Exploration of Gradient-Type Poly(arylene ether)s via an Abb' Monomer System

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EXPLORATION OF GRADIENT-TYPE POLYARYLENE ETHERS VIA AN ABB’ MONOMER SYSTEM

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

By

ALEX DOLGOV
B.S., Wright State University, 2006

2008
Wright State University
WRIGHT STATE UNIVERSITY
SCHOOL OF GRADUATE STUDIES

August 30, 2008

I HEREBY RECOMMEND THAT THE THESIS PREPARED UNDER MY SUPERVISION BY Alex Dolgov ENTITLED Exploration of Gradient-type Poly(arylene ether)s via an ABB' Monomer System BE ACCEPTED IN PARTIAL FULFILLMENT OF THE REQUIREMENTS FOR THE DEGREE OF Master of Science.

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ABSTRACT

Dolgov, Alex. MS., Department of Chemistry, Wright State University, 2008. Exploration of Gradient-type Poly(arylene ether)s via an ABB' Monomer System.

Evidence shows that a gradient like copolymer can be synthesized using nucleophilic aromatic substitution, NAS, chemistry. Using the 4-chloro-3-fluoro-4’hydroxydiphenylsulfone monomer, 5, it is possible to control the ratios of the leaving groups, in this case the fluorine and the chlorine, with the right solvent and temperature. Alternating the temperatures will alter the substitution of the leaving groups, thus forming a polymer backbone of gradient characteristics. Initial reactions to determine the relative rates of displacement of the chlorine and fluorine atoms were carried out using a model compound, 1, which possessed the chlorine and fluorine leaving groups, but not the phenol group. Determining the pattern of leaving group substitution was characterized using $^1$H and $^{13}$C NMR spectroscopy.
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INTRODUCTION

There are a variety of different copolymers being synthesized and used on a daily basis. Some examples of these copolymers are block, alternating, random, gradient, and graft:

![Copolymer Structures](image)

**Figure 1.** Various types of copolymer systems. Listed from the top to the bottom, alternating, random, block, and graft copolymer\(^{14}\).

In a general sense, a block copolymer rapidly transitions from one monomer unit to another. An alternating copolymer alternates every other monomer unit. A random copolymer is synthesized without any structure, and thus is very difficult to predict the monomer sequence. A graft copolymer is a type of branched copolymer, containing branched monomer units that differ from the polymer backbone. Gradient copolymers gradually transition from one monomer unit to the other.

It is also important to understand the underlying principles and common methods of copolymerization synthesis techniques. Step growth polymerization and Chain growth polymerization are two novel synthesis techniques that will be further analyzed along with a few of the different copolymer structures.

In order to understand how polymers are formed, it is essential to first understand how monomer units react with one another. By a general definition of a “copolymer,” it can be considered a product of synthesis of two different monomers, each of which should be able to separately form a homopolymer under suitable reaction conditions\(^{5}\). When two monomers X\(_1\)
and \( X_2 \) are combined in the same vessel and reacted in the presence of an initiator, there are a variety of possibilities of how these monomers will react with one another\(^5\):

1) A homopolymer mixture is formed exclusively from either \( X_1 \) or \( X_2 \).

2) A statistically random copolymer mixture containing \( X_1 \) and \( X_2 \) in the chain. The copolymer will form in the same proportion as with the addition of monomer.

3) An alternating copolymer mixture, where the monomer units alternate in a standard order \( X_1X_2X_1X_2X_1 \).

4) An extreme intermediate copolymer adapting the structures from either the second or third scenario\(^5\). These would include block, graft, and gradient copolymers.

Numerous studies have indicated that monomer units of different reactivities do not favor cross-propagation reactions\(^5\). Therefore, random copolymers have a tendency of forming easiest when the comonomers are similar as reactive species\(^5\). Relative reactivities are controlled by resonance stabilization and polarity. In terms of resonance stabilization, an unstable radical will favor the reaction with a resonance stabilized monomer instead of unstable monomer. Also a resonance stabilized terminal radical will prefer to add to an unstable monomer\(^5\).

**“Q-e” Scheme**

Much of the influence of copolymerization reactions come from the resonance and polar stabilization effects, but the extent of these effects is different for every copolymerization.

Alfrey and Price attempted to quantify the different extents by developing the “Q-e” scheme\(^8\). In the cross propagation reaction:

\[
( \cdots M_i + M_2 \rightarrow \cdots M_2 ) \tag{1}
\]

The relationship amongst the variables was translated to the following equation:

\[
K_{12} = P_1Q_2e^{-e_1e_2} \tag{2}
\]
The variables were identified as such: P is the characterization of the radical state, Q is a measure of the monomer reactivity, and e₁ and e₂ represent the polarization characteristics of the radical and the reacting monomer⁵. In order to relate all monomers, it was essential to find a reference point or a standard of sort. In the end, styrene was selected as the universal standard for this purpose with Q=1 and e=-0.8⁵. The Q and e scheme provides a guide to how monomers will behave while they undergo polymerization reactions. Monomers with similar Q and e values have a tendency to undergo ideal polymerization reactions, whereas in contrast, alternate copolymer synthesis is favored when the Q values are alike, but even more significant, the e values are high and of the opposite sign⁵. The series of qualitative values are listed below in Table 1.

**Table 1.** Monomers and their corresponding Q and e values⁵.

<table>
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<tr>
<th>Monomers</th>
<th>Q</th>
<th>e</th>
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<tr>
<td>Acrylamide</td>
<td>1.120</td>
<td>1.19</td>
</tr>
<tr>
<td>Acrylic Anhydride</td>
<td>1.270</td>
<td>0.51</td>
</tr>
<tr>
<td>Acrylonitrile</td>
<td>0.600</td>
<td>1.20</td>
</tr>
<tr>
<td>1,3-Butadiene</td>
<td>2.390</td>
<td>-1.05</td>
</tr>
<tr>
<td>iso Butylene</td>
<td>0.033</td>
<td>-0.96</td>
</tr>
<tr>
<td>Iso Butyl vinyl ether</td>
<td>0.023</td>
<td>-1.77</td>
</tr>
<tr>
<td>Carbon monoxide</td>
<td>0.100</td>
<td>3.76</td>
</tr>
<tr>
<td>p-Cyanostryre</td>
<td>1.610</td>
<td>0.30</td>
</tr>
<tr>
<td>Cyclohexene</td>
<td>0.002</td>
<td>-1.44</td>
</tr>
<tr>
<td>Ethylene</td>
<td>0.015</td>
<td>-0.20</td>
</tr>
<tr>
<td>Fumaronitrile</td>
<td>0.800</td>
<td>1.96</td>
</tr>
<tr>
<td>Iodene</td>
<td>0.360</td>
<td>-1.03</td>
</tr>
<tr>
<td>Isoprene</td>
<td>3.330</td>
<td>-1.22</td>
</tr>
<tr>
<td>Maleic anhydride</td>
<td>0.230</td>
<td>2.25</td>
</tr>
<tr>
<td>Methyl acrylate</td>
<td>0.420</td>
<td>0.60</td>
</tr>
<tr>
<td>Methyl methacrylate</td>
<td>0.740</td>
<td>0.40</td>
</tr>
<tr>
<td>α-Methylstyrene</td>
<td>0.980</td>
<td>-1.27</td>
</tr>
<tr>
<td>Styrene</td>
<td>1.000</td>
<td>-0.80</td>
</tr>
<tr>
<td>Vinyl acetate</td>
<td>0.026</td>
<td>-0.25</td>
</tr>
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For example, Fumaronitrile (Q = .8 and e=1.96) will form an alternating copolymer with α-Methylstyrene (Q=.980 and e= -1.27).

**Gradient Copolymers**

Gradient Copolymers are a novel class of polymers which started to grab the attention of the scientific community in the early 1990s. With the development of controlled radical polymerization, gradient copolymer research began to flourish. Their unique nature allows 2 or more monomer units to continuously mix and merge with one another, transitioning from one monomer unit into another. More specifically, a gradient copolymer can be defined as a copolymer in which the instantaneous composition varies continuously along the chain contour. This characteristic of course differs from the previously discussed polymers. The synthesis of gradient copolymers is done through controlled living radical polymerization. This technique employs the significant chain breaking reactions that lead to heterogeneity in both composition and molecular weight. There are several techniques amongst controlled radical polymerizations. Amongst those, Atom Transfer Radical Polymerization is the most versatile, practical, and inexpensive method. Fundamental understanding of controlled radical polymerization and Atom Transfer Radical Polymerization is the key to understanding the theory behind gradient copolymers.

Generally speaking, there are two common methods in preparing a gradient copolymer. One method is called the “one-pot” copolymerization, in which the monomer units with different reactivity ratios are combined in one reaction vessel and spontaneously form a gradient structure. The structure of the gradient copolymer depends on the reactivity ratios of the two
monomers, creating a drawback to this method. If the reactivity ratios of the two monomers are similar, a statistical or random copolymer will be created\textsuperscript{4}. Another method of preparation is called a forced gradient copolymerization\textsuperscript{13}. This technique incorporates controlled feeding of one or more monomer units to the reaction vessel, guiding the copolymers into a tailored gradient structure along the polymer backbone\textsuperscript{4}. Force gradient copolymerization is thus a more suitable and practical method of gradient polymer synthesis because it incorporates a wider range of monomers.

**Chain Growth vs. Step Growth Polymerization**

Chain-growth polymerization is known to be one of the most common ways to synthesize polymers\textsuperscript{8}. It can be characterized by a rapid chain reaction of self-addition of monomer units to one another\textsuperscript{14}. In chain growth polymerization, the monomer undergoes the reaction in the presence of an initiator\textsuperscript{15}. The initiator is what continually produces growth centers in the reaction mass, adding monomer units more rapidly onto the polymer chain. Once the reactive center has been generated by the initiator, many of the monomer units quickly attach themselves in a chain reaction to generate a high-molecular-weight polymer\textsuperscript{8}. The sequential addition of monomer molecules to growing centers is the main distinction amongst chain and step growth polymerization\textsuperscript{15}. Monomer units are consumed throughout the course of the polymerization reaction as more chains become initiated and rapidly produce high molecular weight\textsuperscript{8}. Due to the rapid reactivity of chain growth polymerizations, molecular weight of the polymer stabilizes and does not change as the reaction continues. However, the percent conversion of monomer to polymer increases with time of the polymerization\textsuperscript{8}. During the course of chain growth
polymerization, the reaction mixture can contain any of the following components: monomer, growing chain, high molecular weight polymer, and left over initiator.

Step Growth polymerization is characterized by a polymer building up throughout the reaction between the functional groups of the monomers. Unlike chain growth polymerization that occurs quickly, step growth reactions proceed in a step-like fashion with the growth of the polymer being rather slow. The more steps that take place during the synthesis, the higher molecular weight will be. Amongst many available syntheses: addition, condensation, amidation, and ester-interchange remain the most commonly used reactions in step growth polymerization. One of the prominent effects of these reactions is the loss of small molecules.

Polycondensation

Polycondensation can be explained as a reaction in which two monomer units that possess two or more reactive functional groups, condense with one another. A simple reaction capable of demonstrating polycondensation is one of ethylene glycol and adipic acid. If one equivalent of each of the reactants is used, the product will form a monoester as illustrated below.

\[
\text{HOCH}_2\text{CH}_2\text{OH} + \text{HOOCH}_2\bigg(\text{CH}_2\bigg)_4\text{COOH} \rightarrow \text{HOCH}_2\text{CH}_2\text{OOCC}\bigg(\text{CH}_2\bigg)_4\text{COOH} + \text{H}_2\text{O}
\]

Note that the product contains two more reactive groups, one on each end, and can further undergo polycondensation with the hydroxyl group or carboxyl reacting with another equivalent of ethylene glycol or adipic acid. The outcome of this reaction will yield the product as shown in Scheme 2.
The product maintains 2 functional end groups, and can undergo further polymerization upon addition of more ethylene glycol or adipic acid producing a higher molecular weight polymer\(^8\). A generalization for the overall reaction can be depicted by Scheme 3.

**Scheme 3**

\[
\begin{align*}
\text{n HOCH}_2\text{CH}_2\text{OH} + \text{n HOOCH}_2\left(\text{CH}_2\right)_{4}\text{COOH} & \rightarrow \\
\text{HOOC}_2\left(\text{CH}_2\right)_{4}\text{COOCH}_2\text{CH}_2\text{OOC}_2\left(\text{CH}_2\right)_{4}\text{COOCH}_2\text{CH}_2\text{OH} + (2n - 1) \text{H}_2\text{O}
\end{align*}
\]

General guidelines for polycondensation or any step growth polymerization reactions can be summarized by four basic principles:

1. Monomers must have at least two reactive functional groups in order for polymerization to occur\(^8\).

2. Polymerization takes place via a step-wise reaction mechanism between the reactive functional units\(^8\).

3. At any time, polymer synthesis occurs by only one type of reaction amongst the functional groups\(^8\).

4. Once the functional groups react, the polymer still has 2 reactive functional end groups\(^8\).

Gradient copolymers on the other hand, have not been synthesized using step growth or chain growth polymerization but rather controlled radical polymerization.
Controlled Radical Polymerization

Controlled Radical Polymerizations (CRP) are radical polymerizations that have the ability of being terminated and re-initiated by external control\textsuperscript{4}. Within the CRP systems, chain breaking reactions are almost insignificant, because they are suppressed to negligible levels\textsuperscript{3}. Achieving such suppression requires a dynamic exchange between small quantities of active propagating radicals and their dormant species\textsuperscript{6}. Propagation or bimolecular termination reactions do not occur with the dormant species because they lack an active radical site. Suppressing chain-breaking reactions within controlled radical polymerization will result in uniform growth progression of the polymer chain\textsuperscript{6}. One of the most common, inexpensive and effective methods of CRP for synthesizing gradient copolymers is Atom Transfer Radical Polymerization (ATRP). The initial step of the ATRP is the activation of the alkyl halide through a reversible abstraction of the halogen by a transition metal complex to form a radical species, and thus beginning the polymerization\textsuperscript{3}. The halogen abstraction step is reversible, hence a dynamic equilibrium is created between the active, propagating radical site, and the dormant halogen-capped species\textsuperscript{3}. Inside this equilibrium, the rate of activation, $k_a$, is much smaller than the rate of deactivation, $k_d$, the chains remain in their dormant states\textsuperscript{3}. As in a usual radical polymerization, the radical species will propagate, and terminate ($k_p$, $k_t$)\textsuperscript{3}. In an interesting observation, the segment of the terminated chains is drastically smaller than those of the dormant species, and thus this system shows much similarity to living polymerization\textsuperscript{3}. The most frequent gradient copolymers are synthesized using styrene, or styrene derivatives along with butadiene\textsuperscript{12}. Although gradient copolymers are predominantly synthesized using ATRP, it may be possible to synthesize a gradient like polymer using an alternative method such as controlled polycondensation.
Controlled Polycondensation

An interesting topic of exploration is controlled polycondensation. Controlled polycondensation systems can create new polymeric structures with beneficial applications, as well as provide valuable information for other scientific studies\textsuperscript{30}. These reactions possess unique characteristics which can be particularly useful in the industrial process. As opposed to naturally occurring condensation reactions that form an ideally monodisperse polymeric system, synthetic polycondensation reactions behave in a different manner. Synthetic polycondensation systems possess very subtle deviation between the reactivity of the monomer unit and the polymer chain\textsuperscript{30}. Therefore, the only way to obtain control of these polycondensation reactions is to increase the reactivity of the polymer chain while decreasing the reactivity of the monomer\textsuperscript{30}. This would result in a chain growth characteristic by supporting the reaction of the monomer and the growing polymer chain\textsuperscript{30}. A general representation of a “chain-like step growth polymerization” is illustrated in Figure 2\textsuperscript{30} below.

\[ R^* + X\text{--}Y \rightarrow R\text{--}X\text{--}Y^* \]

\[ R\text{--}X\text{--}Y^* \quad nX\text{--}Y \rightarrow R\text{--}X\{\text{--}XY\}_n\text{--}Y^* \]

**Figure 2.** A general representation of a “chain-like step growth polymerization”

\( R^* \) represents the initiator or a core molecule, which is a very reactive species that initially undergoes a rapid reaction with the X unit\textsuperscript{30}. When the initiator \( R^* \) reacts with the X units, the Y unit on the complex becomes more reactive than the Y unit on the monomer. Once the growing chain undergoes activation by the initiator, the growing chain is more likely to react with a monomer, than a monomer is to react with a monomer unit\textsuperscript{30}.  

9
Evidence for controlled polycondensation or “chain-growth polycondensation” reactions has been proposed by Yokozawa, by preparation of polyamides using an initiator\(^{22-23}\). The Yokozawa group used phenyl 4-aminobenzoate derivatives to demonstrate the properties of chain-growth polycondensation reactions. The polymerization is possible by introducing an initiator to the system. The initiator reacts first with a monomer species, increasing the reactivity of the monomer, which proceeds to react with the growing polymer chain as opposed to another monomer\(^{30}\). The reaction done by Yokozawa is illustrated in Scheme 4 below:

Scheme 4

As proposed the initiator initially reacts with the desilylated monomer species\(^{30}\). The initiator has a very strong electron withdrawing group making it much more reactive than the monomer with a strong electron donating aminyl anion\(^{30}\). For this reason, the monomer prefers to undergo a reaction with the initiator instead of another monomer species. The reaction will proceed in a chain like fashion with the radical-monomer species reacting with the growing chain rather than
another monomer by converting the strong electron donating aminyl anion of the monomer species into the weak electron donating amide group of the growing polymer chain\textsuperscript{30}.

**The ABB’ polymer system**

The ABB’ system is a unique and interesting area of polymer science not widely studied by the scientific community. Within the ABB’ system, all of the A and B functional groups are going to be contained in one monomer\textsuperscript{31}. The unique characteristic of this system is that the B groups may or may not be identical leaving groups but they must have the same functionality on the monomer. The B groups possess different reactivity ratios based on their location on the monomer\textsuperscript{31}. This can lead to competitive behavior amongst the B leaving groups\textsuperscript{31}. Competition amongst the B groups can be controlled by factors such as temperature and solvent. The ABB’ system tends to form in a relatively linear manner, leading to more chain entanglements and better mechanical properties\textsuperscript{31}. Scheme 5 illustrates a general representation of the ABB’ polymer system.

**Scheme 5**

Some studies on ABB’ systems have been done by Wang, Jikei, and Kakimoto, who were able to synthesize polyamides using ABB’ monomers\textsuperscript{31}. The purpose of their ABB’ system was to be
able to control the degree of branching of the polymer with varying conditions. Scheme 6 illustrates the synthesis of ABB’ monomer to produce a polyamide polymer.

**Scheme 6**

\[
\begin{align*}
&\text{HOOC} \quad \text{O} \quad \text{NH}_2 \\
&\quad \text{H}_2\text{N}
\end{align*}
\]

1. DBOP
2. TEA
3. NMP

**Nucleophilic Aromatic Substitution**

Nucleophilic aromatic substitution is a two step reaction process. The reaction is much favored by electron withdrawing substituents on the benzene ring to decrease the electron density and ease the approach of a nucleophile. The mechanism advances by the rate determining step of the electron rich nucleophile attacking at the site of substitution, such as an aryl halide, forming a negatively charged Meisenheimer complex allowing the ipso carbon to temporarily bond with the nucleophile. The resonance stabilized intermediate eliminates the halide species in the second step and rearomatizes the benzene ring.

**Scheme 7**

\[
\begin{align*}
&\text{Y} \\
&\text{EWG}
\end{align*}
\]

\[
\begin{align*}
&\text{X}^- \\
&\text{EWG}
\end{align*}
\]

Meisenheimer Complex
Activation Energies ($E_a$) and Electrophilic Strengths

Polycondensation reactions using nucleophilic aromatic substitution must be controlled by following a few fundamental principles. One of these principal parameters is finding electrophilic strengths using $^{13}$C NMR and $^{19}$F NMR to determine chemical shifts. The other important parameter is determining the activation energies ($E_a$) of each of the electrophilic sites.

Important investigations of B$_2$ monomers were conducted by Carter in order to determine the electrophilic strengths of aromatic difluoride B$_2$ monomer compounds that contained electron withdrawing groups in the para positions$^{31}$. NMR spectroscopy was used to determine the electron withdrawing effect of the aryl fluoride substituents because aryl fluorides are activated to undergo nucleophilic aromatic substitution$^{31}$. Inductive and resonance effects were generated due to the substituents developing a positive charge in the ortho or para position$^{33}$. The positive charge built up by the aryl fluoride was easily detected by $^{13}$C and $^{19}$F NMR, making these instrumental methods very sensitive indicators of electron density of the ipso carbon that correlated to the electrophilic site to undergo nucleophilic aromatic substitution$^{31}$. Using $^{13}$C NMR, Carter found the chemical shifts of the electrophilic sites. The electrophilic site in the para position to the electron withdrawing group of the difluoride B$_2$ monomer that underwent polymerization was found in the region of 164.5 to 166.2 ppm$^{33}$. $^{13}$C NMR was also used to determine the chemical shift of the same site in fluorobenzene which was 162.8 ppm$^{30}$. Therefore, due to an electron withdrawing group in the para position, the chemical shift of the ipso carbon is pushed downfield, making the monomer more reactive and susceptible to nucleophilic aromatic substitution.

However, NMR spectroscopy only provides chemical shifts as an estimate for the
electrophilic site. A specific method must be used to obtain more precise data for reactivity of
the electrophilic site by determining the activation energy ($E_a$) which directly relates to the rate
coefficient for the reaction\textsuperscript{31}. The general figure for plots of $k_1/k_2$ for various differences in $E_a$ at
temperatures of 160, 180, and 200°C is shown in Figure 3.

![Figure 3](image)

**Figure 3.** Plots of $k_1/k_2$ for various differences in $E_a$ at temperatures of 160, 180, and 200°C

**Current Project**

The primary focus of the experiments reported here is to synthesize a polymer of gradient
characteristics using controlled polycondensation. It is essential to pick a monomer unit that has
$AB\text{'-type}$ functionality. Typically $AB_2$ and $ABB'$ monomers are used to form branch like
polymers by undergoing substitution at both sites with various reaction conditions. A unique
monomer must be used that possesses different competing B and B' functional groups that
substitute only at one or the other site and proceed to polymerize in a linear manner.
The 4-chloro-3-fluoro-4’hydroxydiphenylsulfone monomer, 5, is an ideal system that possesses all of the right characteristics to apply these data to prepare a gradient type copolymer using nucleophilic aromatic substitution. Compound 5 possesses qualities of the ABB’ system where the chlorine and the fluorine have the same functionality on the monomer. However, unlike other ABB’ monomer systems, these functional groups are not only in different positions on the benzene ring, but possess vastly different reactivities.

![Chemical Structure](image)

**Figure 4.** The 4-chloro-3-fluoro-4’hydroxydiphenylsulfone monomer, 5.

The interesting thing about the compound 5 system, is the positions of the leaving groups. The leaving groups activate the electrophilic site, or the ipso carbon, by pulling electron density toward themselves, making the ipso carbon prone to nucleophilic aromatic substitution. The monomer should essentially polymerize in a linear manner by favoring substitution at only one or the other electrophilic site.
EXPERIMENTAL

Reactant Materials and Solvents:

Unless otherwise noted, all reactions were carried out under a nitrogen atmosphere, and all transfers were done via syringe. The 1-bromo-4-chloro-3-fluorobenzene and 1-bromo-3,4-difluorobenzene were ordered from Fluorochem, and used as received. The 4-methoxy-benzene sulfonyl chloride, benzene sulfonyl chloride, and para-cresol were purchased from Aldrich. Para-cresol was purified by distillation, benzene sulfonyl chloride was purified via distillation, and 4-methoxy-benzene sulfonyl chloride was used as received. Dimethyl sulfoxide (DMSO) and N-methyl-pyrrolidinone (NMP) were dried over and distilled from calcium hydride. Toluene and Tetrahydrofuran (THF) were dried over and distilled from sodium metal.

Instrumentation:

A Hewlett Packard HP 6890 Series GC system, along with a Hewlett Packard 5973 Mass Selective Detector and Agilent 6890 Series Injector were used to acquire the GC/MS data. A Bruker AVANCE 300 MHz instrument was used to acquire $^1$H and $^{13}$C NMR spectra at 300 and 75.5 MHz, respectively. A Viscotek Model 300 TDA instrument was used for all GPC sample analyses. Polymer Laboratories 5 micrometer PL mixed C columns were used with 0.5% LiBr NMP as the eluent. A Thermoseparation Model P1000 pump was used operating at a rate of 0.8 mL/min.
Synthesis of 4-chloro-3-fluorodiphenylsulfone, 1

The procedure for the synthesis of 4-chloro-3-fluorodiphenylsulfone was followed as reported by the Fossum group.\textsuperscript{33}

In a 250 mL round bottom flask equipped with an addition funnel, condenser, and gas inlet were placed 0.54 g (22.175 mmol) of magnesium turnings and enough tetrahydrofuran (THF) to cover the metal. A solution of 4.502 g (21.53 mmol) of 1-bromo-4-chloro-3-fluorobenzene and 25 mL of THF was added slowly to the stirred magnesium at room temperature; upon complete addition, the reaction was stirred and allowed to react for 4 h. The resulting solution of 4-chloro-3-fluorophenylmagnesium bromide was transferred to the addition funnel and added dropwise to a mixture of 3.805 g (21.53 mmol) of benzenesulfonyl chloride in 20 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 acidic water solution, diluted with 500 mL of ethyl ether and transferred to a separatory funnel. The ether layer was washed with distilled H\textsubscript{2}O, saturated NaHCO\textsubscript{3}, and again with distilled H\textsubscript{2}O. The ether layer was dried over MgSO\textsubscript{4}, filtered, and then evaporated to dryness to afford a yellow solid, which was recrystallized from ethanol/water to obtain 0.8590 g of 4-chloro-3-fluorodiphenylsulfone (15.3% yield, mp = 103-104°C).

\textsuperscript{1}H NMR (CDCl\textsubscript{3}): 7.41 (s, 1H), 7.43 (t, 1H), 7.51 (dd, 2H), 7.62 (d, 1H), 7.65 (dd, 1H), 7.88 (d, 2H)

\textsuperscript{13}C NMR (CDCl\textsubscript{3}): 116.3, 123.3, 126.31, 126.73, 128.54, 130.79, 131.73, 139.63, 140.91, 155.21
General procedure for a model reaction of 4-chloro-3-fluorodiphenylsulfone with p-cresol:

In a 25 mL round bottom flask equipped with a stir bar, water condenser, and gas adapter were placed 0.101 g (.3704 mmols) of 4-chloro-3-fluorodiphenylsulfone, 0.04 g (.3704 mmol) of p-cresol, 0.064 g (.463 mmols) of potassium carbonate, and 1.15 mL of solvent. The reaction was heated to various temperatures for various numbers of hours. Aliquots were taken throughout to monitor the reaction and evaluated by GC/MS. Variations of distilled solvents such as DMSO and NMP were used with a concentration of (.32 M) as noted in Tables 2, 3, and 4.

GC/MS – Starting material (4.77 m, 270 m/z), Chloro-substituted product (7.95 m, 342 m/z), fluoro-substituted product (8.23 m, 358 m/z).

Synthesis of 3,4-difluorodiphenylsulfone, 6

The procedure for the synthesis 3,4-difluorodiphenylsulfone was followed as reported by the Fossum group.33

In a 250 mL round bottom flask equipped with an addition funnel, condenser, and gas inlet were placed 0.39 g (16.00 mmol) of magnesium turnings and enough tetrahydrofuran (THF) to cover the metal. A solution of 3.01 g (15.54 mmol) of 1-bromo-3,4-difluorobenzene and 15 mL of THF was added slowly to the stirred magnesium at room temperature; upon complete addition, the reaction was stirred and allowed to react for 4 h. The resulting solution of 3,4-difluoro-phenylmagnesium bromide was transferred to the addition funnel and added dropwise to a mixture of 4.11 g (23.27 mmol) of benzenesulfonyl chloride in 10 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 acidic water 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 with distilled H₂O. The ether layer was dried over MgSO₄, filtered, and then
evaporated to dryness to afford a tan solid, which was recrystallized from hexanes to obtain 0.244 g of 3,4-difluorodiphenylsulfone (6.5% yield, mp = 64-65°C).

\(^1\)H NMR, \(^{13}\)C NMR and \(^{19}\)F NMR spectroscopy are as previously reported by the Fossum group.\(^{33}\)

**General procedure for a model reaction of 3,4-difluorodiphenylsulfone with \(p\)-cresol, 3**

In a 25 mL round bottom flask equipped with a stir bar, water condenser, and gas adapter were placed 0.101 g (.394 mmol) of 3,4-difluorodiphenylsulfone, 0.0425 g (.394 mmol) of \(p\)-cresol, 0.068 g (.492 mmol) of potassium carbonate, and 1.15 mL of NMP. The reaction was heated to 70°C for 24 h. Aliquots were taken throughout to monitor the reaction and evaluated by GC/MS. The resulting solution was precipitated from acidified water, diluted in ether layer and washed with distilled water, saturated sodium bicarbonate and distilled water. The ether was then dried over magnesium sulfate and the volume reduced via rotary evaporation to afford a white solid. The final product was then analyzed using GC/MS and NMR analysis.

\(^1\)H NMR, \(^{13}\)C NMR and \(^{19}\)F NMR spectroscopy are as previously reported by the Fossum group.\(^{33}\)

**General procedure for a model reaction and isolation of fluoro-substituted product from 4-chloro-3-fluorodiphenylsulfone with \(p\)-cresol, 2**

In a 25 mL round bottom flask equipped with a stir bar, water condenser, and gas adapter were placed 0.502 g (1.852 mmol) of 4-chloro-3-fluorodiphenylsulfone, 0.200 g (1.86 mmol) of \(p\)-cresol, 0.32 g (2.321 mmol) of potassium carbonate, and 5.75 mL of NMP. The reaction was heated to 120°C for 24 h. Aliquots were taken throughout to monitor the reaction and evaluated by GC/MS. The resulting solution was precipitated from acidified water, and the precipitate...
collected was recrystallized from methanol to afford a yellow solid. The final product was analyzed using GCMS and NMR analysis. (58% yield, mp = 99-100°C)

$^1$H NMR (CDCl$_3$): 2.37 (s, 1H), 6.85 (d, 2H), 7.06 (d, 2H), 7.33 (t, H1), 7.41 (d, 1H), 7.45 (t, 2H), 7.53 (s, 1H), 7.58 (d, 1H), 7.89 (d, 2H).

$^{13}$C NMR (CDCl$_3$): 19.76, 116.45, 117.84, 121.49, 126.61, 128.37, 129.37, 129.67, 130.57, 132.44, 133.48, 140.04, 152.05.

**Synthesis of 4-chloro-3-fluoro-4’-methoxydiphenylsulfone, 4**

In a 250 mL round bottom flask equipped with an addition funnel, condenser, and gas inlet were placed 1.44 g (59.14 mmol) of magnesium turnings and enough tetrahydrofuran (THF) to cover the metal. A solution of 12.014 g (57.42 mmol) of 1-bromo-4-chloro-3-fluorobenzene and 60 mL of THF was added slowly to the stirred magnesium at room temperature; upon complete addition, the reaction was stirred and allowed to react for 4 h. The resulting solution of 4-chloro-3-fluorophenylmagnesium bromide was transferred to the addition funnel and added dropwise to a mixture of 14.5 g (70.18 mmol) of 4-methoxy-benzene sulfonyl chloride in 35 mL of THF at 0°C. The reaction mixture was stirred overnight. The reaction mixture was quenched with dilute HCl, diluted with ethyl ether and transferred to a separatory funnel. The ether layer was washed with distilled H$_2$O, saturated NaHCO$_3$, and again with distilled H$_2$O. The ether layer was dried over MgSO$_4$, filtered, and then evaporated to dryness to afford a yellow solid, which was recrystallized from ethanol/H$_2$O to obtain 6.2 g of 4-chloro-3-fluoro-4’-methoxydiphenylsulfone. (39% yield, mp = 105-106°C)

$^1$H NMR (CDCl$_3$): 3.78 (s, 1H), 6.98 (d, 2H) 7.44 (dd, 1H), 7.52 (dd, 1H), 7.59 (dd, 1H), 7.88 (d, 2H).
$^{13}$C NMR (CDCl$_3$): 55.73, 114.80, 115.67, 123.70, 126.49, 130.07, 131.66, 131.97, 142.79, 156.22, 163.86.

**Synthesis of 4-chloro-3-fluoro-4'-hydroxydiphenylsulfone, 5**

In a 500 mL round-bottom flask equipped with a stir bar and reflux condenser was charged 6.2 g (20.67 mmol) of 4-chloro-3-fluoro-4'-methoxydiphenylsulfone, 62 mL of glacial acetic acid, and 34 mL of 48% HBr. The reaction mixture was heated to reflux for 48 h. The reaction mixture was slowly poured into 2000 mL of distilled water, and the resulting dark yellow solid was collected via filtration. The solid was recrystallized from toluene using decolorizing charcoal and collected via filtration to yield 4.52 g of clear white crystals. (76% yield, mp = 157-158°C)

$^1$H NMR (CDCl$_3$): 2.28 (s, 1H), 6.94 (d, 2H) 7.27 (dd, 1H), 7.54 (dd, 1H), 7.63 (dd, 1H), 7.81 (d, 2H).

$^{13}$C NMR (CDCl$_3$): 115.61, 116.44, 123.64, 126.84, 130.26, 131.26, 131.70, 142.51, 156.21, 161.27.

**General Procedure for Polymerization of 4-chloro-3-fluoro-4'-hydroxydiphenylsulfone with Azeotropic drying.**

In a 25 mL round-bottom flask equipped with a stir bar, Dean Stark trap, condenser, and gas adapter were placed 0.300 g (1.05 mmol) of 5, 0.18 g (1.31 mmol) of K$_2$CO$_3$, 3.3 mL of NMP, and 3.3 mL of toluene. The Dean Stark trap was filled with toluene and the mixture was heated to 145°C for approximately 3 hours to ensure complete dryness. The toluene was removed and the reaction temperature was raised to 185°C for approximately 8 h. Aliquots were taken throughout to monitor the reaction and evaluated by GPC. The mixture was cooled to room
temperature and slowly poured into 500 mL of vigorously stirred acidic distilled water to afford 0.164 g (53 % yield) of tan solid.

**General Procedure for Polymerization of 4-chloro-3-fluoro-4’-hydroxydiphenylsulfone.**

In a 25 mL round-bottom flask equipped with a stir bar, condenser, and gas adapter were placed 0.300 g (1.05 mmol) of 5, 0.18 g (1.31 mmol) of K$_2$CO$_3$, and 3.3 mL of NMP. The reaction was heated to the desired temperature for various numbers of hours. Aliquots were taken throughout to monitor the reaction and evaluated by GPC. The mixture was cooled to room temperature and slowly poured into 500 mL of vigorously stirred acidic distilled water to afford 0.133 g (34 % yield) of yellow solid.
RESULTS AND DISCUSSION

The main purpose of this project was to explore the possibilities of synthesizing a gradient-like copolymer using nucleophilic aromatic substitution, NAS, chemistry. The 4-chloro-3-fluoro-4’-hydroxydiphenylsulfone monomer, 5, utilized for the polymer synthesis is unique due to the fact that it is a ABB’ type monomer possessing leaving groups, chlorine and fluorine, with considerably different reactivity in NAS reactions. Compound 5 provides an interesting contrast in leaving group ability versus reactive site position, relative to the activating group. Reaction temperature and solvents also play an important role in the kinetics of these reactions. As discussed previously, higher reaction temperatures should yield a lower ratio of the better fluorine, to worse the chlorine, leaving group.

Initial reactions to determine the relative rates of displacement of the chlorine and fluorine atoms were carried out using a model compound, 1, which possessed the chlorine and fluorine leaving groups, but not the phenol group. The model, 1, was synthesized via Grignard chemistry as shown in Scheme 8. Compound 1 was prepared by the reaction of 4-chloro-3-fluorophenylmagnesium bromide with benzenesulfonyl chloride. The crude product was recrystallized from ethanol/H$_2$O to afford 1, as yellow crystals.

Scheme 8

![Scheme 8 Diagram]
The model compound was analyzed for purity and the appropriate molecular weight using the GC/MS and further characterized with \(^1\)H NMR and \(^{13}\)C NMR spectroscopy. Figures 5 and 6 show the \(^1\)H NMR, and \(^{13}\)C NMR spectra of 1, respectively.

![Figure 5](image)

**Figure 5.** The aromatic region of the 300 MHz \(^1\)H NMR spectrum (CDCl\(_3\)) of 1.

Although it is difficult to distinguish the precise peaks amongst the multiplets, the \(^1\)H NMR spectrum shows signals in the desired aromatic region.
The $^{13}$C NMR spectrum shows ten distinct signals which correspond to the labeled carbon signals, confirming the identity of the desired model compound. Key signals include the doublet signal (f) present at 123 ppm, due to the carbon split by the fluorine in the *para* position. The splitting of the carbon atoms by the fluorine are evident because signal (d) that belongs on the aromatic ring without the fluorine is a single peak, whereas signal (e) is a doublet. Other key signals include doublets which belong to (g), (i), (e), (h), and (j) which are carbon signals that are also split by the fluorine atom. The fluorine splitting effect is much smaller in carbons in the *meta* position, which is evident in signals (g) and (e). The J values should be similar in signals (j) and (h) because they are in the *ortho* position in respect to the fluorine, and signals (e) and (g) because they are in the *meta* position in respect to the fluorine. Quaternary carbon signals are not very intense in the NMR spectrum which makes C-Cl (h) easily identified by its low intensity.
Signals (b) and (c) represent 2 identical C atoms, making them the most intense signals in the spectrum.

The interesting thing about the compound 1 system is the position of the leaving groups. The leaving groups activate the electrophilic site, or the ipso carbon, by pulling electron density toward themselves and making the ipso carbon prone to nucleophilic attack. It is also important to consider the stabilization of the intermediate species. The sulfone group provides substantial stabilization of the negatively charged intermediate from the para position, therefore, substitution should be favored in the para vs. the meta position.

**Scheme 9**

The chlorine is the weaker activator of the electrophilic site because it is less electronegative, pulling less electron density away from the ipso carbon and making it less susceptible to nucleophilic attack. However, the chlorine is in the favored para position with respect to the electron withdrawing sulfone, thus providing a more stable intermediate. Fluorine is the stronger activator of the electrophilic site because it is more electronegative, pulling more electron density away from the ipso carbon and making it more susceptible to nucleophilic attack. However, the fluorine is in the less favored meta position, with respect to the electron
withdrawing sulfone, forming the less stable intermediate. The chlorine and fluorine both stabilize the negative charge formed in the intermediate because they are both electron-withdrawing species, however, fluorine should help to stabilize the intermediate much more effectively than chlorine. Thus, the fundamental questions to be answered with the model system are which site favors substitution, and what parameters can be modified to influence the substitution of the leaving groups.

Controlling the temperature is the first factor essential in controlling the ratio of leaving groups. Raising the temperature, in theory, should alter the substitution ratios because an increase in temperature would lead to a smaller ratio of $k_1/k_2$ as illustrated in Figure 3 by the $E_{a1}-E_{a2}$ plot. Solvents also play an important effect in the substitution ratios of this system. The polarity of the solvent, if more polar, should reduce the difference of $E_a$ of the intermediate therefore more polar solvent should decrease the selectivity amongst the chlorine and fluorine.

$^{13}$C NMR can be used to estimate the reactivity of the electrophilic carbon sites $^{33}$. Generally, the farther downfield carbon signals mean that the carbon is more prone to nucleophilic attack. The signal for the ipso carbon attached to the chlorine shows up at approximately 126 ppm. The signal for the ipso carbon attached to the fluorine shows up at approximately 157 ppm, which is more downfield and more willing to undergo nucleophilic attack.
Determination of the relative reactivity of Chloro and Fluoro Sites in 1

Substitution at 70°C

In order to determine the relative reactivity of the 4-chloro and 3-fluoro positions, 1 was treated with one equivalent of p-cresol in DMSO or NMP at 70°C. As shown in Scheme 10 there are two possible products from this reaction, fluoro and chloro-substituted.

Scheme 10

GC/MS provided a relatively straightforward method for determining the product ratios because each product has a distinct molecular weight. A typical GC/MS trace from a sample of the reaction mixture is depicted in Figure 7.
Figure 7. GC/MS of compound 1 reaction with \( p \)-cresol in NMP at 70°C.

The GC/MS spectrum shows three distinct signals that correlate to the starting material and the two possible products of the reaction. The first signal at 4.77 minutes is the starting material with a m/z of 270. The second signal at 7.95 minutes belongs to the chloro-substituted product with a m/z of 342. The final signal found at 8.23 minutes is the fluoro-substituted product with a m/z of 358. The relevant data for these model reactions are summarized in Table 2.

Table 2. Substitution ratios of fluorine and chlorine in system 1 at 70°C.

<table>
<thead>
<tr>
<th>Solvent</th>
<th>Temp (°C)</th>
<th>Time (h)</th>
<th>Cl substituted</th>
<th>F substituted</th>
<th>Residual 1</th>
</tr>
</thead>
<tbody>
<tr>
<td>DMSO</td>
<td>70</td>
<td>96</td>
<td>3.6%</td>
<td>87.1%</td>
<td>9.3%</td>
</tr>
<tr>
<td>NMP</td>
<td>70</td>
<td>96</td>
<td>2.7%</td>
<td>77.5%</td>
<td>17.3%</td>
</tr>
</tbody>
</table>

As shown in Table 2, the substitution occurs at both leaving group sites, with fluorine by far the dominant leaving group. The ratio of fluorine to chlorine displacement for DMSO and NMP is 24.2:1 and 28.7:1 respectively. The solvent polarity shows that fluorine substitution is slightly less favored in the more polar DMSO, than it is in NMP at 70°C. Unfortunately, the data at 70°C
cannot be used as conclusive evidence for the reactivity ratios because the system did not go to completion in either solvent leading to a significant percentage of unreacted starting material. Therefore, subsequent reactions utilized an increased temperature to ensure that reactions went to completion.

**Substitution at 120°C**

Compound 1 was reacted under similar condition as Scheme 10 with one equivalent of \( p \)-cresol, but this time at 120°C.

![Figure 8. GC/MS of compound 1 reaction with \( p \)-cresol in NMP at 120°C.](image)

The GC/MS spectrum shows only two distinct peaks that belong to the chloro and fluoro-substituted products without any trace of starting material. The ratios of products from these reactions are summarized in Table 3.
Table 3. Substitution ratios of fluorine and chlorine in system 1 at 120°C.

<table>
<thead>
<tr>
<th>Solvent</th>
<th>Temp (°C)</th>
<th>Time (h)</th>
<th>Cl substituted</th>
<th>F substituted</th>
<th>Residual 1</th>
</tr>
</thead>
<tbody>
<tr>
<td>NMP</td>
<td>120</td>
<td>24</td>
<td>6.3 %</td>
<td>93.7 %</td>
<td>0 %</td>
</tr>
<tr>
<td>DMSO</td>
<td>120</td>
<td>5</td>
<td>4.8 %</td>
<td>95.2 %</td>
<td>0 %</td>
</tr>
<tr>
<td>Toluene</td>
<td>120</td>
<td>24</td>
<td>0%</td>
<td>21.5 %</td>
<td>76.0 %</td>
</tr>
<tr>
<td>50 NMP/50 Toluene</td>
<td>120</td>
<td>15</td>
<td>8.0 %</td>
<td>92.0 %</td>
<td>0 %</td>
</tr>
</tbody>
</table>

With the increase of reaction temperature to 120°C, no starting material remained after 24 hours in NMP and 5 hours in DMSO. The reaction in NMP was run for an extended period of time to ensure completion. The results also demonstrate that at 120°C, NMP favors substitution in the chloro position by 1.5% more so than DMSO. Even though DMSO is a more polar solvent and proceeds to completion much quicker, the displacement ratio of the chlorine is greater in NMP after 24 hours than in DMSO after 5 hours. The non polar toluene afforded no chlorine substitution; however, 75% of starting material remained, thus making a non polar solvent not an optimal choice for the synthesis of the polymer. The 50 NMP/50 Toluene mixture produced the greatest chlorine displacement product out of all the solvents at 120°C, and would be the preferred solvent mixture to achieve chlorine displacement at lower temperatures.

Unfortunately, 50 NMP/50 Toluene solution would not be ideal at higher temperatures because toluene boils at only 111°C. Thus going up to higher temperatures would not be possible because the reaction mixture would not go beyond the boiling point of toluene. Judging by the preceding data, it interesting to note that the reactions in NMP and DMSO did not go to completion at 70°C, but did go to completion at 120°C.

There was some concern that the presence of residual starting material observed at 70°C may be due to an insufficient amount of added p-cresol. In order to determine if a minimum temperature to reach completion existed, 1 was reacted under similar same conditions with one
equivalent of \( p \)-cresol in NMP at an intermediate temperate of 90°C. After 168 hours, at 90°C in NMP, the substitution ratios of chlorine to fluorine were 7% to 90% with 3% unreacted starting material. As suspected, the ratio of starting material dramatically decreased from the original value of 17% at 70°C, down to only 3% at 90°C. The system was run for an extended period of time to ensure the completion of the reaction. A small portion of starting material remained after 168 hours using exactly one equivalent of \( p \)-cresol. The experiment demonstrated that insufficient quantity of \( p \)-cresol was not the reason for the remaining starting material present in the 70°C reaction. At 90°C, the reaction does not go to completion, even at a prolonged period of time. Based on these data, it was concluded that a temperature of at least 100°C must be used in order to assure the completion of the reaction.

**Substitution at 170°C**

The reaction temperature was then further increased to see the substitution ratio of the leaving groups. According to theory, higher reaction temperatures should yield a lower ratio of fluoro to chloro substitution. Compound 1 was reacted with one equivalent of \( p \)-cresol in NMP as well as DMSO, but at 170°C. The outcome of the reaction was monitored using GS/MS, and a representative chromatogram is shown in Figure 9.
Figure 9. GC/MS of compound 1 reaction with p-cresol in NMP at 170°C.

The GC/MS spectrum shows only two distinct peaks that belong to the chloro and fluoro-substituted products without any trace of starting material. The results are summarized in Table 4.

Table 4. Substitution ratios of fluorine and chlorine in system 1 at 170°C.

<table>
<thead>
<tr>
<th>Solvent</th>
<th>Temp (°C)</th>
<th>Time (h)</th>
<th>CI substituted</th>
<th>F substituted</th>
<th>Residual 1</th>
</tr>
</thead>
<tbody>
<tr>
<td>DMSO</td>
<td>170</td>
<td>1</td>
<td>5.6 %</td>
<td>94.4 %</td>
<td>0 %</td>
</tr>
<tr>
<td>NMP</td>
<td>170</td>
<td>1</td>
<td>15.3 %</td>
<td>84.7 %</td>
<td>0 %</td>
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</table>

As the temperature was increased to 170°C both reactions were complete after only 1 hour. Interestingly, DMSO showed no significant increase in the substitution of the chlorine compared to the 120°C reaction, 5.6 and 4.7 %, respectively. On the other hand, the reaction in NMP showed a dramatic increase in the chlorine substitution rate, going up from 6% at 120°C to 15.3% at 170°C. These data confirmed previous speculation that the less favored chlorine could
be displaced at a greater ratio with higher temperatures. According to these results, it seems that the solvent polarity has a greater influence on the substitution rate at higher temperatures than at lower temperatures.

The model compound reactivity data serve as a starting point for tailoring the composition of chloro and fluoro groups along the polymer backbone. If the polymerization of 1 is carried out at low temperatures such as 70°C, the synthesis will primarily substitute in the fluorine position along the polymer backbone, however, it is anticipated that the reaction will not reach completion. If the temperature is then increased to 120°C, the substitution will slightly increase in the chlorine position. As the temperature is further increased, the polymerization will yield even more chlorine substitution products, forming a gradient conversion along the polymer backbone. Thus, it might be possible to synthesize a gradient polymer using an ABB’ compound and NAS chemistry. Polymerizations were carried out using NMP because it provided the largest window for altering the F/Cl displacement ratio.

**Synthesis of 4-chloro-3-fluoro-4’-hydroxydiphenylsulfone monomer, 5**

To explore the synthesis of a gradient copolymer via NAS chemistry it was necessary to prepare an appropriate ABB’ monomer, 4-chloro-3-fluoro-4’-hydroxydiphenylsulfone, 5. The synthesis of 5 is outlined in Scheme 11. The protected analogue, 4, was prepared by the reaction of 4-chloro-3-fluorophenylmagnesium bromide with 4-methoxy-benzenesulfonyl chloride. The crude product was recrystallized from ethanol/H2O to afford 4 as clean crystals. The methoxy group was deprotected using HBr in AcOH and the resulting phenolic monomer was isolated by precipitating it from water followed by recrystallization from toluene.
The monomer compound was analyzed using the GC/MS for the appropriate molecular weight and characterized with $^1$H NMR and $^{13}$C NMR spectroscopy. Figures 10 and 11 show the $^1$H NMR, and $^{13}$C NMR spectra of 5, respectively.

**Figure 10.** The 300 MHz $^1$H NMR spectrum (CDCl$_3$) of 5.
Figure 11. The 75.5 MHz $^{13}$C NMR spectrum (CDCl$_3$) of 5.

The $^{13}$C NMR spectrum shows the appropriate signals that correspond to labeled carbon atoms of the monomer. Assignments were referenced from Chemdraw predictions, as well as knowledge of the fluorine splitting of the carbons. The $^{13}$C NMR spectrum shows 10 distinct signals which correspond to the numbered carbon signals, confirming the identity of the desired monomer product. Key signals again include the doublet signal (f) present at 123 ppm, due to the carbon split by the fluorine in the para position. Other key signals include doublets which belong to (g), (i), (e), (h), and (j) which are carbon signals that are also split by the fluorine atom. The J values should be similar in signals (j) and (h) because they are in the ortho position in respect to the fluorine, and signals (e) and (g) because they are in the meta position in respect to the fluorine. The fluorine splitting effect is much smaller in carbons in the meta position, which is evident in
signals (g) and (e). The splitting of the carbon atoms by the fluorine is evident because signal (d) that belongs on the aromatic ring without the fluorine is a single peak, whereas signal (e) is a doublet. Quaternary carbon signals are not very intense in the NMR spectrum which makes C-Cl (h) easily identified by its low intensity and doublet splitting. Signals (b) and (c) are symmetric signals, making them the most intense signals in the spectrum. The carbon signal attached to the phenol (a) is found as a singlet downfield. The $^{13}$C NMR chemical shifts for the carbons in the C-Cl and C-F bonds correlate well with the experimental data from the model compound.

**Polymerization of 4-chloro-3-fluoro-4’hydroxydiphenylsulfone monomer, 5**

The polymerization reactions of 5 were carried out under typical NAS conditions as shown in Scheme 12. A variety of reaction parameters were explored such as temperature, concentration, and reaction time and the molecular weight results are summarized in Table 5. Azeotropic drying was used for some, not all, reactions done at higher temperatures. In the azeotropic reactions the toluene was removed after 3 hours and the polymerization was continued. Samples were taken to monitor the progress of the polymerization. GPC was used to determine $M_w$, $M_n$ and $M_w/M_n$ values, and $^1$H NMR and $^{13}$C NMR spectroscopy was used to determine the substitution ratios of chlorine and the fluorine.

**Scheme 12**

![Scheme 12 diagram](image-url)
GPC Analysis

Samples for GPC analysis were taken during the course of several 4-chloro-3-fluoro-4’hydroxydiphenylsulfone, 5, polymerizations.

Table 5. GPC analysis for the polymerization of 5.

<table>
<thead>
<tr>
<th>Temperature(°C)</th>
<th>Concentration (M)</th>
<th>Time(H)</th>
<th>Mₙ</th>
<th>Mₘ</th>
<th>Mₘ/Mₙ</th>
<th>Presence of 3% core molecule</th>
<th>Azeotropic Drying</th>
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</thead>
<tbody>
<tr>
<td>120</td>
<td>.32</td>
<td>24</td>
<td>1894</td>
<td>2623</td>
<td>1.385</td>
<td>Yes</td>
<td>No</td>
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<tr>
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<td>.32</td>
<td>48</td>
<td>2467</td>
<td>4054</td>
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<td>No</td>
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<td>No</td>
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<td>10375</td>
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<td>2.915</td>
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</table>

In terms of temperatures, the experimental data show that polymerization occurs at a temperature of 120°C. The data suggest that there is no significant effect on Mₘ or Mₙ values for polymerization done at high temperatures for short periods of time, or polymerization done at lower temperatures for a prolonged period of time. However, increasing the temperature does have an inverse effect on formation of cyclic species, as fewer cyclic species were formed at higher temperatures. Figure 12 depicts the reduction for the signal of cyclic species in GPC traces for the polymerization of 5 at 120°C and 170°C.
Figure 12. Overlay GPC trace for the polymerization of 5 at 120°C and 170°C.

Further evidence for the presence of cyclic species in the current system is displayed by \(^1\)H NMR spectra in Figure 13.

Figure 13. The 300 MHz \(^1\)H NMR spectra (CDCl\(_3\)) for polymerizations of 5, at 120°C and 170°C.
The small signal present in the approximate region of 6.2 ppm serves as supporting data for the presence of cyclic species, 7. This assignment is based on the observation of a signal present at 6.3 ppm for proton $a$ in the analogous cyclic species prepared by Teasley and Hsiao, 8, shown in Figure 14 below.\textsuperscript{35}

![Chemical Structures](image)

**Figure 14.** Cyclic dimer of ABB’ monomer 5 and cyclic dimer reported by Teasley and Hsiao.

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Altering the concentrations had obvious effects on the polymerization, with higher concentration leading to higher $M_w$ and $M_n$ values. At higher concentrations, the polymer chain grows in a linear manner with reduced formation of cyclic units. The reduction of cyclic units is due to the fact that the monomer molecules are surrounded by more monomer units, and are more likely to react in a linear fashion than reacting with one monomer, forming a cyclic unit, and capping off the reactive end groups. Therefore, intermolecular reactions are favored over intramolecular reactions at higher concentrations.

A core molecule (4,4’-difluorodiphenylsulfone) (3%) was introduced into the system in order to minimize intramolecular cyclization. The core molecule is used to initiate the polymerization in a linear manner which would increase the $M_w$ value. However, experimental data showed that the core molecule did not seem to have a considerable effect on $M_w$ and $M_n$ values, and therefore not a significant factor for increasing $M_w$. The core molecule may have
actually limited the molecular weight of the polymer because it changes the stoichiometric
balance of the system.

Azeotropic drying was also used for several polymerization reactions. Azeotropic drying
is typically used to keep the system free of any moisture by using toluene in a Dean-Stark trap.
After 3 hours the toluene is drained from the Dean-Stark trap, and the reaction is increased to a
higher temperature. Experimental data show that azeotropic drying does not produce any
significant effect on increasing the $M_w$ and $M_n$ values.

**NMR Data**

Carbon Dept NMR data were used to analyze the polymer reactions to determine the ratios of
chlorine and fluorine substitution. This was done by examining one carbon signal in particular to
characterize the polymer product. Using the $^{13}$C Dept NMR spectrum of the protected 4-chloro-
3-fluorodiphenylsulfone monomer, there is a signal at 124 ppm assigned to the carbon in the
*para* position to the fluorine. This signal is away from any overlapping peaks and a doublet, due
to coupling with the fluorine atom, making it a prime candidate for characterizing the
substitution ratios of the polymer.
Figure 15. The 75.5 MHz $^{13}$C NMR Dept spectrum (CDCl$_3$) of 1.

The split carbon doublet signal (f) is assigned to the carbon that is located para to the fluorine in the region of 124 ppm.

Once the carbon of interest was identified, it was necessary to assure the signal indeed belonged to the carbon split by the fluorine in the para position. It was necessary to isolate the chloro substituted (3) and the fluoro substituted (2) compounds and analyze them by $^{13}$C Dept NMR spectroscopy. In order to isolated the fluoro substituted product, the 4-chloro-3-fluorodiphenylsulfone model was reacted with one equivalent of $p$-cresol, 1.25 eq. K$_2$CO$_3$, and NMP at 120°C. The product mixture was recrystallized from methanol and cooled to 0°C to yield pure fluoro substituted product.
The “chloro substituted” product was prepared by reacting 3,4-difluorodiphenylsulfone, 6, with one equivalent of \( p \)-cresol, 1.25 eq. \( \text{K}_2\text{CO}_3 \), and NMP at 70\(^\circ\)C. The product mixture was extracted using acidified H\(_2\)O and dried under vacuum. Preparing the actual chloro-substituted product from compound \( 1 \) would be quite difficult because of the low displacement of the chloride, thus 3,4-difluorodiphenylsulfone was used. The synthesis and isolation of compound 3 is illustrated in Scheme 14 below.

Compounds \( 1, 2, \) and \( 3 \) were analyzed using \(^{13}\text{C} \) Dept NMR spectroscopy to observe the target carbon signal at 124 ppm. Figure 16 illustrates the three \(^{13}\text{C} \) Dept NMRs:
Figure 16. The 75.5 MHz $^{13}$C NMR Dept spectra (CDCl$_3$) of compounds 1, 2, and 3. Compound 1 corresponds to the top spectrum, compound 2 corresponds to the middle spectrum and compound 3 corresponds to the bottom spectrum.

Notice that the doublet is clearly visible only in compounds 1 and 3 due to the fluorine splitting the carbon in the *para* position. However, that peak is not present when the chlorine is substituted as shown in compound 2. It was now possible to apply the same method of analysis to characterize the polymers.

Even though substitution is predominant to the fluorine, the relative rate of substitution of the chlorine should increase at higher temperatures as borne out by the model reactions. The polymer system should essentially behave in the same manner, producing a mixture of chlorine
and fluorine substituted products. However, since the polymer will have a mixture of substituted leaving groups the relative abundance of the doublet at 124 ppm will vary. If more fluorine atoms are substituted then the doublet of the para carbon split by the fluorine will be smaller relative to adjacent carbon peak. If fewer fluorine atoms are substituted, then the doublet of the para carbon split by the fluorine will be greater relative to adjacent carbon peak. The polymerization reactions were analyzed by $^{13}$C Dept NMR spectroscopy to determine the relative abundance of the peak at around 124 ppm. As the polymerization proceeds to substitute more chlorine atoms at higher temperatures, the abundance of that peak will increase. Figure 17 depicts the $^{13}$C Dept NMR spectrum of a polymer prepared at 120°C on the top, and the polymer prepared at 170°C on the bottom.
As shown by Figure 17, the doublet signal is much greater at the higher temperature, demonstrating that higher substitution of the chlorine leads to more abundance of fluorine along the polymer backbone. These data suggests that increasing the temperature in the polymer system follows the predicted trends of the monomers, and at higher temperatures, the polymer will resemble more gradient characteristics.

**Figure 17.** The 75.5 MHz $^{13}$C NMR Dept spectra (CDCl$_3$) of polymers at 120°C and 170°C. The carbon splitting is depicted to have a smaller doublet signal at lower temperatures, and a greater doublet carbon signal at higher temperature.
CONCLUSIONS

The ratio of leaving groups in the monomer can be altered by increasing the temperature, and thus a polymer with gradient characteristics is possible to synthesize by using nucleophilic aromatic substitution. Using the right solvent and gradually increasing the temperature in 5, polymerization will lead to more gradient polymer structure along the backbone. Although a perfect gradient polymer may not be achieved using this method because the substitution ratios are still greatly favored by the fluorine, perhaps at high enough temperatures a higher gradient ratio can be achieved. Targeting specific leaving groups of a polymer can lead to a greater control of the structure of the polymer backbone.
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VITA

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