

SULFONIC ACID IONOMERS: PROTECTION AND DEPROTECTION SCHEMES

By

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A THESIS PRESENTED TO THE GRADUATE SCHOOL  
OF THE UNIVERSITY OF FLORIDA IN PARTIAL FULFILLMENT  
OF THE REQUIREMENTS FOR THE DEGREE OF  
MASTER OF SCIENCE

UNIVERSITY OF FLORIDA

2010

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To Erin

## ACKNOWLEDGMENTS

First and foremost I would like to thank my wife Erin for all her support. She continually amazes me with the grace and ease at which she can uproot her life, move to a new place and excel without missing a beat.

I would also like to thank my mother, sisters, and all my family. They probably did not get as many calls or visits from me as they would like, but they were always supportive and understanding and for that I am truly grateful.

From the Max Planck Institute for Polymer Research, I would like to thank Dr. Irfan Saeed, whom I have never met, but he was nice enough to take an interest in my research from across the Atlantic and provided valuable counseling.

One of the more difficult aspects of getting started in research is getting your feet wet in the lab, so I would like to thank my mentor Dr. Kate Opper for her ideas but most of all for her patience and friendship.

I want to thank all the Wagener Group members. I could not have asked for a better group of folks to work with. I really could not have done this without each and every one of you. You were always willing to help, and for that I am truly grateful.

To all the folks in Leigh 314, thanks for putting up with me over the past year. I will treasure our friendships, and I appreciate all you guys and gals did for me. I learned so much from each of you, and I hope you learned a little something from me.

I would like to thank the United States Air Force Academy Department of Chemistry, as well as the Air Force Institute of Technology for giving me this wonderful opportunity. In particular, I would like to thank Dr. Donald Bird for going the extra mile to help me get into this program at a time when I was not sure where my Air Force

career was going. In the same vein, I would like to thank Major Mike Kazlauskys, who helped me “get my foot in the door”.

I would like to thank the ladies of the Butler Polymer office: Sara and Gina. You guys rock! No doubt you two keep the ship afloat.

Finally, I would like to thank my advisor Professor Ken Wagener. I cannot imagine having been in a better research group. Your guidance in all matters, chemistry and otherwise, has been invaluable to me during my time here. I apologize for all the 15-minute meetings that ran an hour long, but I truly enjoyed our conversations about chemistry and life, and I will miss them. The good news is I am not leaving the group....just changing location.

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Abstract of Thesis Presented to the Graduate School  
of the University of Florida in Partial Fulfillment of the  
Requirements for the Degree of Master of Science

## SULFONIC ACID IONOMERS: PROTECTION AND DEPROTECTION SCHEMES

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December 2010

Chair: Kenneth B. Wagener  
Major: Chemistry

A reliable protection/deprotection scheme for sulfonic acid was investigated for use in the ADMET synthesis of precisely spaced sulfonic acid ionomers. While the protection of sulfonic acid and incorporation into an ADMET polymer is understood, post-polymerization deprotection presents unique challenges.

The use of alkyl moieties in creating sulfonic ester protecting groups yields molecules that are stable in a variety of reaction conditions, yet can be readily deprotected. The nature of the sulfonate anion allows for easy removal of alkyl protecting groups through substitution ( $S_N2$ ) or elimination (E2) chemistry. In post-polymerization reactions, however, these methods do not prove very useful because of solubility issues, as well as the difficulty in affording full deprotection.

A small molecule study was conducted to find a deprotection scheme that could fully deprotect a sulfonic acid functionalized polyethylene polymer. Both isobutyl and neopentyl alkyl protecting groups were studied due to their stability as protecting groups and relative ease of removal.

The deprotection that was ultimately found to be the most promising was the thermolysis of the sulfonate esters in DMF. The reasoning was two-fold. First, it afforded complete deprotection of the small molecules. Second, the alkyl protecting groups were eliminated as gases, which allowed for an easy work-up. While this scheme shows promise, it has not been tested on a macromolecule.

# CHAPTER 1 INTRODUCTION

## Introduction to Fuel Cells

In the 1960s General Electric developed the first proton exchange membrane fuel cell (PEMFC), also called the *solid polymer fuel cell* for use in NASA's manned space vehicles.<sup>1</sup> These fuel cells were advantageous for a few reasons. One is that the polymer electrolytes operated at low temperatures, which meant a PEMFC can start quickly. Another advantage was the 'membrane electrode assemblies' (MEAs) were very thin, allowing for compact fuel cells. Finally, there are no corrosive fluids and the fuel cells can work in any orientation, making them useful for portable applications. The early fuel cells produced for the Gemini spacecraft had an average lifetime of 500h and were fine for the short duration of early manned missions; however, for the longer Apollo missions, water management became a concern, so NASA opted for the alkaline fuel cell.<sup>1</sup> The issue of water management for PEMFCs is still of concern today.

In 1967 Dupont developed Nafion, which was and still is the gold standard by which all other PEMFCs are judged. The backbone of the polymer is simply polyethylene (Figure 1-1) that has undergone perfluorination (Figure 1-2).

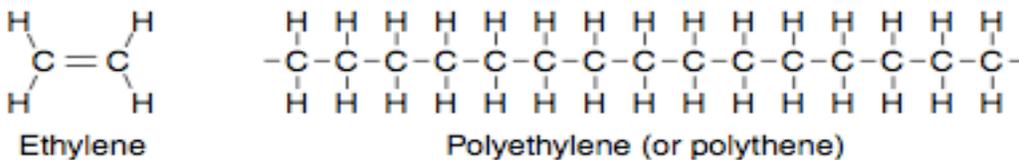


Figure 1-1. Structure of Polyethylene<sup>1</sup>

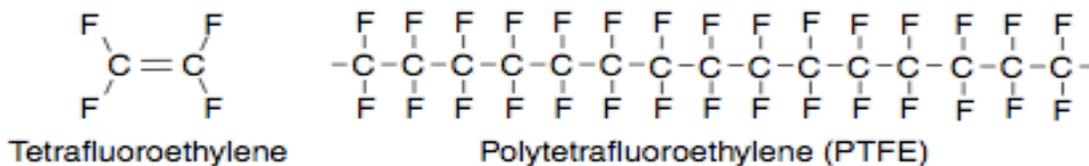


Figure 1-2. Structure of PTFE<sup>1</sup>

The perfluorination of the polyethylene gives a polymer with two important properties. The first is its resistance to chemical reactions due to the strength of the carbon-fluorine bond, and the second is the polymer backbone is hydrophobic, which helps drive water out of the electrode in fuel cells. In order to be utilized in fuel cells the polytetrafluoroethylene (PTFE) is then modified with a sulfonated side chain to yield Nafion, which has electrolytic functionality.<sup>1</sup> The HSO<sub>3</sub> groups are ionically bonded, so the end groups of the side chains are more correctly thought of as SO<sub>3</sub><sup>-</sup> and H<sup>+</sup>, which makes the resulting polymer an *ionomer* (Figure 1-3)..

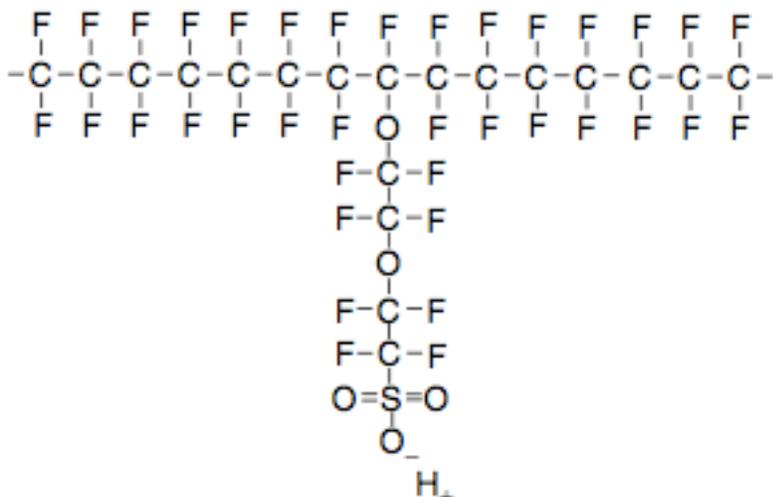


Figure 1-3. Example structure of a sulfonated polyfluoroethylene<sup>1</sup>

Ionomers will be discussed in depth later. For now, we will only consider the attraction between the + and - charges of the each molecule, which results in a clustering of side chains. A key property of sulfonic acid is its hydrophilicity, which with the clustering of SO<sub>3</sub><sup>-</sup> groups, means we now have a polymer with hydrophilic regions within an overall hydrophobic structure. This is a necessity for any polymer to function as a PEMFC.<sup>1</sup>

The hydrophilic clusters allow absorption of large amounts of water, creating essentially two phases, a dilute acid (hydrated) phase within a hydrophobic structure

(Figure 1-4). Within the hydrated phase, the  $H^+$  ions are weakly attracted to the  $SO_3^-$  groups, allowing for conduction.

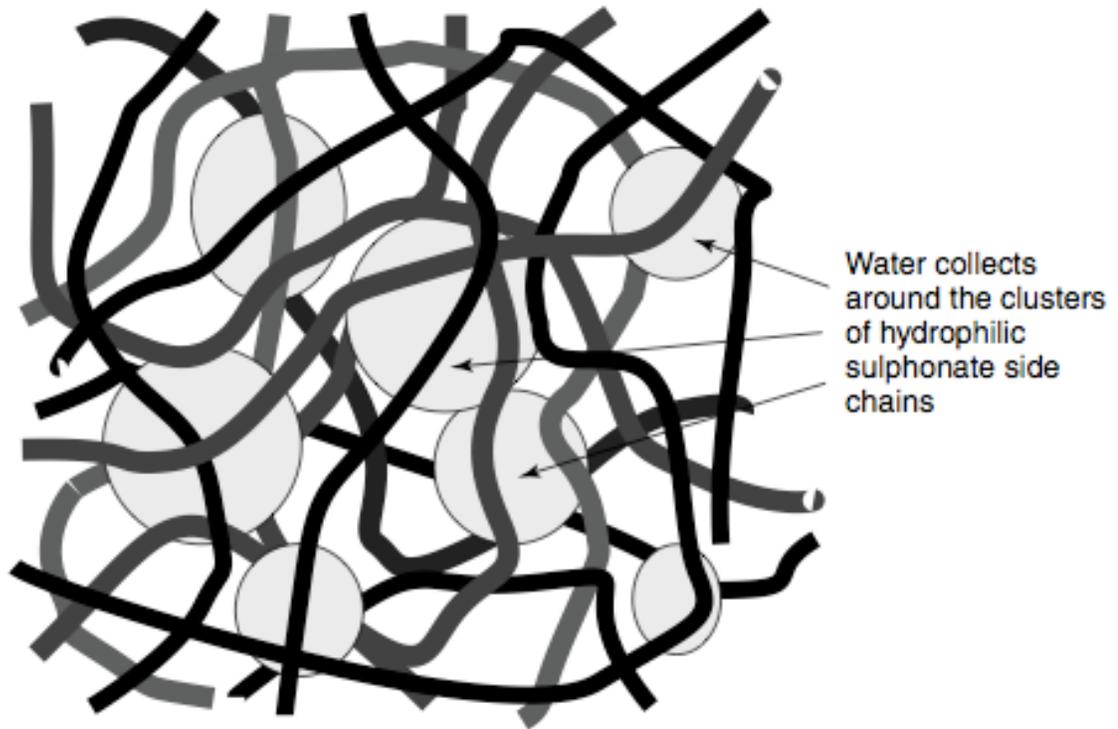


Figure 1-4. The structure of Nafion-type membrane materials. Long chain molecules containing hydrated regions around the sulfonated side chains.<sup>1</sup>

A linear relationship exists between hydration and conductivity, so it is important that the hydrated regions be as large as possible. As water content falls, so does conductivity; however, as mentioned earlier, water management is critical because too much water can cause problems within the fuel cell, such as flooding of the electrodes that are bonded to the electrolyte, which can block the pores in the electrodes or gas diffusion layer. Figure 1-5 gives a brief overview of typical water movement within a fuel cell.

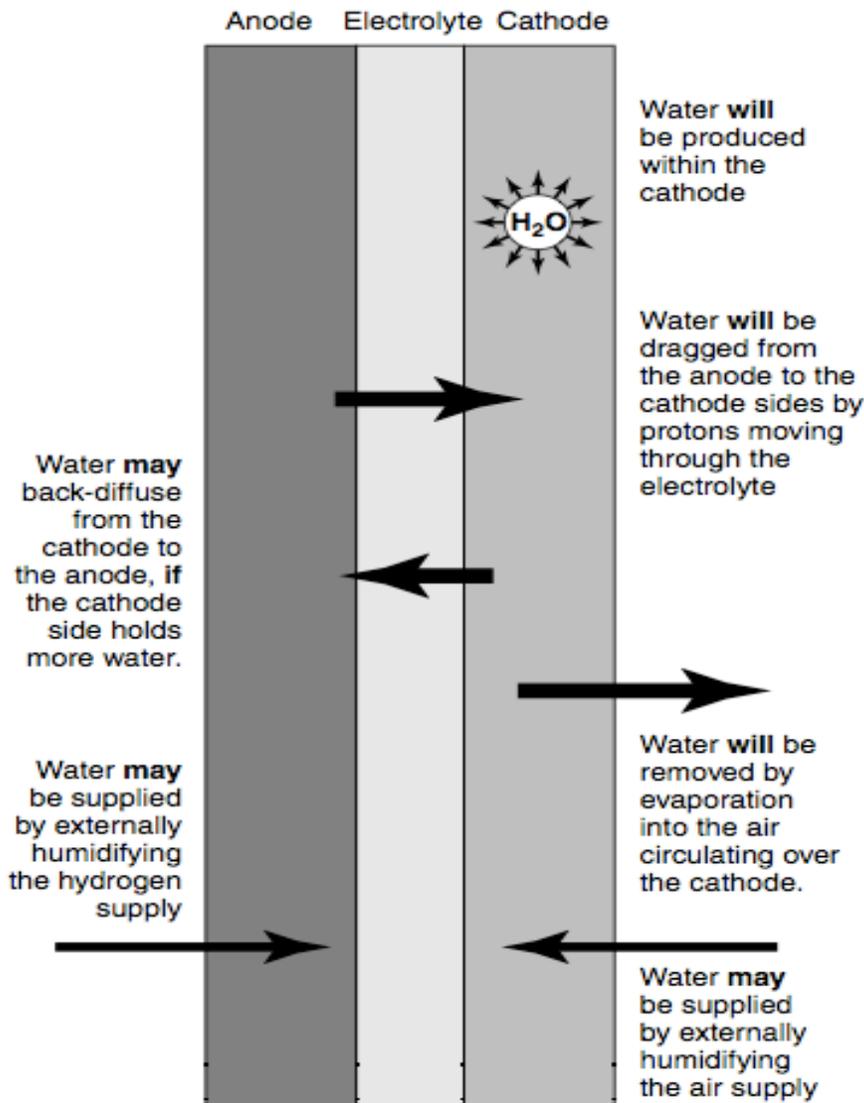


Figure 1-5. Water movement within the electrolyte of a PEM fuel cell.<sup>1</sup>

Development of solid polymer fuel cells essentially stalled in the 1970s and 1980s; however, in the early 1990s, there was renewed interest in this type of cell, and of particular relevance to this thesis, the Army's interest in PEMFCs for small, reliable and portable power delivery systems for soldiers.<sup>1,2</sup> All the advantages previously mentioned are what make PEMFCs ideal for mobile soldiers; however, water management must be addressed to increase fuel cell lifetimes in order for PEMFCs to

find an effective use. The main interest is in sulfonic ionomers, since as with Nafion, they have shown to be the best proton conductors and therefore have the best functionality as solid polymer membranes.

### **Ionomers**

The word *ionomer* historically has been used to describe olefin-based polymers containing a relatively small percentage (below ~15 mol %) of ionic groups, which due to strong ionic interactions, control morphology and in turn physical properties. Eisenberg and Rinaudo defined ionomers as polymers that possess bulk properties governed by ionic interactions in discrete regions of the material (ionic aggregates).<sup>3</sup> As long as ionic aggregates are present in bulk or in a medium of low dielectric constant, the polymer is classified as an ionomer.

Ionomers are of interest because the ionic interactions change the physical properties of the polymers. The modulus, glass transition temperature, viscosity, melt strength, fatigue, transport, and many other properties can be influenced by these ionic interactions.<sup>3</sup> In order to understand these changes in physical properties, one must also understand the organizational (morphological) changes to the polymer. Many ionomers are random with respect to spacing between the ions; however, with the evolution of olefin metathesis, a method of precision placement of these groups has been developed, allowing for a more thorough understanding of how spacing affects morphology and physical properties of ionomers.

### **Olefin Metathesis**

One cannot begin talking about olefin metathesis without acknowledging the work of Karl Ziegler in Germany and Giulio Natta in Italy in the 1950s. Ziegler was studying reactions of ethylene with trialkylaluminum at high temperatures and pressures

and noted molecular weights near 5000; however, upon the addition of a transition metal compound, high-molecular-weight polyethylene formed at low temperatures and pressures.<sup>4,5</sup> This was a remarkable discovery at the time because the typical way of producing polyethylene via radical chemistry yielded low-molecular-weight polyethylene due to the propensity of the propagating chain to undergo various chain transfer or termination reactions, both of which limit molecular weight. Natta followed up on Ziegler's work by achieving stereoselective polymerization of 1-alkenes.<sup>4,6</sup> This was significant because just like polyethylene, high-molecular-weight polymers of 1-alkenes cannot be achieved with radical or ionic initiators.

Their work led to the development of *traditional Ziegler-Natta initiators*. These initiators consist of a group I-III organometallic compound or hydride together with a group IV-VIII transition metal halide or other derivative.<sup>4</sup> The earliest example is titanium tetrachloride with triethylaluminum, and this, as with most Ziegler-Natta initiator systems, participates in a set of reactions involving alkylation and reduction of the transition-metal compound by the group I-III compound as shown below (Figure 1-6).<sup>4</sup>

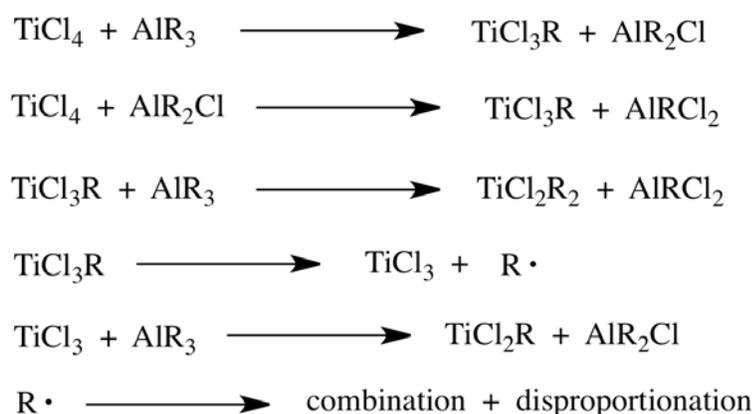


Figure 1-6. Ziegler-Natta alkylation/reduction reactions<sup>4</sup>

The significance of their work earned Ziegler and Natta the 1963 Nobel Prize in Chemistry, and more importantly provided insight and a starting point for further catalyst development and for the evolution of olefin metathesis.<sup>7</sup>

Another important discovery occurred in 1971, when a proposed mechanism submitted by Herrison and Chauvin showed an alkylidene complex reacting with an olefin to give a metallocyclobutane intermediate.<sup>8</sup> The formation of the reaction of the metal-carbene complex with the olefin is a reversible process, and therefore has a productive pathway in which a new olefin is formed and a nonproductive pathway in which the starting materials are regenerated (Figure 1-7).

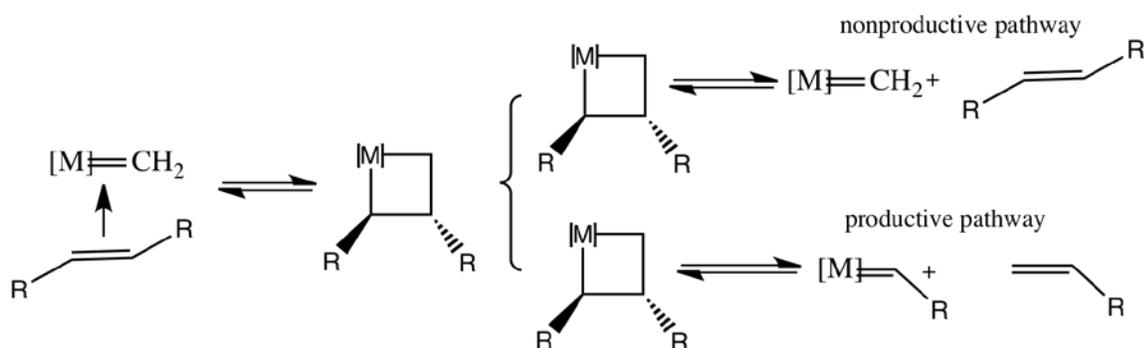


Figure 1-7. Metal carbene metallocyclobutane formation

Extensive catalyst development occurred throughout the 1970s, including the work of Richard Schrock, who worked toward homogeneous catalyst development.<sup>8</sup> Unlike the previous heterogeneous Ziegler-Natta initiator systems, which relied on chiral pockets on the crystal surface to dictate stereoregular monomer insertion, Schrock catalysts and the catalysts that followed were homogeneous, which utilized the symmetry elements of the initiator to control monomer insertion (i.e. the initiators themselves possessed chirality). For the purpose of this thesis, we will not focus on the extensive catalyst development that occurred after Ziegler-Natta, throughout the 1960s

and 1970s but will instead focus on the work of Robert Grubbs and the development of ruthenium based catalysts.

The first breakthroughs in finding metathesis active ruthenium catalysts came from the Robert Grubbs research group at Caltech in the early 1990s.<sup>8</sup> For some time Grubbs had been looking for a Ru(II) alkylidene, with a 16-electron metal center and an olefin binding site but that was also functional group tolerant. After initial synthesis of a Ru(II) catalyst that was found to polymerize norbornene via living ring opening metathesis polymerization (ROMP), Grubbs desired a catalyst that was not limited to strained olefins. It was from this desire that Nguyen and coworkers developed a catalyst that replaced the (PPh<sub>3</sub>) ligands with (PCy<sub>3</sub>), a more electron-donating group.<sup>8</sup> The catalyst was found to initiate metathesis of cis-2-pentene, and it was from this precursor that the traditional Grubbs' first generation (**Ru1**) and second generation (**Ru2**) catalysts were developed.<sup>9-11</sup> Because of their functional group tolerance, reduced air and moisture sensitivity, these catalysts have found a variety of applications in synthetic chemistry and have made acyclic diene metathesis (ADMET) polymerization a useful reaction.

### ADMET

ADMET is a step-growth, condensation-type polymerization, making it very different from the other type of olefin metathesis polymerization ROMP, which is a chain-growth, addition-type. This led to a number of differences seen between polymers prepared via ROMP versus ADMET.

One key difference is that, as with most stepwise reactions, with ADMET high molecular weight polymers are not achieved until high conversions are reached.<sup>8</sup> In step reactions, two monomers react to form dimers, then trimers, tetramers, etc.<sup>4</sup> In this

fashion at low conversions there are many very low molecular weight polymers and with each condensation at low conversion, the number of polymer molecules in the sample is reduced by a small proportion. At high conversion of monomer, now there are a few relatively high molecular weight polymers, and when they combine, molecular weight is dramatically increased, and at the same time the proportion of polymer molecules in the sample is reduced significantly. The number average molecular weight,  $X_n$  versus monomer conversion,  $p$  are related by the Carothers' equation. Because ADMET is an equilibrium reaction, the by-product ethylene (a gas) is driven off in order to force the reaction to completion (high monomer conversion) and subsequently high molecular weights. The polydispersity index (PDI), which is weight average molecular weight,  $X_w$  divided by number average molecular weight  $X_n$ , describes the molecular weight distribution in a polymer sample. As with other condensation polymers, ADMET polymers typically have a PDI that approaches 2 as conversion nears 100%. ADMET's percent conversion versus degree of polymerization curve is in stark contrast to that of ROMP.<sup>8</sup>

Unlike ADMET, ROMP is a chain polymerization; there is a rapid increase in molecular weight at low monomer conversion due to the fast, successive addition of monomer molecules prior to a chain transfer or termination that stops chain growth.<sup>4</sup> This means at higher conversions, since high molecular weight polymers already exist any further additions, chain transfers, or terminations that occur will lead to a negligible change in molecular weight.

One challenge with ADMET, as with any polymer in polycondensation chemistry is competition between polymerization and cyclization.<sup>12</sup> The mechanism involves

backbiting of one of the backbone double bonds of the same chain. For this reason, monomers that would cyclize to form 5, 6, or 7 membered rings should be avoided.<sup>8</sup> Another challenge is monomer purity. Purity is essential because the existence of any monofunctional olefins would act as end-capping reagents, and would limit polymer molecular weight. Also, impurities may cause side reactions that compete with the polycondensation reaction, which would also limit molecular weight.<sup>8</sup>

Another important feature of ADMET is its ability to control branch identity and frequency in the polymerization of  $\alpha,\omega$ -dienes as studied by Wagener and coworkers. It is through the use of  $\alpha,\omega$ -dienes, along with the chemoselectivity of Grubbs' catalyst for metathesis, that allow for precision placement of alkyl and other functional groups along the polymer backbone, which allow for a better understanding of polymer morphology and how it affects physical properties.<sup>13-19</sup> It should be noted that while the chemoselectivity of Grubbs' catalyst for metathesis is excellent for most functional groups, acids will react with the catalyst preferentially and must be protected prior to polymerization.

### **Ionomers via ADMET**

ADMET is useful in the synthesis of ionomers for two reasons. First, it allows for known pendent groups to be regularly spaced along the polymer backbone. Other than ionenes, which are ionic polymers containing mostly quaternary ammonium groups along the chain, regularly spaced ionic groups along a polymer backbone is synthetically difficult to achieve, as most ionomers yield random placement. The second reason ADMET is useful is it overcomes some of the difficulties associated with pendent ions. For example, when incorporating sulfonic acid into a polymer via

copolymerization, one must take care because it can reduce monomer reactivity ratios considerably and make copolymerization impossible.<sup>8</sup> Also, sulfonic acid groups reduce the monomer's solubility making solvent choice difficult. The more common route is postpolymerization sulfonation of aromatic or unsaturated sites, but again with no precision control.

Regularly spaced ionomers are of value because their systematic study will provide insight into how spacing of pendant groups will affect morphology and physical properties. Both carboxylic and phosphonic ionomers have been studied previously, and the results from these studies demonstrated how morphology and physical properties change as branch identity and frequency change.<sup>20-22</sup> These morphological and property changes will certainly be seen in sulfonic ionomers as well, and it is these differences that will most likely result in changes in ion transport ability, which will be crucial in the future development of sulfonate containing PEMFCs.

### **Sulfonic Acid Ionomers via ADMET**

As previously discussed sulfonic ionomers are of particular interest because of their high ion transport ability, which is related to their water uptake ability due to ionic aggregation.

When synthesizing functionalized polyethylene copolymers, ADMET is useful because spacing and branch identity can be controlled, and since it's a metathesis reaction, the reactivity ratio issue can be overcome. One drawback in using ADMET in the case of developing sulfonic acid ionomers is that sulfonic acid groups will disrupt the reaction by killing Grubbs catalysts. It is therefore necessary to protect the acid group prior to incorporation into a monomer molecule and for polymerization.

Sulfonate esters are easily synthesized; however, the difficulty lies in deprotection. There are various ways to deprotect sulfonic esters (acid catalyzed hydrolysis, nucleophilic substitution, etc), but these methods for fully deprotecting a polymer are ineffective because of solubility issues, difficulty in obtaining full deprotection, and difficulty in byproduct removal. The purpose of this thesis is to find a synthetic method that allows for the protection, polymerization, and full deprotection of sulfonic acid to yield a regularly spaced ionomer for morphological study and characterization. Will shorter spacing between groups cause greater aggregation, greater water uptake, and therefore better conductivity? These are questions that with the precision of ADMET will hopefully allow definitive conclusions to be reached, and perhaps an “ideal” spacing found for use in fuel cell membranes.

## CHAPTER 2 EXPERIMENTAL

### Methods

All  $^1\text{H}$ NMR (300 MHz) and  $^{13}\text{C}$  (75 MHz) solution NMR spectra were conducted on a Varian Associates Mercury 300 spectrometer. Chemical shifts for  $^1\text{H}$  and  $^{13}\text{C}$  NMR were referenced to residual signals from  $\text{CDCl}_3$  ( $^1\text{H}$  = 7.27 ppm and  $^{13}\text{C}$  = 77.23 ppm) and  $\text{D}_2\text{O}$  ( $^1\text{H}$  = 4.8 ppm). Thin layer chromatography (TLC) was done on EMD silica gel coated (250 mm thickness) glass plates. Developed TLC plates were stained with iodine adsorbed on silica to produce a visible signature.

Mass spectral data was obtained on a Finnegan 4500 gas chromatograph/mass spectrometer using the electrospray ionization (ESI) mode.

### Materials

All materials were purchased from Aldrich and used as received. Where dry solvent was specified, it was obtained from an MBraun solvent purification system. Lithium diisopropyl amide (LDA) was prepared prior to monomer synthesis. Grubbs' first generation ruthenium catalyst, bis(tricyclohexylphosphine)benzylidene ruthenium(IV)dichloride, was a gift from Materia, Inc.

### Sulfonic Ester Synthesis

#### Isobutyl Methane Sulfonate

In a flame dried, 250 mL round bottom flask equipped with a magnetic stir bar, 10 mL (70 mmol, 1.16 eq) of triethyl amine (TEA) and 70 mL of dry DCM were stirred on ice and under argon for 10 minutes. To this 6.5 mL (65 mmol, 1.1 eq) of isobutyl alcohol was added and stirred for an additional 10 minutes. Finally, 5.0 mL (60 mmol, 1 eq) of methanesulfonyl chloride was added dropwise and allowed to stir overnight.

Upon inspection the next morning, a white precipitate had formed. The reaction mixture was washed three times with approximately 50 mL of deionized water in a separatory funnel. Following the three water washes, the DCM layer was returned to the funnel and washed with brine. The organic layer was then dried over magnesium sulfate and filtered into a 250 mL round bottom flask. The DCM was removed by rotary evaporation to yield a yellow liquid. TLC was then done on the crude product using 1:1.2 hexane:ethyl acetate solvent system and yielded one, possibly two spots. Column chromatography, using the same solvent system afforded the ester in nearly quantitative yield.  $^1\text{H}$  NMR ( $\text{CDCl}_3$ ):  $\delta = 1.00$  (d, 6H), 2.05 (non, 1H), 3.01 (s, 3H), 4.00 (d, 2H).  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ ):  $\delta = 18.87, 28.47, 37.48, 76.00$ . Anal. Calcd for C, 39.45; H, 7.95; O, 31.53; S, 21.07 Found: C, 39.39; H, 8.09.

### **Neopentyl Methane Sulfonate**

In a flame dried, 250 mL round bottom flask equipped with a magnetic stir bar, 6.5 mL (45 mmol, 1.5 eq) of triethyl amine (TEA) and 45 mL of dry DCM were stirred on ice and under argon for 10 minutes. To this 4.0 mL (36 mmol, 1.2 eq) of neopentyl alcohol was added and stirred for an additional 10 minutes. Finally, 2.3 mL (30 mmol, 1 eq) of methanesulfonyl chloride was added dropwise and allowed to stir overnight. Upon inspection the next morning, a white precipitate had formed. The reaction mixture was washed three times with approximately 50 mL of deionized water in a separatory funnel. Following the three water washes, the DCM layer was returned to the funnel and washed with brine. The organic layer was then dried over magnesium sulfate and filtered into a 250 mL round bottom flask. The DCM was removed by rotary evaporation to yield a yellow liquid. TLC was then done on the crude product using 1:1.2

hexane:ethyl acetate solvent system and yielded one, possibly two spots. Column chromatography, using the same solvent system afforded the ester in nearly quantitative yield.  $^1\text{H}$  NMR ( $\text{CDCl}_3$ ):  $\delta = 1.00$  (s, 9H), 3.05 (s, 3H), 3.87 (s, 2H).  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ ):  $\delta = 26.21, 31.88, 37.23, 79.20$ . Anal. Calcd for C, 43.35; H, 8.49; O, 28.87; S, 29.29 Found: C, 42.29; H, 8.57.

### **Sulfonic Ester Deprotection**

#### **Deprotection of Isobutyl Methane Sulfonate (Method 1)**

To a flame dried 250 mL round bottom flask equipped with a magnetic stir bar, 164 mg (1.1 mmol, 1 eq) of isobutyl methane sulfonate, 795 mg (2.2 mmol, 2 eq) of tetrabutylammonium iodide, and 20 mL of acetone were added. The solution was put under argon and heated to  $55^\circ\text{C}$  overnight. TLC was done on the crude solution using a 1:19 methanol:ethyl acetate solvent system. Only 1 spot was detected, so the acetone was removed via rotovap, leaving the sulfonate/tetrabutylammonium salt in the flask.  $^1\text{H}$  NMR ( $\text{D}_2\text{O}$ ):  $\delta = 0.96$  (t, 36H), 1.39 (sextet, 24H), 1.68 (p, 24H), 2.82 (s, 3H), 3.22 (t, 24H).  $^{13}\text{C}$  NMR ( $\text{D}_2\text{O}$ ):  $\delta = 13.01, 19.35, 23.32, 39.77, 58.34$ ,

#### **Deprotection of Isobutyl Methane Sulfonate (Method 2)**

In a 100 mL pressure vessel equipped with a magnetic stir bar, 20 mL (260 mmol, 18.5 eq) of dimethylformamide (solvent) was added to 2 mL (14 mmol, 1eq) of isobutyl methanesulfonate. The sulfonic ester went into solution. The pressure vessel was sealed and submerged in an oil bath that had been heated to  $180^\circ\text{C}$  and was kept in the bath for 6 hours. After approximately 20 min, the solution began getting darker. Approximately 10 min after removing from the oil bath, as the solution began to cool, crystals began to come out of the solution. Following a recrystallization, vacuum

filtration was done to separate the sulfonate salt from the remaining liquid.  $^1\text{H}$  NMR ( $\text{D}_2\text{O}$ ):  $\delta = 2.76$  (s, 6H), 2.84 (s, 3H), 2.89 (s, 1H), 3.04 (s, 1H), 7.95 (s, 1H).  $^{13}\text{C}$  NMR ( $\text{D}_2\text{O}$ ):  $\delta = 31.56, 34.69, 37.07, 38.61, 165.09$ . Anal. Calcd for C, 28.39; H, 6.55; N, 8.28 Found: C, 24.50; H, 7.86; N, 9.14.

### **Deprotection of Neopentyl Methane Sulfonate**

In a microwave reaction vessel, 1.5 mL of neopentyl methanesulfonate was added to approximately 10 mL of DMF. The solution was heated in the microwave to  $180^\circ\text{C}$  for 10 min. Once the vessel was cooled, a precipitate formed. The precipitate was filtered off, recrystallized and an NMR was run.  $^1\text{H}$  NMR ( $\text{D}_2\text{O}$ ):  $\delta = 2.74$  (s, 6H), 2.82 (s, 3H), 2.87 (s, 1H), 3.03 (s, 1H).  $^{13}\text{C}$  NMR ( $\text{D}_2\text{O}$ ):  $\delta = 31.54, 34.69, 37.07, 38.61, 165.09$ . Anal. Calcd for C, 28.39; H, 6.55; N, 8.28 Found: C, 24.99; H, 8.20; N, 9.58.

### **Directly Attached Sulfonic Acid Ester Synthesis**

#### **Isobutyl Tricosa-1,22-Diene-12-Sulfonate**

In a flame dried 3-necked flask equipped with a magnetic stir bar, 2.78 mL (20 mmol, 1 eq) of isobutyl methane sulfonate and 4.4 mL (20 mmol, 1 eq) of 11-bromoundecene were stirred in 20 mL of dry THF under argon. The solution was cooled to  $-78^\circ\text{C}$ , and 0.9 eq of LDA was added dropwise over 30 minutes and stirred for an additional 30 minutes. The solution was warmed to  $0^\circ\text{C}$  and stirred for 2 hours. The solution was brought back to  $-78^\circ\text{C}$ , 0.9 eq of 11-bromoundecene was added slowly and allowed to dissolve. Again, 0.9 eq of LDA was added dropwise over 30 minutes and stirred for an additional 30 minutes. The solution was then warmed to  $0^\circ\text{C}$  and stirred for 3 hours. The reaction was quenched with ice cold water. The mixture was extracted 3 times with 50 mL of diethyl ether, dried over magnesium sulfate and concentrated to a

colorless oil. Column chromatography was done, using 1:19 diethyl ether:hexane as the eluent. The dialkylation product was obtained in 35% recovered yield.  $^1\text{H}$  NMR ( $\text{CDCl}_3$ ):  $\delta = 1.0$  (d, 6H), 1.25-1.65 (br, 32H), 1.9-2.1 (m, 5H), 3.0 (p, 1H), 3.95 (d, 2H), 4.95 (m, 4H), 5.8 (m, 2H).  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ ):  $\delta = 18.92, 26.73, 28.57, 29.08, 29.26, 29.45, 29.59, 29.64, 33.96, 61.24, 74.69, 114.30, 139.29$ . Anal. Calcd for C, 71.00; H, 11.47; Found: C, 70.71; H, 11.89. HRMS calcd for  $\text{C}_{27}\text{H}_{52}\text{O}_3\text{S}$  ( $\text{M}+\text{NH}_4$ ), 474.3975; found, 474.3954.

### Homopolymerization Conditions

In a flame dried 100 mL Schlenk tube, equipped with a magnetic stir bar, approximately 1 g of monomer was added. Prior to this the monomer had been degassed by bubbling argon through it for over 24 hours. Using a 400:1 monomer:catalyst ratio (0.25%), Grubbs' first generation catalyst was added, while under argon. After adding the catalyst, the argon flow was shut off and high vacuum line was opened. The mixture was left under vacuum for over an hour at room temperature. After an hour at room temperature, the tube was lowered into a  $50^\circ\text{C}$  oil bath and was left there for 4 days allowing the removal of ethylene bubbling through viscous polymer. Polymers were quenched by dissolution of polymer in a 1:10 ethyl vinyl ether:toluene solution under argon. The polymers were then precipitated into methanol, filtered, and dried under vacuum.

### Hydrogenation Conditions

A solution of saturated polymer was dissolved in toluene and degassed by bubbling argon through it for approximately an hour. Wilkinson's catalyst  $[\text{RhCl}(\text{PPh}_3)_3]$  was added to the solution along with a magnetic stir bar. The glass sleeve was sealed

in a Parr reactor equipped with a pressure gauge. The reactor was filled to 400 psi hydrogen gas and purged three times while stirring. It was then filled to 800 psi hydrogen and stirred for three days. After degassing the solution, the crude solution was precipitated into ice cold methanol.

## CHAPTER 3 RESULTS AND DISCUSSION

### Introduction

As mentioned in the introduction that while Nafion is the gold standard for PEMFCs, other ionomers containing pendant sulfonic acid groups are highly desired. While ester chemistry is well understood and documented, the protection/deprotection scheme for sulfonic acids, especially as pendant groups on polymers, presents unique challenges. The protection of sulfonic acids is quite facile and proceeds with decent yields, but it is deprotection where problems arise. The most obvious choice for deprotection of an ester is acid catalyzed hydrolysis; however, sulfonate esters are stable in a wide variety of acidic conditions.<sup>23</sup> Also, when trying to get full deprotection of a polymer, two additional problems are present. The first and main problem is a solubility issue. When dealing with a protected sulfonic acid attached to a hydrophobic polyethylene backbone, it is difficult to get the polymer and acid into the same medium. The next issue is getting full deprotection of the polymer. If deprotection is dependent on small acid molecules to find all the pendant sulfonic esters attached to a macromolecule, chances are some will remain in a protected form. So, a reliable deprotection scheme is needed that can transfer from small molecule sulfonic esters to polymers.

### Protection Schemes

With that in mind, small sulfonic esters were synthesized in order to test various deprotection methods. The previously reported reactions utilized are shown below and yield two similar yet distinct sulfonic esters (Figure 3-1).<sup>24</sup> There are a variety of alkyl groups that could be utilized as protecting groups, but these two were chosen due to

their relative stability. It had been previously shown that alkyl moieties attached at a secondary carbon, such as an isopropyl group, are relatively unstable due to the facile heterolysis to yield a secondary carbocation, which can lead to undesirable reactions.<sup>25</sup> Because the neopentyl and isobutyl moieties are attached at a primary carbon, they are less susceptible to heterolysis.

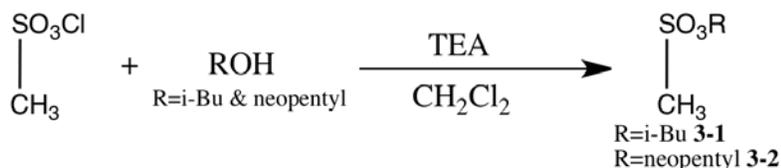


Figure 3-1. Synthesis of isobutyl and neopentyl sulfonic esters

It can be seen from the NMR spectra that the neopentyl (**3-2**) and isobutyl (**3-1**) esters were obtained, and the spectra match reported values (Figure 3-2).<sup>24,26</sup>

A)

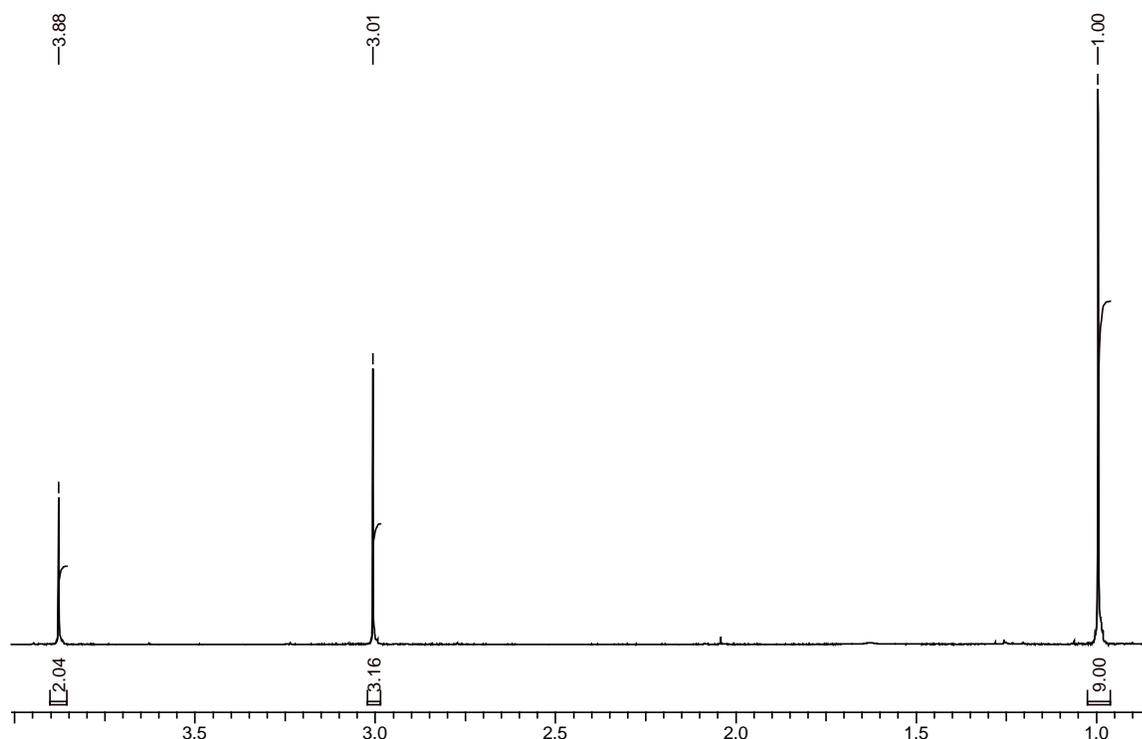
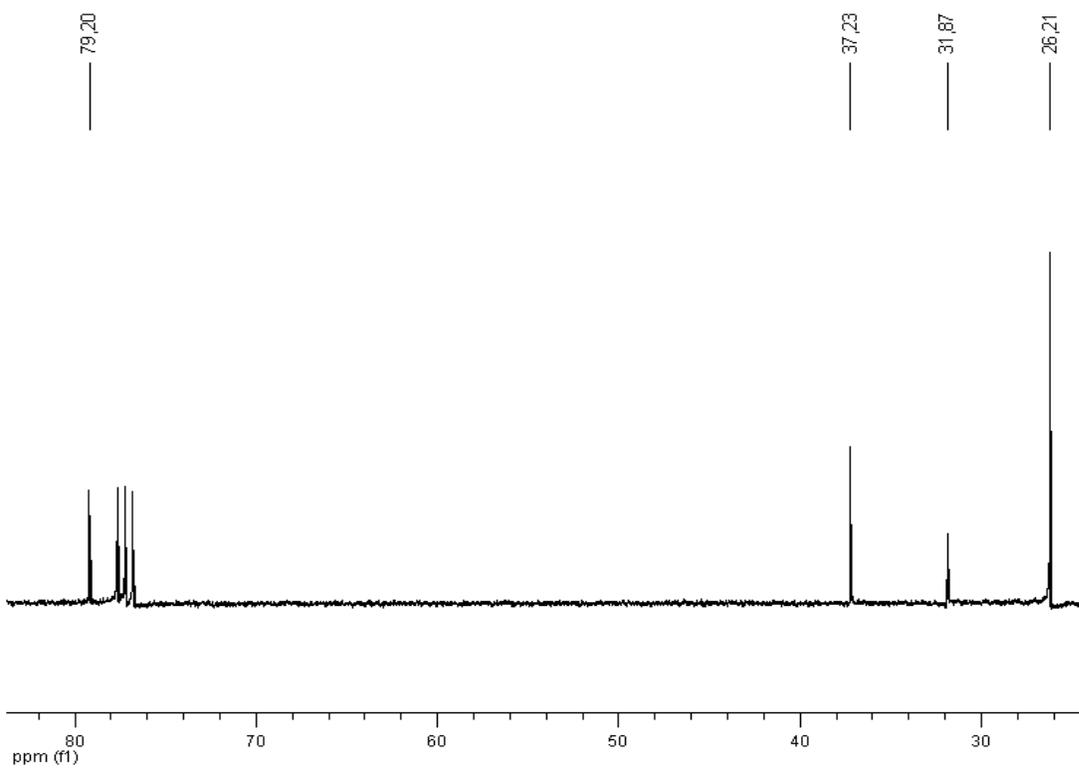


Figure 3-2. A) <sup>1</sup>H NMR of neopentyl methane sulfonate B) <sup>13</sup>C NMR neopentyl methane sulfonate C) <sup>1</sup>H NMR of isobutyl methane sulfonate D) <sup>13</sup>C NMR isobutyl methane sulfonate.

B)



C)

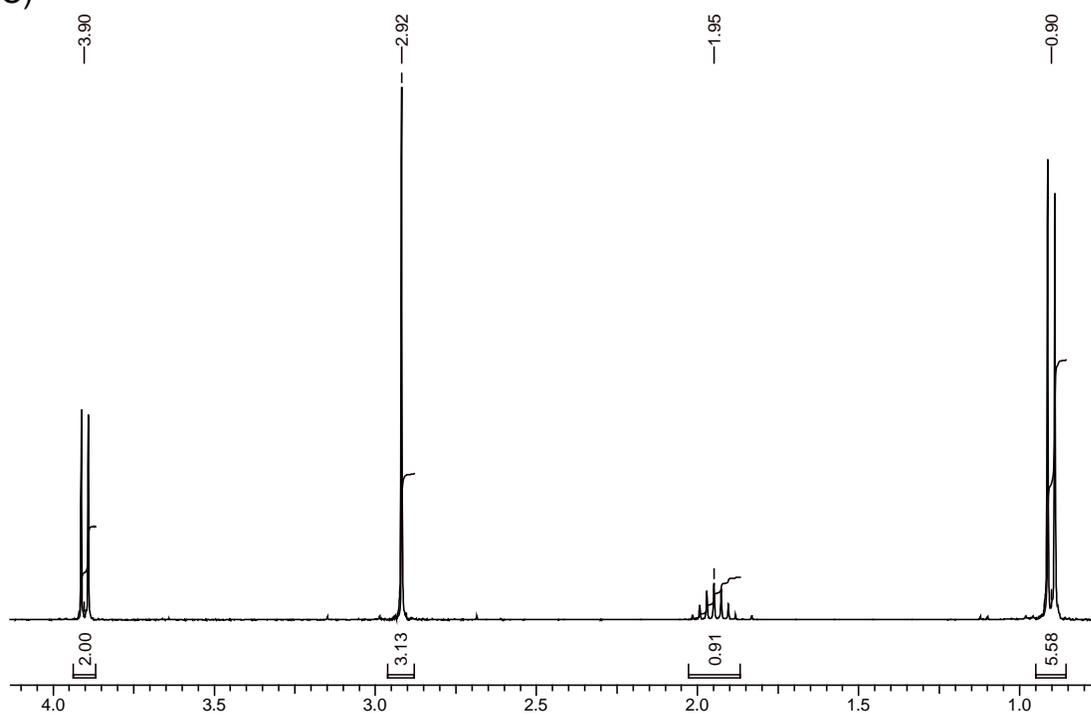


Figure 3-2. Continued

D)

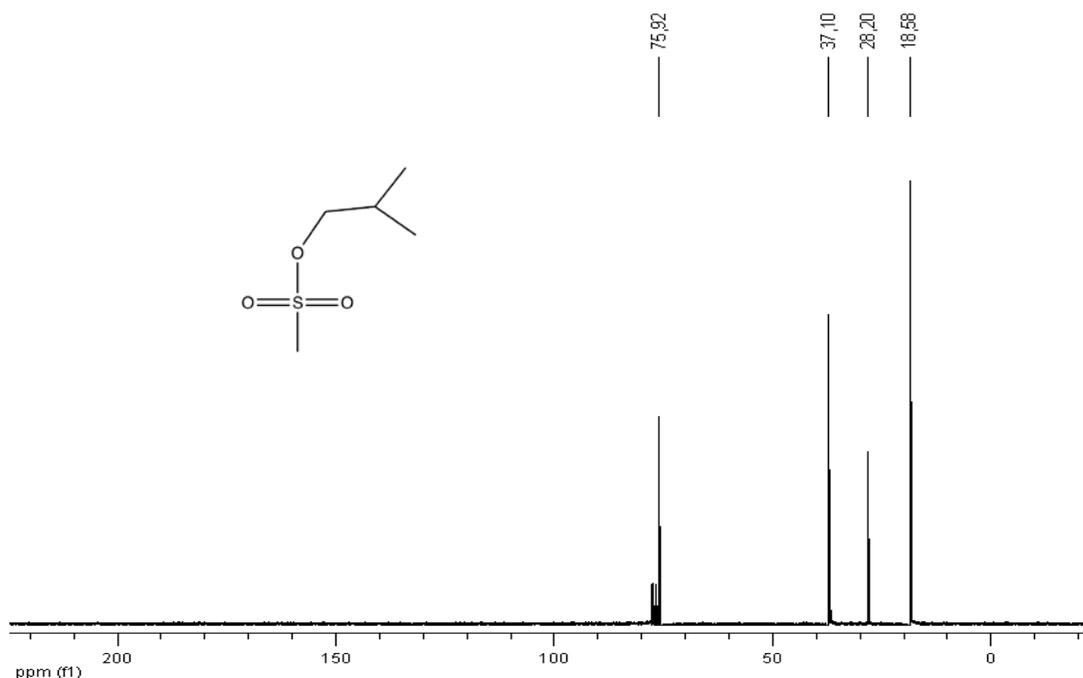


Figure 3-2. Continued

### Deprotection Schemes

#### Isobutyl Ester (3-1) (Method 1)

The first method tested was the reaction of the isobutyl ester with tetrabutylammonium iodide (Figure 3-3).<sup>27</sup> This was expected to proceed via an S<sub>N</sub>2 mechanism, with the iodide displacing the sulfonate group. From the NMR results, it appeared this reaction worked and gave full deprotection.

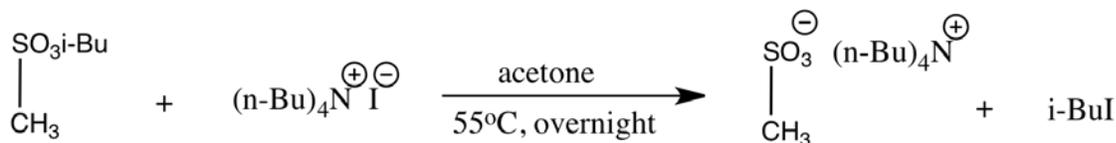


Figure 3-3. Deprotection of Isobutyl ester (Method 1)

In the NMR, the peaks corresponding to tetrabutylammonium iodide are easily recognizable as they all have splitting. The lone peak at approximately 2.8 ppm corresponds to the methyl group of the sulfonate anion. What is a little more

challenging to explain is the integration. As seen in the experimental section, when the integration is set to 3H for the peak at 2.8 ppm, three of the other peaks now integrate to 24H, with the one at 0.9 ppm integrating to 36H (Figure 3-4).

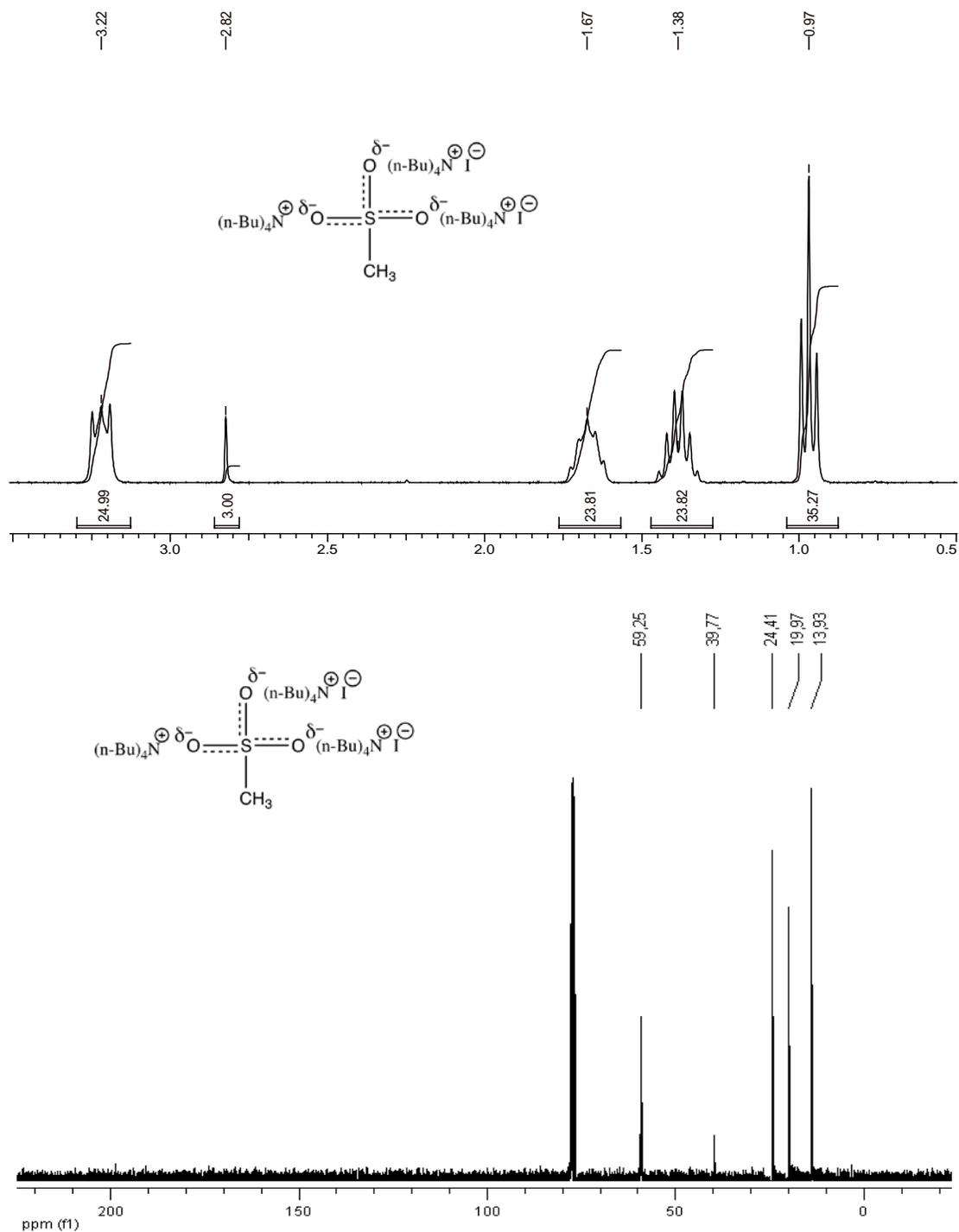


Figure 3-4. NMR spectra from isobutyl deprotection (Method 1)

One way to explain this is to consider the negative charge on the sulfonate anion as being spread over the three oxygen atoms through resonance, so each oxygen has a partial negative charge residing on it. One oxygen associates with one tetrabutylammonium cation and the other two with excess tetrabutylammonium iodide (Figure 3-5).

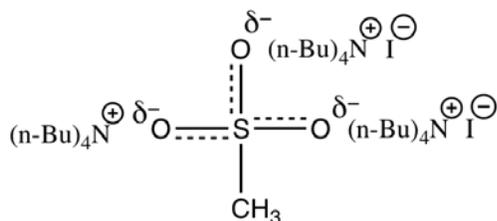


Figure 3-5. Sulfonate/tetrabutylammonium salt w/excess tetrabutylammonium iodide

While this reaction appears to work with a small molecule, the likelihood of this reaction affording full deprotection of pendant groups on a macromolecule is low for the same reasons it is low for acid catalyzed hydrolysis. Thanks to some good fortune, this deprotection method was abandoned for a method much more likely to work on a polymer.

As luck would have it, Dr. Irfan Saeed of the Max Planck Institute for Polymer Research said he had success deprotecting sulfonic ester dendrimers through a thermolysis-type reaction. Dr. Saeed provided his method via a telephone conversation, and it seemed exactly the type of reaction needed to afford full deprotection of a polymer containing sulfonic ester moieties to yield pendant sulfonic acid groups (Figure 3-6). It was in this vein that the bulk of the research proceeded. It was assumed following thermolysis, the sulfonate anion would deprotonate the resulting alkyl cation, giving an olefin that would be lost as a gas at room temperature. As will be

shown later, this proved to be partly correct, but not completely. As it turns out, when the solution is heated to 180°C, more complex reactions must be considered.

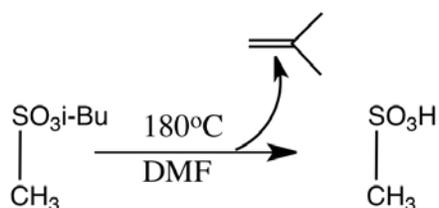


Figure 3-6. Hypothesized thermolysis

### Isobutyl Ester (3-1) (Method 2)

In this reaction, the isobutyl ester deprotection was expected to proceed as shown above (Figure 3-6), but as soon as the reaction vessel cooled, and a precipitate formed, it couldn't have proceeded as above since methanesulfonic acid is a liquid at room temperature. Since there were a limited number of compounds (only two) and there appeared to be a salt, the hypothesis changed to the following (Figure 3-7).

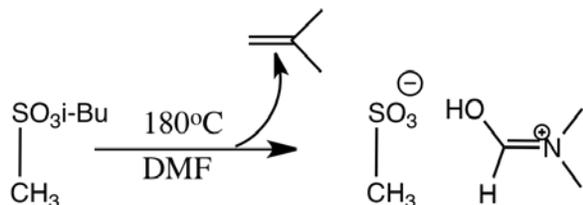


Figure 3-7. Thermolysis w/DMF acting as the base

From the NMR the peak corresponding to the methyl group of the sulfonate anion at 2.84 ppm, which integrated to 3H was readily identified. The other main peak at 2.75 ppm, which integrated to 6H had to be the two methyl groups from DMF, but a singlet did not make sense (Figure 3-8). Neutral DMF has resonance, so that there is a restricted rotation around the amide bond (Figure 3-9). This means the two methyl groups of DMF should have a small difference in chemical shifts, with the one cis to the oxygen being further upfield. Furthermore, if it is DMF that is acting as a base, then its protonated form has no rotation around around the amide bond (Figure 3-10), which

would cause a larger difference in chemical shifts.

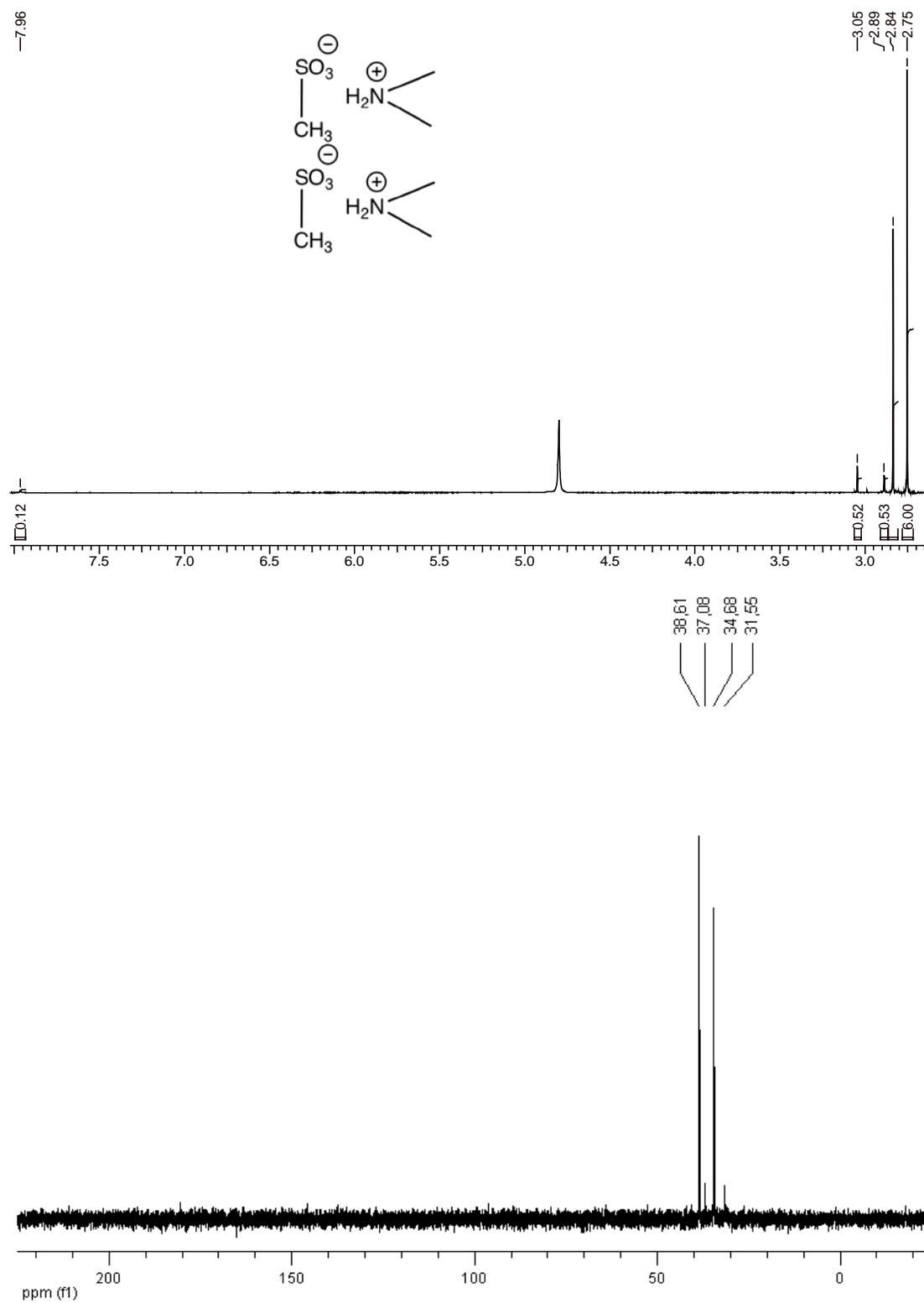


Figure 3-8. NMR from thermolysis of 3-1

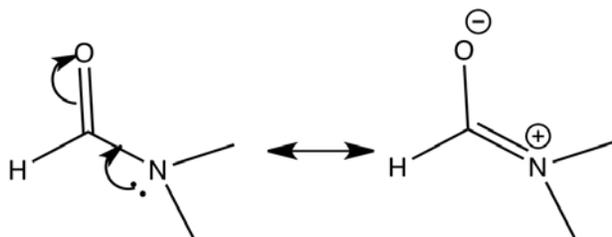


Figure 3-9. Resonance of DMF showing restricted bond rotation

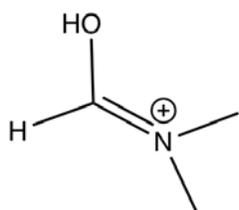


Figure 3-10. Protonated DMF form showing amide bond with full double character

Since the NMR spectrum shows only a singlet, then the second hypothesis (Figure 3-7) is incorrect as well. There must be some other, more complex reaction happening. After doing some literature searches for common reactions involving DMF, it was discovered that DMF, when heated to high temperatures, has been known to decompose into dimethylamine and carbon monoxide.<sup>28</sup> This seemed to be a plausible explanation of what was occurring. If it was then certainly dimethylamine was acting as the base as opposed to DMF, which is a much weaker base. An on-line NMR database was searched, and a proton spectrum on dimethylamine hydrochloride in D<sub>2</sub>O was found. The peak for the methyl groups was a singlet at 2.74 ppm, which is almost exactly the same as the unidentified singlet at 2.75 ppm.<sup>29</sup> To ensure that dimethylammonium ion was present in the salt, the salt was analyzed via mass spectrometry. The mass spec data confirmed the presence of the sulfonate anion,

dimethylamine, and DMF (Figure 3-11). This also explained the difference between the calculated and found values in the elemental analysis.

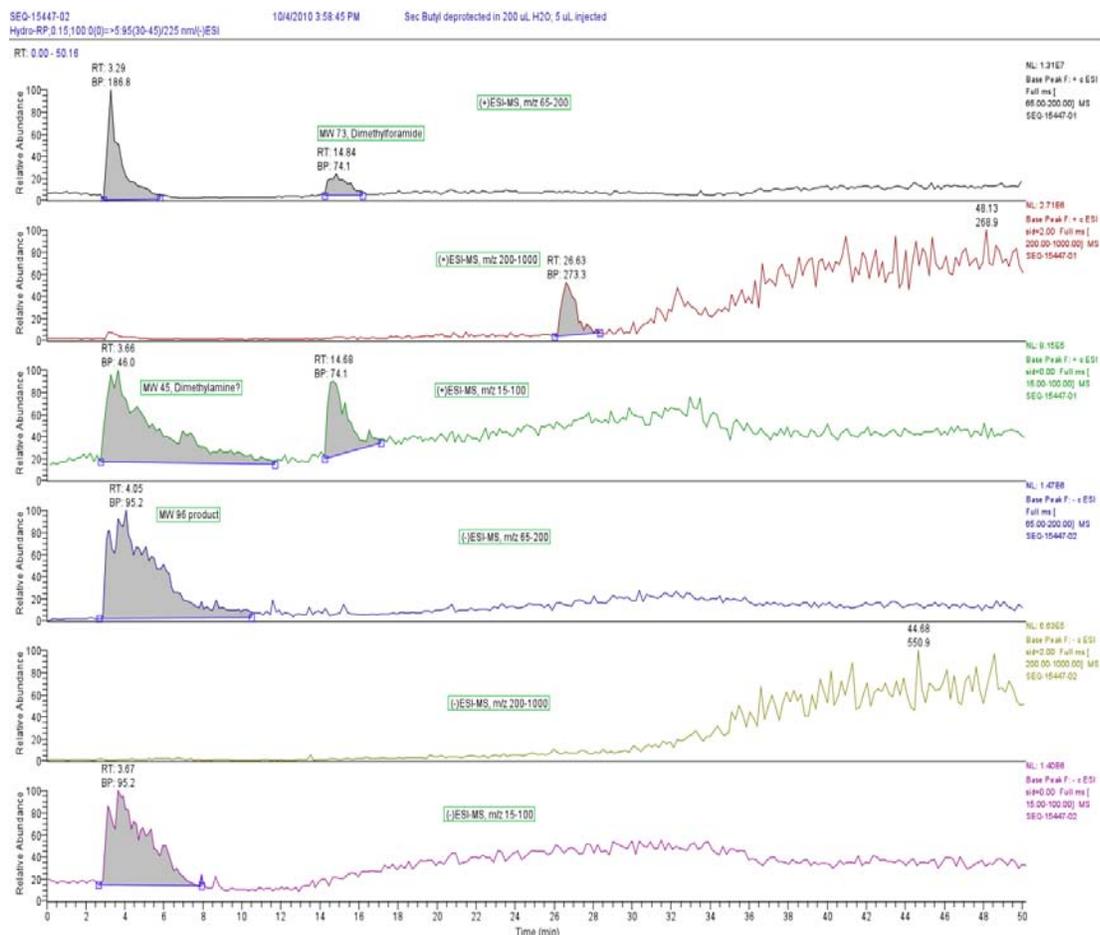


Figure 3-11. Mass spectrum from thermolysis of **3-1**

NMR also supports the existence of trace DMF in the salt, from the peaks at 2.89, 3.04, and 7.95 ppm (Figure 3-8). It appears that the DMF is protonated. The peaks at 2.89 and 3.04 ppm correspond to the methyl groups and have separate chemical shifts as discussed previously, but the methyl groups go from an approximate difference in chemical shift of about 0.08ppm to about double that.<sup>30</sup> This is indicative of protonated DMF, which has no rotation about the carbon-nitrogen bond, causing a larger difference in chemical shift from neutral DMF. The peak at 7.95 ppm corresponds to the aldehydic proton. The <sup>13</sup>C data further supports these conclusions, with the peaks at 38.61 and

34.69 ppm corresponding to the sulfonate methyl and amine methyl groups respectively. The peaks at 31.56 and 37.07 ppm are from the methyl groups of DMF and the carbonyl carbon shows at 165.09 ppm.

### Neopentyl Ester Microwave Deprotection

The results from the deprotection of the neopentyl sulfonic ester mirrored the results from the isobutyl deprotection. The NMR spectra are identical (Figure 3-12), as were the elemental analysis results. So, it appears that the neopentyl moiety, 2-methyl-2-butene, was released as a gas in this reaction as well.

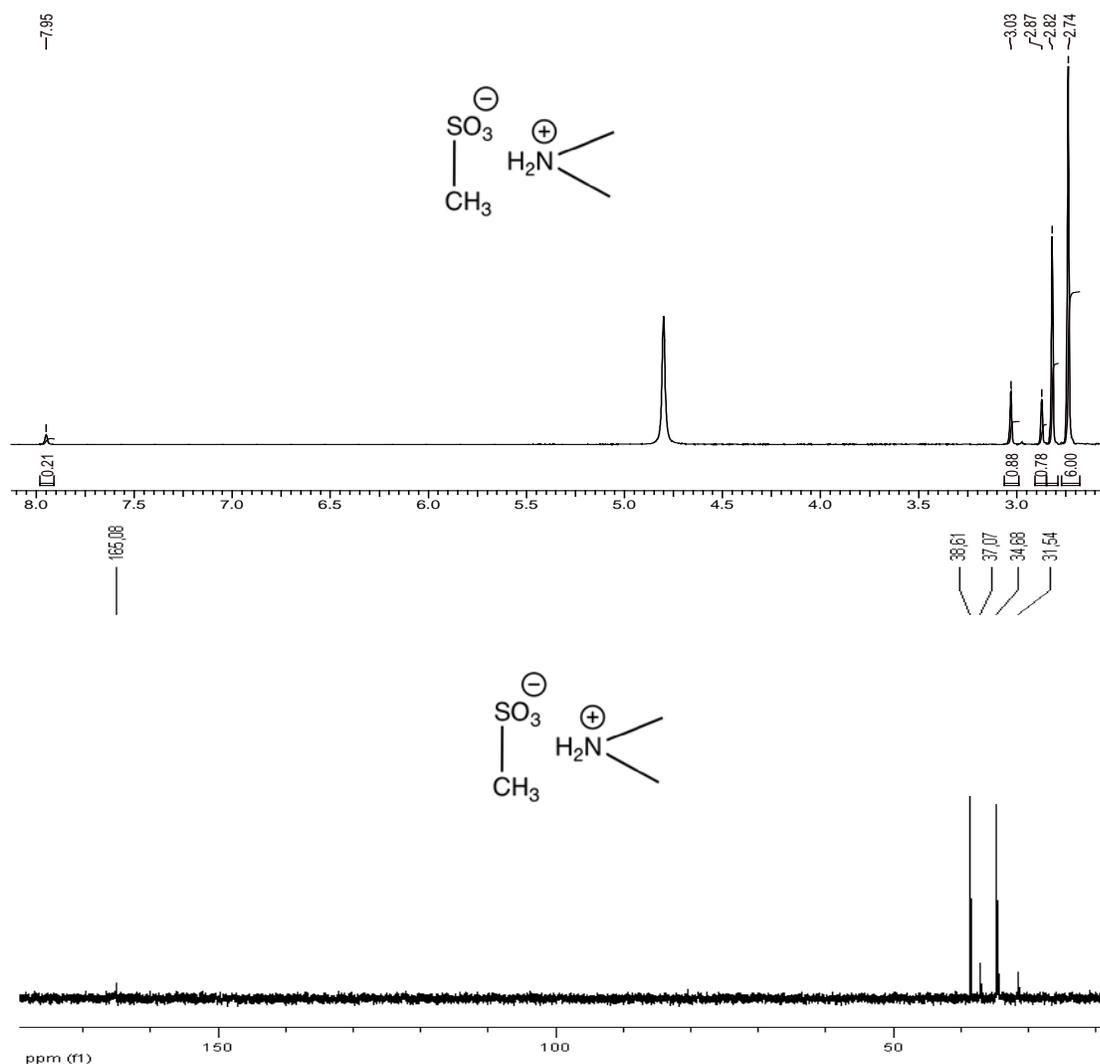


Figure 3-12. NMR spectra from neopentyl sulfonic ester thermolysis via microwave

## Vinyl Ether Study

One other possible protecting group that was attempted, but ultimately failed was using vinyl ethers to form a acetal protecting group. This idea came from previous work using vinyl ether protecting groups for carboxylic acids.<sup>20</sup> The first reaction attempted was the reaction of methane sulfonic acid with ethyl vinyl ether (EVE). The reaction proceeded very rapidly and was quite exothermic, and it left a black viscous substance in the bottom of the flask. Vinyl ethers are well known to polymerize in the presence of acid, and that is exactly what happened in this reaction. The reason the previous carboxylic acid work succeeded in formation of a acetal protecting group is because of the nature of the nucleophile. Consider a carboxylate anion, the negative charge is delocalized over both oxygens, giving each essentially 1/2 (-) charge character. When the sulfonate anion is considered, it can be seen the negative charge is now delocalized over 3 oxygen atoms, giving each a 1/3 (-) charge (Figure 3-13). Because of the additional delocalization, the sulfonate anion is a much weaker nucleophile than the carboxylate anion.

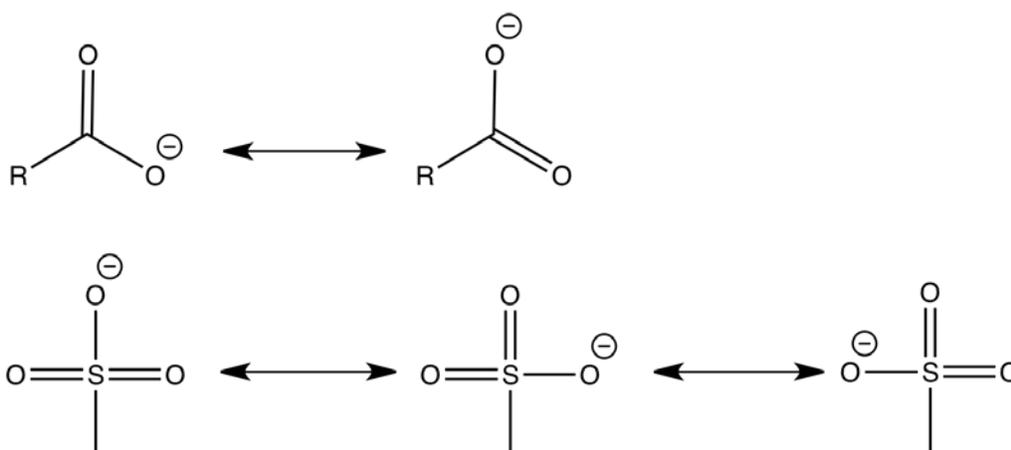


Figure 3-13. Resonance structures of carboxylate and sulfonate anions

It is also important to understand the nature of the ethyl vinyl ether in this reaction as well. Once the EVE is protonated, the oxygen lone pair stabilize the resulting carbocation (Figure 3-14). This also further prevents the already weak sulfonate anion from nucleophilically attacking carbon.

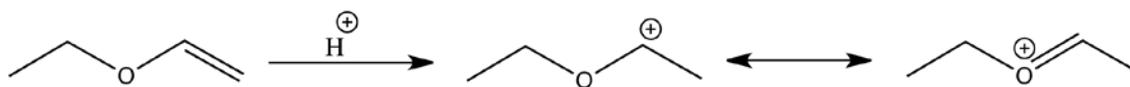


Figure 3-14. Resonance stabilized carbocation of EVE

Another important resonance to consider is EVE itself (Figure 3-15). It can be seen from this resonance that EVE can also act as a nucleophile or in this case a base. So, if the stabilization of the carbocation is preventing the sulfonate anion from adding to the carbon, it stands to reason one might consider electron withdrawing groups that prevent the oxygen from stabilizing the carbocation. This will, however, decrease the basicity as well, which may make the first step of acid/base chemistry more difficult.



Figure 3-15. Resonance of EVE showing nucleophilicity of the double bond

When all the above is combined, it makes sense that the attempted protection reaction of methane sulfonic acid and EVE did not work. The weak nucleophilicity of the sulfonate anion coupled with both the relative stability of the carbocation following protonation of EVE and nucleophilicity of EVE, prevents the sulfonate anion from functioning as a nucleophile. Instead, the stabilized EVE carbocation reacts preferentially with unprotonated EVE in a cationic self polymerization.

Due to time constraints the vinyl ether study was left incomplete. It was hypothesized that if electron withdrawing groups were added to the vinyl ether,

preventing the oxygen lone pair from stabilizing the carbocation, it might force the addition reaction with the sulfonate anion. This ends up being a double-edged sword because as electron withdrawing groups are added, tying up the lone pair of oxygen in resonance, the basicity of the double bond of the vinyl ether is decreased. This will make the first step of protonation more difficult, so it becomes somewhat of a balancing act. There are still compounds left to try, so this may still be a viable option for a sulfonic acid protecting group.

### Conclusions and Further Research

The conclusions to be drawn from this thesis are clear, yet the final desired outcome is not certain. Due to time constraints the research presented here was focused on small molecules. It is clear that an easy, reliable protection/deprotection scheme has been found for small molecule sulfonic acids. What is uncertain is if this same scheme will work for macromolecules. When polymers are involved, many issues begin to arise, the main one being solubility. A fully protected polymer with polyethylene as the backbone will be fairly non-polar and with DMF as the solvent it might be anticipated that the polymer won't go into solution.

After the deprotection success with small molecules, it was decided to attempt a polymerization in order to test this deprotection scheme. The first step was to synthesize monomer **3-3** (Figure 3-16).

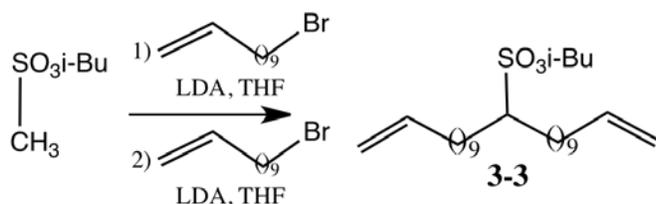


Figure 3-16. Monomer synthesis

By looking at the NMR results, it is seen that the pure monomer was obtained (Figure 3-17). The most telling peaks are at 4.81 ppm and 5.81 ppm, which correspond to the olefin hydrogens. The other peaks of note are at 3.96, 2.98 and 0.99 ppm, which correspond to the isobutyl group.

Following monomer synthesis, a polymerization was done, followed by hydrogenation to yield the saturated polymer (Figure 3-18).

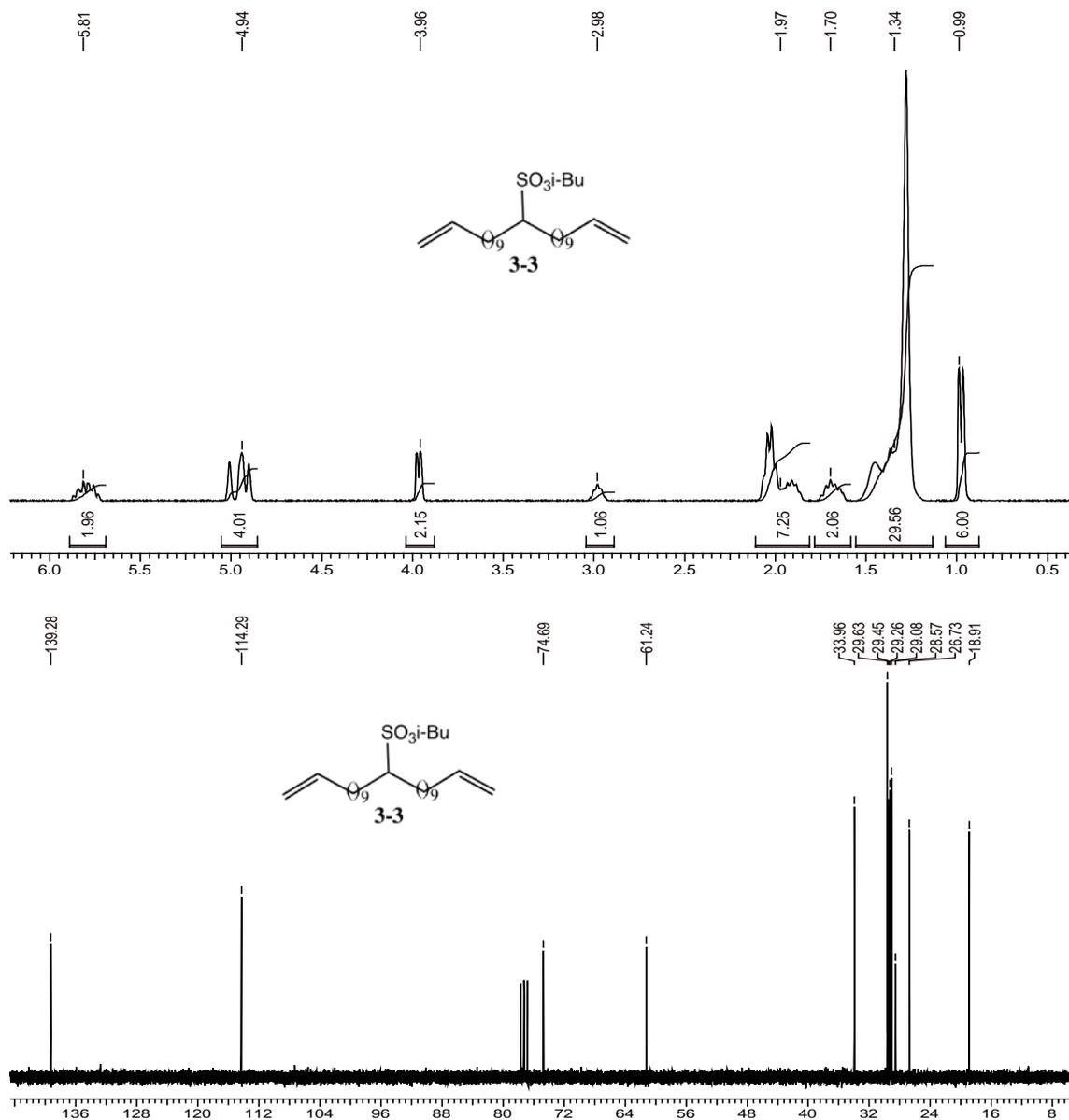


Figure 3-17. <sup>1</sup>H NMR and <sup>13</sup>C NMR of monomer 3-3

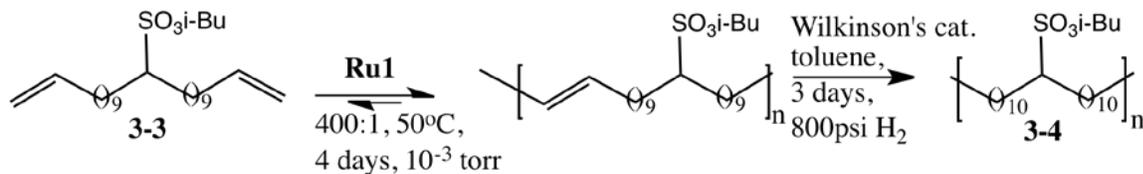


Figure 3-18. Saturated polymer (**3-4**) synthesis

The first polymer with a protected sulfonic acid moiety (isobutyl sulfonate) on every 21st carbon has been obtained with a  $M_n$  of about 34,000. A full characterization of the polymer has not been done, but from NMR it is clear the isobutyl polymer was obtained (Figure 3-19).

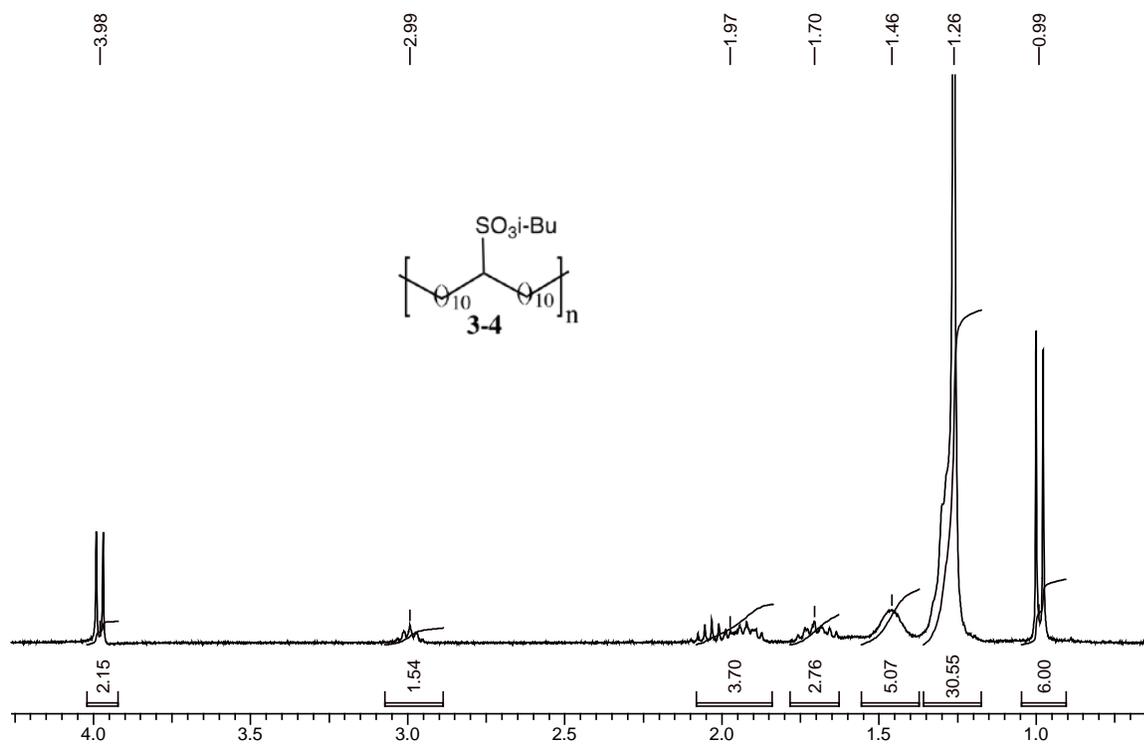


Figure 3-19. <sup>1</sup>H NMR of saturated isobutyl sulfonate polymer

Approximately 200 mg of polymer was added to 10 mL of DMF, and upon heating, the polymer went into solution. The first deprotection reaction was attempted, and it appears this scheme worked (Figure 3-20).

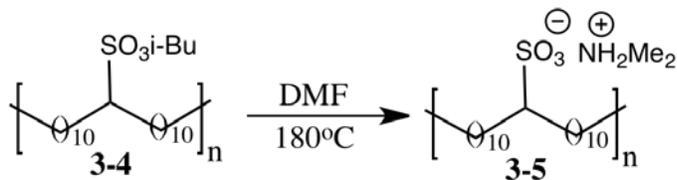


Figure 3-20. Deprotection of saturated polymer (**3-4**)

Although, as in the case with the protected polymer, more characterization needs to be done. One particular area of concern is polymer degradation. Since the deprotection is done with such high heat, there is a possibility that the polymer could degrade, thereby lessening the molecular weight. The most promising observance on the NMR spectra for the deprotected polymer is the absence of isobutyl peaks at 1 ppm and 4ppm, which indicates quantitative deprotection. The large peak at 3.3 ppm is due to water. The NMR was done using DMSO-d<sub>6</sub>, which is often wet, and as discussed earlier, sulfonic acid ionomers absorb water readily, so it's difficult to get a spectrum with no water (Figure 3-21); however, it is highly desired to eventually achieve a spectrum with no water so that the rest of the signals will be magnified. It is hard at this point to see much beyond water and the polymer backbone hydrogens. It is also desired to see the counter ion peak to ensure that the reaction occurred in the same manner as the small molecules.

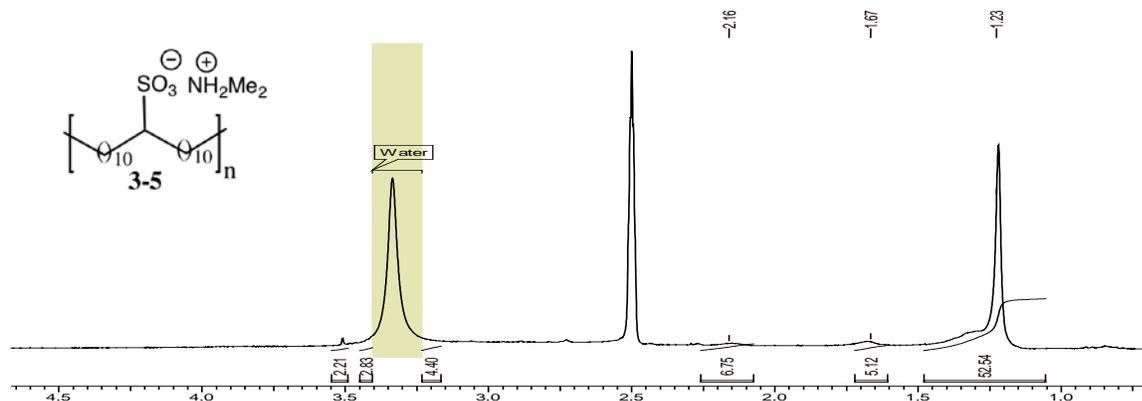


Figure 3-21. Deprotected sulfonic acid ionomer (**3-5**)

The first avenue to pursue would be to reprotonate the sulfonate groups. As shown in the small molecules, it is the DMF that deprotonates the isobutyl group, and the sulfonate anion is such a weak base because of resonance stabilization that it remains anionic. The purpose behind the reprotonation would be to study morphological changes in the polymer due to hydrogen bonding between the pendant sulfonic acid groups.

Next, if it can be shown full deprotection is afforded with a sulfonate group on every 21st carbon, then it would be good to demonstrate that full deprotection is afforded with increased frequency sulfonate groups (every 15th and every 9th carbon). It would also be interesting to see how morphology changes with the increased hydrogen bonding that would be present with increased sulfonic acid substituents. Additionally, water uptake studies would be of interest to see how branch frequency has an effect, since in the end these types of polymers will be of interest in fuel cells, where water management is an issue.

Until further characterization can be done on both the unsaturated and saturated polymers, and in addition, until further data can be obtained that shows unequivocally that full deprotection has occurred without polymer degradation, the previous paragraphs are just ideas and speculation. The main focus now is to get full characterization of the protected polymers, as well as full characterization of the deprotected polymer.

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## BIOGRAPHICAL SKETCH

Captain Lucas Josiah Fisher was born in 1981, to Gordon and Janet Fisher in Bloomington, IN. He spent his childhood on his father's farm in Elnora, IN, where he and his father raised cattle. Upon his high school graduation, he attended the United States Air Force Academy in Colorado Springs, CO. He graduated in 2003 with a Bachelor of Science in chemistry. Following graduation he was commissioned as a Second Lieutenant in the United States Air Force, and he attended Joint Specialized Undergraduate Pilot Training at Vance Air Force Base in Enid, OK. In February 2005, Captain Fisher received his pilot wings and his assignment as a C-17 Globemaster III pilot. After three months of C-17 Pilot Initial Qualification at Altus AFB, OK, he was stationed at Charleston AFB, SC as a C-17 pilot in the 14<sup>th</sup> Airlift Squadron. He logged over 150 combat hours in support of Operations Iraqi and Enduring Freedom. Following his assignment at Charleston, he was selected for the Air Force Academy pipeline program. This program sends Air Force officers to get their masters, followed by an assignment as an instructor at the Academy. After being selected he chose to attend the University of Florida under the direction of Professor Kenneth Wagener, where he studied protection/deprotection strategies for use in acyclic diene metathesis (ADMET) polymerization to create precision sulfonic acid functionalized ionomers.