 1700 cm\(^{-1}\) in the IR disappeared indicating aromatization (Spectrum 5). Anthracene-2-carboxylic acid was then esterified to ethyl-2-anthroate (3) using sulfuric acid/ethanol (Fischer esterification) with a product yield of 48%. The \(^1\)H NMR showed a quartet at 4.25 ppm and a triplet at 1.5 ppm from the ethyl ester and the aromatic region was between 7.5 and 8.8 ppm (Spectrum 6). The IR showed the retention of the carbonyl peak around 1600 cm\(^{-1}\) and a disappearance of the hydroxyl group of the acid at 3000 cm\(^{-1}\) (Spectrum 7). The melting point of the product agreed with the literature value of 137-139°C.

The ester was then taken and reduced with lithium aluminum hydride in diethyl ether to 2-hydroxymethylanthracene (4) in a 90% yield. The \(^1\)H NMR showed the appearance of the aromatic region shifted upfield and is located between 8.5 and 7.5 ppm and a methylene singlet at 4.9 ppm (Spectrum 8). The IR (Spectrum 9) showed a hydrogen-bonded hydroxyl OH stretch at 3500 cm\(^{-1}\) with the disappearance of the carbonyl peak at 1600 cm\(^{-1}\) (ester). The melting point of this compound was 223-225 °C. The final stage of the reaction was to protect the alcohol as an acetate for the Bartlett aromatization conditions (HBr and acetic acid). Protection of the anthracene alcohol the
is necessary to prevent the bromination of the alcohol and using acetate allows transesterification between the solvent and the anthracene ester to regenerate the protecting group. Protection of the alcohol also prevents formation of a carbocation and undergoing subsequent Friedel-Crafts chemistry. Protection was accomplished with N'N-dimethylamino pyridine, triethylamine, and acetic anhydride. The reaction was quantitative and gave 2-anthryl methyl acetate (5) as a pure product by $^1$H NMR and a sharp melting point. The melting point (not reported in the literature) was 172-173°C. The $^1$HNMR peaks important for the characterization of the product are the aromatics at 8.45 and 7.35 ppm, a singlet at 5.3 ppm corresponding to the benzyl ester protons and a singlet at 2.15 ppm corresponding to the methyl protons (Spectrum 10). The IR showed the disappearance of the OH stretch at 3260 cm$^{-1}$ and the appearance of the ester carbonyl at 1701 cm$^{-1}$ (Spectrum 11).

The product 2-anthrylmethylacetate was then reacted with six equivalents of benzoquinone at 162°C in diglyme. After a lengthy workup, the yield was 30% of the presumed Diels-Alder adduct endo 6 and exo 7 (Scheme 4). The $^1$H NMR of the adduct showed the aromatic region between 7.4 and 7.0 ppm, singlets at 6.6 and 5.8 ppm which, corresponded to the bridgehead and unsaturated ketone protons respectively. There was also a peak at 5 ppm corresponding to the benzyl methylene group and a singlet at 2.1 ppm corresponding to the methyl of the acetate. The $^1$HNMR peaks were consistent with the desired product but the peak that corresponds to the $\alpha$ sp$^3$ carbon protons at the bridge are missing (Spectrum 12). Many attempts were made and all of these failed, to resynthesize the adduct and isolate it for further study.
Method B

The new route for the triptycene synthesis is shown in (Scheme 5). This synthesis was developed to optimize the product yields and to produce the reported Diels-Alder adduct. Beginning with the same starting material, this new synthetic route proved to be superior overall. All spectral data and physical properties for the new method corresponded to the method A products where applicable. Since this is a new method of synthesizing these precursors full spectral data will be provided as proof. The synthesis begins with the oxidation of 2-methylanthraquinone (RASM) to anthraquinone-2-carboxylic acid using periodic acid and chromium trioxide in acetonitrile. Anthraquinone-2-carboxylic acid (1) was obtained in 98% crude yield with sufficient purity that it can be used directly in the next step. The \(^1\)H NMR indicated a downfield shift of the aromatic region to 8.62-7.85 ppm (Spectrum 13). The methyl resonance in the starting materials is no longer present at 2.55 ppm. \(^{13}\)C NMR showed the quinone carbons at 182.5 ppm, the carbonyl carbon at 166.5, the aromatics between 128-136.5 ppm and the aromatic carbon bonded to the acid carbonyl is at 135.3 ppm (Spectrum 14). The methyl group in the starting material no longer is present at 22 ppm and the aromatic carbon bonded to the methyl group no longer appears (Spectrum 15). The IR for 2-methylanthraquinone shows only the ketone bands at 1685 cm\(^{-1}\) (Spectrum 16). IR for the product showed a strong and broad band between 3068- 2653 cm\(^{-1}\) indicating the aromatic stretch and the acid hydroxyl respectively. There are also two bands at 1712 and 1685 cm\(^{-1}\) that show the acid and ketone carbonyls (Spectrum 17).

Reduction to anthracene-2-carboxylic acid (2) occurred as described above for method A except that the reaction was refluxed and gave a crude yield of 98%, which
was used directly in the next step. The $^1$HNMR indicated an upfield shift of the aromatic region to 8.8-7.6 ppm showing the disappearence of the ketone carbonyls (Spectrum 18). There also is a resonance at 13 ppm showing the carboxylic acid proton. The $^{13}$CNMR shows (Spectrum 19) the carbonyl carbon at 168 ppm, the aromatic carbon bonded to the acid carbon group at 124.8 ppm, and the 9,10 central ring carbons at 126.7 ppm indicating aromatization since they are absent in the acid quinone. There was also a downfield shift of the aromatic carbons 124-133 ppm. The only significant change in the IR was the disappearence of the ketone band at 1712 cm$^{-1}$ (Spectrum 20). The UV spectra further confirmed the formation of the anthracene acid by displaying three bands between 344-384 nm, which indicate the extended conjugation of a polycyclic aromatic (Spectrum 21). The acid anthracene was then esterified with methanol/benzene/sulfuric acid mixture using a Dean-Stark trap to produce the methyl-2-anthroate (8).\textsuperscript{18} Flash chromatography (SiO$_2$) of the crude mixture gave a pure product in 95% yield. The $^1$H NMR spectra showed no significant change in the aromatic region, a resonance at 4 ppm indicating that the methoxy methyl group of the ester is present (Spectrum 22). The $^{13}$CNMR spectrum (Spectrum 23) shows a resonance at 52.5 ppm indicative of the methoxy methyl group. There are some subtle changes in the aromatic region because of the ester functionality but overall the carbonyl carbon peak and the aromatic carbon bonded to the carbonyl remained in a similar resonance. The IR shows the disappearence of the broad acid peak at 3053 cm$^{-1}$ and the appearance of the ester carbonyl at 1709 cm$^{-1}$ (Spectrum 24). All spectral and physical data from this series of reactions agreed with the original protocol.
The ester anthracene was reacted with benzoquinone in dioxane (Scheme 6) to produce the two diastereomers of 8-methoxycarbonyltriptycene-2,5-dione endo 9a and exo 9b (Diels-Alder adduct). The reported reaction yield was 65% for both diastereomers. The yields we obtained ranged from 10% to 75%, making it difficult to produce large quantities of the Diels-Alder adduct. The $^1$HNMR (Spectrum 25) showed the aromatic region for both isomers is located between 8.1 and 7.19 ppm, 6.37 ppm for the protons on the unsaturated conjugated olefin, a singlet at 4.9 ppm for the triptycene methine, two singlets at 3.89 ppm for the methyl protons of the ester and two singlets at 3.13 and 3.19 ppm for the bridge protons ($\alpha$ protons of sp$^3$ carbon bonded to the ketone). The $^{13}$CNMR resonance at 197 ppm is the bridge carbonyl, 167 ppm is the ester carbonyl, 128 ppm is the $\alpha$, $\beta$-unsaturated alkene, 52 ppm is the methoxy methyl, and 48.7 ppm is both the bridgehead and the saturated $\alpha$-carbons of the ketone, and 124 -127 ppm is the aromatic carbons of both isomers (Spectrum 26). IR analysis shows the ester carbonyl at 1721 cm$^{-1}$ and the ketone band at 1673 cm$^{-1}$ (Spectrum 27). The aromatization was attempted using HBr/acetic acid via the Bartlett protocol but an oily inseparable mixture was produced making purification difficult.

An alternative method was the use of enolate chemistry (base promoted aromatization) to generate the di-phenoxide anion, which would be trapped with an electrophile such as benzyl bromide since all terminal nucleophilic groups in dendrimers are capped to prevent further reaction. The Diels-Alder adduct is treated with sodium methoxide and benzyl bromide in methanol (Scheme 7). The product yield after flash chromatography is 86% of 2,5- bisbenzylxyloxy-8-methoxycarbonyl triptycene 10 ($G_0$ ester). The $^1$HNMR indicated product formation since the peaks at 3.19 ppm and 3.13
ppm were no longer evident indicating the aromatization. The olefinic protons after aromatization moved to 6.6 ppm, the bridgehead (methine) protons shifted downfield to 6.0 ppm, benzyl ether protons appeared at 5.1 ppm, and the ester protons remained where they were at 3.9 ppm (Spectrum 28). $^{13}$C NMR showed the following resonances: 167 ppm for the carbonyl carbon, 148.6 ppm is for the aromatic carbon attached to the ether oxygen, 137.7 ppm for the aromatic carbon connected to the benzyl carbon of the ether, 135.2 ppm for the carbons after aromatization, 124-139 ppm and 145-142 ppm are for the aromatics, 111 ppm for the carbons of the former $\alpha, \beta$-unsaturated ketone, 71.6 ppm for the benzyl carbons, 52.2 ppm for the methoxy methyl of the ester, and 47.8 ppm is for the bridgehead (Spectrum 29). The IR showed the disappearance of the ketones at 1673 cm$^{-1}$ the ester peak at 1720 cm$^{-1}$ and the appearance of the ether bands around 1200 cm$^{-1}$ (Spectrum 30). Mass spectral analysis (EI$^{+}$) indicated a peak at m/z 524.1 in agreement with calculations (Spectrum 31). The ester is then reduced quantitatively (Scheme 8) to the alcohol with lithium aluminum hydride in THF to yield the 2,5-bisbenzyloxy-8-methyl triptycene-ol 11 ($G_0$ alcohol). The $^1$HNMR spectrum remained the same except that the ester peak at 3.9 ppm was no longer evident and a peak appeared at 4.6 ppm indicating the formation of the benzyl alcohol methylene group (Spectrum 32). $^{13}$CNMR showed the same major resonances mentioned above except that the carbonyl carbon and methoxy methyl peaks are no longer there, the new resonance at 65 ppm indicates the benzyl alcohol carbon (Spectrum 33). The IR showed the disappearance of the ester stretch at 1721 cm$^{-1}$ and the appearance of the hydroxyl stretch at 3500 cm$^{-1}$ (Spectrum 34). Mass spectral analysis (EI$^{+}$) shows a peak at m/z = 496 which agrees with the calculated mass (Spectrum 35).
Activation of G₀ Alcohol for Coupling

The G₀ alcohol was converted to the G₀ bromide (12) using two methods (Scheme 9). The first method employed triphenylphosphine and carbon tetrabromide in THF, and the second employed dimethylsulfide and N-bromosuccinamide in methylene chloride (Corey-Kim halogenation). The yields of the reaction were 63% and 73% respectively. The ¹HNMR of the bromide product via the former method was similar to the ¹HNMR of the G₀ alcohol except the benzyl methylene peak moved to 4.4 ppm (Spectrum 36). The latter bromide synthesis gave an identical ¹HNMR (Spectrum 37). ¹³CNMR of the product from the second method showed the same major resonances as G₀ alcohol except for the benzyl alcohol carbon resonance. The new resonance is 34 ppm for the benzyl bromide carbon (Spectrum 38). ¹³CNMR was provided for the latter method since it was superior in yield and purity. Mass spectral analysis (EI+) shows two peaks at m/z = 558 and 560 in agreement with the calculated mass (Spectrum 39) and the two bromide isotopes.

The G₀ alcohol was also activated with methanesulfonylchloride and dicyclohexylamine in toluene to quantitatively generate the G₀ mesyltriptycene (13) (Scheme 10). The ¹HNMR of the mesyltriptycene was similar to the G₀ bromide except for the benzyl methylene at 5.1 ppm and the methyl peak of the mesylate at 2.8 ppm (Spectrum 40). The mesylate was employed as a leaving group since the triptycene could be hindered and the mesylate is more reactive than the bromide.

The final precursor step is the monomer synthesis of 2,5-dihydroxy-8-methoxycarbonyl triptycene (14). The method used resembled the basic aromatization to prepare the G₀ ester, except that the quenching agent was citric acid (Scheme 11). The
The product yield was quantitative. The $^1$HNMR revealed the olefinic protons that are now part of an aromatic system shifted to 6.4 ppm, indicating that the hydroquinone was formed, the bridgehead at 5.8 ppm and an ester peak at 3.99 ppm (Spectrum 41). The IR showed a band at 3400 cm$^{-1}$ indicating a hydrogen bonded hydroxyl, and a band at 1700 cm$^{-1}$ for the ester carbonyl (Spectrum 42). MS (ES-) data (Spectrum 43) also supports the monomer formation with peaks at m/z 342-343 indicating a loss of protons from the hydroquinone (calculated mass of monomer 344 D). Monomer formation was also observed after reducing the product obtained from chromatographing the Diels-Alder adduct (9) with sodium borohydride. Spectral analysis indicated that the aromatized product from the reduction was the same as hydroquinone (14).

**Coupling to form G$_1$**

The final two schemes will describe the attempted couplings to generate the G$_1$ triptycene (15) dendrimer (Figure 2). Scheme 13 illustrates the attempts that utilized the same reagents but different solvents, reaction times, and temperatures. They all showed starting material on TLC after the times described in the scheme. Two further attempts are shown in Scheme 14 where G$_0$ bromide was reacted with either the monomer or the Diels-Alder adduct. The first reaction made use of a homogenous reaction mixture using a strong hindered base DBU in acetonitrile with the Diels-Alder adduct as the monomer. The idea is to generate the phenoxide anions with DBU, and these phenoxides would be trapped by G$_0$ bromide. The result was complete recovery of starting material as indicated by TLC. The second attempt was the classical Frechet
coupling reaction of a benzyl bromide with a dihydroxy ester (monomer 14). After 72 hours the TLC showed a spot that did not correspond to any of the starting materials. After purification using prep TLC, the yield of product was 40%. $^1$H NMR analysis showed the same peaks for the $G_0$ ester except that there were multiple peaks that might be indicative of a successful coupling (Spectrum 44). However, mass spectral analysis (EI+) showed that no significant coupling had occurred. The only indication that some coupling occurred was a small peak at m/z = 1300 (MW of a successful coupling) which was within the baseline noise. The only major fragment was at m/z = 649 indicating a possible homocoupling of the monomers (Spectrum 45).

**Discussion**

The various routes to prepare the triptycene derivatives and the attempted couplings met with different levels of success. Method A (Scheme 3) was carried out following the literature protocol.$^{11}$ All spectral data and physical properties agreed with the reported literature values. The yields obtained via Method A were similar to those reported except for the initial oxidation of 2-methylanthraquinone to anthraquinone-2-carboxylic acid. The product yields obtained were 64% to 70 % of a yellow powder whereas an 83% yield was reported.$^{11}$ The lower yields might be attributed to loss during recrystallization. It is important to use distilled water for all the washes so that no insoluble salt deposits are trapped within in the product. If any insoluble salts are present, they may cause problems during purification in the reduction part of the procedure.
mechanical stirrer is vital because a magnetic stir bar is trapped by the zinc metal and when the reaction refluxes, foaming occurs that causes an eruption. It is imperative to use hot distilled water during the workup to wash the zinc metal free of the product and to avoid any precipitation between the ammonium hydroxide and any heavy ions present in tap water. Hot water also has to be used to increase the solubility of the anthracene acid salts. The acid anthracene was esterified in the same manner described though the yield obtained was 48% of a yellow solid instead of the reported 80%. The lower yield in this case can be attributed to the reversibility of the Fischer esterification. Fischer esterifications produce water as a by product in the presence of the acid catalyst which, can hydrolyze the ester back to the anthracene acid. The reaction going from the ester anthracene to the 2-hydroxymethylanthracene was carried out as reported. No differences were noted and the yield obtained for the yellow solid product was 90% versus the 95% reported yield. Protection of the anthracene methanol as the acetate proceeded quantitatively with DMAP, triethylamine, and acetic anhydride. Use of the triethylamine was not reported in the literature papers cited but as a precaution it was used.

2-Anthrylmethyl acetate was then reacted with benzoquinone via an inverse demand Diels-Alder reaction to produce the triptycene adduct. The reason why the 2-anthryl methyl acetate was used instead of the 2-methanthroate initially was because the former possessed a benzyl carbon that is electron donating while the latter ester isomer is electron withdrawing. The result was a brown solid that had some spectroscopic similarities to the desired adduct. Many attempts were made to try and obtain the solid again but only oily mixtures were isolated.
Method B (Scheme 5) produces many of the compounds substrates as Method A. The yields are generally far better and some of the transformations are carried out after the Diels-Alder reaction rather than before. The initial oxidation to the anthraquinone-2-carboxylic acid with periodic acid and chromium trioxide in acetonitrile is twice as rapid as the Method A oxidation. The yields of this reaction are reproducibly between 95-98% crude; usually pure enough to continue without purification. The preparation of 2-anthroic acid from anthraquinone-2-carboxylic acid is carried out the same way as in Method A except that the reaction is refluxed. The product yield is 98% crude, the most difficult impurity to remove is 2-methylanthracene. Removal is quite difficult since it requires multiple recrystallizations and chromatography is not used since the solubility of the acid is poor in most common organic solvents including acetic acid unless it is heated to boiling. Since the methylanthracene does not react readily with anything it can be carried over to the next step. The Fischer esterification of 2-anthroic acid to the 2-anthroate gives a yield of 95%. This higher yield can be attributed to the removal of water using a Dean-Stark trap thus forcing the equilibrium towards the ester.

The next reaction is the Diels-Alder, which was carried out according to the literature protocol. This reaction worked even with the electron withdrawing group present on the anthracene. Presumably, the ester functionality is sufficiently distant from the central rings for the reaction to proceed. The benzoquinone must be purified prior to the Diels-Alder. A two fold excess of benzoquinone is necessary to avoid a second anthracene from adding to the benzoquinone. Complete reaction required 24 hours using two equivalents of benzoquinone; shorter reaction times could be achieved with more benzoquinone but isolation of the product became more difficult. Overall removal of the
benzoquinone was a significant problem and made it difficult to obtain large quantities of material. The literature procedure called for benzoquinone to be removed by steam distillation. During this method of removal, black decomposition products were formed as well as some retro Diels-Alder products, as observed by TLC. Extraction following distillation required large amounts of benzene to remove the desired product from the black and charred decomposition products. Purification of the crude oily Diels-Alder adduct by recrystallization was also difficult, since there are four stereoisomers: two endo enantiomers and two exo enantiomers. Purification required between 3-6 recrystallizations from ether. The yield of pure adduct was variable; the best result (76%) was obtained with ether, but methanol was more reproducible. Flash chromatography was also used to remove the benzoquinone and anthracene ester impurities. But the Diels-Alder adduct reacted in the presence of air and silica gel to produce a mixture of the original adduct (9), hydroquinone triptycene (14), and the oxidized quinone triptycene. This change in functional groups caused smearing and co-elution of the bulk of the sample. Only a minimal amount of the hydroquinone monomer and quinone triptycene was isolated and characterized.

Once the Diels-Alder product (9) was obtained it served as the source from which the hydroquinone monomer (14) and the G0 monodendron (10) were synthesized. The original literature procedure using HBr7 was found to be inferior to the basic conditions (methoxide).19 This method gave a yield of 86% for the G0 monodendron (10) and quantitative for the monomer (14). When the triptycene adduct is first placed in the methoxide solution it does not dissolve readily but after a few minutes it dissolves and the solution becomes dark red or brown indicating enolate formation. The reduction of
the $G_0$ ester to the $G_0$ alcohol (12) was carried out with LAH in THF at room temperature and gave a quantitative yield. The product is a glassy solid, typically isolated as a foam.

The $G_0$ alcohol was converted to the $G_0$ bromide (12) using two methods. The first method was activation of the $G_x$ generation alcohol to the bromide using triphenylphosphine/carbon tetrabromide in THF, used by Frechet in his poly(aryl ether) synthesis. The product yield using this method was 63%. $^1$H NMR analysis showed that the aromatic region contained extra protons corresponding to the triphenylphosphine that coeluted as a 1:1 complex with the $G_0$ bromide monodendron. The second method (Corey-Kim) gave the $G_0$ bromide from the $G_0$ alcohol in 73% yield as a yellowish wax. This method gave a slightly higher yield with a simpler purification and no contamination. $G_0$ alcohol was also converted into the $G_0$ mesylate (13) to provide a better leaving group than bromide to help counter the sluggish reaction rate due to the triptycene's size. The mesylate was formed in quantitative yield as a colorless oil.

The aromatization of 8-methoxycarbonyl triptycene-3-cyclohexen-2,5-dione (9) to 2,5-dihydroxy-8-methoxycarbonyl triptycene (triptycene hydroquinone monomer) (14) was not carried out as described in the literature report (methanol, HCl gas). Instead, the basic conditions used for production of the $G_0$ ester were employed with citric acid as the quenching agent. Monomer (14) was prepared in quantitative yield as an off-white solid, which did not need further purification. The final step was to couple the $G_0$ bromides and $G_0$ mesylates with the monomer.

Preparation of larger monodendrons requires coupling of the $G_0$ bromides (12) or $G_0$ mesylate (13) with the monomer (14). The first attempted coupling reaction between $G_0$ bromide and the monomer was carried out using THF, 18-C-6, and $K_2CO_3$ (standard
coupling conditions in the Frechet and Hanson poly(aryl ether) syntheses.\textsuperscript{8,9} After 24 hours at reflux the reaction had not progressed by TLC. Given the success of these coupling conditions in the Frechet and Hanson syntheses, the steric bulk of the monomer seemed the more likely cause of low reactivity. Therefore, the reaction was repeated using the same reagents in diglyme at 100°C to help force the reaction. Diglyme was expected to help solubilize the K\textsubscript{2}CO\textsubscript{3} base and also afforded higher temperatures and more forcing conditions. However, after 72 hours the reaction had not progressed as shown by the spot only of starting material on TLC.

G\textsubscript{0} mesylate (13) was then employed as a starting material with monomer (14) using 18-C-6, and K\textsubscript{2}CO\textsubscript{3}, in THF. The mesylate leaving group is more reactive than bromide,\textsuperscript{24} but after 55hrs the reaction showed no progress by TLC. the Frechet/Hanson technique and the result was starting materials on TLC after 55hrs. The mesylate (13) was also unreactive in refluxing dioxane. The greater reactivity of the mesylate leaving group cannot overcome the intrinsic inertness of the triptycene system.

A final set of reaction conditions was attempted on the G\textsubscript{0} ester. The first attempt was modeled from the same reaction used to generate G\textsubscript{0} ester. The Diels-Alder adduct (9) was treated with a strong base and G\textsubscript{0} bromide (12) was then added to try and trap the anions. Methoxide could be used as a base in the G\textsubscript{0} synthesis since it is inexpensive and may be used in excess. For the coupling to G\textsubscript{1} a nonnucleophilic base was preferred to conserve G\textsubscript{0} bromide. The base chosen was DBU: both strong and nonnucleophilic, DBU would also promote a homogenous system that could improve deprotonation efficiency. After 24 hours at room temperature the reaction showed no product formation. The TLC showed only starting materials, with some anthracene ester from
The final attempt was to repeat the typical Frechet and Hanson reaction conditions (THF, 18-C-6, and K₂CO₃) with G₀ bromide (12) and monomer (14). The reaction mixture was refluxed for 72hrs at which time the TLC showed some promise since the monomer was consumed and there was a new spot that did not correspond to the starting materials. MS analysis showed that this was a possible homocoupling of the monomers.

**Possible Uses for the Triptycene System**

Our system uses a variation of the Bartlett method to produce the triptycene since it gives the option of keeping the oxygens after the reaction. We envisioned that a triptycene dendrimer could be synthesized so that not only can higher generations be achieved and applied but applications for the initial structures can also be realized. The dendrimer from triptycene could be used as a chiral stationary phase since it could form cavities that might orient the aromatics in such a way that non-covalent interactions could occur (Figure 3). The dendrimer could also be used for photophysical studies by connecting it to a fullerene. The dendrimer-fullerene system was seen earlier in the introduction. The difference is that the dendrimer used before is a poly (aryl ether) dendrimer that is smaller in size and more flexible. The triptycene dendrimer would be less flexible, larger, and oriented differently in space which could affect the behavior of what happens on the fullerene surface. According to Dougherty benzene rings have binding affinities to cations such as Na⁺, K⁺, etc. It is proposed that synthesizing a lower generation triptycene and connecting it to an iptycene via biphenyls might effectuate ion
trapping in a similar fashion to a liquid like porphyrin (Figure 4). Furthermore, the lower generations given their chirality and steric bulk can be applied as well. The lower generation is a 2,5-dibenzyloxy-8-methoxycarbonyl triptycene (Figure 5). For example, 9-BBN is used to discriminate between various types of alkenes; the less hindered reacts more readily then more hindered. If triptycene is the ligand on the borate (Figure 6) can it be more regioselective or equally regioselective as 9-BBN for hydroborations or boration/oxidation reactions? This would be useful for alkenes that are not very different such as an ethyl to methyl substitution on or near the reactive center. Can hydroboration reductions be carried out stereoselectively and regioselectively on ring systems larger than six? Other possible uses can be as a protecting group similar to the trityl group (Figure 7). Can a triptycene protecting group be more or less sensitive to cleavage than the trityl group by not letting the cleaving reagent diffuse through the caged triptycene system and react with protected group to free it? Can the triptycene induce chirality using steric effects by blocking the faces of molecules and can regioselectively also be controlled as to where protection would occur. One important factor to take into account is that in our system there are benzyl ethers that are prone to cleavage in an acidic reaction media. Therefore, they would have to be changed to some other group that is not acid or base sensitive such as replacing the oxygen with a carbon. Although the way it stands with the ethers, base reactions can be carried out thus not affecting the triptycene system. Other applications can be as a regioselective base used to produce enolates. The usual base is LDA in THF to make enolates out of carbonyls. The idea in the triptycene system is that by possibly using its bulk more control can be gained over the kinetics or thermodynamics of enolate formation in substituted ring systems (Figure 8). The above
applications are for the triptycene dendritic isomer we are constructing although there are other triptycene dendritic isomers and substitution patterns that can be carried out, which will in turn have other properties that can be amplified.
Conclusion

In summary, we were able to prepare the desired AB$_2$ triptycene, both as the G$_0$ monodendron (10) and as the hydroquinone monomer (14). Attempts to couple the monomer (14) with the activated G$_0$ bromide (12) were unsuccessful, however. The G$_0$ monodendrons might be of some interest for testing the applications talked about in the section following the discussion in this chapter.

Method B was preferred over Method A for the preparation of the precursor anthracene, since it provided significantly higher yields. Furthermore, it appears as if the electron withdrawing ester functionality from Method B is distant enough from the central reacting rings to have any affect on the electronics. This in turn eliminates the extra steps that would have been required using Method A. The purification difficulties encountered with the Diels-Alder adduct greatly reduced the overall yield of the triptycene syntheses, however. The benzoquinone route was selected over the benzyne routes to triptycene because of the higher yields of the benzoquinone route, but the purification difficulties may make the benzyne routes attractive for future studies.

Although many modifications could be attempted to improve the yield of triptycenes, the fact still remains that no coupling was observed between the triptycene monomer (14) and the activated G$_0$ triptyceneces (12 & 13). The evidence suggests that the steric problem must be primarily centered at the activated G$_0$ monodendrons (12 & 13). The hydroquinone monomer was able to react effectively as a nucleophile with benzyl bromide to prepare the G$_0$ monodendron (10). Reaction at the site of the triptycene is not impossible, since the G$_0$ monodendron can be converted from the G$_0$ ester (10) to the alcohol (11) with LAH and then to the bromide (12) with either of two reagents (see
above). However, bulky nucleophiles like the triptycene monomer must not be able to access the reactive site for the coupling reaction. If this is true, then our system and any related ones are unlikely to succeed. Other isomers of the triptycene AB$_2$ system, for example, would still require coupling two sterically demanding reagents. Preparation of the triptycene derivatives might require a less sterically demanding coupling reaction.
Experimental Section

General

Melting points were determined on a Thomas Hoover capillary melting point apparatus and are uncorrected.

All $^1$H NMR and $^{13}$C NMR spectra were recorded using DMSO-$d_6$ or CDCl$_3$ (Aldrich) on a Varian 200 MHz NMR or a Varian 500 MHz FT-NMR with a gradient field. NMR units are given in $\delta$ based on an internal tetramethysilane (TMS) standard. $^{13}$C NMR spectra for the synthesis of the lower generation triptycenes were assigned by comparison to standard spectra from Aldrich for analogous compounds. $^1$H NMR spectra of $G_0$Br via triphenylphosphine/carbon tetrabromide was provided by Dr. Wajiha Kahn at Hoffman La Roche. Other $^{13}$C NMR peaks were assigned by calculation of the chemical shift effect of substituents on the aromatic ring using the formula $\delta C = 128.5 + Z_i^{26,27,28}$. Proton chemical shifts for lower generation triptycene generations were compared to literature examples of dendrimers and triptycenes for the determination of benzyl groups and triptycene structures. Some of the abbreviations used when describing NMR resonances are: Bz = benzyl, ArC = aromatic carbon, ArH = aromatic hydrogen, Ph = phenyl.

IR spectra obtained on a Midac Prospect FT-IR using a KBr pellet or a Nicolet MAGNA FT-IR 560 with in line Spectra Tech using a neat sample courtesy of (Steven Toth at IFF) or a Mattson CYGNUS 25 using a KBr pellet. All IR signals are reported in reciprocal centimeters vs. % transmittance.
UV spectra were recorded using a Hewlett Packard 8452 diode array
spectrophotometer in ethanol. The UV signals are reported in absorbance vs. nm.

EI mass spectra were obtained from the Mass Spectrometry Center in Amherst Mass. The spectra were recorded on a JEOL MStation with a source temp of 200°C, acc.
voltage of 10kv, a resolution of 5000 and scan range of 475-575. ES- MS data for the
monomer was taken at Hoffman La Roche courtesy of Dr. Wajiha Kahn.

Analytical TLC was performed using commercially available coated polyester
and aluminum silica gel plates (200-400 mesh, 60 Å) from Aldrich. Silica gel for flash
cromatography (200-400 mesh, 60 Å) was also purchased from Aldrich Chemical
Co.and Bodman.

All solvents and materials were purchased and used as received from Aldrich
except for benzoquinone which was recrystallized from benzene and Norit, followed by
ethanol. THF and dioxane were distilled as needed from sodium/benzophenone, and
methylen chloride was distilled as needed from calcium hydride. Toluene was
purchased from Aldrich as anhydrous.

All reactions were conducted under a nitrogen or argon atmosphere when
specified, otherwise under ambient atmosphere. Syringes used for transfer were always
glass. Reaction vessels where specified were heated with a heat gun or flame under
vacuum followed by inert gas purge.

**Method A** synthesis was carried out as described in the literature.\(^\text{11}\)

Acetylation of anthracene methanol was carried out using a modified literature
procedure.\(^\text{15}\)
Method B

Anthraquinone-2-carboxylic acid (1): A 1 L 3-neck round bottom flask equipped with a mechanical stirrer and condenser was charged with 42g (184 mmol) of HIO₄ in 400 mL of acetonitrile. This suspension was stirred vigorously for approximately 20min. Then 35g (350 mmol) of CrO₃ are added immediately followed by 10g (45 mmol) of 2-methylantraquinone. A deep orange solution appeared followed by an exothermic reaction. At this point a precipitate formed making the solution very viscous and hard to stir. An additional portion of acetonitrile (100 mL) was added to facilitate stirring and the solution was stirred for 4 hours at room temperature. The reaction was monitored using TLC (80%:20%:10 drops ethyl acetate: hexanes: acetic acid). Upon completion the entire mixture was poured into 5 L of water and stirred for 30 min. The precipitate was then allowed to settle to the bottom of the flask and then filtered through a 2 L glass fritted funnel. Subsequent washing removed all of the chromium salts, by washing until the filtrate was colorless. The precipitate was dried overnight on the funnel under vacuum. Crude product yield was 11.1g (98%) as a yellow powder used directly in the next step. Recrystallization with acetic acid was performed to determine the melting point; mp. 291-292°C as reported in the literature.¹¹

¹¹HNMR (DMSO-d₆): δ 8.62-7.85 (m, ArH, 7H), 3.3 (H₂O). ¹³CNMR (DMSO-d₆): δ 182.5 (CO) 166.5 (CO₂H), 136.5-128 (ArC), 135.3 (ArC-CH₃). FTIR (neat): 3063-2653 cm⁻¹ (OH and CH stretch), 1712 cm⁻¹ (CO acid stretch), 1685 cm⁻¹ (CO ketone stretch).

Anthracene-2-carboxylic acid (2): A 2L, 3-neck, round bottom flask equipped with a mechanical stirrer and condenser is charged with 10g (40 mmol) of (1), 45g (688 mmol) Zn dust, and 5g (31 mmol) of CuSO₄. To this mixture of solids was added 500mL of
concentrated NH₄OH and the mixture was stirred vigorously and refluxed for 4 hours after boiling began. Once the reaction has finished (TLC 50:50:4 drops ethyl acetate: hexanes: acetic acid), the entire mixture was filtered through a 2 L glass fritted funnel thoroughly washed with hot concentrated ammonium hydroxide solution followed by hot distilled water. All the filtrates were combined and put aside to cool to room temperature. The remaining Zn was dissolved in concentrated HCl and stirred overnight. The combined filtrates were put them on ice and acidified until it is red to litmus and allowed to stand overnight. The acidic solution where the zinc was dissolved was filtered through a fritted funnel (set up trap to catch HCl vapors from filter flask). The resulting solid was dissolved in a minimum amount of hot acetic acid (it does not matter that the solid is not dry). The acetic acid solution was gravity filtered while hot to remove residual zinc metal. The filtrate was poured into 2L of distilled water. This precipitate and the one acidified previously were then suction filtered. The filter cake was dried on the filter with suction overnight. The crude product yield was 8.6g (98%) as a yellow powder and was used without purification for the next part. Recrystallization with acetic acid was performed to determine the melting point; mp. 283-285°C as reported in the literature for method A.¹¹ ¹H NMR (DMSO-δ₆): δ 8.8-7.7 (m, ArH, 9H), 13.0 (CO₂H, 1H). ¹³C NMR (DMSO-δ₆): δ 168 (CO₂H), 124.8 ((ArC-CH₃), 126.7 (central anthracene carbons), 122-133 (ArC). FTIR (neat): 3050-2666 cm⁻¹ (OH and CH stretch), 1692 cm⁻¹ (CO stretch). UVλmax and conjugated UV bands: 258 nm and 344-384 nm. Spectral data agree with those reported.

2-methylanthroate (8): To a 3-neck 2 L round bottom flask were added 8g (36 mmol) of (2), 40 mL of CH₃OH, 500 mL of C₆H₆ and lastly 7 mL of H₂SO₄. A magnetic stirrer
bar was added to the mixture and condenser with a Dean-Stark trap. The solution was refluxed for 24 hours. TLC of the reaction (10%: 90% ethyl acetate: hexanes) showed no starting material. The first 100 mL of solvent were drained through the trap. The trap was then replaced with a simple downward distillation into a round bottom receiver. The distillate was collected until crystals began to form on the walls of the flask. At this point the heat was removed and the flask cooled to room temperature (a precipitate formed) then cooled on ice to complete crystal formation. The precipitate was filtered and washed with 200 mL of water, followed by 100 mL of cold methanol. The filtrate was put on ice and neutralized with saturated aqueous sodium carbonate. The neutralized filtrate was extracted with ethyl acetate until no product was visible in the organic layer via TLC. The combined organics were extracted with brine and dried over sodium sulfate. The solution was filtered and the solvent removed in vacuo. The solids were recrystallized from ethanol and filtered. The filtrate was concentrated and the resulting solid was dissolved in a minimum amount of ethyl acetate, silica gel was added to this solution and the solvent evaporated. The dry silica gel-compound mixture was loaded on a pre-packed column and chromatographed using ethyl acetate/hexanes. The yield was 8g (95%) of yellow powder with a mp. of 192-193°C. $^1$HMR (CDCl$_3$): $\delta$ 8.8-7.1 (m, ArH, 9H), 4.0 (s, CO$_2$CH$_3$, 3H) $^{13}$CNMR (CDCl$_3$): $\delta$ 167 (CO$_2$CH$_3$), 133.4-124.3 (ArC), 52.5 (CO$_2$CH$_3$). FTIR (neat): 3056-2848 cm$^{-1}$ (CH stretch), 1709 cm$^{-1}$ (CO stretch).

8-methoxycarbonyltriptycene-2,5-dione (9): To a dry 200 mL round bottom flask under nitrogen and covered with aluminum foil was added 7g (30 mmol) of (8) and 30 mL of freshly distilled dioxane. The suspension was heated to 70°C where most of the solid dissolved. To the mixture was added 7g (65 mmol) of twice recrystallized 1,4-
benzoquinone and 10 mL extra dioxane. The mixture was refluxed for 24 hours and monitored using TLC with hexanes: ethyl acetate (80%; 20%). The reaction was then cooled to room temperature and the dioxane evaporated off at the pump. Then using a 1L round bottom single neck flask, a 1:1 mixture of dioxane: water was added using an equal reaction volume and evaporated. This process was repeated 4x to remove the bulk of the benzoquinone. The residue was put under vacuum overnight to further remove benzoquinone. The flask was then charged with 500 mL of water (more added during distillation as necessary) and steam distilled using an external steam source. When no benzoquinone was visible in the distillate (from yellow to clear) the heat was removed and the distillation pot cooled. The gummy/solid black/brown residue in water was extracted with benzene until no appreciable organics were left in the organic layer. The organics were then treated with Norit and sodium sulfate. The resulting yellow solution was filtered through a very thin layer of Celite and concentrated. The resulting oil was recrystallized with methanol. The yield of the reaction varied between 10%-75%. The mp. of the resulting mixture of isomers was 133-135°C. $^1$HNMR (CDCl$_3$): $\delta$ 8.1-7.2 (m, ArH, 7H) 6.37 (s, ketone conjugated olefin, 2H), 4.98 (s, bridgehead, 2H), 3.93-3.89 (two singlets, CO$_2$CH$_3$, 3H ), 3.19-3.13 (two singlets, bridge, 2H), 13CNMR (CDCl$_3$); $\delta$ 197 (bridge carbonyl), 167 (CO$_2$CH$_3$), 128 (ketone conjugated olefin), 124-127 (ArC) 52 (CO$_2$CH$_3$), 48.7-49 (for both bridgehead and bridge). The appearance of two singlets in the $^1$HNMR are due to the different diastereomers present. Multiple peaks in both $^1$H and $^{13}$C exist because of the diastereomers. FTIR (neat): 3064-2949 cm$^{-1}$ (CH stretch), 1721 cm$^{-1}$ (CO ester stretch) 1673 cm$^{-1}$ (CO conjugated ketone stretch), 1614 cm$^{-1}$ (conjugated olefin).
2,5-Bisbenzyloxy-8-methoxycarbonyl triptycene \{G_{6}Ester\} (10): A 250 mL three neck round bottom flask fitted with an efficient condenser, magnetic stirrer, and sealed with one rubber septa and one glass stopper was dried under vacuum with a heat gun (20 minutes), purged with nitrogen for 10 minutes and kept under the inert atmosphere. The round bottom was charged with 100 mL of dry methanol. The nitrogen pressure was increased to keep positive flow pressure when the glass stopper was opened and 0.67g (29 mmol) of sodium metal was put into the reaction vessel. After being sealed the nitrogen pressure was reduced to a slow, steady flow to avoid solvent evaporation. The mixture was stirred until all the sodium metal dissolved completely. Then the nitrogen flow was increased again and 2g (5.8 mmol) of the Diels-Alder adduct (9) was added. The nitrogen pressure was lowered and the mixture stirred for 1.5 hours. At the end of this time, 5.5mL of benzyl bromide were added in one portion and the mixture heated to reflux for 10hrs and monitored using 90%:10% hexanes: ethyl acetate on silica TLC plates. After 10 hours the mixture was cooled to room temperature, and a peach/white precipitate formed. Further cooling with ice for one hour assured complete precipitation. The precipitate was then collected using vacuum filtration and washed copiously with water to remove any methoxide, methanol, or benzyl bromide. The precipitate was tested using TLC and it appeared as one spot. The filtrate was extracted three times with an equal volume of ether. The combined organics were extracted with brine, dried with sodium sulfate, filtered, and concentrated. The residue was then stored under vacuum overnight to assure dryness from residual water. TLC showed the same product spot as the precipitate along with some starting materials. The residue was dissolved in a minimum amount of ether and silica gel was added. The ether was evaporated at the
pump using low heat. This mixture was then dry loaded on a pre-packed silica gel column and flash chromatographed using a gradient mixture of hexane and ethyl acetate. The product yield was 2.6g (86%) with a mp of \(138-140^\circ\text{C}\). \(\text{^1H} \text{NMR (CDCl}_3\): } \delta 8.1-7.0 (m, ArH, 17H), 6.6 (s, hydroquinone, 2H), 6.0 (s, bridgehead, 2H), 5.1 (s, BzCOPh, 4H), 3.93 (s, CO\textsubscript{2}CH\textsubscript{3}, 3H). \(\text{^13C} \text{NMR (CDCl}_3\): } \delta 167 (CO\textsubscript{2}CH\textsubscript{3}), 148.6 (ArC-O-C), 137.7 (ArC-C-O), 135.7-135.2 (former bridge), 111 (former olefinic \(\alpha,\beta\) unsaturated), 71.6 (ArC-C-O), 52.2 (CO\textsubscript{2}CH\textsubscript{3}), 47.8 (bridgehead), 124-129, 144.5-146.2, 151.5 (remaining aromatics). \(\text{FTIR (KBr pellet): } 3064-2946 \text{ cm}^{-1} \) (CH stretch), 1720 cm\(^{-1}\) (C=O ester stretch), 1271 and 1054 cm\(^{-1}\) (C-O ether/ester). \(\text{EI}^+ \text{ m/z (524.20) and composition C}{}_{36}\text{H}{}_{28}\text{O}_4\). 

\textbf{2,5-bisbenzyloxy-8-triptyceneol (G\textsubscript{o}OH) (11): } A 3-neck, 100 mL round bottom flask equipped with a magnetic stir bar, one rubber septa, and an addition funnel was dried under vacuum with a heat gun. After cooling, the system was flushed with N\(_2\) and kept under the same atmosphere throughout the reaction. 2.3g (4.4 mmol) of (10) was dissolved in a minimum amount of dry THF and transferred via an oven dried and desiccated syringe through the septa into the round bottom. Then more THF was used to wash the vessel and bring the total volume of THF to 30mL. A 1M LAH/THF solution (13mL) was added through the addition funnel over a period of 30min. The solution was then stirred for 3hrs at room temperature and monitored using TLC (70%: 30% ethyl acetate: hexanes). No starting material was then present. The nitrogen line was removed from the system and the flask cooled with ice. The cooled reaction was slowly quenched with saturated Na\textsubscript{2}SO\textsubscript{4} until there was no more evolution of H\(_2\) gas, and then stirred for 10min. The solution was then vacuum filtered to remove any precipitate. The precipitate
was washed with ether until the filtrates showed no more product via TLC. The filtrates were collected and diluted with an equal volume of water, and extracted with ether 3 times. The organics were extracted with an equal volume of brine and dried over sodium sulfate for 15min. The solution was filtered and evaporated on a rotovap, then pumped overnight for further drying. A white foamy solid was obtained. Further purification was not needed since the reaction is quantitative (2.2g). The mp of the compound is 70-72 °C.

$^1$HNMR (CDCl$_3$): δ 7.6-6.9 (m, ArH, 17H), 6.5 (s, hydroquinone, 2H), 5.9 (s, bridgehead, 2H), 5.1 (s, BzCH$_2$OPh, 4H), 4.5 (s, BzCH$_2$-OH, 2H). $^{13}$CNMR (CDCl$_3$): δ 148.6 (ArC-O-C-Ph), 137.7 (ArC-C-O-Ph), 136 (former bridge), 111 (former olefinic α,β unsaturated), 71.8 (BzC-OPh), 47.8 (bridgehead), 65 (BzC-OH) 122.5-134, 138-146.2, 150.5 (remaining aromatics). FTIR (KBr pellet): 3100-2900 cm$^{-1}$ (CH stretch), 3600-3200 cm$^{-1}$ (OH stretch), 1210 cm$^{-1}$ (C-O ether). EI+ m/z (496.1) and composition C$_{33}$H$_{28}$O$_3$.

2,5-dibenzoxytriptycene-8- benzylbromide {G$_0$Br} [method 1] (12): A 3-neck, 50 mL round bottom flask equipped with a magnetic stir bar, one rubber septa, one glass stopper, and a tube adapter was dried under vacuum with a heat gun. After cooling, the system was flushed with N$_2$ and kept under N$_2$ throughout the reaction. 1.7g (3.4 mmol) of (11) was dissolved using dry THF and transferred via a dry and desiccated syringe into the reaction vessel. While stirring, the nitrogen pressure was increased and 1.5g (4.5 mmol) of CBr$_4$ and 1.2g (4.6 mmol) of PPh$_3$ were added. The system was then sealed and the pressure reduced. The reaction was stirred at room temperature for 2 hours while being monitored using TLC with 80%: 20% hexanes: ethyl acetate. After 2 hours the reaction appeared to be complete with a precipitate of triphenyl phosphine oxide. The
reaction was filtered into an equal volume of water and the precipitate was washed with a small amount of toluene. The filtrate was extracted 3 times with an equal volume of methylene chloride. The combined organics were dried with sodium sulfate and concentrated. The resulting residue was dissolved in a minimum amount of ethyl acetate and silica gel added. The ethyl acetate was evaporated and the resulting silica gel/GoBr was dry loaded on a pre-packed column and gradient flash chromatographed using ethyl acetate/hexanes. The yield was 1.2g (63%) of a yellow oily residue. \(^1\)HNMR (CDCl\(_3\)): \(\delta\) 7.5-7.0 (m, ArH, 17H), 6.8 (s, hydroquinone, 2H), 5.9 (s, bridgehead, 2H), 5.1 (s, BzCH\(_2\)OPh, 4H), 4.4 (s, BzCH\(_2\)-Br, 2H).

2,5-dibenzyloxytriptycene-8-benzylbromide {GoBr} [method 2] (12): A 3-neck, 50 mL round bottom flask equipped with a magnetic stir bar, one rubber septa, one glass stopper, and a tube adapter was dried under vacuum with a heat gun. After cooling, the system was purged with N\(_2\) and kept under N\(_2\) throughout the reaction. To a suspension of 60mg (0.34 mmol) of NBS in 10 mL of anhydrous methylene chloride was added at 0\(^\circ\)C over a period of 3 min 0.03mL (0.025g, 0.41 mmol) of dimethylsulfide. The reaction temperature was then cooled to -20\(^\circ\)C and over a period of 5 minutes was added 0.120 g (0.24 mmol) of 11. The reaction was then allowed to warm to 0\(^\circ\) and stirred at this temperature for 4hrs. The reaction was monitored using TLC with 70%: 30% hexanes: ethyl acetate as the mobile phase. After the 4hrs the reaction mixture was poured into 30mL of ether and washed 3 times with an equal volume of water and then one time with an equal volume of brine brine. The solution was dried with sodium sulfate, filtered and evaporated. The residue was chromatographed using the same conditions as for method 1. The product yield was 0.098g (73%) of an off white solid after pumping under vacuum.
$^1$HNMR (CDCl$_3$): $\delta$ 7.5-7.0 (m, ArH, 17H), 6.8 (s, hydroquinone, 2H), 5.85 (s, bridgehead, 2H), 5.1 (s, BzCH$_2$OPh, 4H), 4.4 (s, BzCH$_2$-Br, 2H). $^{13}$CNMR (CDCl$_3$): $\delta$ 148.6 (ArC-O-C-Ph), 137.7 (ArC-C-O-Ph), 136 (former bridge), 111 (former olefinic $\alpha,\beta$ unsaturated), 71.8 (BzC-OPh), 47.8 (bridgehead), 33.8 (BzC-Br) 124-129, 138-145, 149 (remaining aromatics). EI+ m/z (558, 560), (479.1 loss of Br$^-$), (297.1 loss of Br$^-$ and two tolyl cations) and composition C$_{35}$H$_{27}$O$_2$Br.

2,5-dibenzyl oxytriptylene-8- benzylmesylate (G$_0$Mes) (13). A 3-neck, 25 mL round bottom flask equipped with a magnetic stir bar, one rubber septa, one glass stopper, and a tube adapter was dried under vacuum with a heat gun. After cooling, the system was purged with N$_2$ and kept under N$_2$ throughout the reaction. 50mg (0.1 mmol) of (11) in 10 mL of dry toluene was added to the reaction vessel with a dry and desiccated syringe. The reaction flask was cooled to 0°C in an ice bath. Dicyclohexylamine (0.03ml, 0.027g, 0.15 mmol) was then slowly added using the same syringe. The solution was stirred for two minutes and then to the cold solution was added 0.02ml (0.029g, 0.26 mmol) of methanesulphonyl chloride. The resulting solution was stirred while maintaining the temperature as close to 0°C as possible, for 1 hour. An equal volume of methylene chloride was then added to the mixture and the solution was filtered. The precipitate was washed thoroughly and then discarded. The organics were then washed with an equal volume of water. The aqueous layer was back extracted 2 times with equal volumes of methylene chloride. The combined organics were washed with 0.5M HCl, 5% NaHCO$_3$, and brine. The organics were then dried over magnesium sulfate and filtered. The filtrate was concentrated to afford quantitatively (0.06g) of the G$_0$Mes as a colorless oil used immediately for coupling. $^1$HNMR (CDCl$_3$): $\delta$ 7.5-7.0 (m, ArH, 17H), 6.8 (s,
hydroquinone, 2H). 5.85 (s, bridgehead, 2H), 5.2 (s, BzCH$_2$SO$_3$-CH$_3$, 2H), 5.1 (s, BzCH$_3$OPh, 4H), 2.8 (s, BzCH$_2$SO$_3$-CH$_3$, 3H).

2,5-dihydroxy-8-methoxycarbonyl triptycene (monomer) (14). A 3-neck, 250 mL round bottom flask equipped with a magnetic stir bar, one rubber septa, one glass stopper, and a tube adapter was dried under vacuum with a heat gun. After cooling, the system was purged with N$_2$ and kept under N$_2$ throughout the reaction. To the round bottom was added 150 mL of anhydrous methanol with a syringe through the septa. The N$_2$ pressure was increased 0.3g (13 mmol) of sodium metal were added. The N$_2$ pressure was reduced, the mixture was then stirred until all the sodium dissolved. Then 1.0g (2.9 mmol) of (9) was added. The reaction mixture was stirred for 2 hours. At the end of 2 hours the reaction was slowly quenched using a saturated solution of citric acid to generate the hydroquinone triptycene (14). After a substantial addition of the citric acid solution, the reaction mixture was stirred for another 2 hours while monitoring with TLC using 80%: 20% hexanes: ethyl acetate as mobile phase. At the end of this 2 hours the starting material was no longer visible on TLC. The mixture was treated with an equal volume of ether and extracted with water to remove any citric acid, methanol, or methoxide. The extraction must be performed quickly to avoid oxidation to the benzoquinone triptycene. The organic layer was then extracted with brine, treated with Norit and vacuum filtered a very thin layer of Celite. The Celite was washed with methanol and ether to assure removal of the product. The filtrate was then and concentrated. The off white crystalline product yield is quantitative (approx. 1.0g).

$^1$HNMR (CDCl$_3$): $\delta$ 8.1-7.1 (m, ArH, 7H), 6.6 (s, hydroquinone, 2H) 5.8 (s, bridgehead, 2H), 3.9 (s, CO$_2$CH$_3$, 3H). FTIR (KBr pellet): 3600-3400 cm$^{-1}$
(OH stretch) 3100-2900 cm\(^{-1}\) (CH stretch), 1200-1300 cm\(^{-1}\)

(C-O-C ether/ester), 1700 cm\(^{-1}\) (C=O ester stretch). ES- m/z 342-343 (loss of hydroquinone protons).

**G\(_1\) Triptycene (15)** A 3-neck 50 mL round bottom flask equipped with a magnetic stir bar, one rubber septa, one glass stopper, and a tube adapter was dried under vacuum with a heat gun. After cooling, the system was purged with N\(_2\) and kept under the same atmosphere throughout the reaction. The round bottom was charged with 15mg (.11 mmol) of potassium carbonate, 5mg (0.02 mmol) of 18-crown-6, 15mg (0.044 mmol) of the monomer (14), and 10 mL of dry THF. The solution was stirred under nitrogen for 5 minutes. Afterwards, 50mg (0.09 mmol) of G\(_0\)Br (12) were added with an additional 15mL of THF and then the reaction mixture was refluxed for 72 hours. After 72 hour, TLC showed no more monomer, some G\(_0\)Br, and a spot corresponding to none of the starting materials. The reaction was cooled to room temperature, poured into water and extracted with 3 times with equal volume of ethyl acetate. The organics were dried with magnesium sulfate, filtered, and concentrated. The resulting oil was pumped on overnight. The reaction mixture was then chromatographed using prep-TLC using 60%: 40% hexanes: ethyl acetate yielding 0.02g of a solid. \(^1\)H NMR (CDCl\(_3\)) showed similar peaks that are visible for G\(_0\)Br and the monomer consistent with coupling. EI m/z (647.3) was not consistent with (15), so the reaction was considered to have failed. All other attempted couplings were carried out with same proportions of base, catalyst, substrates, and solvent (see Schemes 13 & 14 for reagents and reaction times).
References

15. Modification Procedure of DMAP: 5g of anthracene methanol as added to 180mL of anhydrous THF. This mixture was followed by addition of 1g of DMAP, 5ml of triethylamine, and finally 5 ml of acetic anhydride. The reaction was refluxed for 2.5hrs and monitored using 2:3 ethyl acetate: hexanes. The reaction mixture is cooled and added to a separatory funnel along with an equal volume of methylene chloride. To the sep. funnel was added a solution of chilled 1M HCl. The organics were extracted three times with acid to remove any amine bases. Then the organics were extracted another three times using saturated sodium bicarbonate to remove residual acid and anhydride. Wash organics with water to remove any residual base and THF. Re-extract the organics with brine to remove any water traces. Dry the organic layer with anhydrous sodium sulfate, filter, and evaporate. Dry in vacuo overnight. Yield of the yellow powder was quantitative (Data are given in the results section).


**Bibliography**

Scheme 1. Retro-synthetic analysis for the synthesis of the monomer via Method A
Scheme 2. Retro-synthetic analysis for the synthesis of the monomer via Method B
Figure 1. (Top) Shows the space between the reactive nucleophiles and the later activated nucleophilic center. (Bottom) The difference in size between the two respective generations. Both figures show possibilities that may alter reactivity and reaction efficiency.
**Method A**

Scheme 3. Synthetic route to form the Diels-Alder precursor (5)
Spectrum 1. $^1$H NMR of 2-Methylanthraquinone (SM)
Spectrum 3. I.R. of Anthraquinone-2-carboxylic acid (1)
Spectrum 7. IR of 2 - Anthroate (3)
Spectrum 9. IR of 2-Hydroxymethylanthracene (4)
Spectrum 10. $^1$H NMR of 2-Anthrylmethyl acetate (5)
Spectrum 11. I.R. of 2-Anthrylmethyl acetate (5)
Scheme 4. Attempted Diels-Alder reaction to produce the triptycene adduct before monomer generation.
METHOD B

Scheme 5. Optimized synthesis and preparation of Diels-Alder precursor 8

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Spectrum 14. $^{13}$C NMR of Anthraquinone-2-carboxylic acid via Method B (1)
Spectrum 15. $^{13}$C NMR of 2-Methylantraquinone (SM)
Spectrum 16. IR of 2-Methylandranthraquinone (SM)
Spectrum 17. IR of Anthraquinone-2-carboxylic acid via Method B (1)
Spectrum 18. 1H NMR of 2-Anthraic acid via Method B (2)
Spectrum 20. IR of 2-Anthraic acid via Method B (2)
Spectrum 23. $^{13}$C NMR of 2-Methylanthroate (8) via Method B
Spectrum 24. IR of 2-Methylanthroate (8) via Method B
Scheme 6. Synthesis of Diels-Alder diastereomeric adducts 9a,b
Spectrum 25. $^1$H NMR of 8-Methoxycarbonyltriphyene-2,5-dione (9) via Method B
Spectrum 26. $^{13}$C NMR of 8-Methoxycarbonyltriptycene-2,5-dione (9) via Method B
Spectrum 27. IR of 8-Methoxycarbonyltriphyene-2,5-dione (9) via Method B
Scheme 7. Synthesis of Goester via enolate chemistry.
Spectrum 28. $^1$H NMR of 2,5-Bisbenzoyloxy-8-methoxycarbonyl tripycene $G_0$ ester (10)
Spectrum 29. $^{13}$C NMR of 2,5-Bisbenzyloxy-8-methoxycarbonyl triptycene

$G_0$ ester (10)
Spectrum 30. IR of 2,5-Bisbenzyloxy-8-methoxycarbonyl triptycene

$G_0$ ester (10)
Spectrum 31. MS 2,5-Bisbenzoyloxy-8-methoxycarbonyl triptycene

G_0 ester (10)
Scheme 8. Reduction of $G_0$ ester 10 to $G_0$ alcohol 11
Spectrum 34. IR of G₀ alcohol (11)
Scheme 9. Two methods to generate the bromide reactive triptycene.
Spectrum 36. $^1$H NMR of $G_0$ bromide via PPh$_3$/CBr$_4$ (12)
Spectrum 37. $^1$H NMR of $G_0$ bromide via Corey-Kim halogenation (12)
Spectrum 39. MS of G₀ bromide via Corey-Kim halogenation (12)
Scheme 10. Synthesis of the highly reactive G₀ mesylate
Scheme 11. Synthesis of monomer via enolate chemistry
Spectrum 41. $^1$H NMR of 2,5-dihydroxy-8-methoxycarbonyl triptycene (monomer) (14)
Spectrum 42. IR of 2,5-dihydroxy-8-methoxycarbonyl triptycene (monomer) (14)
Spectrum 43. Ms of Monomer: 2,5-dihydroxy-8-methoxycarbonyl triptycene (monomer 14)
Figure 2. Illustration of first generation coupling reaction.
Scheme 13. Failed attempts to produce G₅ triptycene using various leaving groups, temperatures, and solvents
Scheme 14. Final coupling attempts to form G₁ triptycene.
Spectrum 44. $^1$H NMR of failed G1 (15) coupling reaction
Spectrum 45. MS of failed $G_1$ (15) coupling reaction with possible homocoupling of monomer
Figure 3. An example of a G_x triptycene that could be used as a chiral stationary phase. It is evident from the picture that the chirality comes from the bridgehead positions that also form cavities that can aid as "filters" to separate copounds.
Figure 4. Lower generation triptycenes being used as sterically hindered ligands with biphenyls that can close the face of one of the cavities and trap an ion. This molecule has a face above the plane (A) and one below the plane (B). It is also possible to study if the triptycene interferes with ion trapping.
Figure 5. The lower generation triptycene (G<sub>0</sub>ester) that can be used to access various derivatives for uses in reactions and photophysical studies. This molecule can be changed not only at the ester position but also the benzyl ethers can be removed and other functionality can be introduced.
If hydroboration occurs here, the boron reagent goes to the less hindered side but in this particular molecule the disimilarity is not great therefore, will there be a difference between the two reagents above.

**Figure 6.** This G0-triptycene borate can be used as a hydroborating reagent. The sterics in this molecule can aid in discriminating between similar functional groups that would otherwise nearly react equally with usual reagents such as 9-BBN.
$R$ is a substrate that requires hydroxyl protection or induction of stereochemistry at a particular position.

**Tirtyl protecting group**

**Triptycyl protecting group that can possibly be used to induce long range chirality**

**Figure 7.** A triptycene system that can be used like the trityl system to protect and induce chirality with possible enhanced cleavage stability and selective protection.
Figure 8. A triptycene system that may be better than LDA to form enolates regio, chemo, and stereoselectively because of its size and rigid conformation.
Chapter 3

Synthesis and Characterization of Hyperbranched Poly(phenylene sulfide) via the use of 3,4-dichlorothiobenzene Monomer and SEC-LALLS/QELS Characterization: Kinetic Studies and Optimized Synthesis
In the Introduction, numerous examples were discussed about the various monomers and methods used to synthesize hyperbranched systems. Among these types of polymers was one example of a hyperbranched poly(phenylene sulfide). To our knowledge this is the only literature report to date that deals with some of the aspects in producing highly branched phenylene sulfides with improved solubility and enhanced glass temperatures. Unfortunately this report does not discuss any thermogravimetric analysis, any kinetic findings with regards to the polymerization, any size exclusion chromatography or light scattering data to support their $M_w$ values and polydispersities. They also do not include any data or give any insight as to the approximate radius of the polymer they produced. Furthermore, their polymer follows the usual synthetic trend of using 1,3,5-AB$_2$ monomers. The interest in synthesizing sulfide polymers lies with their industrial utility as engineering thermoplastics. The first evidence of poly (phenylene sulfide) [PPS] was reported by Friedel and Crafts in the late 19th century. In the 1940’s and 1950’s many attempts to produce this material failed. In 1967 Edmond Hill of Phillips Petroleum Company produced this polymer on a commercial scale using 1,4-dichlorobenzene with sodium sulfide, and Phillips marketed it under the name Ryton. The main interest in this polymer is a result of its high resistance to chemicals, hydrolysis, high temperatures, and radiation. The difficulties with making this polymer is that the synthesis involves high temperatures and pressure and the resulting polymer does not dissolve below 200°C.

The polymer we propose simplifies the preparation of the hyperbranched sulfide to a one pot synthesis instead of the multistep synthesis described by Kakimoto.
monomer is a 1,3,4- AB₂ system that would generate an unsymmetrical polymer. With the 1,3,5 -AB₂ system, Kakimoto achieved an 80% degree of branching (DB) presumably because the steric crowding around the B groups is less. The 1,3,4- AB₂ can in principle be used to study how equally the B groups react given their different environments. We also conducted thermal studies using DSC and TGA (Chapter 5), SEC-LALLS to study the reaction kinetics, quasi elastic light scattering for radii determination, ¹H NMR (Chapter 4) to determine the DB, MALDI to determine the accuracy of the LALLS Mₙ and elemental analysis (EA) (Chapter 4). We also oxidized the sulfide polymer to the sulfone polymer and study its properties. The retrosynthetic analysis shows the synthetic methodology used to produce the hyperbranched poly(phenylene sulfone) [HPPSO] by oxidizing hyperbranched poly(phenylene sulfide) [HPPS]. HPPS is synthesized by S₉Ar of a 1,3,4- AB₂ system where A = S⁻ and B = Cl (Figure 1). Evidence for S₉Ar by sulfur on ipso positions of halogenated aromatics are shown in Figure 2.¹⁰,¹¹,¹²,¹³

Our kinetic studies were conducted using an SEC with inline refractive index and laser light scattering detectors. Light scattering is an absolute method to determine the Mₙ. Incident polarized light is passed through a sample cell containing the solvent and polymer sample. The polarized light consists of an electric field oscillating perpendicularly to a magnetic field. When this light collides with a polymer molecule, the electrons will experience a force because of the electric field component of the incident light. The collisions cause a perturbation that induces a dipole moment. It is this induced dipole that scatters the light to the detector giving rise to the signal.¹⁴ When using light scattering instruments with multiple angles, the radius of gyration, the Mₙ, and the shape of the molecule can be determined by the following equation:
where \( \frac{Kc}{\Delta R_g} \) is the Rayleigh ratio, \( M_w \) is the weight average MW, \( n_0 \) is the refractive index of the medium, \( \lambda_o \) is the wavelength of the light in a vacuum, \( S^2 \) is the squared z average radius (\( R_g \) : radius of gyration), \( \theta \) is the scattering angle, \( A_2 \) is the second virial coefficient that describes solvent–solute or solute-solute interactions, and \( c \) is concentration in mg/mL.\(^{15,16}\) This equation is typically plotted as \( \sin^2 \theta/2 \) vs. Rayleigh ratio. Then by extrapolating the data from the various angles to \( c=0 \) the \( M_w \) and the 2\(^{nd}\) virial coefficient are obtained. When the 2\(^{nd}\) virial coefficient is positive, then the solvent is considered good and the measurements and calculations describe the polymer as a separate entity in solution. When the 2\(^{nd}\) virial coefficient is negative then the solvent is considered poor since it allows for polymer-polymer interactions that give rise to calculation errors because of aggregation (Figure 3).

When the light scattering system contains only two lower angles than \( \sin^2 \theta/2 \) becomes very small thus the equation is transformed into:

\[
\frac{Kc}{\Delta R_g} = \frac{1}{M_w} + 2A_2c
\]

such that the only parameters that can be obtained are the \( M_w \) and \( A_2 \).\(^{14,15,16}\)
The simplified equation is then applied to obtain $M_w$ using only two angle detectors as is the case with LALLS (low angle laser light scattering). Our SEC-LALLS uses another form of the simplified equation as the basis to calculate the $M_w$:

$$M_w = \frac{BI_{\text{scatt}}}{A I_o S I G_{RI} (dn/dc) P \theta}$$

where $B/AI_0$ are instrumental parameters obtained from a calibration typically conducted using polystyrene standards of low polydispersity. Also within the $A$ parameter are found constants and variables common to the K term (complete derivation can be found in reference 10). $SIG_{RI}$ and $I_{\text{scatt}}$ are measured by the instrument, $P(\theta)$ is a correction factor for large molecules defined as the ratio of scattered intensity at angle $\theta$ / scattered intensity at angle 0, and $dn/dc$ is known or can be measured by the instrument if the exact concentration of the solution in mg/mL is obtained. The following equation is used by the instrument to calculate $dn/dc$:

$$SIG_{RI} = B(dn/dc)c$$

The $dn/dc$ is the change in refractive index / change in concentration, $c$ is concentration in mg/mL, and $B$ is the instrument parameter discussed above. The refractive index detector (mass detector) measures the change in the index of refraction of the polymer solution relative to the blank (cell containing only solvent). In an SEC system, the $dn/dc$ is the sum of the slices of the RI detector peak. Each point during elution of the peak on the chromatogram represents a different concentration with a corresponding index of
refraction. Therefore, for a specific polymer of known concentration in a specific solvent with known index of refraction, the measured RI signal will give rise to a dn/dc which is constant for that solute-solvent system at a particular temperature. When injecting samples after the dn/dc is calculated the concentration is no longer critical because the dn/dc is known. One drawback of all light scattering techniques is sensitivity to contamination by dust. Another major drawback is that if the polymer being studied has a radius of less than 10nm, static light scattering systems will generally not be able to measure the radius of gyration. Therefore, another method known as quasi elastic light scattering (QELS) is used to measure radii. The radii measured using this method are drag radii or hydration radii. The QELS system measures the translational diffusion of a molecule as it moves randomly through a solution caused by solvent-solute collisions (Brownian motion). Since the light scattered from a diffusing molecule or particle will generate an autocorrelation function relative to its motion, diffusion coefficients can be determined. Consequently, diffusion can be related to the size and shape of the molecule, molecular weight, and solvent interactions. One major advantage of this technique is that polymers of less than 10nm can be measured giving insight as to the approximate radius of the polymer or particle. Since hyperbranched and dendritic systems at higher MW exhibit globular structural behavior, spherical shapes are usually assumed for these systems. The following equation shows this relationship for presumed spherical systems:

\[ D_{1}^{\theta} = \frac{kT}{f} = \frac{kT}{3\pi\eta d} \]
where, D is the translational diffusion coefficient at infinite dilution, k is Boltzmann’s constant, f is the molecular frictional coefficient (Stokes-Einstein relation), η is the fluid viscosity at a given T, and d is the diameter of the polymer or particle.9,14,15,17 Once the diffusion is measured the diameter can be calculated since all the other parameters are known constants. The hydrodynamic radius is half of the observed diameter. In our hyperbranched sulfur systems QELS was the method used to obtain the size of the polymer since the particles were less than 10nm and could not be calculated by our LALLS system.

Results and Discussion

Preliminary polymerization studies were performed by self-condensing commercially available 3,4-dichlorobenzenethiol for 48 hours in both N,N-dimethylformamide (DMF) and N-methylpyrrolidone (NMP) solvents using potassium carbonate as a base at four temperature: 25°C, 50°C, 100°C, and 150°C (Scheme 1). The lower temperatures (25°C and 50°C) resulted in the formation of only small oligomers (dimers-tetramers). The higher temperatures (100°C and 150°C) resulted in the formation of high MW polymers, including a significant fraction of precipitated insoluble solids. The results led us to choose 100°C and 150°C for further kinetic studies. The 48 hour test reactions resulted in polymers that were insoluble. Some shorter reaction time should result in tractable polymers of high MW and will aid in the determination of how reaction time affects the rate of polymerization.
Kinetic Studies

Kinetics were performed by maintaining identical conditions: the same volume of solvent (DMF) or (NMP), the same quantity of monomer and base. The samples obtained from the kinetic studies were measured by SEC-LALLS/RI to determine the effect of temperature and reaction time on the rate of polymerization. Kinetic runs were performed in DMF and NMP at 100°C and 150°C. Aliquots of the reaction mixture were removed at 3, 6, 24, 27, and 30 hours. All SEC samples for the kinetic runs were 2mg/mL. The data was used to establish a value for dn/dc of 0.192. Figure 4 shows the retention times and components for the polymers produced in DMF at 100°C at various times during the reaction. Table 1 below is a summary of the results observed on the chromatograms.

<table>
<thead>
<tr>
<th>Entry</th>
<th>Reaction Temperature °C</th>
<th>Aliquot Removal (hrs)</th>
<th>M_w</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>25-100</td>
<td>0</td>
<td>179 (Mon. Mw)</td>
</tr>
<tr>
<td>2</td>
<td>100</td>
<td>3</td>
<td>649</td>
</tr>
<tr>
<td>3</td>
<td>100</td>
<td>6</td>
<td>1,102</td>
</tr>
<tr>
<td>4</td>
<td>100</td>
<td>24</td>
<td>12,501</td>
</tr>
<tr>
<td>5</td>
<td>100</td>
<td>27</td>
<td>9,426</td>
</tr>
<tr>
<td>6</td>
<td>100</td>
<td>30</td>
<td>8,850</td>
</tr>
</tbody>
</table>

Table 1. M_w values obtained after every aliquot removal in DMF solvent.
The calculated M\textsubscript{w} (except the monomer value that is included to show that initially upon heating the only species is monomeric) values directly correlate to what is observed in the chromatograms. The second and third entries indicate that the polymer although increasing in M\textsubscript{w} includes smaller species as illustrated in the first two chromatographs where there are longer retention times and multiple peaks. In the second chromatograph there is a shoulder at a shorter retention time indicating the existence of a larger species. In Table 1 this is indicated by the larger M\textsubscript{w} after 6 hours. The fourth entry in Table 1 shows that after 24 hours the M\textsubscript{w} is significantly larger. Chromatogram 3 indicates this by overall shorter retention times and peak narrowing corresponding to the reduction of smaller species in the solution. However, there are indications that larger and smaller species are contained within the bulk of the polymer since there are shoulders to the left (larger) and right (species) of the central peak. Until this point as the reaction progresses larger M\textsubscript{w} are observed indicated by shorter retention times. Entries five and six indicate that after 24hrs, the polymer begins to degrade. This is shown in the table by a reduction in the M\textsubscript{w}. In chromatograms 4 and 5 there is a small increase in the retention time but more importantly, the formation of smaller species is observed as a shoulder growing to the right of the main peak towards higher retention times as the reaction progresses from 27-30 hrs. This can occur if at longer reaction times and at high temperatures sulfur nucleophiles from monomers or other smaller polymeric constituents attack the ipso positions of other sulfurs causing the fragmentation. Figure 5 is a plot of Table 1 showing the gradual increase in M\textsubscript{w} (as is observed in self condensations)\textsuperscript{15} with a rapid increase after certain reaction time except that in our case instead of the plot leveling off, it begins to decrease showing a degradation profile.
Considering that the polymer in DMF began degrading after 24 hrs at 100°C, it was possible that in NMP at 150°C the degradation would occur earlier. Figure 6 shows the retention times and components for the polymers produced in NMP at 150°C at various times during the reaction. Table 2 below is a summary of the results observed on the chromatograms.

<table>
<thead>
<tr>
<th>Entry</th>
<th>Reaction Temperature °C</th>
<th>Aliquot Removal (hrs)</th>
<th>M_w</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>25-150</td>
<td>0</td>
<td>179 (Mon. M_w)</td>
</tr>
<tr>
<td>2</td>
<td>150</td>
<td>3</td>
<td>12,052</td>
</tr>
<tr>
<td>3</td>
<td>150</td>
<td>6</td>
<td>12,729</td>
</tr>
<tr>
<td>4</td>
<td>150</td>
<td>8.5</td>
<td>12,695</td>
</tr>
<tr>
<td>5</td>
<td>150</td>
<td>24</td>
<td>10,533</td>
</tr>
</tbody>
</table>

Table 2. M_w values obtained after every aliquot removal in NMP solvent.

The results obtained for the reaction kinetics in NMP solvent illustrate that there is no significant change throughout the reaction times as observed in Table 2 except that after 8.5 hours degradation of the polymer began. Nevertheless the degradation was not as significant as in DMF since the chromatograms in Figure 6 all have nearly the same retention times and similar distribution of the peaks. The degradation is indicated by the lowering of the M_w value in entry 5. Figure 7 is the graphical representation of Table 2 showing a rapid increase in M_w followed by a near leveling off and then a small amount of
degradation. The most probable reason for the marked difference in the distributions as illustrated in the chromatographs is that in NMP at 150°C the polymerization reaches completion more quickly and that the reactive ends of the polymer branches under these vigorous conditions react more readily. In DMF at 100°C the rate at which the reaction occurs is slower and that at the lower temperatures the reactive ends of the polymer branches are less reactive. Kinetic runs were also performed in NMP at 100°C but the result was nearly identical to the DMF data. The reaction was not performed in DMF at 150°C since decomposition of DMF at its boiling point could produce side reactions. The optimum conditions to produce batch quantities of the hyperbranched poly(phenylene sulfide) for the polymerizations are therefore DMF 24 hours/ NMP 8.5 hours at 100°C and 150°C respectively.

_Synthesis and Characterization Using Optimized Conditions_

The path used in the optimized procedure is the same as in Scheme 1 except that the reaction conditions are DMF 100°C 24 hours and NMP 150°C 8.5 hours (no core reactions). Other studies were also be conducted by adding core former (1,3,5-trichlorobenzene a B3 core). The core former reactions were conducted using the same reaction conditions as the "no core reactions" in each respective solvent except that a 300:1 and a 50:1 monomer: core ratio was added (Scheme 2). The reason for the core formers is to reduce the number of reactive ends and possibly decrease the polydispersity of the polymer sample. Table 3 below summarizes all the results obtained from the no core and core reactions in DMF and NMP. Table 3 also shows the $M_n$ values obtained by
the SEC-LALLS system. These values will be compared to the approximate MALDI $M_n$ values (Chapter 4).

<table>
<thead>
<tr>
<th>Reaction Solvent</th>
<th>Reaction Temp/Time $(^\circ C$/hrs)</th>
<th>Monomer: Core ratio</th>
<th>$M_w$</th>
<th>$M_n$</th>
<th>PD</th>
</tr>
</thead>
<tbody>
<tr>
<td>DMF</td>
<td>100/24</td>
<td>$\infty$:1</td>
<td>16,823</td>
<td>8,376</td>
<td>2.00</td>
</tr>
<tr>
<td>DMF</td>
<td>100/24</td>
<td>300:1</td>
<td>13,018</td>
<td>8,477</td>
<td>1.50</td>
</tr>
<tr>
<td>DMF</td>
<td>100/24</td>
<td>50:1</td>
<td>8,447</td>
<td>7,206</td>
<td>1.17</td>
</tr>
<tr>
<td>NMP</td>
<td>150/8.5</td>
<td>$\infty$:1</td>
<td>15,578</td>
<td>10,409</td>
<td>1.49</td>
</tr>
<tr>
<td>NMP</td>
<td>150/8.5</td>
<td>300:1</td>
<td>19,628</td>
<td>12,268</td>
<td>1.50</td>
</tr>
<tr>
<td>NMP</td>
<td>150/8.5</td>
<td>50:1</td>
<td>13,098</td>
<td>9,984</td>
<td>1.30</td>
</tr>
</tbody>
</table>

Table 3. Comparison of $M_w$ and PD between no core and core reactions.

Figure 8 shows the retention times and curve shapes of the DMF no core ($\infty$: 1), 300:1 monomer: core, 50: 1 monomer: core. The DMF ($\infty$: 1) peak shows a wide distribution since the peaks are from a low retention (high MW) to a high retention (low MW). The 300:1 monomer: core reaction in DMF shows a reduction in PD and a lower MW than the DMF reaction with no core. The peak of the core terminated reaction is narrower, although there is a shoulder after the main peak. This indicates the presence of some smaller molecular weight constituents. The 50: 1 monomer: core reaction in DMF
narrower, although there is a shoulder after the main peak. This indicates the presence of some smaller molecular weight constituents. The 50:1 monomer: core reaction in DMF shows a significant reduction in PD and a significant decrease in the MW relative to the other DMF reactions (Table 3). The peak is narrower and the retention time has increased. The result is as expected; reducing the number of reactive ends would control the reaction.

Figure 9 illustrates the chromatograms obtained when using NMP at 150°C with no core (∞: 1), 300:1 monomer: core, and 50:1 monomer: core. NMP (∞: 1) shows a narrow distribution. It is possible that at the NMP temperature the reaction completion is higher indicating that its polydispersity is lower. As observed in Table 3 the PD of DMF is 2 while in NMP it is 1.49. In NMP with a 300:1 monomer: core ratio the same effect was not observed. In other examples, when the core former fails to yield the expected result, secondary processes\textsuperscript{18,19} that overwhelm the effectiveness of the core former have been shown to be present. In our case the rapid reaction at 150°C in NMP may overshadow the effect of such a small amount of core former. Further studies would be required to establish the exact cause of this unexpected result. In Table 3 the two 300:1 monomer: core DMF and NMP entries show that in DMF the MW and PD decreased with introduction of the core while the NMP showed no change in PD but an increase in MW with addition of the core. The NMP 50:1 monomer: core reaction showed a decrease in molecular weight and PD, as expected (Table 3).

In order to rely on the data obtained, the DMF reactions and NMP reactions are plotted vs. some polystyrene standards to obtain a rough estimate as proof that the $M_w$ reported are accurate (Figures 10 & 11). The MW calculated by the instrument for the
systems fall within the range of the retention times obtained for the polystyrene standards, supporting the MW calculations. Another important observation is that the order of the DMF curves is sequential. The reaction in DMF with no core was retained the least followed by the 300:1, and then the 50:1. In the NMP case when comparing it to the polystyrene standards, it shows that the MWs calculated are correct since the curves correspond to the polystyrene curve retentions. In the NMP overlay the least retained curve is the 300:1 monomer: core reaction followed by the no core reaction, then the 50:1 core.

Another important property of the polymer is its radius. In our case the SEC-LALLS cannot provide radii since the polymer molecules are less than 10nm. Therefore, QELS was used to measure the radii of the hyperbranched poly (phenylene sulfides). The reported hydrodynamic radii represent the DMF/NMP HPPS with no core and the DMF/NMP 50:1 monomer: core HPPS since these samples show the significant effect supported by the theory of core formers (Table 4).

<table>
<thead>
<tr>
<th>Sample Name</th>
<th>$R_h$ nm</th>
</tr>
</thead>
<tbody>
<tr>
<td>DMF ∞:1</td>
<td>5.4</td>
</tr>
<tr>
<td>DMF 50:1</td>
<td>1.35</td>
</tr>
<tr>
<td>NMP ∞:1</td>
<td>3.64</td>
</tr>
<tr>
<td>NMP 50:1</td>
<td>2.92</td>
</tr>
</tbody>
</table>
The QELS data supports the SEC-LALLS data by showing a decrease in radius from the no core systems to the core terminated systems. In the SEC-LALLS paralleled by the increase in retentions and decrease in MW.

The hyperbranched sulfide polymers prepared above were then oxidized in acetic acid using 30% H$_2$O$_2$ (Scheme 3). The solution was quenched with saturated sodium bicarbonate and the resulting precipitates were filtered and washed thoroughly with water. The hyperbranched poly(phenylene sulfones) were obtained as white flaky powders. Like its linear counterpart, the sulfone was sparingly or completely insoluble in all solvents necessary to carry out any solution studies. Therefore, the only studies that were conducted were solid state thermal studies (Chapter 5) and IR (Chapter 4).
Conclusion

The syntheses of hyperbranched polymers are known to be less costly and more efficient than dendrimer syntheses. Furthermore, hyperbranched systems offer an attractive alternative to linear polymers by being able to enhance solubility and processing. The synthesis of hyperbranched poly (phenylene sulfide) presented shows a simple and efficient way to synthesize moderately large polymers using inexpensive materials via a one pot method with moderately high temperatures and simple isolation procedures. The sulfide polymer showed good solubility in THF and chloroform at room temperature. The oxidation to the sulfone, although simple and efficient, produces a polymer that is insoluble at room temperature in organic solvents. SEC-LALLS proved to be a reliable and rapid method to separate the polymer chains by molecular weight and monitoring the polymerization reactions. SEC-LALLS also provided the PD of the resulting polymers. This is revealing since hyperbranched systems may achieve a perfect dendritic structure but have varying MW. QELS radii corresponded to the SEC-LALLS retention times showing that the change in retention time was in fact due to decrease in polymer size. Future studies can focus on other aromatics to produce hyperbranched systems, including other benzene isomers and polycyclics like naphthalene and anthracene. Copolymerization of linear (AB) and branching (AB$_2$) monomers would also provide interesting materials.
Experimental

Anhydrous DMF, NMP, 3,4-dichlorobenzenethiol, hexanes, and 1,3,5-trichlorobenzene were purchased and used without further purification from Aldrich. Potassium carbonate was dried 24hrs in an oven at 200°C. Reactions were run in three necked round bottom flasks with condenser, efficient magnetic stirrer, and N₂ line. All reaction setups were dried with a heat gun under vacuum and then flushed with N₂ for 15min. Temperatures were maintained by a Thermo-watch LS1000. Air was excluded to avoid any sulfur oxidation. Moisture was excluded to avoid any competing nucleophilic attacks by water or residual hydroxide. Normal THF for sample purification and inhibitor free THF for SEC and LS studies were purchased from Pharmco. 30% hydrogen peroxide solution was used as received from Fisher Scientific.

All polymer samples were dissolved in normal THF, precipitated into hexanes, stirred vigorously for two hours, filtered, and dried thoroughly under vacuum. The dissolving and precipitation steps were repeated twice before putting the sample under vacuum. Before injection into SEC, all samples were filtered using a 0.45µ cameo filter into pre-rinsed vials using inhibitor free THF. The SEC LALLS/RI used was a Waters 510 HPLC Pump with an inline degasser and an inline Waters 410 differential refractometer with a Precision Detectors 2000 Low Angle Laser Light Scattering Unit with 15° and 90° detectors. The size exclusion stationary phase was a crosslinked poly (vinyl styrene) column from Polymer Laboratories (5µ particle size, 500Å pore size) with a guard column. Chromatograms were run at 1mL/min flow rate with an injection volume through a Rheodyne injector of 50µL and a sample concentration of 2mg/mL. Column temperature was maintained at 30°C for all sample runs. Inhibitor free THF was used to dissolve the
polymer samples for QELS studies. The polymer solution was filtered directly into a pre-rinsed scintillation vial using a 0.45µm cameo filter and inhibitor free THF. The QELS unit with batch capability was used to calculate the hydrodynamic radius. The QELS system is supplied by Wyatt Technology Corporation.

**Kinetic studies procedure:**

5g of 3,4-dichlorobenzenethiol were added to 6.7g of K$_2$CO$_3$ in 40 mL of anhydrous DMF/NMP and the reaction was heated 100°C or 150°C respectively. The reaction in DMF produces a lemon yellow color while in NMP the reaction color is a dark black/green. 5mL aliquots were removed from the reaction mixtures at 3, 6, 24, 27, and 30 hours for DMF and 3, 6, 8.5, 24, and 30 hours for NMP. The aliquots were carefully poured into 20 mL of 6M HCl. The precipitate was vigorously stirred for 10 minutes and then filtered. The resulting precipitate was dried and then dissolved with stirring in a minimum amount of normal THF. The THF solution was added dropwise into a test tube containing 20 mL of hexanes and stirred for 10 minutes. The resulting precipitate was then filtered, washed with hexanes, and dried. The precipitates obtained from DMF were white finely divided powders. The precipitates obtained from NMP were a light brown colored powder.

**General procedures: DMF or NMP, no core:**

10g of 3,4-dichlorobenzenethiol were added to 13.4g of K$_2$CO$_3$ in 80 mL of DMF/NMP and the reaction was heated to 100°C for 24 hours and 150°C for 8.5 hours, respectively. The reaction in DMF produced a yellow lemon color while in NMP the reaction color is a dark black/green. The reactions were then cooled and diluted with an equal volume of water and carefully poured into 300 mL of 6M HCl. The precipitate was vigorously
stirred for 1 hr and then filtered. The resulting precipitate was dried thoroughly and then dissolved with vigorous stirring in a minimum amount of normal THF. The THF solution was added dropwise into a beaker of hexanes (5 times the volume of THF) with vigorous stirring over a period of 2 hrs. The resulting precipitate was then filtered, washed with hexanes and dried. The precipitates obtained for DMF were white finely divided powders. The precipitates obtained form NMP were a light brown colored powder. The final quantity of sample obtained after the precipitates were worked up was 7-7.5 grams in most cases.

**General core reactions DMF or NMP:**

5 g of 3,4-dichlorothiobenzene were added to either 0.1 g (50:1) or 0.017 g (300:1) of 1,3,5-trichlorobenzene core and 6.7 g of K₂CO₃ in 40 mL of DMF/NMP. The reactions were heated to 100°C in DMF for 24 hours and 150°C in NMP for 8.5 hours. The workup was the same as the general polymerization protocol. The reaction solution color and the final product precipitates had the same appearance with core as without core. The final amount of product sample obtained was approximately 4 g in most cases.

**General Oxidations:**

200 mg of sulfide polymer was added to 12 mL of 30% H₂O₂ and 20 mL of glacial acetic acid. The resulting suspension was refluxed for 4 hrs (the reactions are heterogeneous since the sulfide and resulting sulfone are poorly soluble in acetic acid), cooled and precipitated slowly with stirring into a beaker containing a solution of saturated sodium bicarbonate. The resulting precipitate was then filtered, washed thoroughly with water to remove residual bicarbonate, and dried. The products obtained were white finely divided powders. The quantity obtained after reaction was approximately 150 mg in all cases.
References

4. Refer to the text and references in Chapter 1 Part 3 for a complete discussion.
Figure 1. Retrosynthetic analysis to produce hyperbranched sulfide/sulfone polymers via a one pot method.
Figure 2. Examples of $S_N Ar$ reactions showing ipso substitutions of halogens by sulfide anion.$^{11,12,13}$
Figure 3. Example of a Zimm plot\textsuperscript{16}

\[ M_w = (1\pm 0.7) \times 10^7 \text{ g/mol} \]
\[ r_g = 586\pm196 \text{ nm} \]
\[ A_2 = 4\times10^{-6} \text{ mol ml/g}^2 \]
Scheme 1. Preliminary polymerization by self condensing 3,4-dichlorobenzenethiol for 48hrs at 25°C, 50°C, 100°C, and 150°C.
Figure 4. Chromatograms of DMF kinetic runs.
Figure 5.
DMF Kinetic Data with 179g/mol on the starting point where at 0hrs the Mw is equal to the monomer.
Figure 6. Chromatograms of NMP Kinetec runs.

A. NMP 150°C

B. NMP 160°C

C. NMP 170°C

D. NMP 180°C

E. NMP 190°C
Figure 7.
NMP Kinetic Data with 179g/mol on the starting point where at 0hrs the Mw is equal to the monomer.
Scheme 2. Synthesis of hyperbranched poly(phenylene sulfide) with core former.
Figure 8. Chromatograms of DMF core and non-core reactions
Figure 9. Chromatograms of NMP of core and non-core reactions
Polystyrene vs. DMF HPPS

Figure 10. Overlays of polystyrene and DMF core and non-core reactions.
Polystyrene vs. NMP HPPS

![Graph showing overlays of polystyrene and NMP core and non-core reactions.]

**Figure 11.** Overlays of polystyrene and NMP core and non-core reactions.
Scheme 3. Oxidation of hyperbranched PPS to hyperbranched poly (phenylene sulfone).
Chapter 4

Characterization of Hyperbranched Poly(phenylene sulfide) and Poly(phenylene sulfone)
Introduction

Some common instrumental techniques used to determine the approximate structure of a polymer include NMR, IR, MALDI, and elemental analysis (EA). All give structural information: NMR connectivity, IR functionality, MALDI MW, and EA gross chemical composition. Hawker and Frechet both have used NMR to determine the composition of a hyperbranched polymer since it contains different repeat unit environments.\(^1\)\(^2\) The different environments present in a symmetrical hyperbranched system based on an AB\(_2\) monomer are linear, dendritic, and terminal (Figure 1). The ratio of these environments gives insight as to how dendritic or "perfect" the polymer structure is. The ratio is known as the degree of branching (DB) and is described by the following equation:

\[
DB = \frac{T + D}{T + D + L}
\]

where D is the number of dendritic monomer units, T is terminal, and L is linear. The relative numbers of monomer units in the different environments are obtained from the integration provided by the NMR spectrum. The closer DB is to unity the more the polymer approaches a completely dendritic or "perfect" architecture with no linear units. The number of terminal groups and dendritic groups approach a 50:50 ratio as the polymer approaches infinite polymerization. The DB is always reported as a percent: a 60% DB, which is typical of hyperbranched systems, describes a polymer that is 30% terminal, 30% dendritic and 40% linear. Other insights can be gained as to how reactive
each B group is in an AB₂ system. It is usually assumed that all B groups react equally but as each polymer molecule grows, the steric and electronic environment of the different B groups become more diverse, and the reactivity of the B groups also becomes diverse. There is one report by Feast⁴ indicating 100% DB for a hyperbranched analogue of Tomalia’s PAMAM dendrimer. Although the polymer is dendritic it does not mean that its PD is unity, since it can be structurally perfect with a range of Mₗ. The typical methodology used to ascertain the DB is to synthesize model compounds that represent the various monomer isomers within the polymer and compare the polymer and model compound chemical shifts by ¹H NMR. This technique is not applicable in all cases since significant peak broadening can occur rendering inconclusive assignments. In these cases ¹³C NMR can sometimes be used instead.

Results and Discussion

¹H NMR Determination of the Degree of Branching

The hyperbranched poly(phenylene sulfide) polymer described in Chapter 3 has a 1,3,4- structure rendering it unsymmetrical whereas the majority of other hyperbranched systems are 1,3,5 (Figure 2) including the sulfide polymer by Kakimoto.⁵,⁶ Furthermore, unlike other hyperbranched systems our polymer. This unsymmetrical structure makes the ¹H NMR method for obtaining DB more difficult to employ, since there are two linear cascading units rather than one (Figure 3). Model compounds {D} (1) and {L₁} (2) were synthesized using previously reported protocols,⁷,⁸ {L₂} (3) was purchased from Chem. Services and {T} (4) was synthesized from a procedure employed in our lab (Figure 4). Spectroscopic data of the starting materials, the products
(supporting the literature reports), the protocol devised in our lab, and the compound obtained from Chem. Services are detailed in the experimental section at the end of this chapter.

To successfully use NMR for determining DB, there need to be unique resonances for the different isomeric model compounds. The next step is to recognize the same unique peaks in the hyperbranched polymer, which in our case are unique aromatic proton resonances. In Figure 5 are the $^1$H NMR aromatic regions of the model compounds. Spectrum 1 is representative of the terminal monomer environment [T]. The aromatic region has two unique peaks at 7.3 ppm and 7.9 ppm while the remaining peaks are common to the other isomers and cannot be used to make an assignment. Spectrum 2 shows the dendritic monomer environment [D] with a unique peak at 7.18 ppm. Spectra 3 and 4 (meta substituted [L$_2$] and para substituted [L$_4$] respectively) are the linear components whose peaks coincide with the remaining peaks of both the terminal and dendritic and cannot be used to make an assignment. In the polymer samples (Polymer Spectra 1-6) because of peak broadening the assignments made are tentative providing only an approximate DB. The two terminal peaks correspond to the broad peaks at 7.65 ppm and 7.54 ppm. The dendritic peak in the polymer samples corresponds to the broad peak at 7.4 ppm. Using the above formula the DB was found to be 53% (calculation table is in Experimental Section) on average for all samples. The result obtained is consistent with other reported DBs for hyperbranched polymers of 50-60%. This means that 26.5% of our polymer is terminal and 26.5% is dendritic, while the remaining 47% is linear. The significance of this result is directly related to both steric and electronic effects. As the polymer grows larger the ability to accommodate branched units becomes
increasingly difficult. Furthermore, the steric hindrance reduces the ability for A groups to interact with all B groups. In our case the 3,4 orientation of the chloro B groups increases the sensitivity to steric effects. Electronic effects also have an affect on reactivity. As the number of sulfurs increases the less likely the aromatic system is activated towards nucleophilic aromatic substitution since sulfide moieties are electron donating and deactivate the system.

**IR, Elemental Analysis, and MALDI**

NMR studies could not be conducted on the sulfone polymers since they are essentially insoluble. The only spectroscopic technique available was FT-IR. Spectrum 12 is the infrared spectrum of hyperbranched poly (phenylene sulfide). The main peaks of interest are at 3100 cm\(^{-1}\) (C-H stretch), 2540 cm\(^{-1}\) (S-H stretch), 1600 cm\(^{-1}\) (aromatic C=C), 1700-1900 cm\(^{-1}\) (asymmetrically substituted aromatic), and 600 cm\(^{-1}\) (C-Cl). The oxidation of hyperbranched poly(phenylene sulfide) can produce both hyperbranched poly (phenylene sulfone) hyperbranched poly (phenylene sulfoxide). The relevant stretches for the sulfone hyperbranched polymer (Spectrum 13) that do not appear in the hyperbranched sulfide polymer are the peaks at 1050 cm\(^{-1}\) (S=O symmetric) and 1375 cm\(^{-1}\) (S=O asymmetric) indicating that the oxidation did take place. The S-H stretch of the hyperbranched sulfide polymer is also no longer present indicating oxidation. Sulfoxide formation (Spectrum 13) from incomplete sulfur oxidation may have occurred since there is a weak band present at 1225 cm\(^{-1}\) (peak next to the S=O asymmetric stretch). However, the intensity of the peak is too small, thus indicating an insignificant amount of hyperbranched poly (phenylene sulfoxide) present. Therefore, it appears that the majority
of the hyperbranched sulfide polymer was oxidized successfully to the sulfone. The IR spectra were the same for all hyperbranched poly(phenylene sulfide) samples. The same was observed for all hyperbranched poly(phenylene sulfone/sulfoxide) samples.

Elemental analysis (EA) was conducted to support the structural determinations made by NMR and IR. Table 1 below shows the % composition of the various hyperbranched poly (phenylene sulfides) obtained from EA and the % composition we calculated for a theoretically perfect sulfide dendrimer and linear sulfide polymer. Our calculations virtually agree with all the EA results. Any numbers obtained from EA that are significantly different from our calculations can also be attributed to solvents or reagents that might have been present in the sample at the time of analysis thus affecting the percentages obtained. Furthermore, the results agree with the DB calculation showing that the ratio of the branched: linear is nearly the same (Figure 6-7).

<table>
<thead>
<tr>
<th>Polymer Sample</th>
<th>% C Obtained from EA analysis</th>
<th>% H Obtained from EA analysis</th>
<th>% Cl Obtained from EA analysis</th>
<th>% S Obtained from EA analysis</th>
<th>% O Obtained from EA analysis</th>
</tr>
</thead>
<tbody>
<tr>
<td>DMF ∞: 1</td>
<td>50.46</td>
<td>2.36</td>
<td>26.78</td>
<td>20.4</td>
<td>/</td>
</tr>
<tr>
<td>DMF 300:1</td>
<td>41.46</td>
<td>2.42</td>
<td>39.33</td>
<td>16.79</td>
<td>/</td>
</tr>
<tr>
<td>DMF 50: 1</td>
<td>51.34</td>
<td>2.64</td>
<td>24.95</td>
<td>20.1</td>
<td>/</td>
</tr>
<tr>
<td>NMP ∞: 1</td>
<td>49.93</td>
<td>2.93</td>
<td>27.14</td>
<td>20</td>
<td>/</td>
</tr>
<tr>
<td>NMP 300: 1</td>
<td>51.53</td>
<td>2.48</td>
<td>24.86</td>
<td>21.13</td>
<td>/</td>
</tr>
<tr>
<td>NMP 50: 1</td>
<td>51.52</td>
<td>2.66</td>
<td>23.95</td>
<td>20.04</td>
<td>/</td>
</tr>
</tbody>
</table>

Our Calculated values for linear and dendritic polymeric forms HPPS

<table>
<thead>
<tr>
<th>% C</th>
<th>% H</th>
<th>% Cl</th>
<th>% S</th>
<th>% O</th>
</tr>
</thead>
<tbody>
<tr>
<td>50.5</td>
<td>2.10</td>
<td>24.9</td>
<td>22.5</td>
<td>/</td>
</tr>
</tbody>
</table>
Table 2 below shows the EA % composition and our calculated % composition for hyperbranched poly (phenylene sulfone). Taking the sum of the EA analysis and subtracting it from 100 provided as a remainder the oxygen composition thus proving oxidation. The result for dendritic vs. linear composition was nearly the same showing that the DB obtained for hyperbranched poly (phenylene sulfide) and our structural assumption based on NMR is accurate (Figure 8). Furthermore, in Table 2, a calculation is provided for any evidence of sulfoxide from partially oxidized sulfurs. The calculated % composition obtained for sulfoxide presence is significantly different from the EA results thus showing that if there is any sulfoxide in the sample it is inconsequential. This further supports the IR evidence for insignificant sulfoxide formation (Figure 9).

<table>
<thead>
<tr>
<th>Polymer Sample</th>
<th>% C Obtained from EA analysis</th>
<th>% H Obtained from EA analysis</th>
<th>% Cl Obtained from EA analysis</th>
<th>% S Obtained from EA analysis</th>
<th>% O Obtained from subtracting the EA sum of all other atoms from 100</th>
</tr>
</thead>
<tbody>
<tr>
<td>DMF ∞: 1</td>
<td>41.32</td>
<td>2.02</td>
<td>20.64</td>
<td>17.86</td>
<td>18.16</td>
</tr>
<tr>
<td>NMP ∞: 1</td>
<td>40.79</td>
<td>2.05</td>
<td>19.98</td>
<td>17.47</td>
<td>19.71</td>
</tr>
<tr>
<td>Our Calculated values for sulfone/sulfoxide polymers</td>
<td>% C</td>
<td>% H</td>
<td>% Cl</td>
<td>% S</td>
<td>% O</td>
</tr>
<tr>
<td></td>
<td>41.2/45.6</td>
<td>1.72/1.9</td>
<td>20.3/22</td>
<td>18.4/20.3</td>
<td>18.3/10.1</td>
</tr>
</tbody>
</table>
Matrix Assisted Laser Desorption Ionization (MALDI) in polymer chemistry is used to determine $M_n$ values and also to validate the $M_n$ values obtained from light scattering techniques. In our hyperbranched polymer system we used MALDI for the same purpose. However, the MALDI $M_n$ values we obtained are only approximate values since the polydispersity of our molecule makes an exact determination quite difficult. Nevertheless, the shape of the MALDI spectra obtained (shape was persistent for all hyperbranched poly (phenylene sulfide) samples.) is consistent with step-reaction polymer kinetics where in the initial stages of the polymerization there are higher concentrations of low molecular weight species and monomer present which decrease as polymerization time increases with slow increases in molecular weight (Spectra 14-19). Table 3 below shows the values of the MALDI ($M_n$) vs. SEC-LALLS ($M_n$). The $M_n$ values we obtained were calculated by taking the average of the MWs between the highest intensity MW and as low as 2.5% intensity MW (representative calculation shown in Figure 10).

<table>
<thead>
<tr>
<th>Polymer Sample</th>
<th>$M_n$ Obtained from MALDI</th>
<th>$M_n$ Obtained from SEC-LS</th>
</tr>
</thead>
<tbody>
<tr>
<td>DMF 1:1</td>
<td>9,344</td>
<td>8,376</td>
</tr>
<tr>
<td>DMF 300:1</td>
<td>9,292</td>
<td>8,477</td>
</tr>
<tr>
<td>DMF 50:1</td>
<td>8,049</td>
<td>7,206</td>
</tr>
<tr>
<td>NMP 1:1</td>
<td>9,637</td>
<td>10,409</td>
</tr>
<tr>
<td>NMP 300:1</td>
<td>7,241</td>
<td>12,268</td>
</tr>
<tr>
<td>NMP 50:1</td>
<td>8,419</td>
<td>9,984</td>
</tr>
</tbody>
</table>

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As can be seen in Table 3, the MALDI $M_n$ values obtained using our calculation technique provided us with results that were acceptable and comparable to the $M_n$ values obtained from the SEC-LALLS. The average difference between the two values obtained is approximately 5 monomer units (monomer MW = 179 g/mol) although the NMP 300:1 value is low for the MALDI calculation (28 monomer unit difference; the NMP 300:1 sample was also significantly different in $M_w$ value as compared to the others according to SEC-LALLS). Nevertheless, MALDI is an excellent technique that can be used to approximate $M_n$ values for hyperbranched polymers and to also provide a check for light scattering. MALDI data was not obtained for hyperbranched poly (phenylene sulfone) since its lack of sufficient solubility made it impossible to obtain its spectrum.
Conclusion

The DB results obtained by \(^1\)H NMR analysis are consistent with the majority of literature precedents for step growth polymerizations used to produce hyperbranched systems. These methods generally yield polymers with DB between 50%-60%. Kakimoto reported a DB of 80% for the 1,3,5 symmetrical hyperbranched poly(phenylene sulfide).\(^5\) Our polymer is further complicated by the presence of two linear systems thus increasing the difficulty of determining the DB. \(^{13}\)C NMR might be a useful alternative method as a check for the \(^1\)H NMR MALDI analysis although difficult to interpret since the PD of the polymers are > 1 does give insight as to the accuracy of the \(M_n\) values obtained from SEC-LALLS. Finally, EA analysis does confirm that the polymer is nearly identical linearly and branched since the calculation of the EA based on linear and dendritic models give nearly the same percentages of atoms.
Experimental

General

All starting materials and solvents for the synthesis of model compounds were purchased from Aldrich and used without purification. 1,3-bis(isopropylthio) benzene was purchased from Chem. Services. All reaction apparati were thoroughly dried using a heat gun while the assembly was under vacuum and reactions were carried out under N₂ atmosphere. Moisture must be excluded to avoid any competing nucleophilic reactions that could interfere with the sulfur nucleophiles. 2-Propane thiolate was prepared and dried before use. Polymer samples were dissolved in THF and precipitated in hexanes with vigorous stirring for two hours before filtration of the precipitate (repeated 2x). ¹H NMR solvents were purchased from Aldrich in ampoules. THF-d₈ was used for the polymer and model compound analysis unless otherwise noted. Acetone-d₆ was also used for model compound analysis; no significant difference between the chemical shifts was noted using either THF-d₈ or Acetone-d₆. D₂O used for propanethiolate analysis was purchased from Aldrich. ¹H NMR spectra were recorded using a Varian 500 MHz NMR with gradient field. All values are reported in δ units using TMS as an internal standard. FT-IR spectra were recorded using a Midac Prospect FT-IR Spectrophotometer with Windows 3.1 operating system. IR signals are reported in % transmittance vs reciprocal centimeters. Solid samples were analyzed using KBr pellets. Oily samples were analyzed neat on NaCl plates. Elemental Analysis was obtained from Schwarzkopf Microanalytical Laboratory (Woodside N.Y.) MALDI analysis was obtained from the Mass Spectrometry Laboratories at the University of Illinois at Urbana Champaign using a Voyager 4066
System. Analytical TLC was performed using commercially available coated polyester and aluminum backed silica gel plates (200-400 mesh, 60 Å) from Aldrich. Silica gel for flash chromatography (200-400 mesh, 60 Å) was also purchased from Aldrich and Bodman.

Starting material $^1$H NMR and IR spectra for comparison to products.

2-Propanethiol: $^1$HNMR (CDCl$_3$): δ 3.1 (spt, 1H), 1.6 (d, 1H $S-H$), 1.3 ppm (d, 6H).

1,2-Dichloro-4-nitrobenzene: $^1$HNMR (Acetone-$d_4$): δ 8.5–7.9 (m, 3H).

IR (KBr): 3200 cm$^{-1}$ (C-H aromatic), 1600 cm$^{-1}$ (C=C, aromatic), 1550 cm$^{-1}$ (N=O, assym.), 1355 cm$^{-1}$ (N=O, symm.), 1035 cm$^{-1}$ (C-Cl aromatic).

1,2,4-Trichlorobenzene: $^1$HNMR (Acetone-$d_4$): δ 7.5–7.3 (m, 3H). IR (neat): 3200 cm$^{-1}$ (C-H aromatic), 1600 cm$^{-1}$ (C=C, aromatic), 1035 cm$^{-1}$ (C-Cl aromatic).

3,4-Dichlorobenzenethiol: $^1$HNMR (Acetone-$d_4$): δ 7.8–7.3 (m, 3H), 4.6 (s, 1H $S-H$) IR (neat): 3200 cm$^{-1}$ (C-H aromatic), 2600 cm$^{-1}$ (S-H), 1600 cm$^{-1}$ (C=C, aromatic), 1035 cm$^{-1}$ (C-Cl aromatic).

Product protocols, $^1$H NMR, and IR.

Propanethiolate. To a three neck, 100 mL round bottom flask containing a solution of 30 mL anhydrous ethanol with 7.4g of sodium methoxide was slowly added with vigorous stirring 8.5 mL of 2-propanethiol. After the reaction was stirred at room temperature for 2 hours, the solvent was evaporated. The solid white residue was then filtered and washed with ether and set to dry under vacuum. Caution: Both starting material and product produce a severe stench. Reactions should be performed under a well ventilated hood.

$^1$HNMR (D$_2$O): δ 1.3 (d, 6H), 2.8 (m, 1H).
1,4-Bis(isopropylthio)-2-chlorobenzene. In a three neck, round bottom flask containing 1g of 1,2-dichloro-4-nitrobenzene in HMPA was added 1.2g of propanethiolate. The resulting solution was stirred vigorously for 2 hours where 3 spots appeared on TLC using 99:1 petroleum ether: ether (reaction did not go to completion). The reaction mixture was then poured into water and extracted with ether. The combined organics were dried with NaSO₄, filtered, and concentrated. The residue was chromatographed on silica using 99:1-→ 98:2 petroleum ether: ether (low boiling petroleum ether fraction) as clear oil. The product yield was 62%. ¹HNMR (THF-d₈ or Acetone-d₆): δ 7.4-7.0 (m, 3H), 3.45 (spt, 1H), 3.3 (spt, 1H), 1.3 (d, 6H), 1.25 (6H). IR (neat): 2800 cm⁻¹ (C-H aliphatic and aromatic), 1600 cm⁻¹ (C=C aromatic).

1,2,4-Tris(isopropylthio)benzene. To a three neck, round bottom flask, containing HMPA and 2.9g of isopropylthiolate was added 900mg of 1,2,4-trichlorobenzene. The reaction mixture was then heated with vigorous stirring at 100°C for 1.5 hours. The reaction was then cooled to room temperature, poured into a brine solution and extracted with ether. The ether layers were then extracted with water, dried using NaSO₄, filtered and concentrated. The resulting oil was chromatographed using silica gel and 98:2 petroleum ether: ether. The yield of the colorless oil was 86%. ¹HNMR (THF-d₈ or Acetone-d₆): δ 7.4-7.2 (m, 3H), 3.4 (spt, 1H), 1.3 (d, 6H). IR (neat): 2800 cm⁻¹ (C-H aliphatic and aromatic), 1600 cm⁻¹ (C=C aromatic).

3,4-Dichloro-1-thioisopropylbenzene. (This reaction need not be anhydrous). 630mg of finely ground KOH was added to 20 mL of DMF and stirred for 15 minutes. To this solution was added 3,4-dichlorothiobenzene and stirred for 5 minutes (polymerization would not occur because room temperature is too low to cause SₐNAr). Finally 2-
chloropropane was added and the solution was stirred for 3 hours. The reaction mixture was then poured into ether and extracted with methanolic potassium hydroxide (Claisen’s Alkali) to remove any unreacted benzene thiol compound. The organics were then washed with water, brine, dried with NaSO₄, filtered and concentrated. The product was obtained quantitatively as colorless oil. ¹HNMR (THF-d₈ or Acetone-d₆): δ 7.6–7.3 (m, 3H), 3.58 (spt, 1H), 1.3 (d, 6H). IR (neat): 2800 cm⁻¹ (C-H aliphatic and aromatic), 1600 cm⁻¹ (C=C aromatic), 1035 cm⁻¹ (C-Cl aromatic).

**Polymer samples.**

Syntheses of various polymers are discussed in chapter 3. The ¹HNMR chemical shifts concentrate on the aromatic region (Table 4).

<table>
<thead>
<tr>
<th>Sample Name</th>
<th>Area under terminal ({T})</th>
<th>Area under dendritic ({D})</th>
<th>Total area under aromatic peaks (D+T+L)</th>
<th>% DB = (\frac{D+T}{D+T+L}) *100</th>
</tr>
</thead>
<tbody>
<tr>
<td>DMF ∞ : 1</td>
<td>2.63 + 18.23</td>
<td>32.59</td>
<td>100</td>
<td>53%</td>
</tr>
<tr>
<td>DMF 300 : 1</td>
<td>2.80 + 17.51</td>
<td>34.02</td>
<td>100</td>
<td>54%</td>
</tr>
<tr>
<td>DMF 50 : 1</td>
<td>2.36 + 16.93</td>
<td>35.31</td>
<td>100</td>
<td>55%</td>
</tr>
<tr>
<td>NMP ∞ : 1</td>
<td>2.73 + 19.14</td>
<td>32.38</td>
<td>100</td>
<td>54%</td>
</tr>
<tr>
<td>NMP 300 : 1</td>
<td>2.34 + 17.44</td>
<td>31.29</td>
<td>100</td>
<td>51%</td>
</tr>
<tr>
<td>NMP 50 : 1</td>
<td>2.08 + 15.66</td>
<td>33.21</td>
<td>100</td>
<td>51%</td>
</tr>
</tbody>
</table>

Table 4. Calculation of the DB for hyperbranched poly(phenylene sulfide).
References

Figure 1. Hyperbranched monomer environments of a symmetrical $AB_2$ system.
Figure 2. Hyperbranched poly (phenylene) sulfides produced from poly (sulfonium cation).
Figure 3. Hyperbranched Poly(phenylene sulfide) monomer environments in a 1,3,4-AB₂ system.

F = focal point
D = dendritic
L₁, L₂ = linear
T = terminal
Figure 4. Synthesis of monomer model compounds for NMR determination of DB.

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Figure 5. $^1$H NMR aromatic region of model compounds representing the different environments.
Polymer Spectrum 1. NMR of HPPS with No Core Former (∞ : 1) [DMF Reaction Conditions]
Polymer Spectrum 2. NMR of HPPS with 300 : 1 Monomer : Core Ratio [DMF Reaction Conditions]
Polymer Spectrum 3. NMR of HPPS with 50:1 Monomer:Core Ratio [DMF Reaction Conditions]
Polymer Spectrum 4. NMR of HPPS with No Core Former (∞ : 1) [NMP Reaction Conditions]

DB = .54
Polymer Spectrum 5. NMR of HPPS with 300 : 1 Monomer : Core Ratio [NMP Reaction Conditions]
Polymer Spectrum 6. NMR of HPPS with 50:1 Monomer:Core Ratio [NMP Reaction Conditions]
Spectrum 12. IR of hyperbranched poly (phenylene sulfide)
Spectrum 13. IR of hyperbranched poly(phenylene) sulfone
Dendritic Composition at Infinite Polymerization

\[
\text{C}_{12}\text{H}_6\text{S}_2\text{Cl}_2 = 285
\]

\[
\% \text{ Element} = \frac{\# \text{ of atoms} \times (\text{Atomic mass})}{\text{MW of linear repeat Unit}}
\]

\[
C = 50.5
\]

\[
H = 2.10
\]

\[
\text{Cl} = 24.9
\]

\[
S = 22.5
\]

At infinite polymerization the dendritic and terminal units in a branched polymer assuming 100% DB are at a 50:50 ratio. The focal unit contributes negligibly to the total and therefore the elemental analysis depends solely on the terminal and dendritic unit.

Figure 6. Theoretical structure in calculating elemental analysis results
Linear Composition at Infinite Polymerization

C₆H₃SCl = 142.6

C = 50.5

H = 2.10

Cl = 24.9

S = 22.5

% Element = \frac{\text{# of atoms} \times \text{(Atomic mass)}}{\text{Mw of linear repeat Unit}}

At infinite polymerization the focal and terminal units in a linear polymer chain contribute negligibly to the total Mw and therefore the elemental analysis depends solely on the repeat unit.

Figure 7. Theoretical structure in calculating elemental analysis results
Oxidized Linear Composition at Infinite Polymerization for Sulfone

\[ \text{C}_6\text{H}_3\text{ClSO}_2 = 174.6 \]
\[ C = 41.2 \]
\[ H = 1.72 \]
\[ Cl = 20.3 \]
\[ S = 18.4 \]
\[ O = 18.3 \]

\[ \% \text{Element} = \frac{\# \text{of atoms} \times (\text{Atomic mass})}{\text{Mw of linear repeat Unit}} \]

At infinite polymerization the focal and terminal units in a linear polymer chain contribute negligibly to the total Mw and therefore the elemental analysis depends solely on the repeat unit.

Figure 8. Theoretical structure in calculating elemental analysis results
Oxidized Linear Composition at Infinite Polymerization for Sulfoxide

\[ \text{C}_6\text{H}_3\text{ClS}O = 158 \]

\[ C = 45.6 \]

\[ H = 1.90 \]

\[ Cl = 22.0 \]

\[ S = 20.3 \]

\[ O = 10.1 \]

\[ \frac{\text{# of atoms} \times (\text{Atomic mass})}{\text{Mw of linear repeat Unit}} \]

At infinite polymerization the focal and terminal units in a linear polymer chain contribute negligibly to the total Mw and therefore the elemental analysis depends solely on the repeat unit.

Figure 8. Theoretical structure in calculating elemental analysis results
Spectrum 14. MALDI of HPPS with No Core Former (∞ : 1) [DMF Reaction Conditions]
Spectrum 15. MALDI of HPPS with 300 : 1 Monomer : Core Ratio [DMF Reaction Conditions]
Spectrum 16. MALDI of HPPS with 50:1 Monomer : Core Ratio [DMF Reaction Conditions]
Spectrum 17. MALDI of HPPS with No Core Former (∞ : 1) [NMP Reaction Conditions]
Spectrum 18. MALDI of HPPS with 300 : 1 Monomer : Core Ratio [NMP Reaction Conditions]
Spectrum 19. MALDI of HPPS with 50:1 Monomer:Core Ratio [NMP Reaction Conditions]
The $M_n$ is the average MW between 50% intensity and 2.5% intensity.

**Figure 10.** Sample calculation for the determination of $M_n$. 
Chapter 5

Thermal Analysis of Hyperbranched Poly(phenylene sulfide) and Hyperbranched Poly(phenylene sulfone) via Thermo-gravimetric Analysis and Differential Scanning Calorimetry
Introduction

Thermal analysis of polymers is a useful technique in the determination of physical properties. Two of the most commonly used methods of analysis are thermogravimetric analysis (TGA) and differential scanning calorimetry (DSC). In TGA a sample is placed into a pan (usually platinum) suspended from a sensitive balance. The pan and sample are then placed in a furnace with a controlled atmosphere (usually nitrogen or air). The sample is then heated to determine at what temperature degradation processes occur that cause the extrusion of low molecular weight volatiles. The volatiles and the residue in the pan (if any) can then be analyzed by spectroscopic techniques to determine their structure and composition. Materials will often behave differently in the different atmospheric environment; nitrogen (or other inert gas) reveals the intrinsic stability of the material, while air is the most likely operating environment and may cause oxidation processes not apparent with an inert gas.

DSC can be used to obtain parameters for Gibb’s equation variables to study a reaction path equilibrium process, or obtain specific heat. In the study of polymers DSC offers insight as to the crystallinity or amorphicity of a polymer structure. Crystalline or semicrystalline structures (generally linear systems although exceptions are known) usually exhibit a $T_g$ (glass transition temperature or a state of frozen liquidity), $T_c$ (crystallization temperature), and a $T_m$ (melting temperature). All are transitions where the polymer goes through a phase change. The glass transition is usually an endotherm because the polymer absorbs heat as bond rotation and molecular movements increase in the liquid state. A $T_c$ is an exotherm because the molecule releases energy as it becomes ordered into a
into a crystalline structure. The $T_m$ is an endotherm that indicates that the polymer is completely melted or is in a liquid state. $T_m$ is only observed if the polymer is crystalline or a $T_c$ is observed. Samples for DSC are usually placed in aluminum hermetic pans. As the heat is applied the difference in the heat capacity of the sample pan and an empty reference pan will determine the transition temperatures described above. If the heat capacity is to be measured then the sample must be accurately weighed, otherwise weighing is not necessary. Structural properties, atomic connectivity, hydrogen bonding etc. all have an effect on decomposition and the various transition temperatures described above.

Highly branched systems like dendrimers or hyperbranched polymers generally do not exhibit crystalline or melting temperatures because of their amorphous structures. They do however exhibit glass transitions that typically are higher temperatures than those of linear polymers. This increase is a consequence of the branched structure not being able to freely rotate so that the molecules do not flow past one another as easily as in a linear system. Another effect is the number of functional groups that a highly branched system can contain, due to the many chain ends. If a hyperbranched or dendritic system contains hydroxy or carboxy functionalities, their hydrogen bonding can further hinder rotation. In the case of ketones or thiol ketones rotation or freedom may be restricted by lone pairs on the hetero atoms. Onset of decomposition from TGA for highly branched systems often begins earlier because of terminal groups. Furthermore, multi-functionality can lead to domino effects that cause complete and rapid decay of the polymer relative to a linear system of similar atomic composition.
The TGA and DSC of hyperbranched poly (phenylene sulfide) and hyperbranched poly (phenylene sulfone) will be analyzed to determine if these general observations from other hyperbranched systems would apply to our system. DSC analysis of Kakimoto's hyperbranched PPS revealed amorphous polymers with a T_g of 102-124 °C (T_g increased with higher MW). No T_m was observed, indicating a lack of crystallinity in these polymers. Linear sulfur polymers such as poly (phenylene sulfide) (PPS) and poly (phenylene sulfones) are well-known and useful engineering thermoplastics. Furthermore, PPS has high chemical resistance, is stable at very high temperatures (T_d > 300°C) is an excellent coating agent, and has low flammability. Among the unique characteristics of linear PPS are its thermal properties. PPS is a semicrystalline polymer with T_g near 85 °C and T_m near 285 °C and excellent thermal stability. Polysulfones (polysulfone, polyethersulfone, and polyphenylsulfone) are amorphous thermoplastics that have oxidative resistance, good mechanical strength and stiffness. Polysulfones do not have melting temperatures even though they are linear structures. Generally, polysulfones have T_g between 185 °C and 220 °C and T_d > 500 °C. High glass transitions are important for producing transparent materials for high temperature applications. Some polysulfones are used in microwave products that allow the visualization of food being cooked without having to buy expensive glass products. Low glass transitions can also be important for producing plastics with flexibility and strength.
Results and Discussion

TGA

Perng, Li, and Seo have studied the degradation of linear poly(phenylene sulfides) and poly(phenylene sulfones) using pyrolytic GC-MS to induce degradation followed by chromatographic separation and mass spectrometric detection. They indicated that under nitrogen, the sulfide polymer's initial degradation profile begins with end group scission, followed by main chain scission, producing low molecular weight volatiles such as H₂S, thiobenzene, and benzene. Higher temperatures after initial decomposition led to loss of components from the main chain such as diphenyl sulfides, biphenylthiol, biphenyl, and dibenzothiophene. Under an air atmosphere, not only do the above processes occur but also oxidation of any sulfides and aromatics. This is followed by SO₂, CO, and CO₂ extrusion leaving small amounts of graphitized polymer sample. Our TGA is not equipped with an inline GC-MS. We envisioned that since our sulfide polymers are atomically similar in composition, and our HPPS polymer degradation curve was similar in shape to both a commercial TGA curve (Figure 1) and measured TGA curve in our lab of a commercial PPS in air and nitrogen (Figures 2-3), we can assume a similar degradation profile in air and nitrogen for our HPPS.

Thermogravimetric analysis was performed in both nitrogen and air. The initial maximum decomposition indicated by the 1st derivative of the degradation curve of the hyperbranched PPS produced in DMF is near 458 °C in N₂ (except for the 300:1 monomer: core sample where maximum decomposition began at 502 °C) (Figures 4-6). The polymer produced in NMP began maximum decomposition near 475 °C for all
samples (Figures 7-9). Figure 10 is an overlay of all the HPPS polymer degradation curves obtained under a nitrogen atmosphere. The main observation is that the polymer molecular weight and preparation conditions generated only small effects on the maximum decomposition. In air, the HPPS polymer from DMF followed the same trend with a maximum decomposition of 440 °C except for the 300:1 monomer: core sample, which decomposed at 490 °C (Figures 11-13). The polymer from NMP also began maximum decomposition at 450 °C for all samples (Figures 14-16). Figure 17 is an overlay of the degradation profiles in air of HPPS. The most significant difference between the polymer samples under the two different atmospheres is the mass retention: 25% - 30% of the mass remains at 700 °C in N₂, while only 1% - 18% remains at 700 °C in air.

When nitrogen was used as the gas the decomposition can be attributed to non-oxidative processes. Depolymerization (DEP) and main chain scission (MCS) sulfide processes dominate under these conditions where the initial decomposition (DEP) releases H₂S, thiobenzene, benzene (presumed from literature reports on linear PPS).9 Higher temperatures after initial decomposition would lead to loss of components from the main chain such as diphenyl sulfides, biphenylthiol, biphenyl, and dibenzothiophene. The difference in the percentages of residual mass between air and nitrogen experiments are mainly due to SO₂ extrusion that occurs in sulfide samples exposed to air between 480-615 °C. Sulfur dioxide extrusion begins a domino effect that may further produce radicals forming more thiobenzene, diphenylthioether, and dibenzothiophene decomposition products. Initial decomposition before sulfur dioxide formation and extrusion can be attributed to depolymerization and main chain scission as under nitrogen. This may be the reason why nearly all the sample is lost in the air experiment. Our polymer also contains
numerous chlorine atoms thus some pyrolytic loss can come from loss of chlorobenzene, 
HCl, or even the starting material used for polymerization. Nevertheless, the polymer 
remains rather resilient. Overall the sulfide polymers in nitrogen are relatively stable: the 
mass levels off around 480 °C. This may be indicative of possible sulfide crosslinks or 
graphitic structures that are produced.

The same analysis was conducted using hyperbranched poly(phenylene sulfone) 
under nitrogen and air atmospheres. TGA analysis revealed that the decomposition 
temperature for the sulfone polymers under N\textsubscript{2} is 458 °C (some samples showed multiple 
processes, therefore, the global maximum was used as the maximum decomposition). The 
sample under nitrogen shows rapid mass loss due to S\textsubscript{0}2 extrusion and possibly some 
decomposition as explained above for the sulfides polymers. Since both processes may be 
occurring at the same time, a definitive 1st derivative curve with one global maximum may 
not be apparent (Figures 18-24). The sulfones under air appear to have more 
decomposition processes than the nitrogen experiment (Figures 25-31). The maximum 
decomposition temperature under air is higher than that of hyperbranched poly(phenylene 
sulfone) under nitrogen. This can be attributed to the higher temperature for oxidation of 
sulfides to sulfones and sulfoxides thus causing the polymer to completely degrade. This 
is evident because the sulfone polymer in nitrogen begins early but retains substantial mass 
well above 650 °C under N\textsubscript{2}. Hyperbranched poly (phenylene sulfone) in air decomposes 
at higher temperatures but degrades rapidly to nearly 0% of the initial mass immediately 
following initial decomposition. These processes are presumably loss of SO\textsubscript{2} and oxidation 
of any residual sulfides to sulfones followed by extrusion. Our polymers contain
substantial chlorine therefore it is also possible to lose HCl and SO₂Cl as well as other components.

**DSC**

DSC thermal analysis was conducted by comparing our results with Kakimoto’s DSC analysis⁶ and it showed that our system had a Tₘ of 110-130 °C (in agreement with the reported hyperbranched PPS). We also compared our results to a commercial DSC source (Figure 32)¹² and a DSC obtained of linear PPS in our laboratory (Figure 33). The exception is the DMF polymerization with no core, which gave a Tₘ similar to the linear polymer. This may be due to plasticization by residual solvent (Figures 34-39). HPPS has no melting temperature, unlike linear PPS indicating an amorphous system due to extensive branching. The higher Tₘ of the hyperbranched HPPS may be attributed to restricted chain rotations also a result of extensive branching. Figure 40 is an overlay of all the DSC curves for HPPS samples along with the linear PPS confirming our analyses.

DSC analysis of the sulfone polymers revealed a Tₘ of 220-250 °C and no Tₘ indicating a glassy, amorphous polymer (Figures 41-47). This is consistent with the higher Tₘ associated with sulfone polymers relative to the sulfide systems (both linear and highly branched). In the case of hyperbranched poly (phenylene sulfone) not only are steric chain restrictions a factor but also dipole-dipole attractions are stronger, and lone pair repulsions increase rotational barriers decreasing molecular movement.
Conclusion

Thermal analyses were conducted on hyperbranched poly(phenylene sulfides) and poly(phenylene sulfones). Our results were compared to commercial linear sources and literature sources on other hyperbranched sulfur systems. The results corresponded to theoretical predictions that highly branched polymers would have different glass transitions because of restricted molecular movement and no melting temperature because of their amorphous structure. Onset of decomposition was earlier in our branched system than in the linear system possibly because of the larger number of halogens as the end groups that could initiate early degradation through halogen scission. This behavior is in agreement with other literature reports\textsuperscript{13} that show that multiple functional groups can alter degradation patterns by either enhancing or decreasing thermal stability.
Experimental

All solvents were purchased from Pharmco or Aldrich. Polymer samples were dissolved in THF and precipitated in hexanes with vigorous stirring for two hours before filtration of the precipitate (repeat this operation twice). Samples must be thoroughly dried before DSC or TGA can be conducted to avoid solvent interference in the results. In TGA the solvent may disrupt the % mass in the decomposition curve. In DSC the solvent may plasticize the sample and may volatilize causing pan rupture.

TGA analysis was conducted using a TA Instruments Hi-Res TGA 2950 Thermogravimetric Analyzer using a platinum pan sample holder. The pan was tared automatically by the instrument prior to sample loading. The analysis was conducted under a nitrogen or air atmosphere using a sample heating increment of 10°C/min from 30 °C - 700 °C. TGA plots were recorded using T °C vs. % Mass loss with a 1'st derivative inset curve to show maximum degradation profiles.

DSC analysis was conducted using a TA Instruments DSC 2920 Modulated Differential Scanning Calorimeter. The sample holder was an encrypted aluminum hermetic pan. The analysis was conducted under ambient atmosphere using a heating increment of 10°C/min from 30 °C - 330 °C. Samples were not weighed since no specific heat calculation was done. Higher temperatures were not attempted as the aluminum pans would begin to deform. DSC plots were recorded using T °C vs. Heat Flow (W/g) with Exo Up as an indicator of sample thermal heat release and Endo down as an indicator of sample thermal heat absorption.
References

13. Refer to papers cited in the hyperbranched section of Chapter 1.
TGA of Commercial Linear PPS

Figure 1
Figure 2: TGA of Linear PPS in Air

- Weight (%) vs Temperature (°C)
- Deriv. Weight (%/°C) vs Temperature (°C)
TGA of Linear PPS in Nitrogen

Figure 3
TGA of HPPS in Nitrogen (DMF ∞:1  Mon.: Core)

Figure 4
Figure 5
Figure 6
Figure 7

TGA of HPPS in Nitrogen (NMP ∞: 1 Mon.: Core)
Figure 8: TGA of HPPS in Nitrogen (NMP 300:1 Mon.: Core)
TGA of HPPS in Nitrogen (NMP 50:1 Mon.: Core)

Figure 9
Overlay of HPPS in Nitrogen

Figure 10
TGA of HPPS in Air (DMF ∞ : 1 Mon. : Core)

Figure 11
TGA of HPPS in Air (DMF 300 : 1 Mon. : Core)

Figure 12
TGA of HPPS in Air (DMF 50: 1 Mon. : Core)
TGA of HPPS in Air (NMP 300 : 1 Mon. : Core)

Figure 15
TGA of HPPS in Air (NMP 50 : 1 Mon. : Core)

Figure 16
Figure 17

Overlay of HPPS in Air

Weight (%) vs. Temperature (°C)

- DMF 50:1 Mon.: Core
- NMP 50:1 Mon.: Core
- NMP 300:1 Mon.: Core
- NMP 50:1 Mon.: Core
- DMF 300:1 Mon.: Core
- DMF 50:1 Mon.: Core
- DMF 1:1 Mon.: Core
TGA of HPPSO in Nitrogen (DMF $\infty : 1$ Mon. : Core)

Figure 18
TGA of HPPSO in Nitrogen (DMF 300 : 1 Mon. : Core)

Figure 19
TGA of HPPSO in Nitrogen (DMF 50 : 1 Mon. : Core)

Figure 20
Figure 21
TGA of HPPSO in Nitrogen (NMP 300 : 1 Mon. : Core)

Figure 22
TGA of HPPSO in Nitrogen (NMP 50 : 1 Mon. : Core)

Figure 23
Overlay of HPPSO in Nitrogen

Figure 24
TGA of HPPSO in Air (DMF∞ : 1 Mon. : Core)

Figure 25
TGA of HPPSO in Air (DMF 300 : 1 Mon. : Core)

Figure 26
Figure 27

TGA of HPPSO in Air (DMF 50 : 1 Mon. : Core)
TGA of HPPSO in Air (NMP α : 1 Mon. : Core)

Figure 28
Figure 29

TGA of HPPSO in Air (NMP 300 : 1 Mon. : Core)
Figure 30

TGA of HPPSO in Air (NMP 50 : 1 Mon. : Core)
Overlay of HPPSO in Air

Figure 31
DSC of Commercial Linear PPS

Figure 32
Figure 33: DSC of Linear PPS
DSC of HPPS (DMF $\infty$ : 1 Mon. : Core)

Figure 34

Heat Flow (W/g) vs. Temperature (°C)
DSC of HPPS (DMF 300 : 1 Mon. : Core)

Figure 35
Figure 36: DSC of HPPS (DMF 50 : 1 Mon. : Core)

Heat Flow (W/g) vs. Temperature (°C)
DSC of HPPS (NMP∞ : 1 Mon. : Core)

Figure 37
DSC of HPPS (NMP 300 : 1 Mon. : Core)

Figure 38
DSC of HPPS (NMP 50 : 1 Mon. : Core)

Heat Flow (W/g)

Temperature (°C)

Figure 39
Overlay of HPPS and Linear PPS

Figure 40
DSC of HPPSO (DMF ∞ : 1 Mon. : Core)

Figure 41
DSC of HPPSO (DMF 300 : 1 Mon. : Core)
DSC of HPPSO (DMF 50 : 1 Mon.: Core)

Figure 43
Figure 45

DSC of HPPSO (NMP 300 : 1 Mon. : Core)
DSC of HPPSO (NMP 50 : 1 Mon. : Core)

![Graph showing DSC of HPPSO](image-url)

**Figure 46**
Figure 47
Chapter 6

Final Conclusion for Hyperbranched Poly(phenylene sulfide) and Poly(phenylene sulfone)
Conclusion

The synthesis of hyperbranched polymers is more efficient and less costly than the synthesis of dendritic polymers. Hyperbranched polymers also exhibit similar solubility and thermal properties relative to their dendritic counterparts. To this end we synthesized a novel hyperbranched system. We successfully constructed hyperbranched poly (phenylene sulfide/sulfone) since sulfur containing hyperbranched systems have not been extensively studied. We chose to use 3,4-dichlorobenzenethiol as the monomer since it not only introduced sulfur connectivity but also gave an unsymmetrical structure to the overall polymer. Furthermore, hyperbranched systems offer an attractive alternative to linear polymers by being able to enhance solubility and processing. The synthesis of hyperbranched poly (phenylene sulfide) proposed shows a simple and efficient way to synthesize moderately large polymers using inexpensive materials. Oxidation to the sulfone, although simple and efficient, produces a polymer that is insoluble at room temperature in organic solvents. Therefore, its structural characterization was limited to IR, MALDI, and EA. SEC-LALLS proved to be a reliable and rapid method to determine the molecular weights ($M_w$ and $M_a$) and PD of the polymerization reactions. QELS hydration radii were obtained since the polymer chains were less than 10nm and could not be measured accurately using LALLS. Nevertheless, they supported the SEC-LALLS retention times showing that the change in retention time was in fact due to a change in polymer size.

The DB results obtained by $^1$H NMR analysis are consistent with the majority of literature precedents for step growth polymerizations used to produce symmetrical
hyperbranched systems (for the most part) containing one linear environment along with dendritic and terminal environments. Our polymer contains two linear systems thus increasing the difficulty of determining the DB. However, enough clarity in the aromatic region was obtained to gain insight into the structure of the compound. MALDI analysis although difficult to interpret since the PD of the polymers are > 1 does support the $M_n$ values obtained from SEC-LALLS. EA analysis supports the DB calculated by NMR by showing that the polymer is nearly identical linearly and branched.

Thermal analyses conducted on hyperbranched poly(phenylene sulfide) were compared to commercial linear sources and literature sources of other hyperbranched sulfur systems. The results corresponded to theoretical predictions that highly branched polymers would have different glass transitions and no melting temperature because of their amorphous structure. Hyperbranched poly(phenylene sulfide) had a higher glass transition than the linear sulfide and a comparable glass transition to the symmetrical system presented by Kakimoto. Hyperbranched poly (phenylene sulfone), like its linear counterpart, exhibited a very high glass transition. TGA analysis showed that decomposition of our hyperbranched sulfide occurred earlier than in the linear sulfide system, nonetheless it showed that it has comparable thermal stability. Hyperbranched poly(phenylene sulfone) was subjected to the same conditions (air or nitrogen) that hyperbranched poly(phenylene sulfide) was. The sulfone polymer was also thermally resistant, but its degradation pattern was more complex because of the presence of SO$_2$.

In conclusion, a hyperbranched sulfur polymer was synthesized that agreed with the overall theoretical predictions. Spectroscopic techniques were used to gain insight into its structure and elemental analysis was performed to obtain its composition. SEC-
LALLS proved to be a simple and accurate technique to obtain MWs, which corresponded to QELS data. Finally, thermal analysis also agreed with theoretical predictions about glass transitions, melting temperatures, and degradation patterns obtained when highly branched structures are heated to high temperatures.