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TAILORING BRANCHING FOR POLY (ARYLENE ETHER)S VIA REACTIVITY
RATIO CONTROLLED POLYMERIZATIONS

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

By

AMANDA IKE

B.S., The Ohio State University 2000

2007

Wright State University

WRIGHT STATE UNIVERSITY
SCHOOL OF GRADUATE STUDIES

July 9, 2007

I HEREBY RECOMMEND THAT THE THESIS PREPARED UNDER MY SUPERVISION BY Amanda Ike ENTITLED Tailoring Branching for Poly(arylene ether)s via Reactivity Ratio Controlled Polymerizations BE ACCEPTED IN PARTIAL FULFILLMENT OF THE REQUIREMENTS FOR THE DEGREE OF Master of Science.

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ABSTRACT

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Tailoring Branching Via Reactivity Ratio Controlled Polymerizations of Poly(arylene ether)s.

The ability to control physical and mechanical properties of polymer systems has become an important aspect of polymer science. In order to tailor the branching in polymer systems, an understanding into the reactivity of the electrophilic sites in the monomer is important. Kinetic methods have been explored in order to determine the reactivity of monomers in preparing poly(arylene ether)s and to predict the degree of branching that will occur in a polymer of this kind. The reactivity of AB₂ sulfones and phosphine oxides was explored, along with the reactivity of ABB'B'' sulfones. NMR spectroscopy was used as a probe into the reactivity of the electrophilic sites in the above mentioned systems. Both ¹³C and ¹⁹F NMR spectroscopy were used to analyze model compounds, in order to study the relative reactivity of electrophilic sites in a certain monomer of interest. While NMR spectroscopy is an efficient tool in analyzing the reactivity of the electrophilic sites in a monomer, it is only a guide. A better guide into reactivity would be to actually determine the reactivity, or to calculate the activation energy of the electrophilic site, E_a, via kinetic methods. Once determining the E_a of the electrophilic sites in the monomer, the reactivity of these monomers will aid in determining the branching that will occur in these monomer systems. Once branched polymers have been constructed, the endgroups of these polymers can then be modified for specific applications.

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DEDICATION

To my family and friends who have provided love and support over the course of my education and career.

INTRODUCTION

The field of polymer science is rapidly expanding to encompass many new methods of synthesizing polymers. With this rapid expansion, comes a greater ability to produce polymers with advantageous physical and mechanical properties. The ability to control polymerization processes at the molecular level affords the opportunity to predetermine the macroscopic properties of these polymer systems. One parameter that can be utilized to tune the physical properties of polymers is the level of branching in hyperbranched systems. The degree of branching (DB) affects a number of material properties, such as solubility, as well as thermal and mechanical properties. If one possesses the ability to control branching, polymer systems can be prepared with specific purposes and applications in mind. Branched polymers have been used for a variety of applications, including but not limited to, drug delivery, microelectronics, catalysis, optics, coatings and resins, and in numerous types of engineering plastics.¹

Why branching matters

The ability to tune the chemical and physical properties of branched polymers is possible, largely due to the ability to control the degree of branching within polymer systems. Representations of linear and branched polymers are shown in Figure 1. Hyperbranched systems possess properties with many advantages such as 1) a large number of endgroups, 2) low intrinsic viscosities and 3) excellent solubility. It is due to these properties that branched polymers are relatively easy to process when compared to

linear systems. In Figure 2, the relationship between viscosity and molecular weight is shown. Linear systems tend to have higher viscosities, which in turn, make these systems more difficult to process. Hyperbranched and dendritic systems have lower viscosities, making processing these branched systems much easier. It is well understood that the reason for the low viscosity values is a lack of chain entanglements, which, unfortunately, also leads to poor mechanical properties.

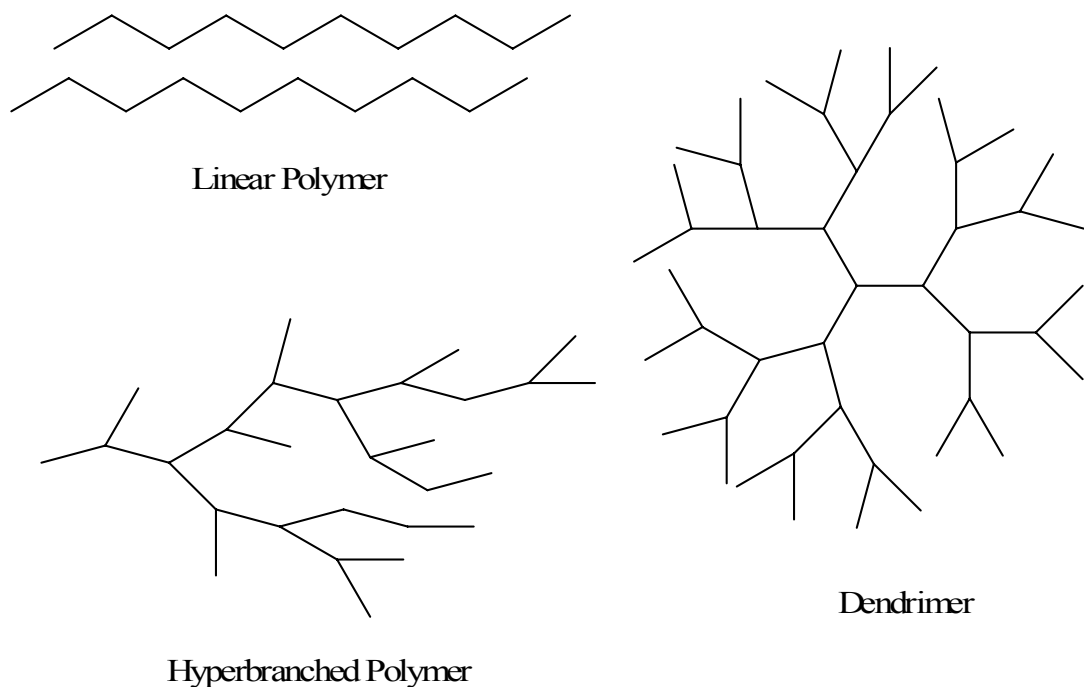


Figure 1. The structure of linear and branched polymers.

Figure 3 shows the relationship between physical properties and branching. Linear polymers tend to have better physical properties than the corresponding hyperbranched and dendritic systems. Establishing the proper balance between the advantageous

physical properties of linear systems and the ease of processing in branched systems would seem to be very beneficial.

A direct result of varying the DB within a polymer is that the number of endgroups in that polymer can be controlled. The endgroups in branched polymer systems can be modified to correlate with specific applications. As stated above, hyperbranched systems are easier to process than their linear counterparts. When compared to their dendritic counterparts, hyperbranched systems are much easier, and much less expensive to synthesize than dendrimers.

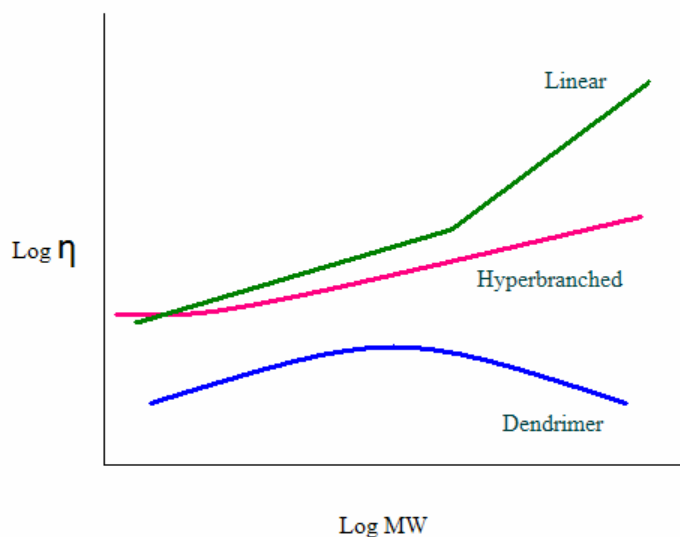


Figure 2. The relationship between viscosity and molecular weight.



Figure 3. The relationship between physical properties and branching.

The synthesis of hyperbranched polymers can be achieved via a number of methods including: 1) polycondensation of AB_n monomers²⁻¹⁰, 2) self-condensing vinyl polymerizations¹¹⁻¹⁶, 3) $A_2 + B_3$ routes¹⁷⁻²⁴ and 4) $AA^* + B_2B^*$ routes²⁵⁻²⁸.

Degree of Branching

Flory was the first to develop the concept of branched polymers using AB_n -type monomers to synthesize polymers in which cross-linking would not occur.⁵ The extent to which a polymer has branched is defined as the degree of branching (DB). There are three different units that can exist within a branched polymer system: terminal, linear and dendritic, which are depicted in Figure 4. In a terminal unit, the polymer is growing in only one direction and thus, has terminal functional groups that are available for substitution. In a linear unit, the polymer is growing in two directions and has one or more functional groups available for substitution. In a dendritic unit, the polymer is growing in three directions, having a branched structure. A dendritic unit may or may not have any functional groups available depending on the monomer used for polymerization.

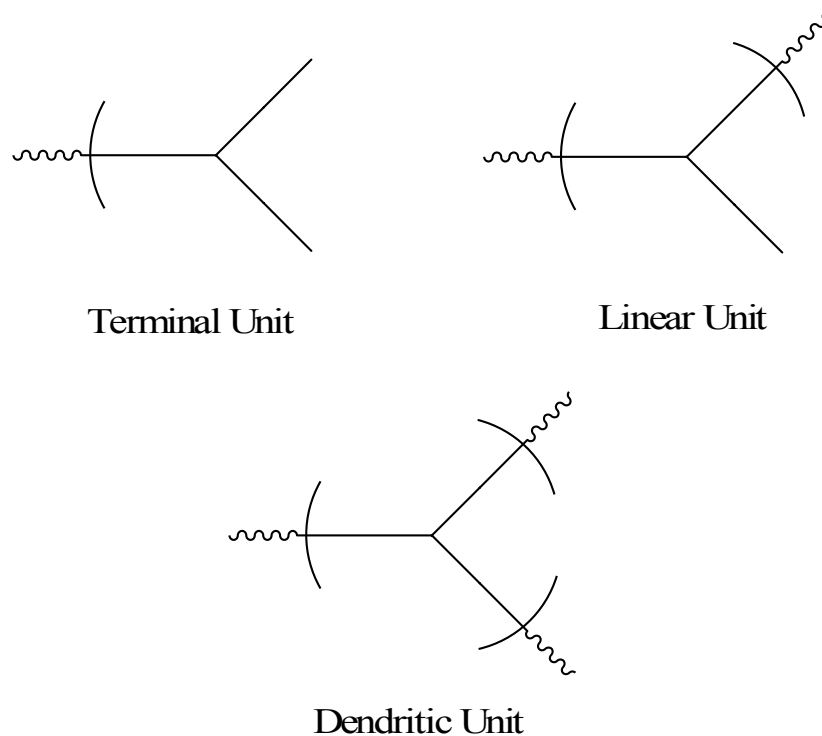


Figure 4. Generic structures of the possible repeat units in a branched polymer.

In order to calculate DB values, the relative number of each fragment needs to be determined. Typically, this is achieved via the use of NMR spectroscopy and a series of model compounds to enable the assignment of the proper signals. The relative areas of the assigned peaks, corresponding to specific fragments, terminal, linear, and dendritic are determined and the DB values are calculated using equation (1).⁸

$$DB = \frac{D + T}{D + T + L} \quad (1)$$

In this equation D represents the number of dendritic units in the system, T represents the number of terminal units in the system and L represents the number of linear units in the system. As stated above, these numerical values are obtained via integration of NMR spectra. The degree of branching for a linear polymer would have a value of 0 (at very

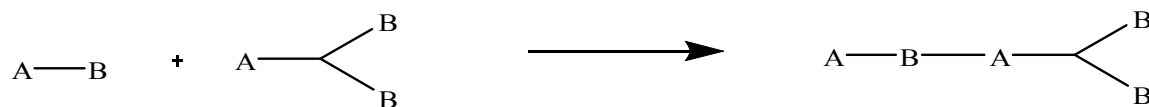
high molecular weight), as linear polymers lack branching. A perfectly branched dendrimer would have a degree of branching value of 1, while hyperbranched systems, statistically, have a value of 0.5 which results from a 1:2:1 ratio of T:L:D units.^{7,29}

Systems to control branching

There are many systems that can be used to control branching in polymer systems prepared via polycondensation chemistry including 1) $AB + AB_n$ ³⁰⁻³³, 2) $A_2 + B_3$ ^{17-24, 34}, 3) ABB' ^{10, 35} and 4) AB_2 acting as ABB' ²⁻⁴. The most critical aspects of any branched system are the degree of branching within that system and the placement of the branch points along the polymer. Each of these systems has its own unique advantages and disadvantages with regards to the final polymer characteristics.

In an $AB + AB_n$ route, there is an introduction of a linear segment in the otherwise growing hyperbranched polymer. Generally in AB_2 systems, the distance between branching points is very random. The addition of the linear AB segment allows for more control over the distance between branching points, but the placement of the branch points will depend on the relative reactivity of the monomers utilized. The number of branch points is controlled by the ratio of AB/AB_2 . As the concentration of AB monomer increases, the polymer contains more linear segments and therefore has a lower degree of branching. This, in turn, improves the mechanical properties of the polymer because chain entanglements are more likely with less branching. Scheme 1 depicts a copolymerization of generic AB and AB_2 monomers.

AB/AB₂ Polymerization Scheme



Scheme 1. Generic AB + AB₂ polymerization

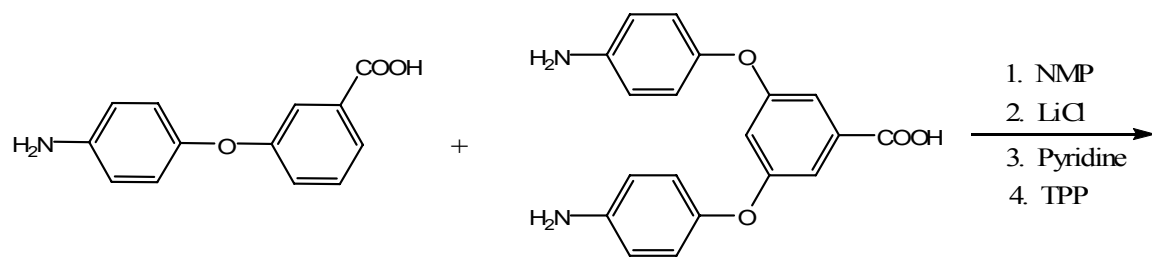
Jikei, et al. reported a series of polymerization reactions employing the AB + AB_n route resulting in the formation of branched poly(amides). These included the “one-pot” copolymerization of the AB and AB₂ monomers, stepwise polymerization of the AB₂ monomer with a slow addition of the AB monomer and stepwise polymerization of the AB monomer with a slow addition of the AB₂ monomer.³⁰ Scheme 2 shows the monomers used by Jikei, et al. in the AB + AB_n copolymerization to form polyamides.

The “one-pot” copolymerization was a typical polycondensation reaction in which both the AB and AB₂ monomers were polymerized in a one-step reaction to produce a hyperbranched polymer. Although the ratio of monomers in this case was 1:1, the growing polymer contained more AB₂ units in the early stage of polymer growth, with more AB monomer units being incorporated later in the polymerization. This is thought to be because of the difference in the number of B groups in each monomer. The AB monomer contains only one B group, while the AB₂ monomer contains two B groups, giving it twice as many B groups to react. The resulting polymer had a viscosity value of 0.29 dL/g and was soluble in NMP, DMSO, DMF and *m*-Cresol.

In the first stepwise polymerization, AB monomer was added dropwise to an already growing AB₂ polymer. In the beginning of the polymerization, only AB₂ units

were present and were allowed to polymerize for 30 minutes. This allows for a hyperbranched structure to grow first, before the incorporation of an AB monomer. As the AB monomer was added slowly to the growing polymer over 150 minutes, linear segments were introduced into the polymer. The resulting polymer was composed of many dendritic units due to the fact that branching occurred first before the linear segments were introduced. It also had a higher viscosity value, 0.35 dL/g, than the one-pot synthesis and was only soluble in NMP and DMSO.

The other stepwise polymerization began with AB monomer being polymerized for 30 minutes, resulting in a linear polymer. AB₂ monomer was added slowly over 150 minutes and incorporated branching into the linear segments that had already formed. The resulting polymer had long linear chains because the linear polymer was allowed to form first before incorporating the AB₂ monomer. The resulting polymer had a 0.40 dL/g viscosity value, which was higher than the previous two polymerizations, and just as the first slow addition polymerization, was only soluble in NMP and DMSO. The “one-pot” copolymerization resulted in lower viscosities and higher solubilities in a number of polar solvents, relative to the stepwise polymerizations. This is thought to be because of the more random architecture of these copolymers.



Scheme 2. Copolymerization to produce polyamides by Jikei, et al.

Jikei, et al. have also worked with other AB + AB_n systems, copolymerizing 3-(4-aminophenoxy) benzoic acid and 3,5-bis (4-aminophenoxy) benzoic acid, using triphenylphosphite (TPP) and pyridine as condensing agents.³³ These copolymerization reactions were carried out with various ratios of AB₂ monomer to AB monomer. As the ratio of AB₂/AB decreased, or with increasing AB, the viscosities of the polymers increased. This is due to the increasing linearity of the polymers as more AB is incorporated, resulting in chain entanglements in the polymers. Similar work was also done by Baek, et al. to synthesis poly(ether ketone)s³¹ and poly(phenylquinoxaline)s³⁶.

Another route to hyperbranched polymers is an A₂ + B₃ system. There are many different examples of A₂ + B₃ systems including those by Lin, et al. with poly (aryl ester)s and poly (arylene ether)s^{20, 21}, Unal et al. who have worked with poly (ethylene glycol) and 1,3,5-benzenetricarbonyl trichloride²⁴, and poly (urethane urea) elastomers³⁴, Monticelli, et al. have worked with poly aramids²², Czupik, et al with poly (arylene ether phosphine oxide)s¹⁸, Hao et al. with polyimides¹⁹, and Chen et al. with photosensitive hyperbranched polyimides¹⁷. Unal et al. have also recently worked with polyurethanes and polyureas, as they have previously made the linear counterparts to these systems.

These A₂ + B₃ systems are attractive compared to other systems because they contain only one type of functional group per monomer unit. A general scheme of an A₂ + B₃ system is shown in Scheme 3. As in other systems to prepare branched polymers, the A functional groups can react only with B functional groups, not with themselves, and *visa versa*. In previously discussed systems, both the A and B functional groups are within the same monomer and as a result, the polymerization and the branching, are random. In an A₂ + B₃ system, the functional groups are within separate monomers and

the linearity and branching of the polymer is controlled by varying the length between functional groups in the A_2 or B_3 component.

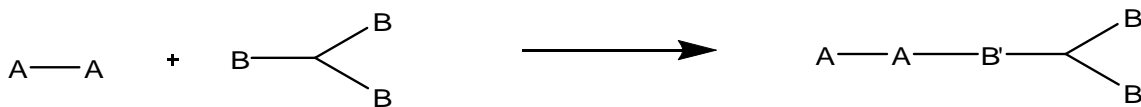
In an $A_2 + B_3$ system, the idea is to maintain the advantageous properties of branched polymers, such as high solubilities, low viscosities and a large number of end groups, while also improving the mechanical properties to approach those shown by linear polymers. In order to keep the balance between the positive properties of branched and linear polymers, the reaction conditions in these polymerization reactions must be carefully controlled. As stated earlier, AB_2 polymer systems have low viscosities, high solubilities and a large number of endgroups that can be modified, but they have poor mechanical properties. The branching in these systems is random and cannot be controlled. In the $AB + AB_n$ polymer systems, branching is still random, but controlling the number of branch points is possible based on the ratio of AB_2/AB monomer. These systems still have low viscosities, good solubilities and endgroups that can be modified. With the $A_2 + B_3$ polymer system, there is more control over the distance between branch points by control of the A_2 monomer. By varying the molar mass of the A_2 monomer, the distance between the branch points in the polymer can be controlled. Therefore, the length of linear segments in the polymer can be controlled and a balance of branched and linear segments can be tailored in order to obtain the most advantageous properties of both linear and branched polymers.

However, there is one major risk associated with the $A_2 + B_3$ systems, the possibility of gelation. Gelation occurs when a 3-D network is formed due to crosslinking between growing polymer chains, typically accompanied by a dramatic increase in the viscosity, approaching ∞ . The point at which the polymeric system begins

to gel is called its critical conversion. This leaves the polymer insoluble in all organic solvents and prevents solution phase processing.

In order to prevent gelation, it is extremely important to closely monitor all reaction conditions in these systems. Most $A_2 + B_3$ systems that have an A:B ratio of 1:1, have a critical conversion of 0.72, meaning that gelation will occur when 72% of the A functional groups have been consumed. This value is based on the assumption that the reactivity of the functional groups remains the same throughout the polymerization and that there is no intramolecular cyclization. The critical conversion of the system can be pushed higher by varying the A:B ratio. For example, at an A:B ratio of 1:2, Monticelli et al. were able to push the critical conversion to 1.00 or 100% conversion of the A functional group²², but at the expense of producing very low molecular weight materials.

$A_2 + B_3$ Polymerization Scheme

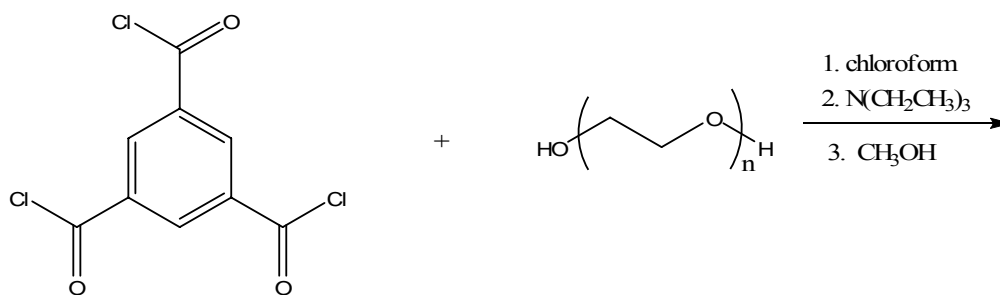


Scheme 3. General $A_2 + B_3$ polymerization.

Unal et al. choose specific reaction conditions for the purpose of avoiding gelation in their system, which used polyethylene glycol (PEG) and 1,3,5-benzene tricarbonyl trichloride (BTC) as shown in Scheme 4. Unal et al. ran a series of polymerization reactions in which variations of the A monomer were made by using A_2 monomers with molar masses varying from 200-3400 g/mol in dilute solutions. These variations were made in an effort to control and vary the distance between branch points in these polymers. Copolymerization reactions of $A_2 + B_3$ monomers generally results in

crosslinking, however, a slow addition of A_2 to B_3 was utilized in order to prepare completely soluble, branched polyesters while avoiding crosslinking.

Fossum and Czupik had previously shown that by adding a dilute solution of A_2 slowly to a dilute solution of B_3 , mostly linear polymer was produced initially, followed by a more highly branched product at latter stages of the addition of A_2 . Alternatively, when adding a dilute solution of B_3 slowly to a dilute solution of A_2 , highly branched products were formed initially and the risk of crosslinking was still minimized.



Scheme 4. Polymerization of poly(aryl ester)s by Unal et al.

Lin et al also carried out polymerizations with an $A_2 + B_3$ system. Their goal was similar to Unal et al. given above, which was to create hyperbranched polymers and avoid gelation. This goal was achieved by carrying out polymerization reactions in which a dilute solution of one monomer was added slowly to a dilute solution of another monomer. The order in which a monomer is added is crucial in these polymerizations. When a dilute solution of A_2 was added slowly to a dilute solution of B_3 , the resulting polymer was high yielding, 90%, and gelation was avoided. However, when the reverse situation was carried out, in which dilute B_3 solution was slowly added to dilute A_2 solution, gelation did occur. This is thought to be because the B_3 monomer contains three functional groups causing a high local concentration effect that could lead to crosslinking, where the A_2 monomer contains only two functional groups. The molar

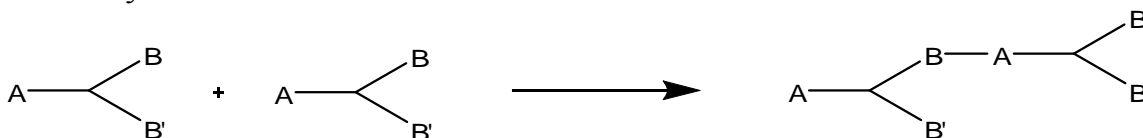
ratio of $A_2:B_3$ was kept at 1:1 in order to build similar polymers to those produced through typical AB_n systems and the overall concentration did not exceed 0.080 M to avoid gelation.

The degree of branching in these systems was much harder to calculate than in other hyperbranched systems. This is due to the numerous cyclic structures that can be created when dilute solutions are employed. However, typical branching units, dendritic, linear and terminal, are found within these systems just as with others. The degree of branching was calculated based on the relative percentages of the different units, found in the 1H NMR spectrum of the polymer. The DB values of this system were near 50%, which is what is expected in typical AB_n type systems.

More recently, the use of ABB' -type monomers to tailor the branching in both poly(imide)s and poly(amide)s has been reported. A general ABB' polymerization is shown in Scheme 5. In an ABB' system, the A and B functional groups are on the same monomer, therefore branching will be random, just as it was in the $AB + AB_n$ system. In a typical ABB' monomer, the two B groups are of the same functionality, but they have different reactivity based on their position in the monomer. This can lead to competition among the sites and as a result a varying degree of branching. The ABB' system tends to have a lower degree of branching than other systems, making it more linear than other systems, which leads to more chain entanglements and better mechanical properties. As stated before, with linear polymers, along with good mechanical properties come poor solubility, high viscosity and a small number of endgroups. This also applies to the ABB' systems with a low degree of branching. However, endgroup modification can counter poor processing properties. For example, modification with amino groups can

lead to hydrogen bonding which can enhance the good mechanical properties and aid in solubility in organic solvents.

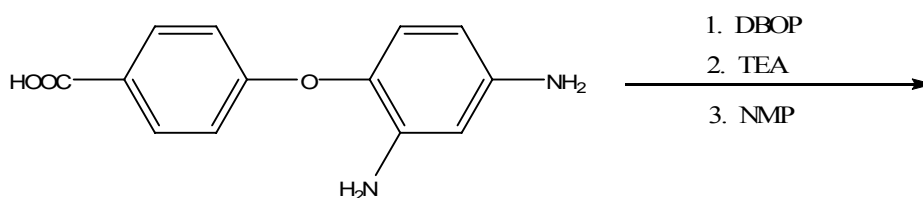
ABB' Polymerization Scheme



Scheme 5. General ABB' polymerization.

These systems have not been well explored, but Wang, Jikei and Kakimoto have recently synthesized polyamides and polyimides from ABB'-type monomers^{10, 35}. Scheme 6 shows their polymerization to form polyamides from an ABB'-type monomer. Their polymerizations to produce polyamides involved varying the reaction conditions, specifically the condensing agent, in order to produce polymers that had varying degrees of branching. In the first ABB' polymerization reaction, (2,3-dihydro-2-thioxo-3-benzoxazolyl) phosphonic acid diphenyl ester (DBOP) and triethylamine (TEA) were used as condensing agents at room temperature to produce a polymer (PA1) with a DB value of 0.1. In the second ABB' polymerization reaction, triphenylphosphite (TPP) and pyridine were used at 100 °C, to produce a polymer (PA2) with a DB value of 0.2. The PA1 polymer that was produced was modified with both amino and imine groups resulting in viscosity values that ranged from 0.39 dL/g to 0.73 dL/g. In the PA2 polymer, that was also modified with amino and imine groups, the viscosity values ranged from 0.31 dL/g to 0.34 dL/g. The lower viscosity values observed in PA2 are due to the higher degree of branching which in turn resulted in fewer chain entanglements within the polymer. Lower viscosities were also observed when very bulky groups were used for modification. This is probably because of the lack of chain entanglements due to

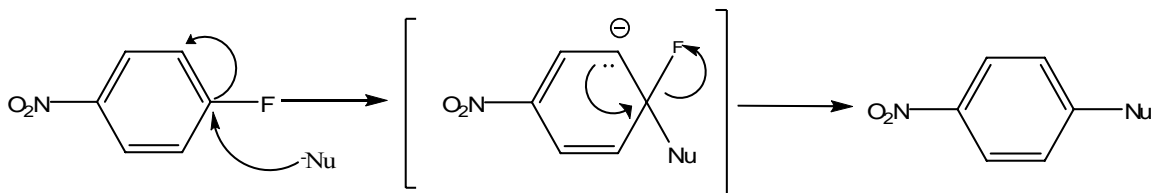
bulky group interference. They also found that film formation was directly related to chain entanglements. Those polymers that were able to entangle, produced films that could be peeled intact. They also concluded that the amino-modified polymers had stronger tensile properties due to hydrogen bonding within the polymer. The lower DB polymers produced better films and had higher tensile strength than their high DB counterparts.



Scheme 6. Polymerization of an ABB' polyamide.

Nucleophilic Aromatic Substitution

The mechanism for the polycondensation reactions in this project is nucleophilic aromatic substitution (Scheme 7) which is commonly used for the production of poly(arylene ether)s. Nucleophilic aromatic substitution takes place in two steps. The first, rate determining, step is the attack of an electron rich nucleophile on the *ipso* carbon atom of an activated aryl halide. Activation of the *ipso* carbon is typically provided by a strongly electron withdrawing group, located in the *ortho* or *para* position. This step leads to a stable intermediate, known as a Meisenheimer complex. In the second step, the halide ion is eliminated, reforming the aromatic structure.



Scheme 7. General scheme for Nucleophilic Aromatic Substitution.

Electrophilic Strength and Reactivity

In order to understand how and why a system, prepared via nucleophilic aromatic substitution, branches to the extent that it does, the strength of electrophilic sites must be determined. Two approaches will be utilized to determine the strength of the electrophilic sites in the monomers 1) determination of the ^{13}C and ^{19}F NMR chemical shifts and 2) the determination of the activation energy, E_a , for each electrophilic site using standard kinetic studies. The resulting data will provide a guideline to prepare systems with varying degrees of branching.

Carter et al. previously investigated the electrophilic strength of aromatic difluoride B_2 monomers, which contained electron-withdrawing groups in the *para* positions. They were able to use NMR spectroscopy to evaluate these systems due to the fact that aryl fluorides are activated to undergo nucleophilic aromatic substitution. They found that this electron-withdrawing group caused the development of a partial positive charge at the ortho or para position through both inductive and resonance effects.³⁷ It was determined that both ^{13}C and ^{19}F NMR spectroscopy were very sensitive probes of the electron density of the ipso carbon atoms which correlated well with the ability of the electrophilic site to undergo nucleophilic aromatic substitution. The reactivity of electrophilic sites was determined via ^{13}C and ^{19}F NMR spectroscopy, by comparing the relative values of the chemical shifts in each of the two methods with the results of competition reactions between the various monomers. It was found that the more reactive sites typically had ^{13}C and ^{19}F NMR chemical shifts that were considerably downfield of the less reactive species.

Unfortunately, NMR spectroscopy is only a probe of electron density at an electrophilic site. In order to determine the actual reactivity of an electrophilic site, the activation energy of that site must be determined, as this directly relates to the rate coefficient for the reaction. The activation energy, E_a , for the electrophilic sites in **1b-3b** will be determined by standard kinetic procedures. Figure 5 shows a general scheme of the k ratios for various E_a differences at various reaction temperatures.

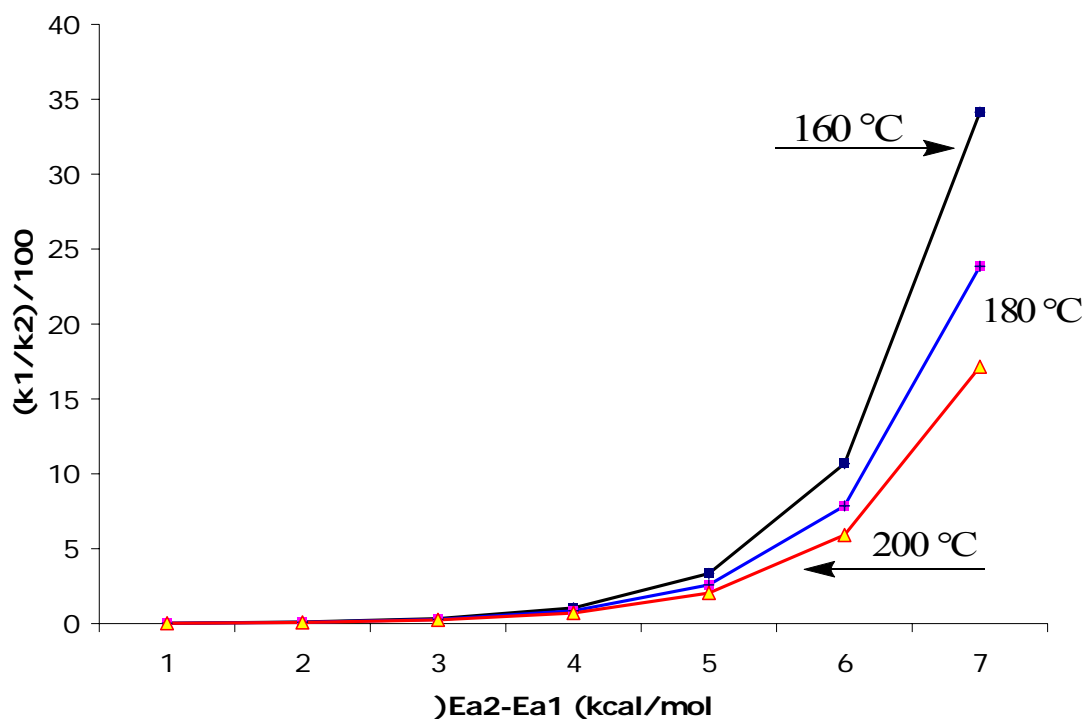


Figure 5. Plots of k_1/k_2 for various differences in E_a at 160, 180 and 200 °C.

This Project

In this project, the polymerization behaviors of two different AB_2 monomers, **1** and **2**, designed to produce poly(arylene ether sulfone)s and poly(arylene ether phosphine oxide)s, respectively, have been studied. These polymerizations have been conducted in order to determine the extent to which these systems can act as ABB' systems after one electrophilic site has reacted, in turn, changing the reactivity of the second electrophilic

site. Hyperbranched polymers have been constructed by the polymerizations of 1) AB₂ monomers in the presence of core molecules and 2) an ABB'B'' monomer via nucleophilic aromatic substitution, NAS, at a variety of reaction temperatures. The monomers for these polymerizations are shown in Figure 6.

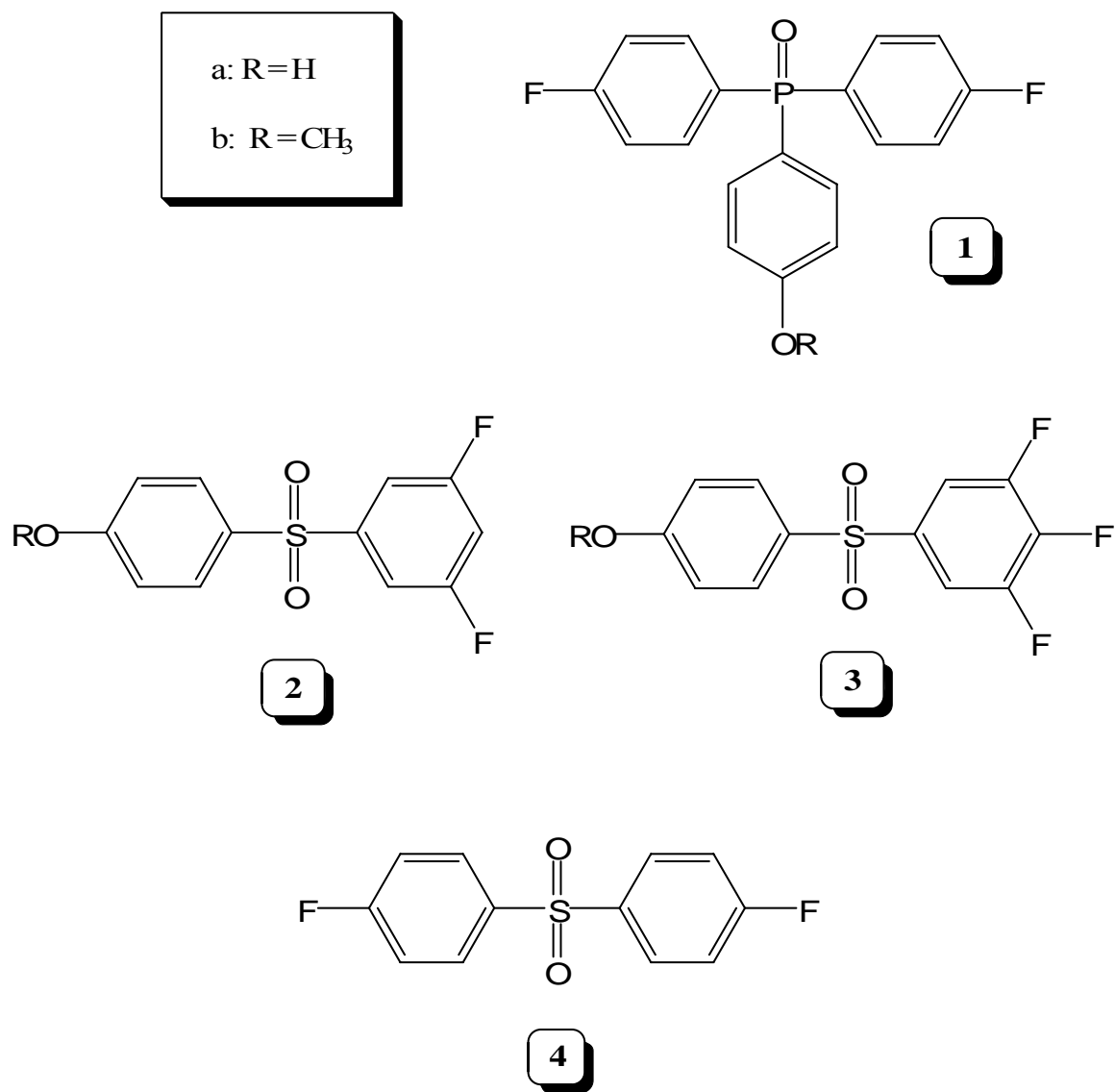


Figure 6. The monomers and core molecule used for polymerizations of hyperbranched systems.

EXPERIMENTAL

Materials

All reactions were performed under a nitrogen atmosphere and all transfers were done using syringes or cannula as necessary. THF and toluene were dried over sodium metal and distilled under nitrogen prior to use. N-methyl-pyrrolidinone (NMP) and dimethyl sulfoxide (DMSO) were dried over CaH₂ and distilled under nitrogen prior to use. 4-Fluorophenyl sulfone, 4-Hydroxy benzenesulfonic acid, sodium salt dihydrate and 4-Methoxy-benzene sulfonyl chloride were purchased from Aldrich. 4-Fluorophenyl sulfone and 4-Hydroxybenzenesulfonic acid, sodium salt dihydrate were used without any further purification and 4-Methoxy-benzene sulfonyl chloride was purified via recrystallization from hexanes prior to use. 1-bromo-4-fluorobenzene, 1-bromo-3,5-difluorobenzene, and 1-bromo-3,4,5-trifluorobenzene were purchased from Fluorochem and used without any further purification. 4-Methoxy phenylphosphonic dichloride was purchased from TCI and distilled prior to use.

Instrumentation

¹H and ¹³C NMR spectra were acquired using a Bruker Avance 300 MHz instrument operating at 300 and 75.5 MHz respectively. ¹⁹F NMR spectra were acquired using a Bruker Avance 400 MHz instrument operating at 376.5 MHz with 10% CFC₃ as an external standard, and the instrument set relative to the lock signal. Samples were

dissolved in (methyl sulfoxide)- d_6 or deuterated chloroform- d . SEC analysis was performed using a Viscotek Model 300 TDA system equipped with refractive index, viscosity, and light scattering detectors operating at 70°C. Polymer Laboratories 5 μ m PL gel mixed C columns were used with NMP (with 0.5% LiBr) as the eluent and a Thermoseparation Model P1000 pump operating at 0.8 mL/minute.

Synthesis of 3,5-Difluoro-4'-methoxydiphenyl sulfone, 2b

The procedure for the synthesis of 3,5-difluoro-4'-methoxydiphenyl sulfone was followed from the previous method as reported by the Fossum group.⁴

In a 250 mL round bottom flask equipped with an addition funnel, condenser, and gas inlet were placed 1.304 g (53.7 mmol) of Mg turnings and enough tetrahydrofuran (THF) to cover the metal. A solution of 10.056 g (52.1 mmol) of 1-bromo-3,5-difluorobenzene and 30 mL of THF was added slowly to the stirred Mg at room temperature; upon complete addition, the reaction was stirred and allowed to react for 4 h. The resulting solution of 3,5-difluorophenylmagnesium bromide was transferred to the addition funnel and added dropwise to a mixture of 10.77 g (52.1 mmol) of 4-methoxybenzene sulfonyl chloride in 30 mL of THF at 0°C. The reaction mixture was stirred overnight, followed by heating to reflux for 3 h. The reaction mixture was quenched with saturated ammonium chloride solution, diluted with 500 mL of ethyl ether and transferred to a separatory funnel. The ether layer was washed with distilled H₂O, saturated NaHCO₃, and again distilled H₂O. The ether layer was dried over MgSO₄, filtered and then evaporated to dryness to afford a tan solid, which was recrystallized from ethanol/water to obtain 11.59 g of 3,5-Difluoro-4'-methoxydiphenyl sulfone (79% yield, mp = 119-121°C, literature mp = 119-121°C).

^1H NMR, ^{13}C NMR and ^{19}F NMR spectroscopy are as previously reported by the Fossum group.⁴

Synthesis of 3,5-Difluoro-4'-hydroxydiphenyl sulfone, 2a

The procedure for the synthesis of 3,5-difluoro-4'-hydroxydiphenyl sulfone was followed from the previous method as reported by the Fossum group.⁴

In a 250-mL round bottom flask, 5.34 g (18.8 mmol) of 3,5-Difluoro-4'-methoxydiphenyl sulfone was dissolved in a mixture of 60 mL of glacial acetic acid and 27 mL of 48% HBr and heated at reflux for 48 h. The reaction mixture was cooled and slowly added to 600 mL of water; and the resulting precipitate was isolated by filtration and dissolved in ethyl ether. The resulting product was extracted using 0.2 M sodium hydroxide. The layers were separated, the aqueous solution was acidified, and the precipitate was filtered off. The product was recrystallized from ethanol/water to yield 2.84 g of product (56 % yield, mp = 184-186°C, literature mp = 184-186 °C)

^1H NMR, ^{13}C NMR and ^{19}F NMR spectroscopy are as previously reported by the Fossum group.⁴

Synthesis of Bis-(4-fluorophenyl)-4-methoxyphenylphosphine oxide, 1b

The procedure for synthesis of Bis-(4-fluorophenyl)-4-methoxyphenylphosphine oxide was followed from the previous method as reported by the Fossum group.³

In a 500 mL round-bottom flask equipped with a Claisen adapter, condenser, addition funnel, gas inlet and stir bar was placed 4.33 g (178 mmol) of Mg turnings and enough THF to cover the metal. To the addition funnel was added 130 mL of freshly distilled THF and 29.72 g (113 mmol) of 1-bromo-4-fluorobenzene. Approximately 10%

of this mixture was added to the magnesium metal to start the reaction, after which time the remaining solution was added at such a rate as to maintain a gentle reflux. After complete addition of the bromide the resulting brown solution was heated to reflux for 3 h at which time the reaction mixture was cooled to 0 °C with an ice bath. Subsequently, a solution of 17.7 g (78.7 mmol) of 4-Methoxyphenylphosphonic dichloride in 62 mL of THF was added over a period of 30 min. The reaction mixture was allowed to warm to room temperature overnight with stirring, and the excess Grignard reagent was quenched with dilute HCl. The organic material was extracted into ether; washed with water, 5% sodium hydroxide, and water; followed by drying over magnesium sulfate. The solvents were removed via rotary evaporation followed by vacuum to afford 24.30 g of a light yellow, viscous oil that was used without further purification (89.7 % yield).

¹H NMR, ¹³C NMR and ¹⁹F NMR spectroscopy are as previously reported by the Fossum group.³

Synthesis of Bis-(4-fluorophenyl)-4-hydroxyphenylphosphine oxide, 1a

The procedure for synthesis of Bis-(4-fluorophenyl)-4-hydroxyphenylphosphine oxide was followed from the previous method as reported by the Fossum group.³

In a 500 mL round-bottom flask equipped with a stir bar and reflux condenser was charged 24.30 g (70.4 mmol) Bis-(4-fluorophenyl)-4-methoxyphenylphosphine oxide, 78 mL of glacial acetic acid and 109 mL of 48% HBr. The reaction mixture was heated to reflux for 48 h. The reaction mixture was slowly poured into 2600 mL of distilled water, and the resulting tan solid was collected via filtration. The solid was dissolved in 800 mL ethyl acetate, washed with distilled water and dried over magnesium sulfate. The solution was filtered and the volume reduced to approximately 50 mL via rotary

evaporation to induce crystallization. The desired compound was isolated as a light yellow powder, 14.93 g (64.1 % yield, mp = 224-226°C, literature mp = 224-226 °C).

¹H NMR, ¹³C NMR and ¹⁹F NMR spectroscopy are as previously reported by the Fossum group.³

Synthesis of 3,4,5-Trifluoro-4'-methoxydiphenyl sulfone, 3b

In a 500 mL round-bottom flask equipped with a Claisen adapter, condenser, addition funnel, gas inlet and stir bar were placed 2.37 g (97.6 mmol) of Mg turnings and enough THF to cover the metal. A solution of 20.0 g (94.8 mmol) of 1-bromo-3,4,5-trifluorobenzene and 100 mL of THF was added slowly to the Mg at room temperature; upon complete addition, the reaction was stirred and allowed to react for 4 h. The resulting solution of 3,4,5-trifluorophenylmagnesium bromide was transferred to the addition funnel and added dropwise to a mixture of 24.49 g (119 mmol) of 4-methoxybenzene sulfonyl chloride in 55 mL of THF at 0°C. The reaction mixture was stirred overnight, followed by heating to reflux for 3 h. The reaction mixture was quenched with dilute HCl, diluted with ether and transferred to a separatory funnel. The ether layer was washed with distilled H₂O, dilute NaHCO₃, and again distilled H₂O. The ether layer was dried over MgSO₄, filtered and then evaporated to dryness to form a tan solid, which was recrystallized from methanol to afford 9.00 g of 3,4,5-Trifluoro-4'-methoxydiphenyl sulfone (31.5 % yield, mp =121-122 °C).

¹H NMR (DMSO-*d*₆): 3.85 (s, 3H), 7.15 (d, 2H), 8.0 (m, 4H)

¹³C NMR (CDCl₃): 55.57, 112.9 (m), 115.1, 130.2, 131.1, 139.3 (m), 143.9 (t), 150.5 (m), 163.53.

¹⁹F NMR (DMSO-*d*₆): -131.44 (d, 2F), -153.29 (dd, 1F)

Elem. Anal. Calcd. For $C_{13}H_9F_3O_3S$: C, 51.66%; H, 3.00%. Found: C, 51.85%; H, 3.24%.

Synthesis of 3,4,5-Trifluoro-4'-hydroxydiphenyl sulfone, 3a

In a 500 mL round-bottom flask equipped with a stir bar and reflux condenser was charged 9.0 g (29.8 mmol) of 3,4,5-trifluoro-4'-methoxydiphenyl sulfone, 90 mL of glacial acetic acid, and 88 mL of 48% HBr. The reaction mixture was heated to reflux for 48 h. The reaction mixture was slowly poured into 1300 mL of distilled water, and the resulting tan solid was collected via filtration. The solid was dissolved in ether, washed with distilled water, saturated sodium bicarbonate and distilled water. The solution was then dried over magnesium sulfate, filtered and the volume reduced via rotary evaporation. The desired compound was then recrystallized from ethanol/water, stirred and heated in toluene, and recrystallized again in methanol to yield 2.4634 g of clear needle-like crystals (28.7 % yield, mp =198-199 °C).

1H NMR (DMSO-*d*₆): 6.95 (d, 2H), 7.86 (d, 2H), 7.96 (t, 2H), 10.8 (s, 1H)

^{19}F NMR (DMSO-*d*₆): -153.59 (dd, 1F), -131.51 (d, 2F)

Elem. Anal. Calcd. For $C_{12}H_7F_3O_3S$: C, 50.00%; H, 2.45%. Found: C, 50.64%; H, 2.63%.

Synthesis of Monosubstituted Model Compound for AB₂ sulfone

In a 25 mL RB flask equipped with a stir bar, water condenser, and gas adapter were placed 1.0 g (3.52 mmol) of 3,5-Difluoro-4'-methoxydiphenyl sulfone, 0.380 g (3.52 mmol) of *p*-cresol, 0.729 g (5.28 mmol) of potassium carbonate and 11.0 mL of NMP. The reaction was heated to 75 °C for 24 h.

Synthesis of Monosubstituted Model Compound for AB₂ phosphoryl

In a 25 mL RB flask equipped with a stir bar, water condenser, and gas adapter were placed 0.5 g (1.45 mmol) of Bis-(4-fluorophenyl)-4-methoxyphenylphosphine oxide, 0.157 g (1.45 mmol) of p-cresol, 0.301 g (2.18 mmol) of potassium carbonate and 4.53 mL of NMP. The reaction was heated to 100 °C for 24 h.

Synthesis of Monosubstituted Model Compound for ABB'B'' sulfone, 5b

In a 15 mL RB flask equipped with a stir bar, water condenser, and gas adapter were placed 0.2 g (0.662 mmol) of 3,4,5-Trifluoro-4'-methoxydiphenyl sulfone, 0.0715 g (0.662 mmol) of p-cresol, 0.137 g (0.993 mmol) of potassium carbonate, and 2.07 mL of NMP. The reaction was heated to 40 °C for 48 h. Aliquots were taken throughout to monitor the reaction and evaluated by GCMS. The resulting solution was precipitated from water, diluted in ether and washed with distilled water, saturated sodium bicarbonate and distilled water. The ether was then dried over MgSO₄ and the volume reduced via rotary evaporation to afford a white solid. The final product was then analyzed using GCMS and NMR analysis.

¹H NMR (DMSO-*d*₆): 2.26 (s, 2H), 3.37 (s, 3H), 3.87 (s, 3H), 6.91 (d, 2H), 7.16 (t, 2H), 7.95 (d, 2H), 8.10 (dd, 2H).

¹³C NMR (DMSO-*d*₆): 55.85, 112.69, 115.23, 130.28, 131.28, 132.82, 134.96, 138.98, 153.40, 154.61, 156.79, 163.60.

¹⁹F NMR (DMSO-*d*₆): -123.38 (s)

Synthesis of Disubstituted Model Compound for ABB'B'' sulfone, 6b

In a 15 mL RB flask equipped with a stir bar, water condenser, and gas adapter were placed 0.2 g (0.662 mmol) of 3,4,5-Trifluoro-4'-methoxydiphenyl sulfone, 0.0715 g (0.662 mmol) of p-cresol, 0.137 g (0.993 mmol) of potassium carbonate, and 2.07 mL

of NMP. The reaction was heated to 80 °C for 216 h. Aliquots were taken throughout to monitor the reaction and evaluated by GCMS. The resulting solution was precipitated from water, diluted in ether and washed with distilled water, saturated sodium bicarbonate and distilled water. The ether was then dried over MgSO₄ and the volume reduced via rotary evaporation to afford a white solid. The final product was then analyzed using GCMS and NMR analysis.

¹⁹F NMR (DMSO-*d*₆): -124.31 (s)

Synthesis of Trisubstituted Model Compound for ABB'B'' sulfone, 7b

In a 15 mL RB flask equipped with a stir bar, water condenser, and gas adapter were placed 0.2 g (0.662 mmol) of 3,4,5-Trifluoro-4'-hydroxydiphenyl sulfone, 0.0715 g (0.662 mmol) of p-cresol, 0.137 g (0.993 mmol) of potassium carbonate, and 2.07 mL of NMP. The reaction was heated to 120 °C for 504 h. Aliquots were taken throughout to monitor the reaction and evaluated by GCMS. The resulting solution was precipitated from water, diluted in ether and washed with distilled water, saturated sodium bicarbonate and distilled water. The ether was then dried over MgSO₄ and the volume reduced via rotary evaporation to afford a white solid. The final product was then analyzed using GCMS and NMR analysis.

General Procedure for Determination of Activation Energy

In a 25 mL round bottom flask equipped with a stir bar, water condenser and gas adapter were placed 0.300 g (0.993 mmol) of monomer **3a**, 1 equivalent p-cresol, 1.5 equivalents of potassium carbonate, and 3.10 mL of NMP. The reaction was heated at temperatures varying from 50 °C to 70 °C. Aliquots were taken throughout to monitor the reaction and evaluated by GCMS.

General Procedure for Polymerization of 3,5-Difluoro-4'-hydroxydiphenyl sulfone and 4-Fluoro-4'-fluorodiphenyl sulfone with Azeotropic drying.

In a 25 mL round-bottom flask equipped with a stir bar, Dean Stark trap, condenser, and gas adapter were placed 0.500 g (1.86 mmol) of **2a**, 0.0141 g (0.056mmol) of **4** (3%), 0.384 g (1.86mmol) of K₂CO₃, 2.90 mL of NMP, and 2.90 mL of toluene. The Dean Stark trap was filled with toluene and the mixture was heated to 165°C for approximately 3 hours to ensure complete dryness. The toluene was removed and the reaction temperature was raised to 200 °C for approximately 1 h. The mixture was cooled to room temperature and slowly poured into 500 mL of vigorously stirred acidic distilled water to afford 0.414 g (87.2 % yield) of white solid.

¹⁹F NMR (DMSO-*d*₆): -105.27 (d); -105.84 (m); -106.04 (s)

General Procedure for Polymerization of Bis-(4-fluorophenyl)-4-hydroxyphenylphosphine oxide and 4-Fluoro-4'-fluorodiphenyl sulfone with Azeotropic drying.

In a 25 mL round-bottom flask equipped with a stir bar, Dean Stark trap, condenser, and gas adapter were placed 0.500 g (mmol) of **1a**, 0.0230 g (mmol) of **4** (3%), 0.630 g (mmol) of K₂CO₃, 4.75 mL of NMP, and 4.75 mL of toluene. The Dean Stark trap was filled with toluene and the mixture was heated to 165°C for approximately 3 hours to ensure complete dryness. The toluene was removed and the reaction temperature was raised to 180 °C for approximately 1 h. The mixture was cooled to room

temperature and slowly poured into 500 mL of vigorously stirred acidic distilled water to afford 0.870 g (90.8 % yield) of white solid.

^{31}P NMR (CDCl_3): 27.25 (s); 27.45 (s); 27.65 (s).

General Procedure for Polymerization of 3,4,5-Trifluoro-4'-hydroxydiphenyl sulfone, 3a

In a 25 mL round-bottom flask equipped with a stir bar, condenser and gas adapter were placed 0.5 g (1.74 mmol) of 3a, 0.359 g (2.60 mmol) of potassium carbonate and 3.5 mL of NMP. The mixture was heated to 40 °C for 48 h and then cooled to room temperature and added dropwise to vigorously stirring acidic water to precipitate the polymer as 0.397 g of white solid (95.2% yield). The solid, 0.287 g, was then dissolved in THF, and was added slowly to vigorously stirring methanol to afford 0.160 g of a white solid (56% yield).

^{19}F NMR (CDCl_3): -119.96 (s); -120.05 (s); -128.71 (d); -150.55 (d).

RESULTS AND DISCUSSION

The main goal of this project was to control the degree of branching in several poly(arylene ether) systems via the use of kinetic parameters, specifically reactivity ratio differences. Tuning the degree of branching in these systems allows the physical and mechanical properties of these materials to be altered systematically. By controlling the branching in a polymer chain, the number of endgroups in a polymer can also be controlled, and these endgroups can then be modified for specific applications. In order to achieve the main goal of this project, the reactivity of the electrophilic sites in three different monomers designed to undergo nucleophilic aromatic substitution reactions was determined. The reactivity of these sites was probed via a combination of NMR spectroscopy, model reactions, and determination of their individual activation energies, E_a . Once the kinetic parameters were determined, they provided an operating window for controlling the physical and mechanical properties of these systems.

Similarities of AB_2 and ABB'

In an AB_2 system, there are two different types of functional groups, A and B, and two different reactivities in an unsubstituted monomer. A general AB_2 system is shown in Figure 7. The A functional group is the only functional group of its kind with its own independent reactivity. It is assumed that the A functional group can only react with a B functional group and *vice versa*. Initially, the B groups are of equal reactivity due to their equivalent positions in the monomer. This is true only in the unsubstituted

monomer, however, AB_2 systems are not quite what they seem to be in terms of reactivity. Once reaction of one of the B groups has taken place, the reactivity of the second B group may change considerably. During the polymerization process this change in reactivity of the second B group would then lead to either a higher or lower reactivity relative to any unreacted B groups on remaining monomer species. In essence, this makes the AB_2 system act much more like an ABB' system in which the B functional groups are different in reactivity from the outset. Even small differences in reactivity are important at lower temperatures. A negative change in reactivity would result in less branching while a positive change in reactivity would afford a more branched structure. At higher temperatures, the difference in reactivity is smaller, making the B sites more competitive and resulting in more branching in the polymer.

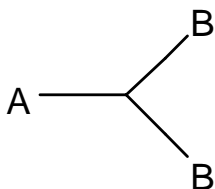


Figure 7. The general structure of an AB_2 monomer.

In an ABB' system, there are two different functional groups with three different reactivities. A general ABB' system is shown in Figure 8. Once again, the A group can only react with a B functional group and *vice versa*. The B groups are of the same functionality, yet, due to their placement in the monomer, may have significantly different reactivities. It is this difference in reactivity at the B sites that allows for variations in branching in this system. At lower temperatures, the reactivity difference between the B sites is very large, which should result in the formation of mostly linear polymer. As the reaction temperature increases, the reactivity difference between the two

sites decreases, allowing more branching to take place because the B sites are more competitive.

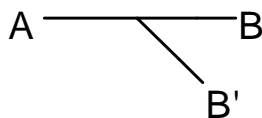


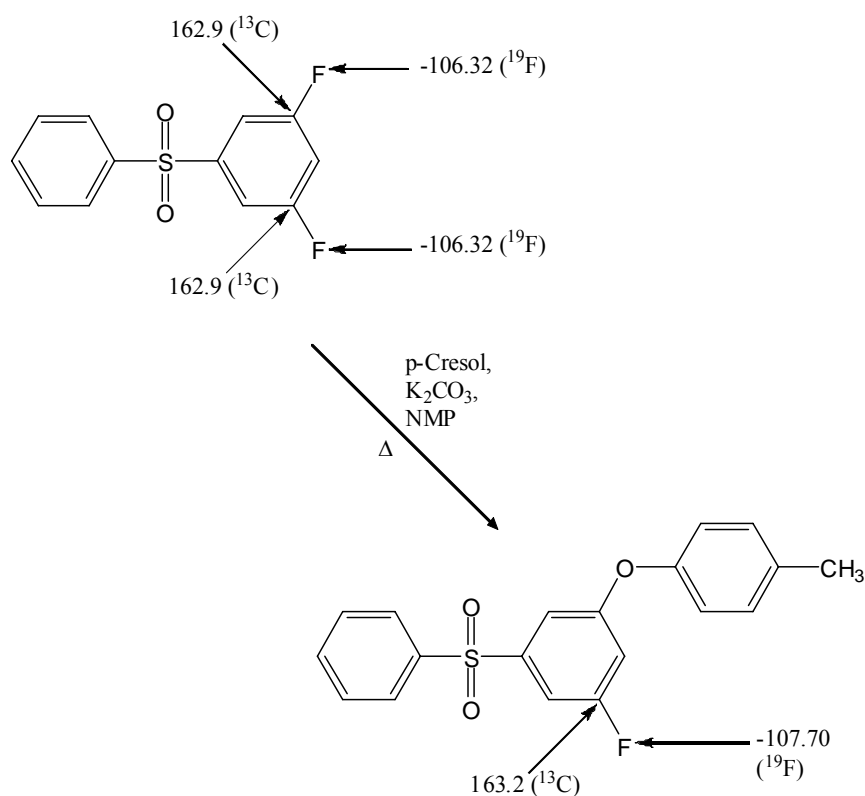
Figure 8. The general structure of an ABB' monomer.

Electrophilic Strength and Reactivity of AB₂ systems

The ability to tailor the branching in poly(arylene ether)s rests on the inherent differences in the reactivity of the electrophilic (B) sites in the monomers. Model reactions were used to determine the relative reactivity of the electrophilic sites for monomer **2a**. The reactions to produce the monosubstituted and disubstituted model compounds were carried out as previously described in the literature using the corresponding B₂ monomer, that does not possess the A functional group.³⁸ In these reactions, 1 equivalent of the monomer of interest, along with 1 equivalent of *p*-cresol, were reacted with K₂CO₃ and NMP at various temperatures to produce the desired substituted products as shown in Scheme 8.

The ¹³C and ¹⁹F NMR chemical shifts of this system can provide a rough guide of relative reactivity for electrophilic sites. The un-substituted B₂ monomer exhibits a ¹³C NMR chemical shift of 162.9 ppm for the *ipso* carbon atoms and a ¹⁹F NMR chemical shift of -106.32 ppm. The monosubstituted B₂ monomer displays ¹³C and ¹⁹F NMR chemical shift values of 163.2 ppm and -107.70 ppm, respectively. The downfield shift in the ¹³C spectrum indicates an increase in electrophilic strength of the carbon atom and therefore the second site is more reactive once the first site is substituted. However, the

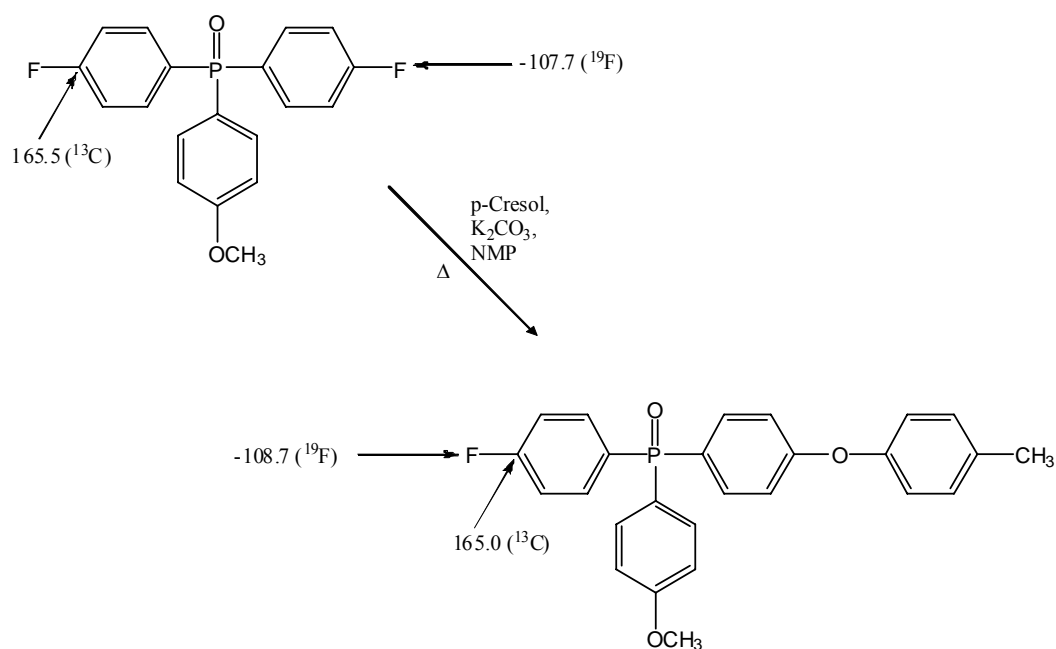
upfield shift in ^{19}F indicates a decrease in the electrophilic strength of the *ipso* carbon, therefore making the fluorine less likely to leave via substitution. These data for determining reactivity are conflicting, but it is generally accepted that ^{19}F NMR chemical shifts seem to be a better guide, in part due to their greater sensitivity.



Scheme 8. Model reaction using B_2 monomer representing an AB_2 sulfone system.

Model reactions were also used to determine the relative reactivity of the electrophilic sites in monomer **1a**. The reactions to produce the monosubstituted and disubstituted model compounds were carried out previously by the Fossum group. In these reactions, 1 equivalent of the monomer of interest, along with 1 equivalent of *p*-cresol, were reacted with K_2CO_3 and NMP at various temperatures to produce the desired

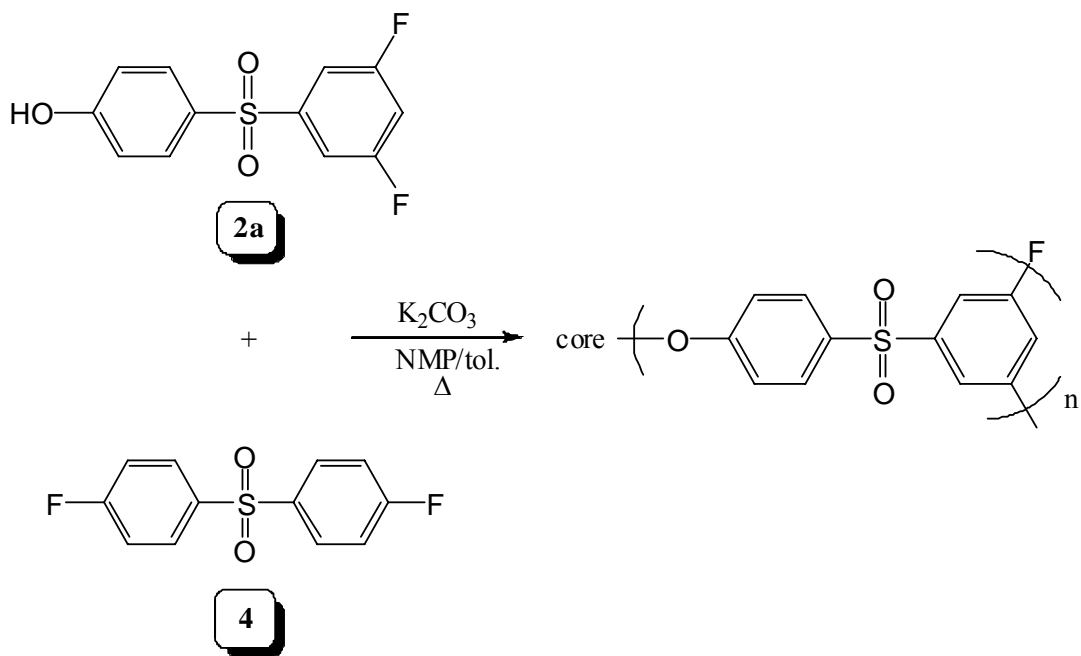
substituted products as shown in Scheme 9. The ^{13}C and ^{19}F NMR chemical shifts of these species can provide a guide to relative reactivity for this system. The unsubstituted AB_2 monomer shows a ^{13}C NMR chemical shift of 165.5 ppm for the *ipso* carbon atoms and a ^{19}F NMR chemical shift of -107.7 ppm for the two fluorine atoms. The monosubstituted AB_2 monomer has ^{13}C and ^{19}F NMR chemical shift values of 165.0 ppm and -108.70 ppm, respectively. The ^{13}C upfield shift indicates a slight decrease in electrophilic strength of the *ipso* carbon and a decrease in reactivity of the second site once the substitution of the first site has taken place. The ^{19}F upfield shift also indicates a decrease in the electrophilic strength of the *ipso* carbon, therefore making the fluorine less likely to leave via substitution.



Scheme 9. Model reaction of AB_2 phosphoryl system.

Polymerization of Monomer 2a

The polymerization reactions of the AB₂ sulfone monomer, **2a**, were carried out as depicted in Scheme 10. The monomer was reacted in the presence of 3% core, **4**, under typical nucleophilic aromatic substitution conditions. Azeotropic drying was used in reactions that occurred at 160, 180 and 200 °C. The reaction was azeotropically dried at the corresponding temperature for 3 hours, the toluene removed, and the reaction was allowed to progress to completion. Aliquots were taken both during and after completion of the polymerization reaction in order to monitor molecular weight and PDI development.



Scheme 10. Polymerization of AB₂ sulfone monomer with a core molecule.

The AB₂ sulfone polymer samples were subjected to ¹H, ¹³C and ¹⁹F NMR studies to confirm their structures and provide degree of branching information. The data showing

the results of the AB₂ sulfone polymerizations are shown in Table 1. As the reaction temperatures increased, the molecular weight and PDI of each polymer remained relatively constant, but the degree of branching (DB) increased gradually. Equation (2) was used to calculate the DB values for the AB₂ sulfone system. The degree of branching, DB, of each polymerization was determined via the use of ¹⁹F NMR spectroscopic studies to find the number of dendritic and linear units in the poly(arylene ether sulfone)s. The possible structural units of the hyperbranched polymer are shown in Figure 9.

$$DB = 2ND / (2ND + NL) \quad (2)$$

Examination of the DB data for this system reveal the general trend that an increase in reaction temperature results in increased branching within the polymer system. The DB values range from 0.65 to 0.77, showing systems that are more than 50% branched. The results are not consistent with the predictions of reactivity ratios based on ¹⁹F NMR chemical shifts and reactivity ratios within the AB₂ monomer system. Based on the decreased reactivity of the second site one would actually expect a DB value below 0.5 (the statistical number), however, this is not observed.

The observation that all of the DB values are above 0.5 may simply be a result of how they are determined. Without any firm spectroscopic handle to determine the number of dendritic units present in the polymer, this number must be inferred from the number of terminal units. A lower molecular weight material would appear to have a higher number of terminal units, relative to linear units. This would also be the case with a linear polymer. For example, a linear polymer, with 100 repeat units, would have 2 endgroups (ratio 98 L: 2 T or 49:1) while a linear polymer, with 50 repeat units would still have 2

end groups (ratio 48 L: 2 T or 24:1). Therefore, one must use caution in putting any real value on the DB calculations performed with these types of polymers. However, what is clear with this system, is that there exists a subtle trend toward a more branched structure as the reaction temperature is increased.

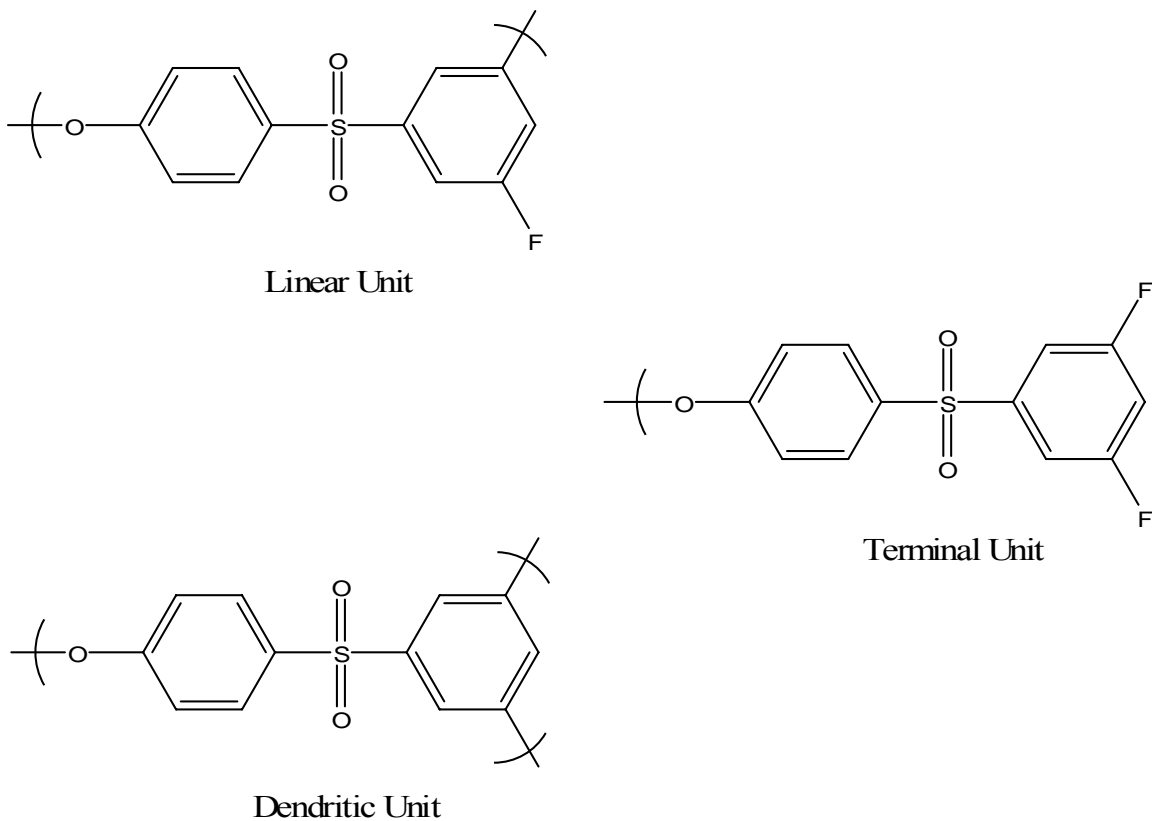


Figure 9. General structures of the possible repeat units in a branched polymer.

Table 1: AB₂ sulfone polymerization data

Reaction	Temperature	[M]	M _n	PDI	% Yield	DB	T _g
1	140	.64	5,647	5.4	85.5	0.651	159.32
2	160	.64	4,206	2.9	85.4	0.765	175.72
3	180	.64	4,290	2.7	90.9	0.756	144.44
4	200	.64	3,677	4.5	87.2	0.766	151.91

Thermal Analysis of AB₂ sulfone system

Thermal analysis on the AB₂ sulfone polymers was conducted via DSC, or differential scanning calorimetry. This is a technique in which the instrument measures the amount of heat absorbed by a particular polymer sample as compared to a reference substance. The polymer sample will absorb more or less energy than the reference substance, causing for a negative or positive peak, showing whether the transition the polymer undergoes is exothermic or endothermic.

The possible transitions that a polymer may undergo are 1) the glass transition at temperature, T_g, 2) crystallization at temperature, T_c, and 3) melting at temperature, T_m. In this case we will be strictly measuring the glass transition temperature. By definition the glass transition temperature is the temperature at which the amorphous regions of the polymer soften and are able to move. Figure 10 shows a DSC trace for a polymer made from an AB₂ sulfone monomer with a T_g of 175.72 °C. Himmelberg et al. were able to obtain a T_g value of 205 °C for a polymer synthesized with the AB₂ sulfone monomer at 165 °C.⁴ The difference in these values is thought to be due to differences in molecular

weights. Himmelberg et al. obtained a polymer with a M_n value of 6,180 compared to the current polymer with an M_n value of 4,206.

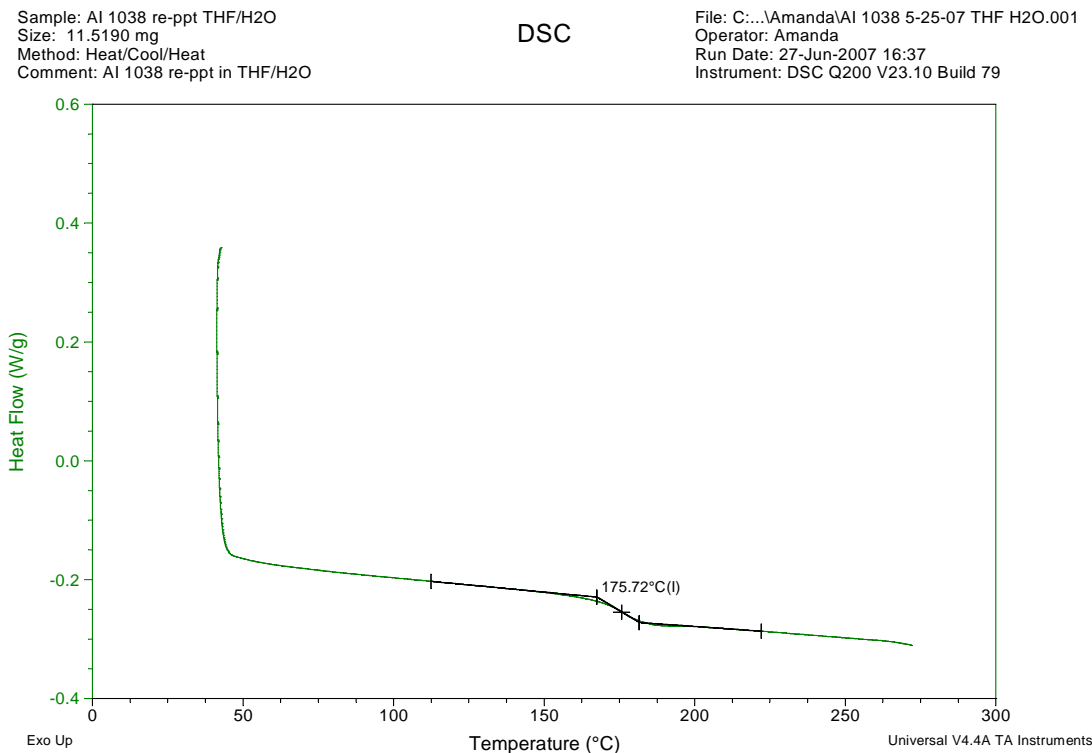
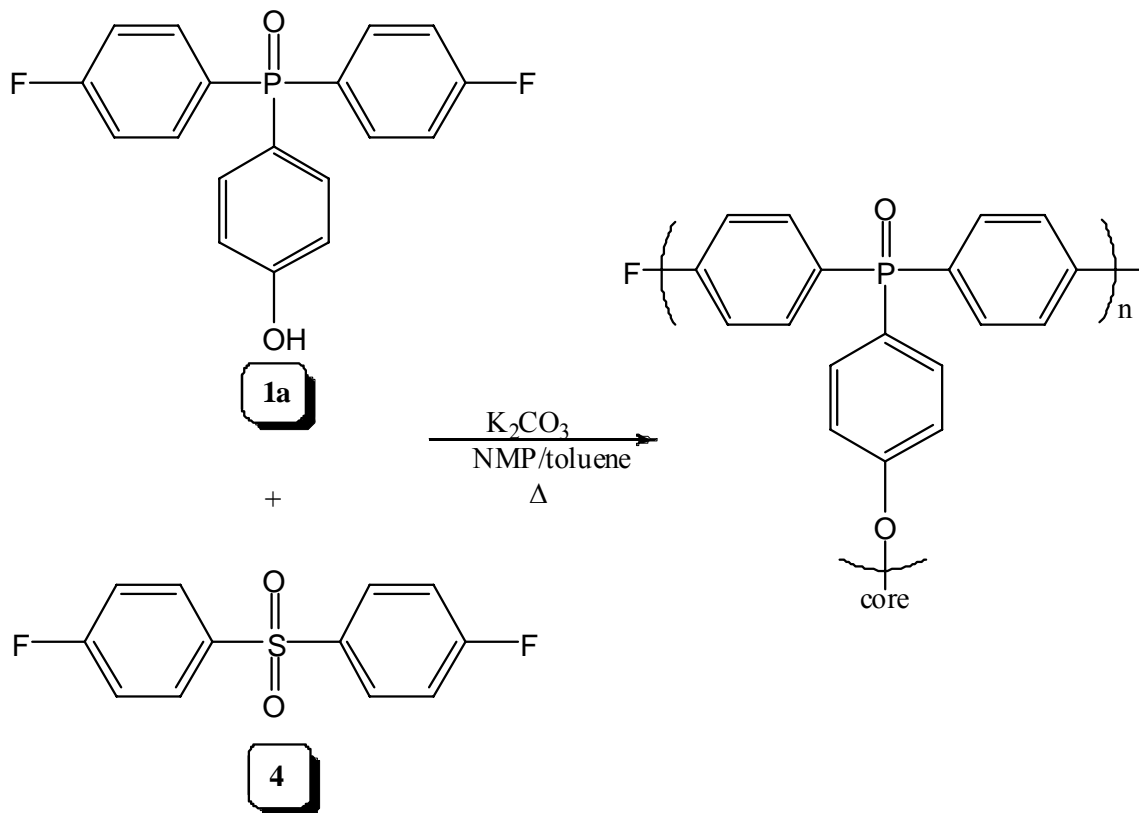


Figure 10. DSC trace for AB₂ sulfone polymerization at 160 °C.

Polymerization of Monomer 1a

The polymerization reactions of the AB₂ phosphoryl monomer, **1a**, were carried out as depicted in Scheme 11. The monomer was reacted in the presence of 3% core, **4**, under typical nucleophilic aromatic substitution conditions. Azeotropic drying was used in reactions that occurred at 160, 180 and 200 °C. The reaction was azeotropically dried at the corresponding temperature for 3 hours, the toluene removed, and the reaction was allowed to progress to completion. Aliquots were taken both during and after the polymerization reaction in order to monitor molecular weight and PDI.



Scheme 11. Polymerization of AB₂ phosphoryl monomer with a core molecule.

The phosphoryl polymer samples were subjected to ¹H and ³¹P NMR studies to confirm their structures and provide degree of branching information. The data showing the results of the AB₂ phosphoryl polymerizations are shown in Table 2 and the ³¹P spectra used to calculate DB values are shown in Figure 11. As the reaction temperatures increase, the molecular weight and PDI of each polymer remain relatively constant, while the degree of branching (DB) increases. The degree of branching, DB, of each polymerization was determined via NMR studies by calculating the number of dendritic and linear units in the phosphoryl polymerizations and using Equation (3). This shows the same general trend that was present in the AB₂ sulfone system, in which increases in reaction temperature result in increased branching within the polymer system. However, the AB₂ sulfone system is slightly more sensitive to temperature changes, as is shown by

the greater range of DB values over the course of the temperature changes. The AB₂ phosphoryl DB values ranged from 0.47 to 0.54 as opposed to the range of 0.65 to 0.77 for the AB₂ sulfone system. This is mostly likely due to the close proximity of the electrophilic sites in the AB₂ sulfone system leading to electronic effects enhancing the reaction sites. The results for the phosphoryl system are consistent with the predictions based on ¹⁹F NMR chemical shifts and reactivity ratios within the AB₂ phosphoryl monomer system. These data match perfectly with what would be expected for a statistical system (DB = 0.5) at 160 °C and then tailoring of DB both below and above that temperature. The phosphoryl monomer is likely less sensitive to temperature due to the lack of proximity of the electrophilic sites. They are not as close together as the sites in the corresponding sulfone system and do not have the increased competition for reaction.

$$DB = 2 ND / (2ND + NL) \quad (3)$$

Table 2: AB₂ phosphoryl polymerization data

Reaction	Temperature	[M]	M _n	PDI	% Yield	DB	T _g
1	120	.64	5,980	2.3	66.0	0.470	185.68
2	140	.64	7,936	8.4	78.3	0.495	165.68
3	160	.64	4,983	2.4	95.3	0.499	196.29
4	180	.64	8,036	2.5	96.0	0.559	165.84
5	200	.64	6,293	3.3	93.7	0.543	193.29

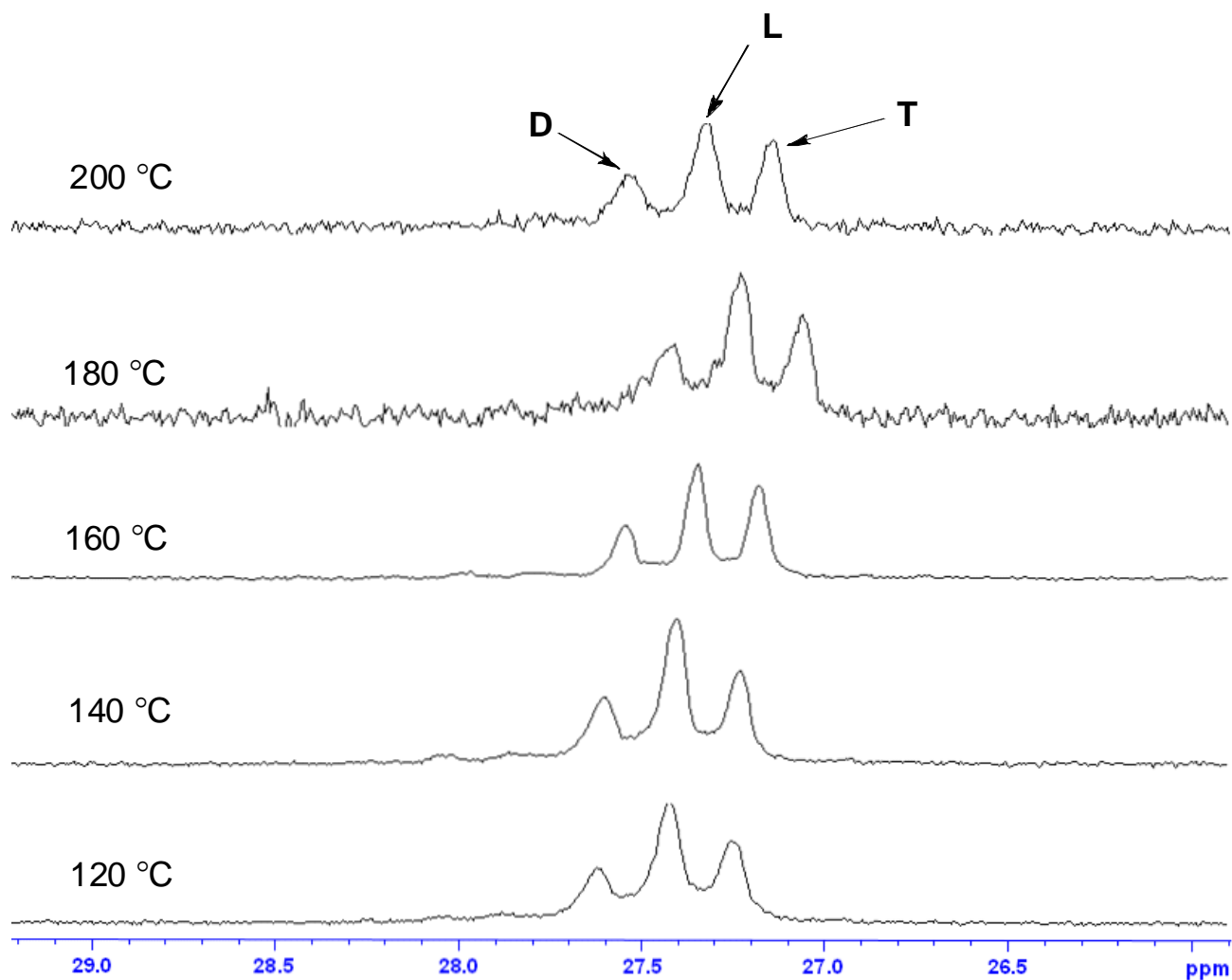


Figure 11. ^{31}P NMR overlay used to calculate DB values.

Thermal Analysis of AB_2 phosphoryl system

Differential scanning calorimetry, DSC, was again the thermal analysis of choice in this system in order to determine the glass transition temperatures, T_g , of the AB_2 phosphoryl system. A representative DSC trace for an AB_2 phosphoryl is shown below in Figure 12, in which the T_g is 185.68 °C. This glass transition temperature is higher than that found in the preceding AB_2 sulfone system.

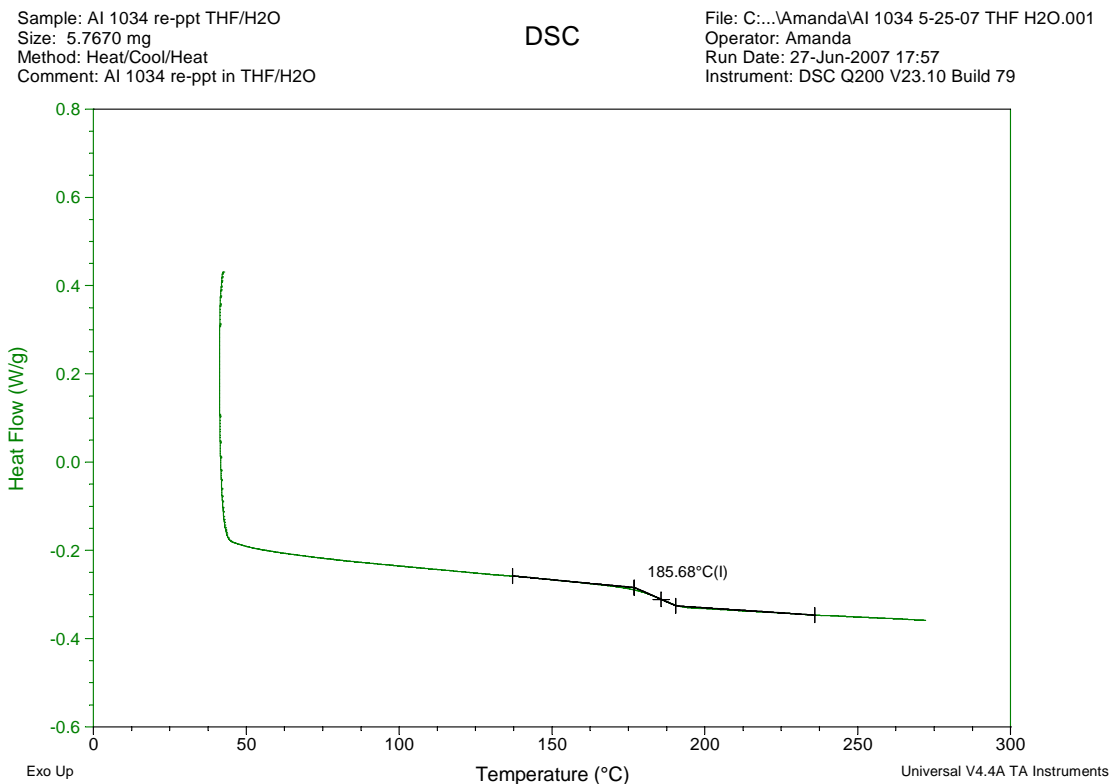


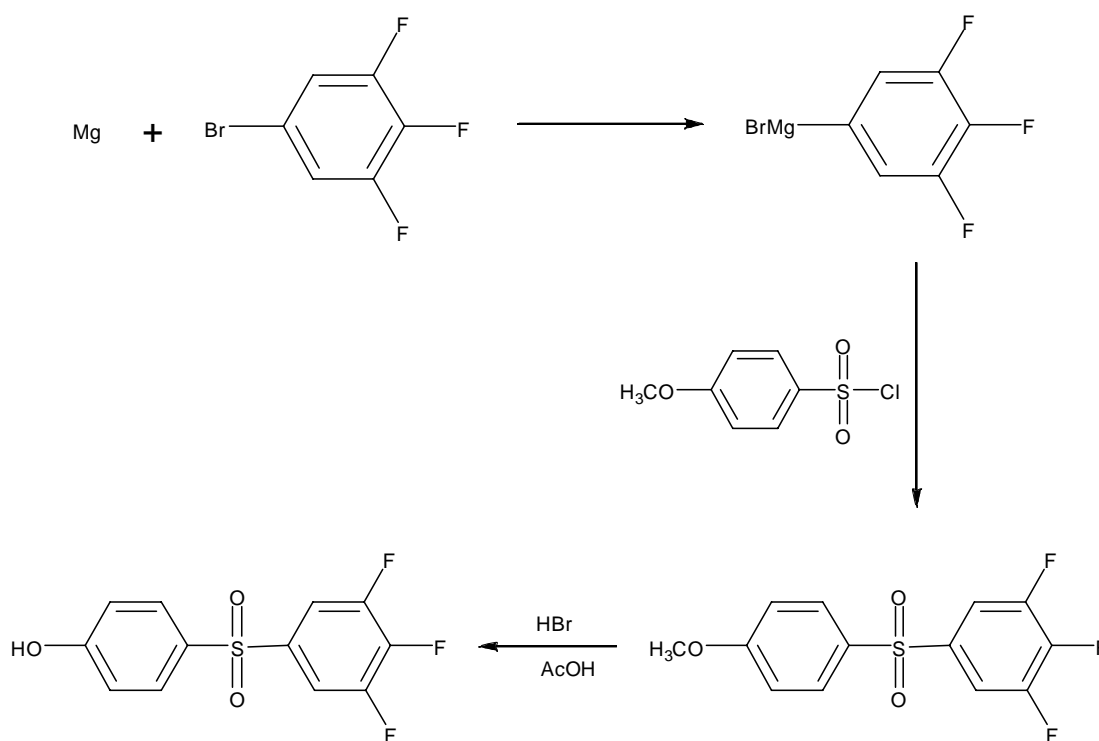
Figure 12. DSC trace for an AB₂ phosphoryl polymerization at 120 °C.

Synthesis of Monomer 3a

Due to the limited success in tailoring branching using AB₂-type structures, a monomer was designed to have significantly different reactivities of the electrophilic sites. The synthesis of 4-(3,4,5-trifluorophenylsulfonyl)phenol, **3a**, is outlined in Scheme 12. The reaction of 1.0 equivalent of 3,4,5-trifluorophenylmagnesiumbromide with 1.5 equivalents of 4-methoxybenzene sulfonyl chloride in tetrahydrofuran provided the corresponding monomer precursor, **3b**, in 31.5% yield after recrystallization from ethanol/water. Subsequent deprotection of the phenol group using HBr followed by a recrystallization from methanol afforded **3a** in 28.7% yield as transparent, cylindrical crystals. Analysis by ¹H, ¹³C, and ¹⁹F NMR along with GC/MS and elemental analysis

confirmed its structure. The ^1H NMR and ^{19}F NMR spectra are shown in Figures 13 and 14, respectively.

The ABB'B'' monomer, 3,4,5-trifluoro-4'-hydroxydiphenyl sulfone, **3a**, is a hybrid of the previous AB₂ and ABB' systems of the Fossum group, where the B groups are of the same functionality but all three have different reactivities. It is assumed that the *para*-position will be the most reactive based on basic chemistry principles and the *meta*-positions would seem to be of equal reactivity, at least initially. However, just as in the previous AB₂ systems, once substitution of one electrophilic site has occurred, the reactivity of the remaining sites will change.



Scheme 12. Synthesis scheme for the preparation of the ABB'B'' sulfone monomer, **3a**.

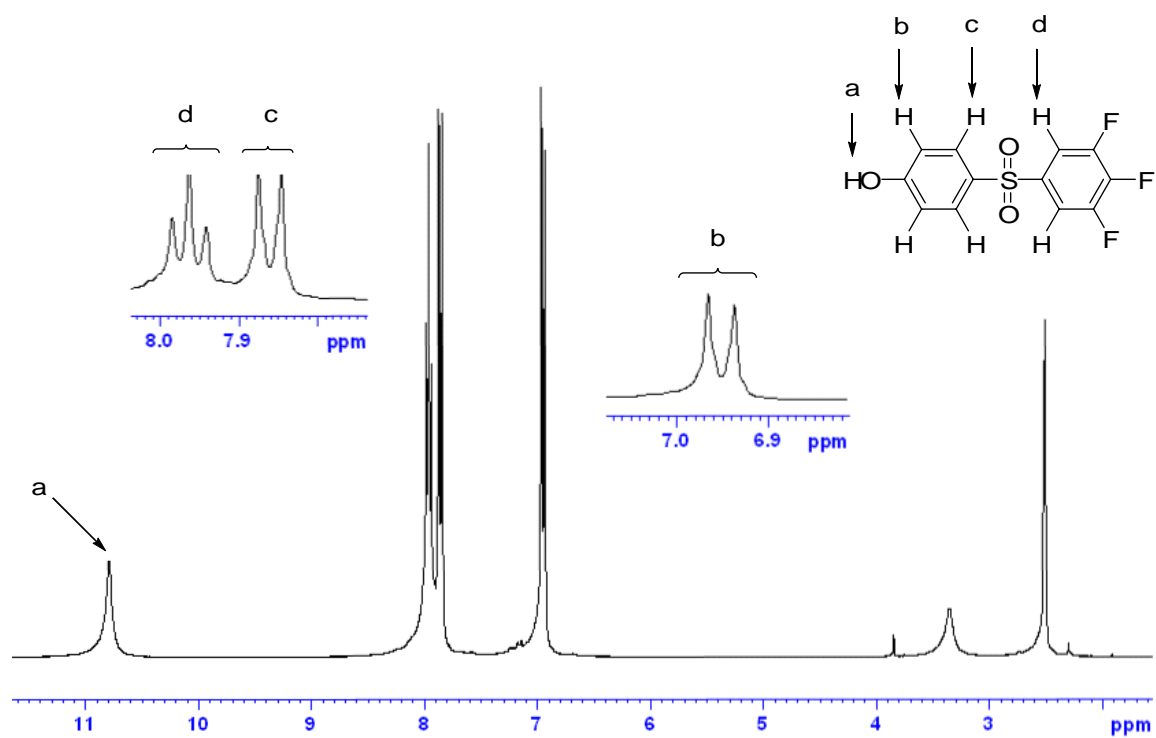


Figure 13. ^1H NMR spectrum of monomer **3a**.

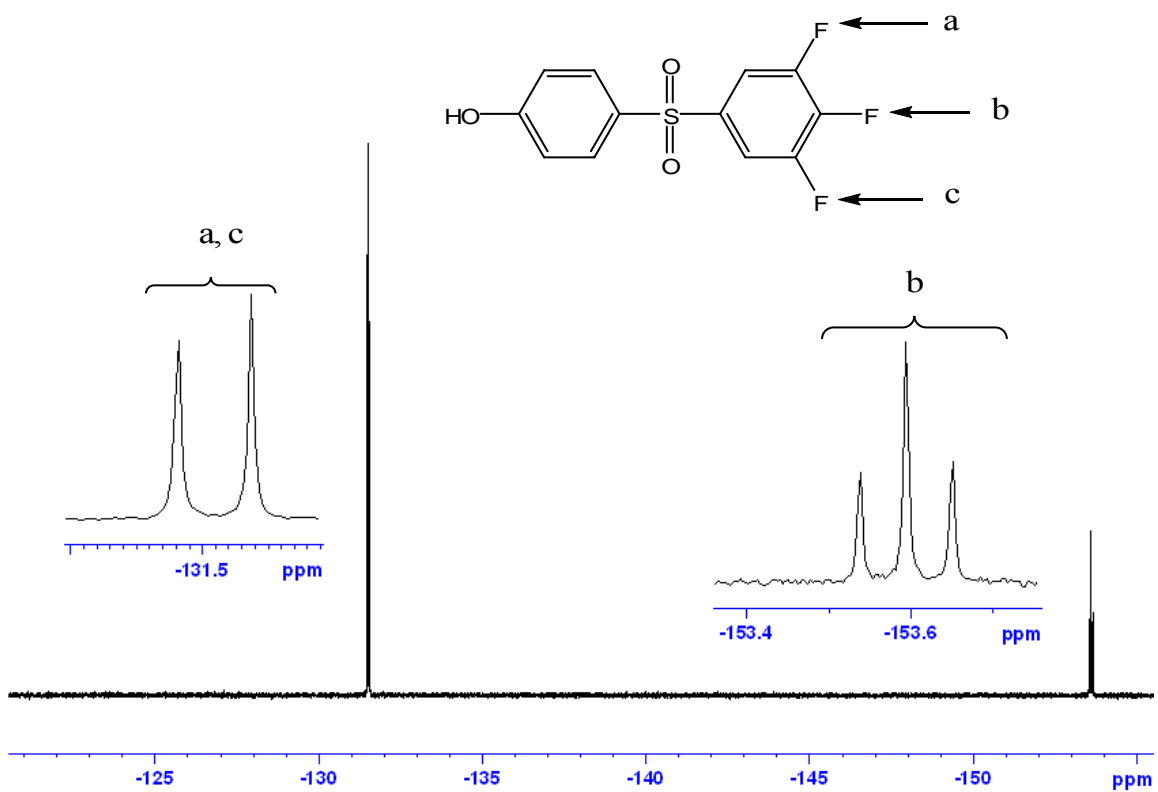


Figure 14. ^{19}F NMR spectrum of monomer 3a.

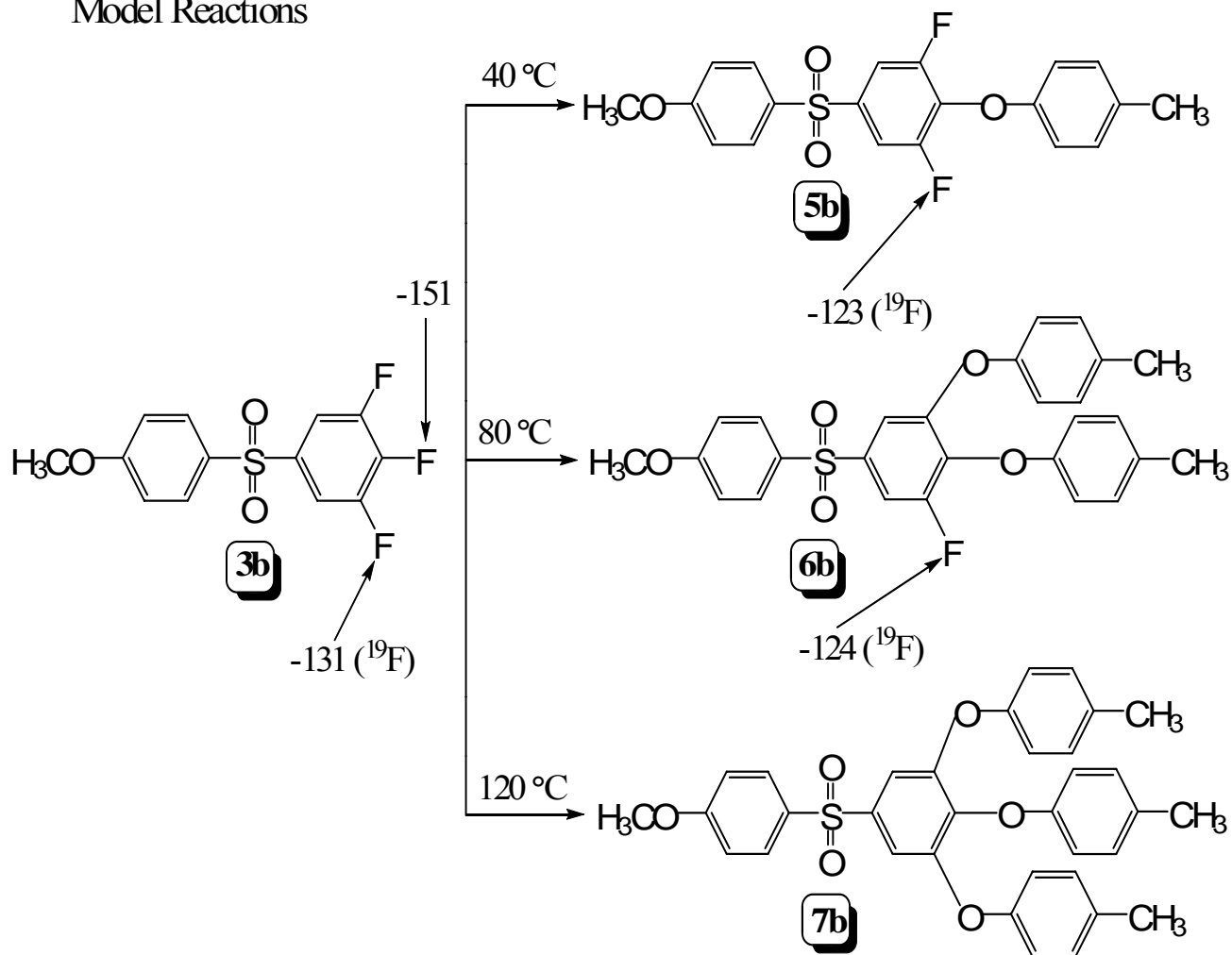
Electrophilic Strength and Reactivity of ABB'B'' sulfone

Model reactions were used to determine the relative reactivity of the electrophilic sites for monomer **3b** as shown in Scheme 13. In these reactions, 1 equivalent of **3b**, along with 1 equivalent of *p*-cresol, were reacted with K₂CO₃ and NMP at various temperatures to produce the corresponding mono-substituted product, **5b**. The ¹⁹F NMR spectra for the model compounds are shown in Figure 15.

The ¹⁹F NMR chemical shifts of this system can provide a guide of relative reactivity for the electrophilic sites. The unsubstituted ABB'B'' monomer shows a ¹⁹F NMR chemical shift of -151 ppm for the *para*-position and a ¹⁹F NMR chemical shift of -131 ppm for the two fluorine atoms in the *meta*-positions. The monosubstituted ABB'B'' monomer produced only a single ¹⁹F NMR chemical shift at -123 ppm which could only result from substitution that was solely at the *para*-position leaving the two identical fluorine atoms in the *meta*-positions untouched. The ¹⁹F upfield shift indicates an increase in electrophilic strength of the ipso carbon, therefore making the fluorine more likely to leave via substitution.

Upon further reaction with another equivalent of *p*-cresol, at 80 °C, the *di*-substituted model compound, **6b**, was produced. A ¹⁹F NMR chemical shift of -124 ppm is observed for the remaining fluorine atom in the *meta*-position. The slight upfield shift in the ¹⁹F resonance indicated a marginal decrease in the electron density present on the *ipso* carbon atom, therefore making the fluorine less likely to leave via substitution. With another equivalent of *p*-cresol and a temperature increase to 120 °C, virtually all of product was the tri-substituted compound, **7b**, as determined by GCMS analysis.

Model Reactions



Scheme 13. Model reactions of ABB'B'' sulfone system.

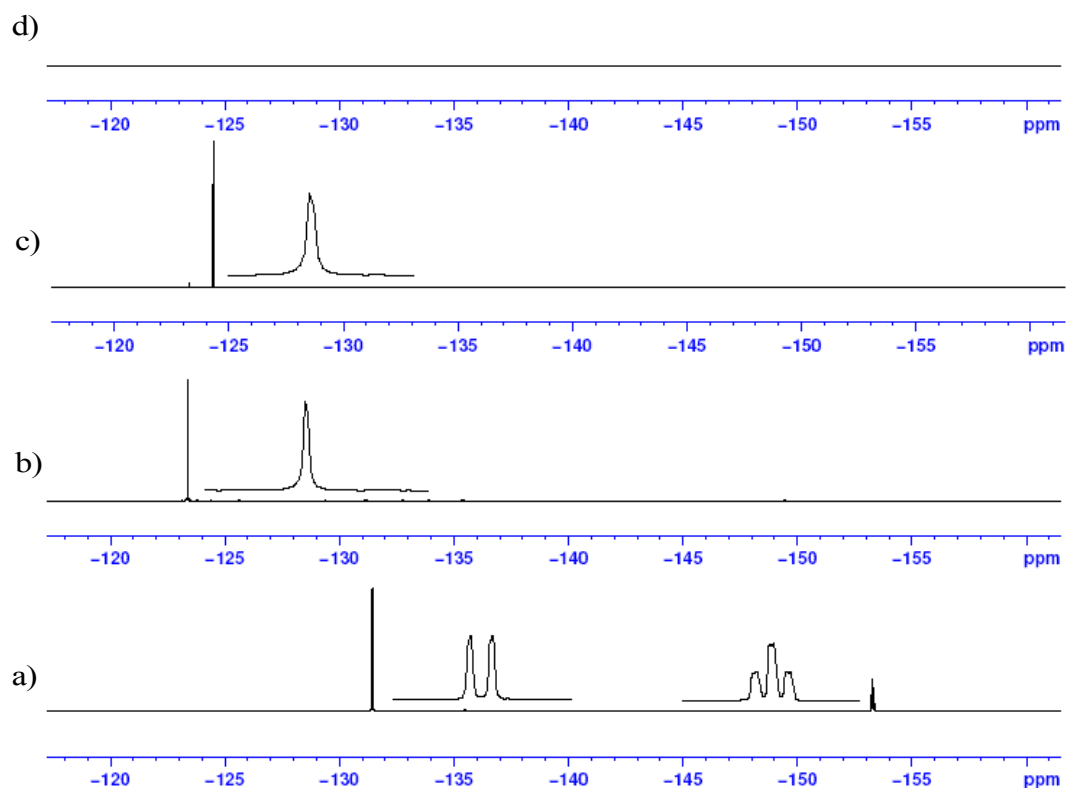
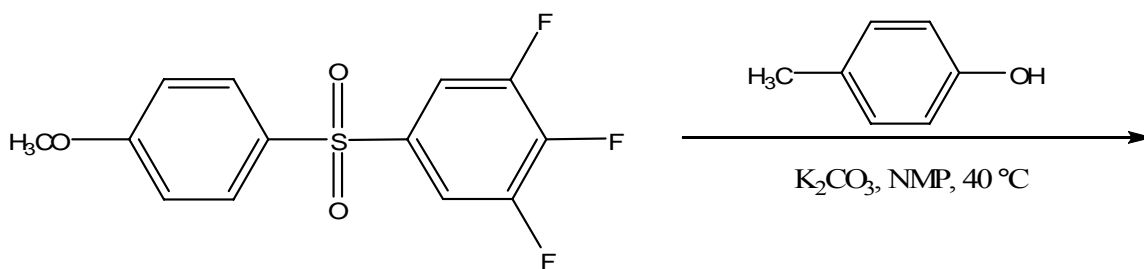


Figure 15. ^{19}F NMR spectra for a) unsubstituted b) monosubstituted c) disubstituted and d) trisubstituted model compound.

Determination of Activation Energies for ABB'B'' sulfone

NMR spectroscopy has been used to probe the reactivity of AB_2 sulfone and phosphoryl systems and also in the ABB'B'' sulfone system. While this is a good indication of the relative reactivity of the electrophilic sites in the system, it is really only to be used as a guide in determining reactivity. A better technique is to actually determine the E_a values kinetically with model compound reactions. The model reaction is shown below in Scheme 14.



Scheme 14. A model reaction of the ABB'B'' system to determine E_a .

The activation energy for the reaction with monomer **3b** was determined by performing a series of reactions at 50, 60 and 70 °C, with *p*-cresol, under typical nucleophilic aromatic substitution conditions. Since this reaction is assumed to be second order, then $[A] = [B]$, and the rate of the reaction is, $\text{rate} = k[A][B]$ or $\text{rate} = k[A]^2$. A linear plot can then be constructed as $1/[A]_t$ vs. time in which the slope of this line will be k , the rate coefficient of the reaction of the first electrophilic site. As stated previously, three reactions, each at different temperatures were conducted in order to produce three rate constants for the first electrophilic site. In each reaction, aliquots were taken at appropriate times and the concentration of monomer, $[A]$, was determined via GCMS analysis. Figure 16 shows the plot of $1/[A]$ vs. time for the three reactions. The slope of each of these lines gave a rate constant, k , which can then be used to determine the E_a of the first electrophilic site. A second plot of the natural log, \ln , of the rate coefficient, k , vs. $1/T$ (K) of each reaction afforded a linear plot whose slope is equivalent to $-E_a/R$. This plot is shown in Figure 17. The equation was then solved to find the E_a for the first electrophilic site of monomer **3a**, which was determined to be 18 kcal/mol.

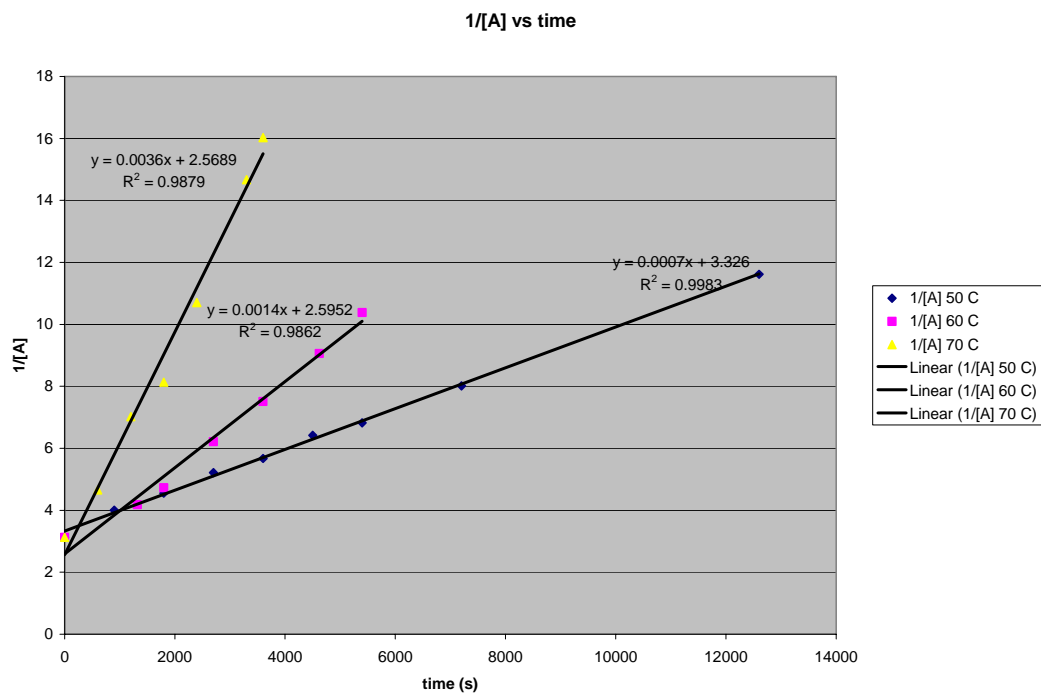


Figure 16. Plot of $1/[3b]$ vs. time (sec.) for reaction of **3b** at 50, 60 and 70 °C.

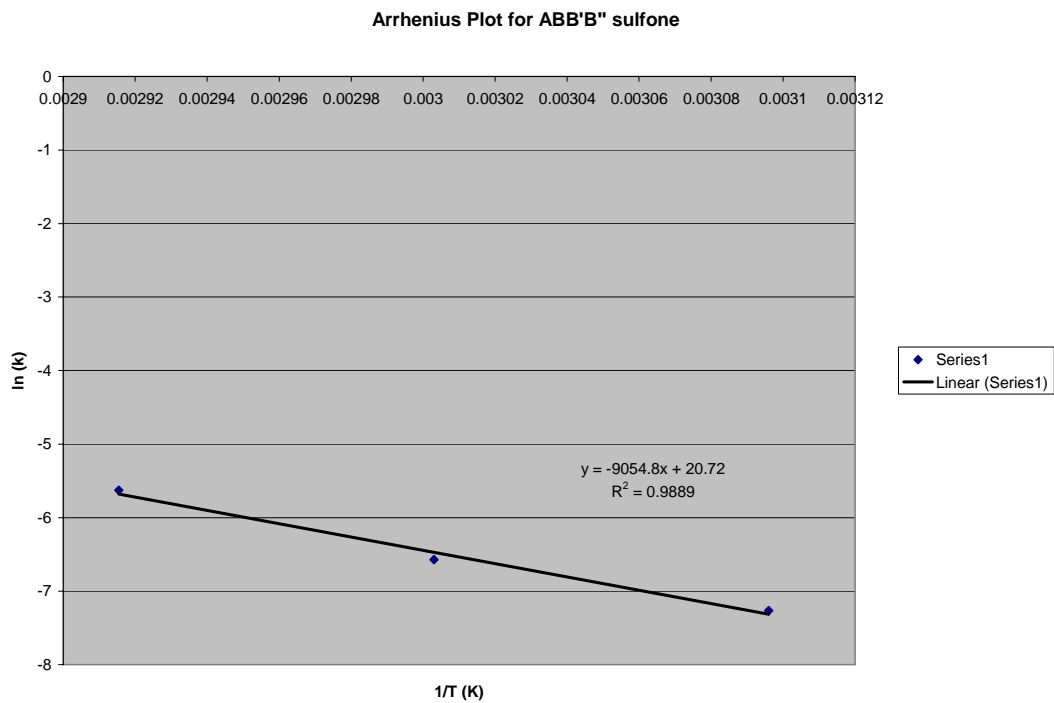


Figure 17. Arrhenius plot for **3b**.

The ability to tailor the branching in poly(arylene ether)s rests on the inherent differences in the reactivity of the electrophilic sites. Determination of the E_a for the electrophilic sites in the methoxy protected analogues allows the ratios of rate constants for linear growth versus branching growth to be estimated according to equation 4.

$$k_1/k_2 = e^{[-(E_{a1}-E_{a2})/RT]} \quad (4)$$

As an example of the utility of this equation, if values of 25 and 30 kcal/mol are employed for the E_a 's of the first and second electrophilic sites, respectively, the ratio of k_1/k_2 at 180 °C is approximately 250. Plots of the ratios of rate constants for different values of E_a at a number of different temperatures are shown in Figure 18.

Unfortunately, the E_a for the second site in **3b** has not yet been determined.

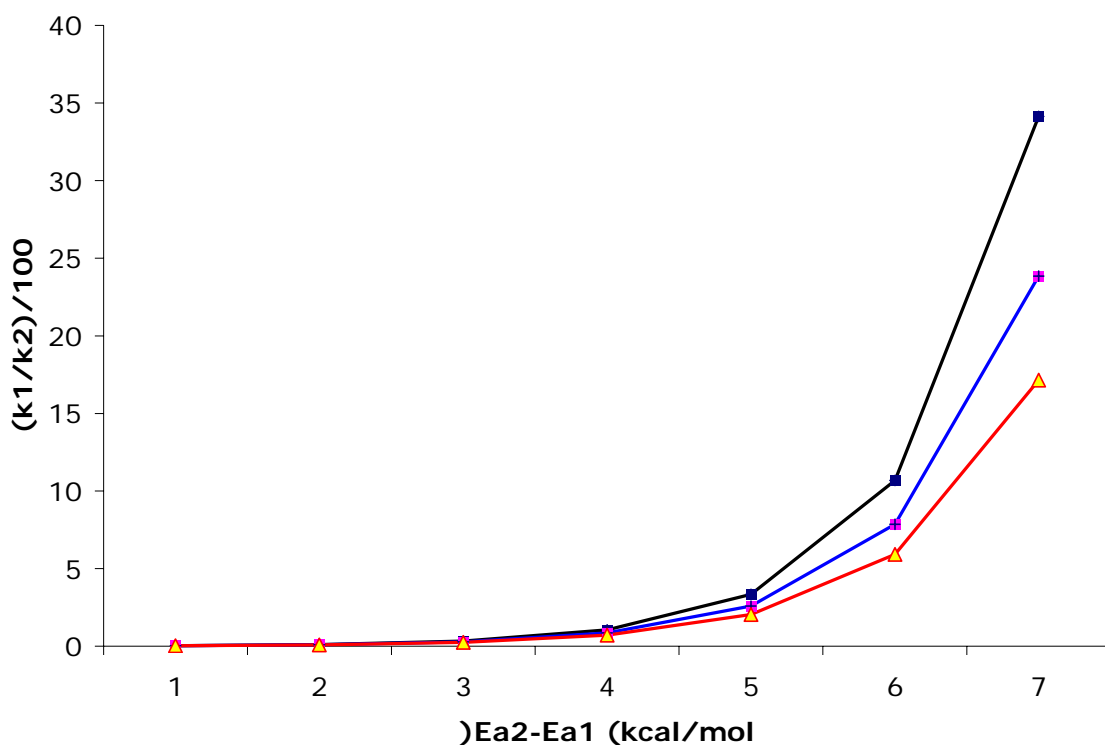
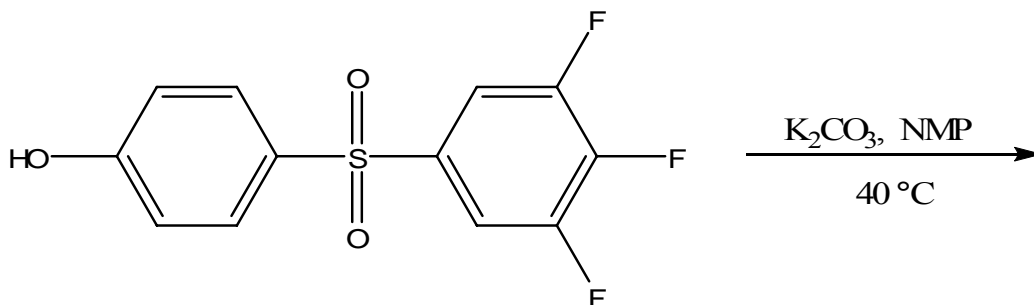


Figure 18. Plot of k ratios vs. difference in E_a .

The ABB'B'' monomer was reacted under typical nucleophilic aromatic substitution conditions, without a core molecule, unlike the previous AB₂ systems. A general ABB'B'' polymerization is shown in Scheme 15. Polymerization reactions were carried out at temperatures ranging from 40 to 200 °C in NMP and from 80 to 200 °C in DMSO. The 200 °C reaction was a microwave reaction as opposed to the typical heating with an oil bath. The reaction was monitored by removing aliquots both during and after the polymerization reaction for analysis by GPC to determine molecular weight and PDI. In order to maintain a consistent solvent polarity, azeotropic drying was not conducted on these systems as in the previous AB₂ systems. The result of these polymerizations is shown in Table 3.



Scheme 15. Polymerization of ABB'B'' sulfone monomer.

The DB values for the ABB'B'' systems shows a similar trend as with the AB₂ systems, where DB increases with increasing temperature. However, in the ABB'B'' system, the range of values for the DB is much greater than in the previous systems, showing that this system is more sensitive to temperature changes. The T_g values, glass transition temperatures, also show a trend in which the T_g decreases as the branching increases.

Table 3: ABB'B'' sulfone polymerization data

Reaction	Temperature	Solvent	[M]	M _n	PDI	% Yield	DB	T _g
1	40	NMP	0.32	8,328	7.162	95.2	0	219.82
2	80	NMP	0.32	7,930	7.452	91.8	0.182	218.59
3	120	NMP	0.32	11,778	3.074	88.4	0.348	207.99
4	160	NMP	0.32	13,543	3.092	82.5	0.415	207.72
5	200	NMP	0.32	7,121	1.885	93.7	0.434	195.49
6	80	DMSO	0.32	11,942	2.052	96.4	0.264	213.26
7	120	DMSO	0.32	9,009	2.114	95.1	0.311	209.44
8	160	DMSO	0.32	8,968	1.804	91.2	0.467	206.55
9	200	DMSO	0.32	7,086	1.463	89.6	0.589	195.6

Viscosity values would also be useful in determining the branching in a system.

As stated previously, linear systems have relatively higher viscosity values than do their branched counterparts. By measuring the viscosity of a series of polymers, a trend in branching, or lack thereof, could be determined. Although in this case we are unable to obtain exact viscosity values, a trend in viscosity can be determined using the relationship between the RI (Refractive Index) and DP (Differential Pressures) of the polymers in the ABB'B'' system. A plot of the RI values, used to measure concentration, is shown in Figure 19 and a plot of DP values is shown in Figure 20. Typically, as the RI plots remain constant in a series of polymers, the DP values should decrease to show a decrease in viscosity. By taking the ratio of DP to RI and plotting this ratio vs. temperature, we are able to see a trend in our ABB'B'' system in which it shows the viscosity of the ABB'B'' polymers is decreasing as the reaction temperature increases. This is yet another piece of

evidence to confirm that branching is increasing in this system, with increasing reaction temperature. The plot of DP/RI vs. temperature is shown in Figure 21.

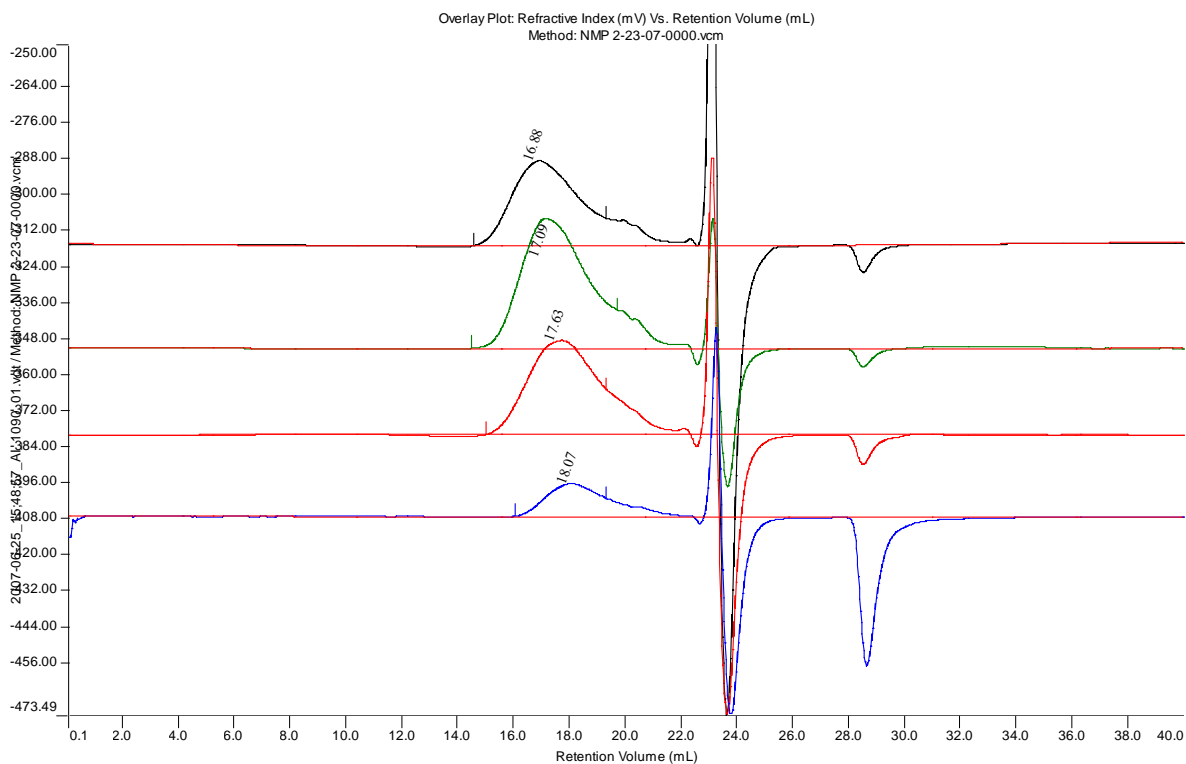


Figure 19. SEC overlay of ABB'B'' polymerizations at 80 °C (black), 120 °C (green), 160 °C (red) and 200 °C (blue) in DMSO.

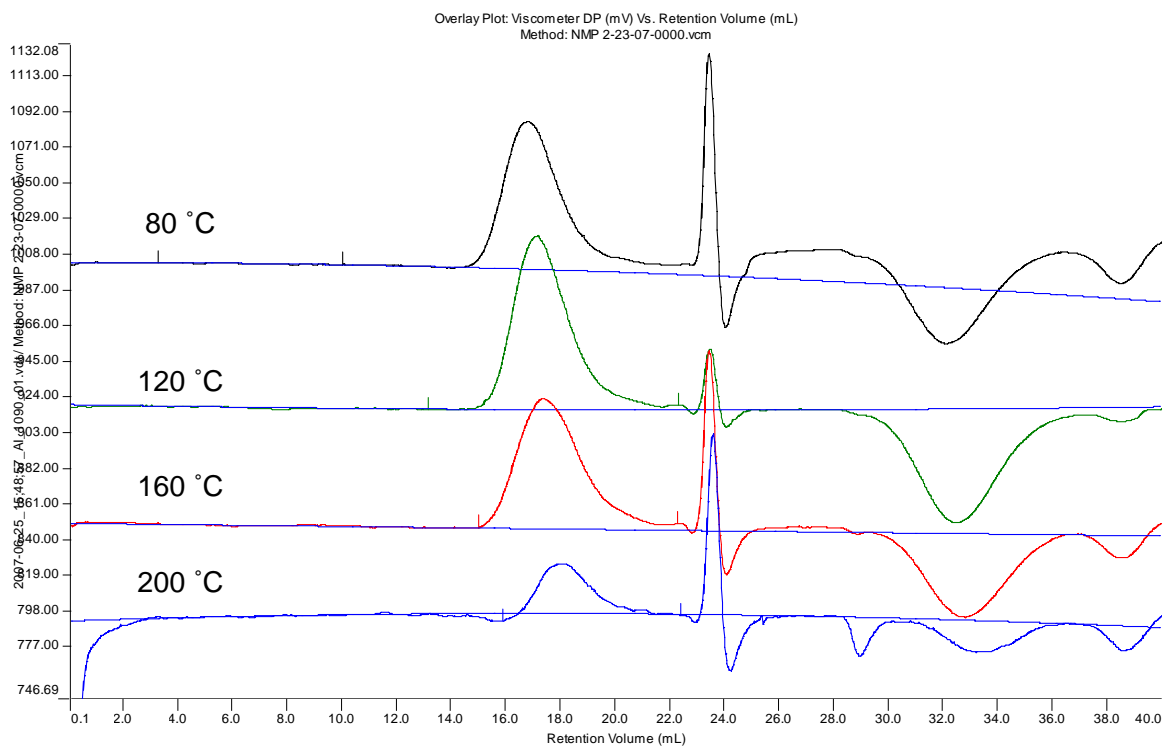


Figure 20. SEC traces showing viscosity values for ABB'B'' polymerizations in DMSO.

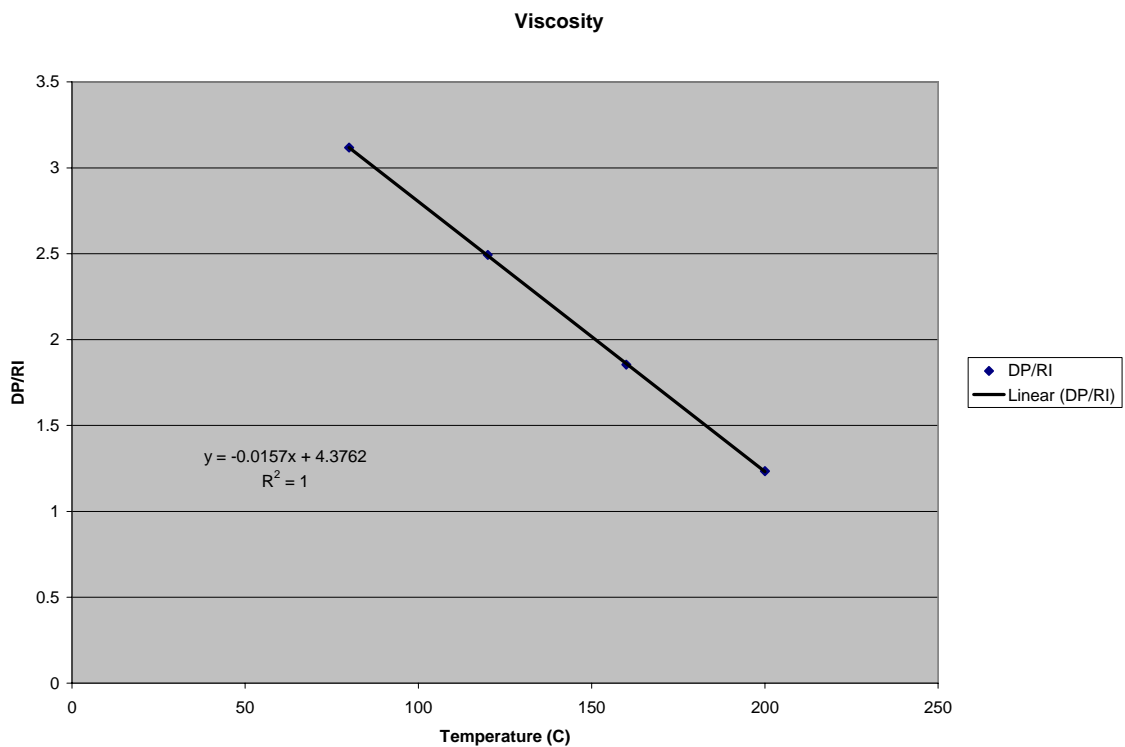


Figure 21. The relationship between viscosity and temperature.

Thermal Analysis of an ABB'B'' sulfone system

Differential scanning calorimetry, DSC, was again the thermal analysis of choice in this system in order to determine the glass transition temperatures, T_g , of the ABB'B'' sulfone system. An overlay of the DSC traces for an ABB'B'' sulfone is shown below in Figure 22. It is apparent in these traces that as the reaction temperature increases the glass transition temperature is decreasing.

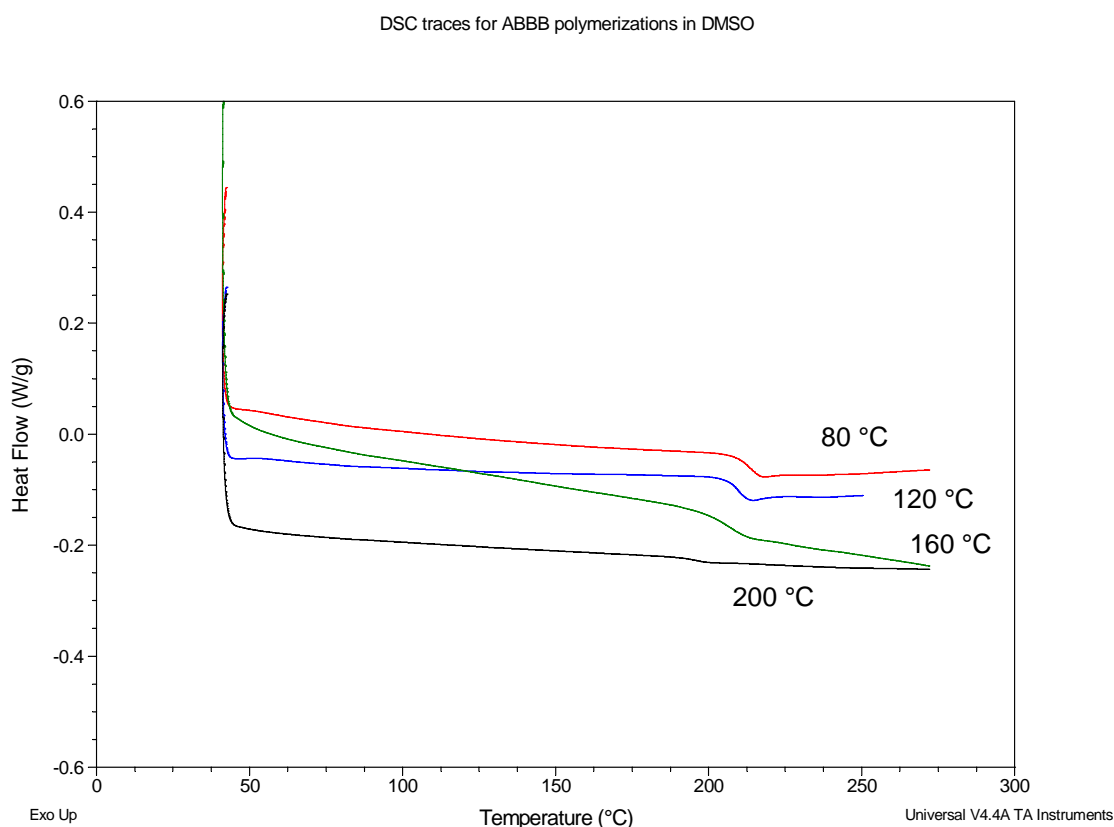


Figure 22. A DSC overlay plot of the ABB'B'' polymerizations in DMSO.

Degree of Branching

The degree of branching within these systems was determined via NMR spectroscopy. The degree of branching, DB, of each polymerization was determined via NMR studies by calculating the number of, linear and dendritic units in the

polymerizations. The sulfone polymer samples were subjected to ^1H , ^{13}C and ^{19}F NMR studies to confirm their structures and provide degree of branching information, while the phosphoryl polymer samples were subjected to ^1H and ^{31}P NMR. For the ABB'B'' sulfone systems, in NMP and DMSO, the NMR samples were obtained in two different solvents, DMSO-*d*6 and CDCl_3 in order to obtain the best spectrum in order to integrate peaks for DB calculations. The ^{19}F NMR spectra for these polymers, using two different solvents for NMR spectroscopy, CDCl_3 and DMSO-*d*6 are shown below in Figures 23-26. The NMR spectra obtained using CDCl_3 were chosen to calculate DB values due to the ease of integrating the appropriate peaks.

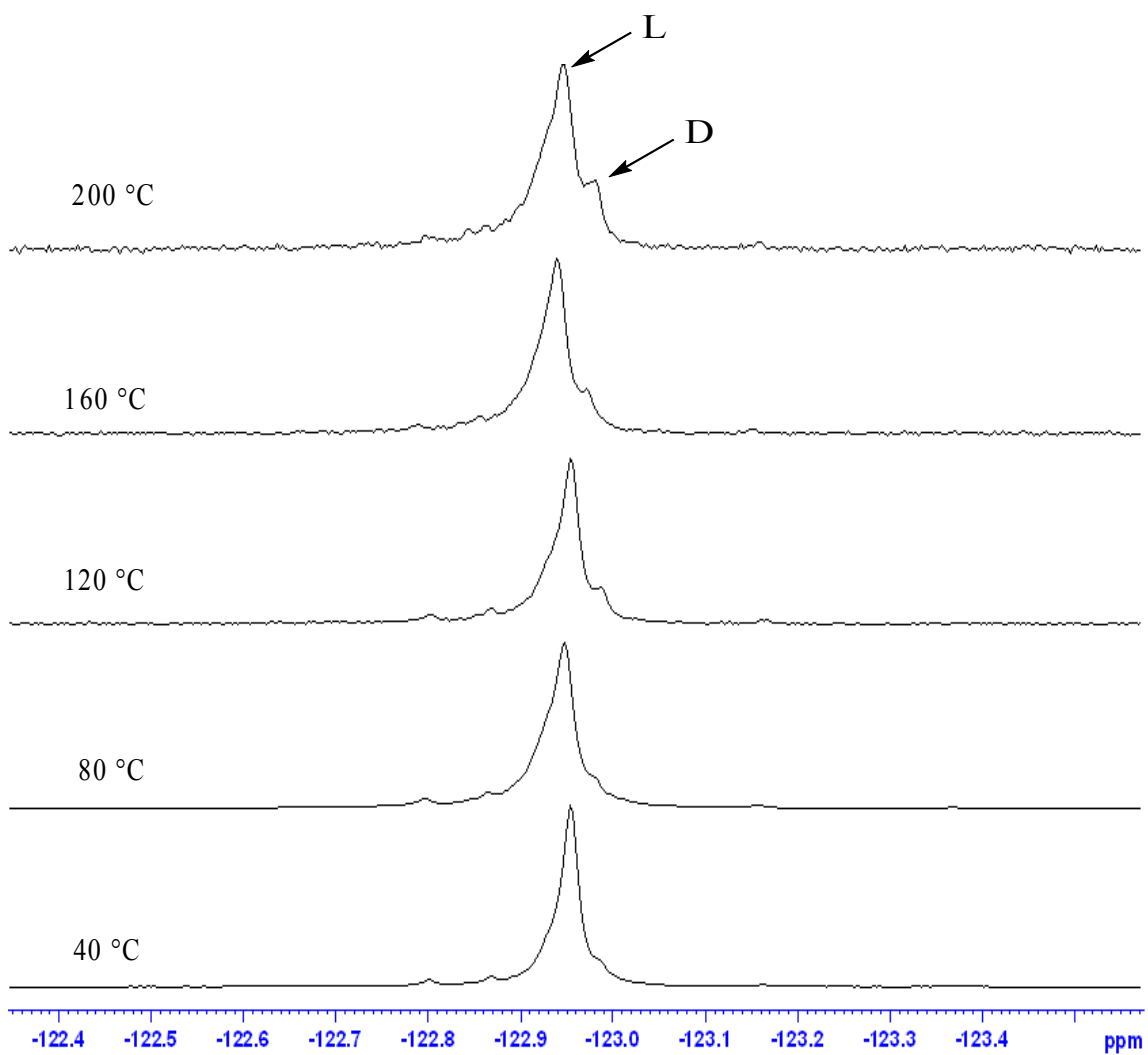


Figure 23. ^{19}F NMR of ABB'B'' sulfone polymerizations in NMP using DMSO- d_6 .

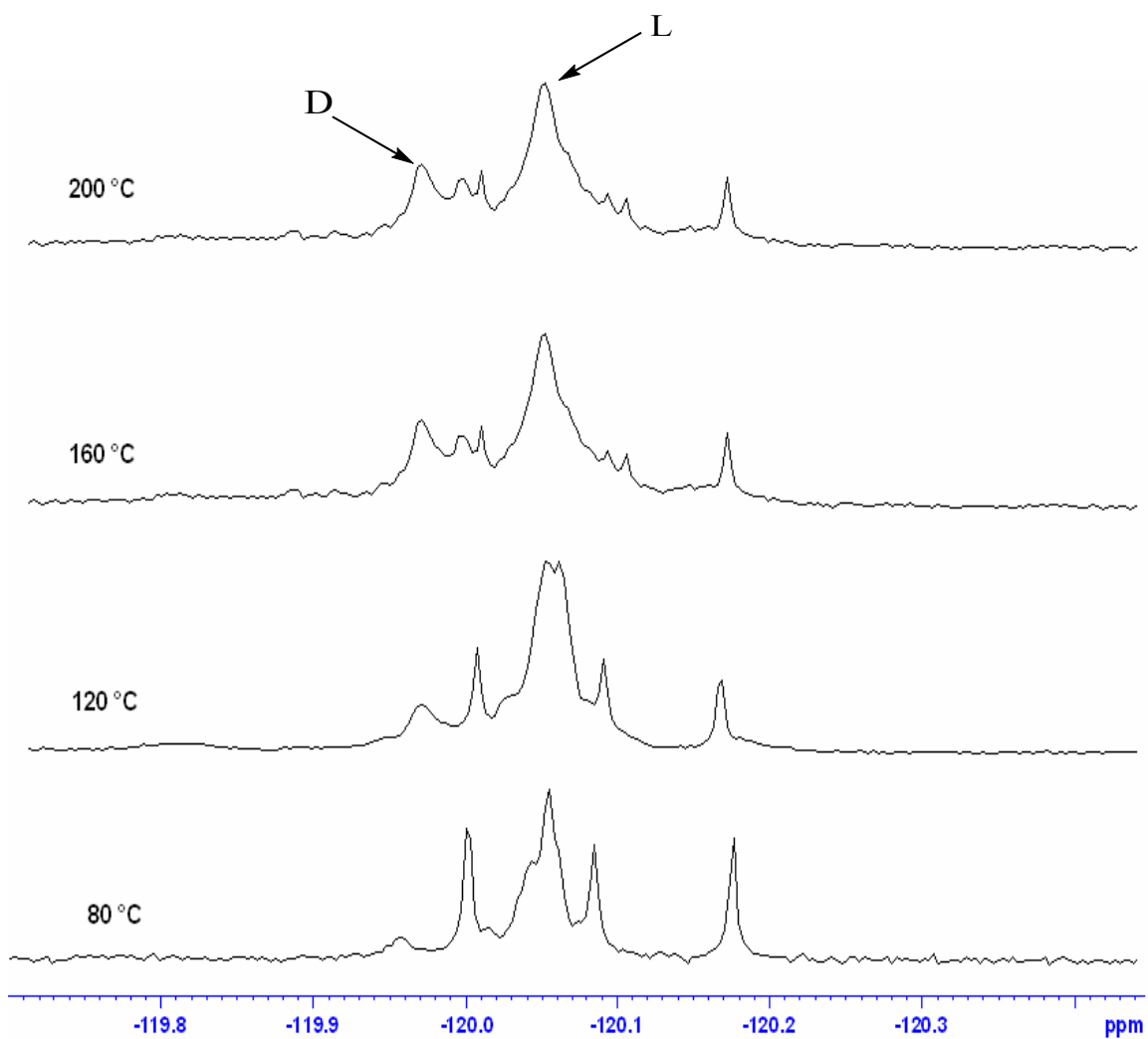


Figure 24. ^{19}F NMR of ABB'B'' sulfone polymerizations in NMP using CDCl_3 .

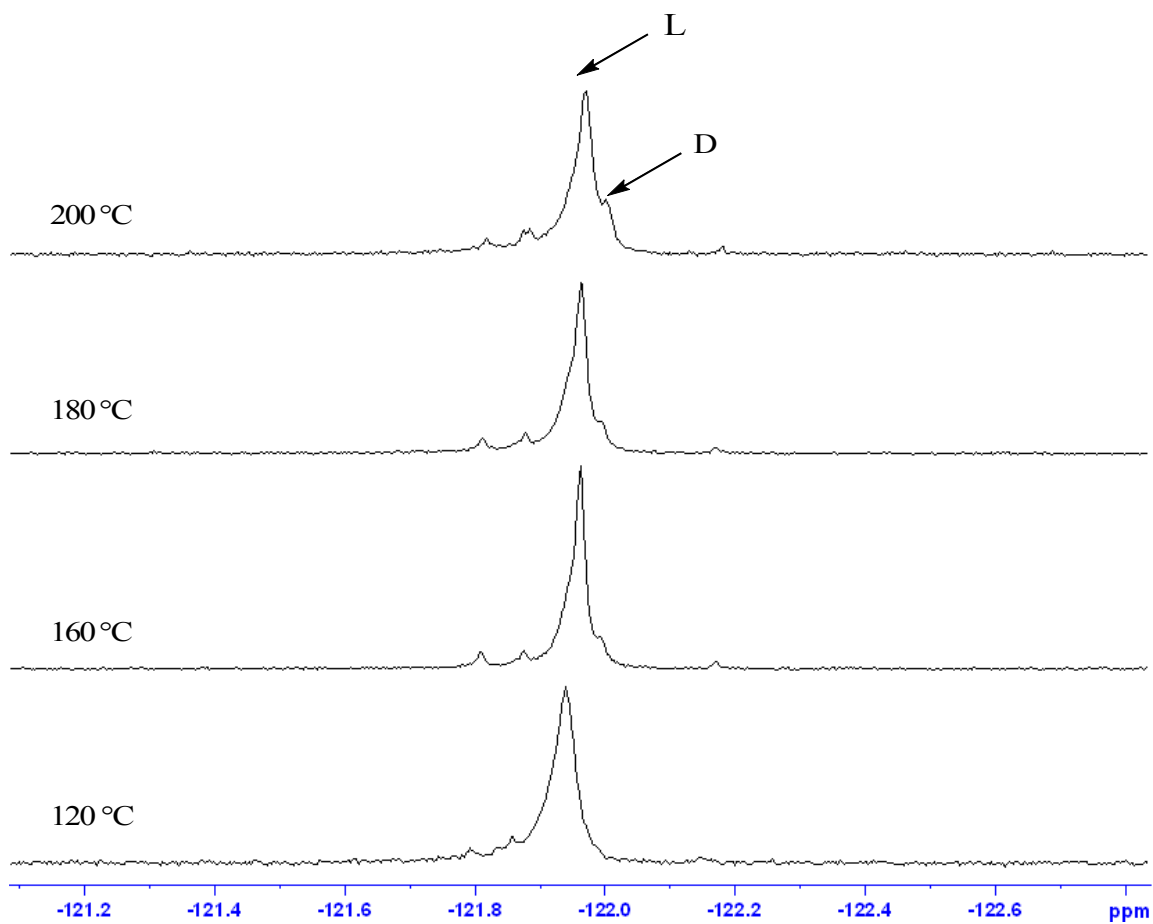


Figure 25. ^{19}F NMR of ABB'B'' sulfone polymerizations in DMSO using DMSO-*d*₆.

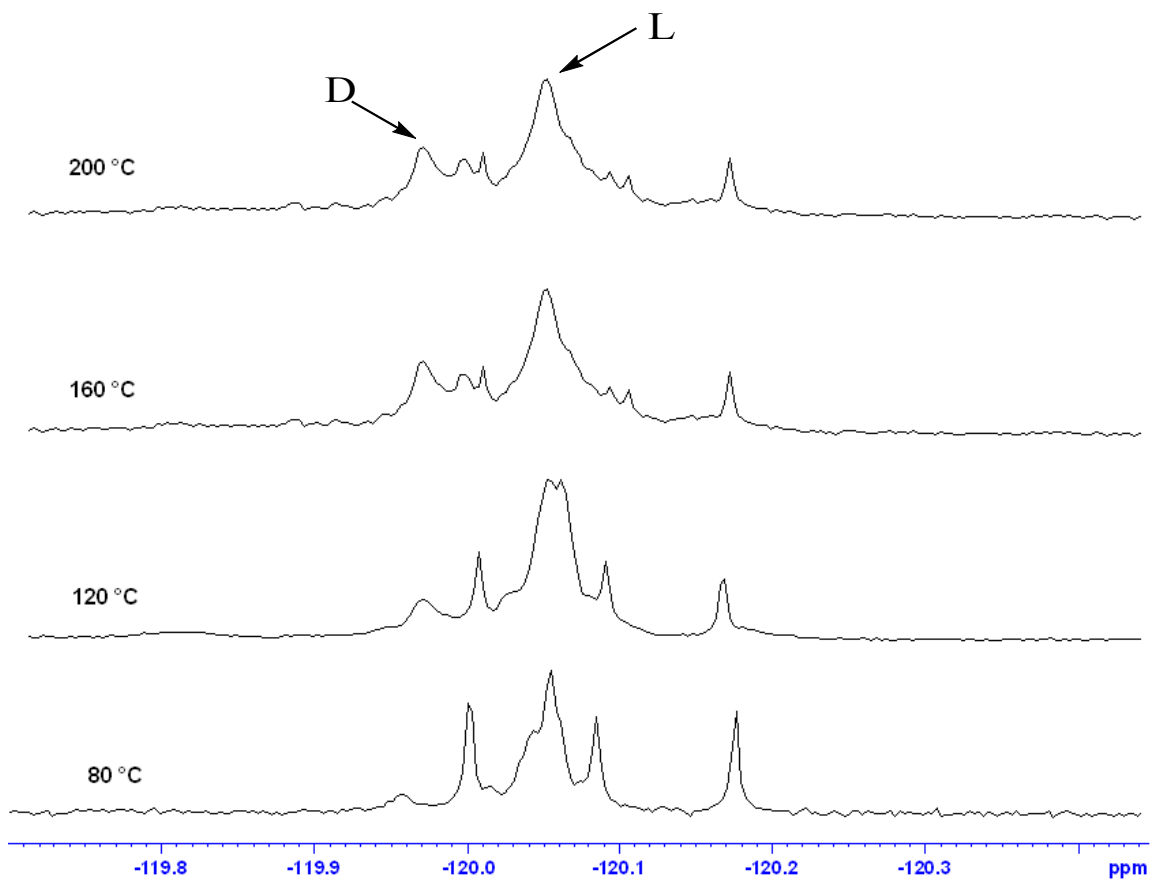


Figure 26. ^{19}F NMR of ABB'B'' sulfone polymerizations in DMSO using CDCl_3 .

Conclusions

The degree of branching in hyperbranched poly(arylene ether) systems can be varied by changing the reaction temperature. These polymerization reactions show a trend in which degree of branching increases with increasing temperature, without significant change in molecular weight. The ABB'B'' sulfone system is much more sensitive to changes in temperature than the AB₂ sulfone and phosphoryl systems. Both ¹³C and ¹⁹F NMR spectroscopy are sufficient guides to determine relative reactivity in these monomer systems. Determining activation energies of electrophilic sites will be the greatest measure of reactivity in these systems and will enable predictions about branching in polymer systems to be made. The ability to control DB in these systems results in an ability to control the number of end-groups in the polymer. The endgroups in these branched polymers can then be modified for specific applications. Studies directed toward determining the effect of degree of branching on the thermal and mechanical properties of these systems are currently underway.

Future Work

The evaluation of kinetic parameters in these polymer systems will continue, specifically with the determination of the E_a value for the second electrophilic site in the ABB'B'' sulfone monomer. Upon determining this value, a better understanding of the true reactivity of this monomer and the ability to control the branching in this system will be obtained. Reactions to obtain the E_a values for AB₂ monomers will also be carried out.

In producing branched polymers, endgroup modification is an important aspect that must be studied in order to determine how these modifications will affect polymer

properties. Endgroup modification reactions for each system will be carried out and analyzed using SEC and NMR spectroscopy. Investigations into the exact viscosity values for polymers will also be underway.

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