SYNTHESIS OF IONIC LIQUID MONOMERS USING FLUORINATED SULFONYL IMIDE ANIONS AND THE 1,3-DIALKYLIMIDAZOLIUM CATION

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SYNTHESIS OF IONIC LIQUID MONOMERS USING FLUORINATED SULFONYL IMIDE ANIONS AND THE 1,3-DIALKYLMIDAZOLIUM CATION

A Dissertation
Presented to
the Graduate School of
Clemson University

In Partial Fulfillment
of the Requirements for the Degree
Doctor of Philosophy
Inorganic Chemistry

by
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Accepted by:
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ABSTRACT

With their unique material and solvent properties, ionic liquids have seen an amazing, exponential increase in interest. After a brief introduction of select areas of interest for these compounds, this thesis mainly focuses on the development of novel polyfunctional ionic liquids and polymeric ionic liquids.

One of the preferred anions for ionic liquids is the bis((trifluoromethyl)sulfonyle) imide anion, first introduced by our group in 1982. It shows excellent thermal stability and the desired resonance delocalization of a negative charge for ionic liquids. A series of monofunctional, difunctional, and multi-functional bis(perfluoroalkylsulfonyle)imides, along with 1,3-dialkylimidazolium cations were prepared by direct methylation of the alkylimidazole when possible, and by anion metathesis when necessary.

The resonance stabilization of the bis(perfluoroalkylsufonyl)imide anion serves two important purposes in this research. First, it provides delocalization of negative charge necessary to minimize interionic attractions in ionic liquids. Second, this same delocalization also renders the N-alkyl derivatives of the bis(perfluoroalkylsufonyl)imide anion good alkylating agents. This property is exploited in this research.

For potential electrochemical applications, polyfunctional ionic liquids were prepared to explore the properties of poly-anionic based materials. Concurrently, the effects of the organic cations, including polycations were examined. Novel ionic liquids of the following types were prepared.
In order to have a polymeric ionic liquid containing the fluoroalkyl sulfonated anion in the polymer backbone, a novel monomer of the following type was prepared.

\[
\text{CF}_3\text{SO}_2[\text{NSO}_2(\text{CF}_2)_x\text{SO}_2]_y\text{NSO}_2\text{CF}_3
\]

\[
x = 2 \text{ or } 4
\]
\[
y = 1 \text{ or } 2
\]

\[
R-N-N-R' \quad \text{and} \quad R-N-(\text{CH}_2)_z-N-N-R
\]

\[
z = 3 \text{ or } 7
\]

The trifluorovinyl aryl ethers can undergo step-growth polymerization by a thermal [2 +2] cycloaddition reaction. The thermally initiated cycloaddition was possible with the ionic liquid functional group present but made processing the polymer difficult because of the low glass transition temperature.

An alternative approach to fluorinated polymeric ionic liquids is to have the anion/cation on a pendant group on a polymeric chain. For this purpose a vinyl sulfonyl fluoride monomer was prepared.
Cyclopolymerization of this monomer with tetrafluoroethylene was successfully carried out to give a novel ionomer.
DEDICATION

I dedicate this work to my family and all who have been supportive of me through the years. This work would not exist without them.
ACKNOWLEDGMENTS

All of my work could not have been completed without the support of many special people. I am especially grateful to my advisor, Dr. Darryl. D. DesMarteau, whose creativity and knowledge of chemistry seems boundless, has contributed greatly to my development as a chemist and as a person. His incredible scientific capability and impeccable moral character have been an inspiration through my pursuit of this Ph.D. degree.

I would also like to thank Dr. Stephen Creager for valuable creative discussions and advice on these novel ionic liquids. And gratitude goes to my committee members Dr. Dennis W. Smith, Jr. and Dr. Bill Pennington for providing their beneficial insights regarding my research work. Group members, Dr. Rama Rajagapol, Dr. Hua Mei, Dr. Monika Mujkic and the rest of the Fluorine Group members, past and present, have enriched my work and life with their help in the laboratory, and simply with their encouragement, support, and friendship.

I dedicate this thesis to my family; my father, Tom Hickman; my aunt, Sandra Wallace; and my grandmother, Faye Fox Hickman, who passed away in March 2006, all who provided me with the example that through hard work and perseverance that anything is possible.
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CHAPTER I
INTRODUCTION

Preface

This thesis can be divided into two areas of research targeting potential industrial applications of ionic liquids: one is the synthesis of novel ionic liquids utilizing a halide-free methodology, and the other is the incorporation of ionic liquids into polymer systems by copolymerizing an ionic liquid monomer with other compatible comonomers, such as tetrafluoroethylene. The common thread between these two areas is the fluorinated sulfonyl imide anion and the 1,3-dialkylimidazolium cation.

In this introduction, some background for each project is presented along with the motivation underlying the research. Synthetic and characterization details of these novel ionic liquids are discussed in the succeeding chapters. Ionic liquids are presented first, followed by a short overview about perfluoroalkyl sulfonimide compounds and the 1,3-dialkylimidazolium cation. Incorporating the perfluoroalkyl sulfonimide functionality into polymer systems provides the potential for electrochemical applications as well as other uses, such as non-volatile plasticizers.

Ionic Liquids

Ionic liquids (ILs) are organic salts with melting points, by convention, under 100 °C, often below room temperature. They are comprised entirely of ions and exhibit interesting and sometimes unusual physical properties. Negligible vapor pressure, variable miscibility, favorable solvation behavior, and high thermal stability of ionic liquids has resulted in ionic liquids receiving considerable attention for their potential to deliver as “green” reaction media.¹² Ionic liquids also show substantial potential for use
in electrochemical devices as they have a wide electrochemical window, high conductivity, high ionic mobility, and wide operating temperature range; all of which make them attractive candidates for use as electrolytes in advanced electrochemical devices, including supercapacitors,\(^3\) lithium batteries,\(^4\) polymer-electrolyte fuel cells,\(^5\) deposition of metals and semiconductors, for catalysis, for separation and crystallization, in nanoscience, and many others. Most ionic liquids have viscosities comparable to those of oils, orders of magnitude greater than those of typical organic solvents. This high viscosity is a major disadvantage in many industrial applications as they depend on mass transfer and mixing. Viscosity also impacts on conductivity and thus the use of ionic liquids in electrochemical devices.\(^6\)

The first report of an IL goes back to 1914 and was reported by Paul Walden, of Walden inversion fame, and synthesized by the neutralization of ethylamine with nitric acid to form ethylammonium nitrate (EAN).\(^7\) Organic chloroaluminates were first mentioned in 1951 and studied extensively for applications in battery electrolytes and electrodeposition.\(^8\) However, these chloroaluminate ionic liquids are subject to rapid hydrolysis and required an inert-gas atmosphere. In the 1990s, 40-plus years later, the advent of air and moisture stable ILs has made them increasingly popular in academia and industry.\(^9\) Regarded as uncommon and a mere curiosity in the 1990s, today there are over 300 ionic liquids available commercially.\(^10\)

Walden’s EAN and the chloroaluminates were referred to as “room temperature molten salts” at the time and later termed “room temperature ionic liquids” (RTILs) because the expression “molten salt” had always been associated with high temperature
inorganic salts. The terms “room temperature ionic liquids” or RTILs and the shortened term “ionic liquids” (ILs) has become the preferred nomenclature today.

The design of ionic liquids is conceptually quite simple: minimize ionic coordination for a low melting point. These interesting compounds either incorporate a bulky asymmetric cation with floppy alkyl groups to preclude good crystal packing and/or include an anion for which there is considerable delocalization of the electron cloud. This weakens interaction with the cation and lowers viscosity. The most common classes of anions and cations are illustrated in Figure 1.1.

Typical anions
AlCl$_4^-$, Al$_2$Cl$_7^-$
PF$_6^-$, BF$_4^-$, SbF$_6^-$
[(CF$_3$SO$_2$)$_2$N] - (TFSI), (C$_4$F$_9$SO$_2$)$_2$N$, CF_3$CO$_2^-$
ROSO$_3^-$, RSO$_3^-$

Typical cations

![Diagram of 1,3-dialkylimidazolium and N-alkylpyridinium](image)

**Figure 1.1:** Examples of anions and cations commonly used to synthesize ionic liquids

From the families shown, a number of potential cation and anion combinations and their many substitution patterns allow the desired properties to be chosen. Even with
this array of variables at hand, a large percentage of ionic liquids synthesized utilize the
1,3-dialkylimidazolium cation due to its thermal stability and versatility for creating
derivatives. The bis((trifluoromethyl)sulfonyl)imide anion is one of the most effective
anions for low melting points and thermostability.

There’s no escaping the simplicity of how ILs are made. The synthesis of ionic
liquids can generally be divided into two sections: formation of the desired cation,
usually through a quaternization reaction on a nitrogen atom, whether it is a pyridine, an
imidazole, or an amine, and commonly done with an alkyl halide; and then followed by
anion metathesis to pair the cation with the desired anion. This is illustrated in the
following scheme for an ammonium salt.  

![Scheme 1.1: Typical synthetic paths for ionic liquids](image)

For example, if an alkyl imidazole is quaternized by reacting with an alkyl halide,
a halide salt will form. Now the bulky asymmetric cation is present, but not the desired
anion capable of limiting coordination through resonance. Then the second step is
chosen based on the target IL. The Lewis acid approach is typical of the
chloroaluminates. On the right side, three ways of performing anion metathesis are available and the appropriate choice is made based on availability, solubility differences, and potential for impurities. There is no avoiding trace metal, protic, or halide contamination when performing anion metathesis. This may or may not be a concern for the application of the IL but obviously can affect physiochemical properties. One of the goals of this research was to synthesize the IL within the top step – make the quaternized cation and the delocalized anion at the same time, thus preventing possible protic or halide contamination. This goal is made possible with the use of the N-alkyl bis((perfluoroalkyl)sulfonyl) imide moiety. The Queen's University Ionic Liquid Laboratories (QUILL) touts a patented halide-free synthetic method that utilizes a trifluoroacetate ester or sulfonic ester as an alkylating agent to the nucleophilic alkyl imidazole.\textsuperscript{12} This step requires 2-5 days for alkylation and then must be followed by neutralization with the acid form of the desired anion. The bis((perfluoroalkyl)sulfonyl) imide moiety alkylates in one step.

**Bis((Perfluoroalkyl)sulfonyl)imides and Their Derivatives**

An introduction to the bis((perfluoroalkyl)sulfonyl) imide moiety could possibly begin with its predecessor, imidobis(sulfuryl fluoride), (FSO\textsubscript{2})\textsubscript{2}NH. The reaction of imidobis(sulfuryl fluoride) with xenon difluoride in dichlorodifluoromethane at 0°C, reported by the DesMarteau group in 1974, provided the first example of xenon bonded to an element other than oxygen or fluorine.\textsuperscript{13} To form reasonably stable xenon compounds of this type, the substituent must have high group electronegativity and be resistant to degradative fluorination or oxidation.
Several bis((perfluoroalkyl)sulfonyl) imide, \((R_f\text{SO}_2)\text{NH}\), compounds were reported by Meussdoerffer and Niederprum in 1972 and realized that having two sulfonyl groups on nitrogen drastically increases the acidity of the proton.\(^{14}\) These bis((perfluoroalkyl)sulfonyl) imide compounds also meet the above requirement of being highly electronegative and resistant to degradative fluorination or oxidation. Years later, the DesMarteau group, intrigued by the bis((perfluoroalkyl)sulfonyl) imide’s acidity, successfully used a new sulfonimide to form yet another compound possessing a xenon-nitrogen bond.\(^{15}\) The parent member of the series, \((\text{CF}_3\text{SO}_2)\text{NH}\), was synthesized and reacted with trimethylsilane to form the silylimide, \(\text{Me}_3\text{SiN(SO}_2\text{CF}_3)\text{2}\), which then was reacted with \(\text{XeF}_2\) to form \(\text{Xe}[\text{N(SO}_2\text{CF}_3)\text{2}]_2\). The silicon-fluorine bond is extremely strong (582 kJ mol\(^{-1}\)) and clearly the driving force for this reaction.\(^{16}\)

Meussdoerffer and Niederprum’s later gas phase acidity measurements indicated that the relative acidity based on the \(R_f\) group of \((R_f\text{SO}_2)\text{NH}\) could not be solely based on the \(R_f\) group.\(^{17}\) Their claim was that the remarkable acidity could be attributed to three major substituent effects: (i) correctly oriented dipolar substituent/anion interaction (F effect), (ii) polarizable substituent/anion interaction (P effect), and (iii) substituent/\(\pi\)-electron-acceptor interaction (R effect) which preferentially stabilizes the strong electron-pair donor anion forms compared to the corresponding weaker \(\pi\)-donor conjugate acid forms. The acidity of the bis(perfluoroalkyl sulfonyl) imide is also due to the delocalization of the conjugate base charge over the O-S-N skeleton.
The conjugate bases of these acids are extremely weak nucleophiles and thus their coordination with metals and other cations is weak. Poor coordination to cations and their lack of hydrogen bonding capability is what makes the perfluoroalkyl sulfonyl imide anion attractive for ionic liquids. The anion, (CF$_3$SO$_2$)$_2$N$, is also an effective anion in producing low melting points for these same reasons.

While the TFSI anion is generally considered to be non-coordinating there have been a small number of publications reporting crystal structures. It was found that the TFSI salts of the oxophilic Group I metal cations lithium, sodium, potassium, cesium and rubidium exhibit strong metal-anion interactions to the sulfonyl oxygens, resulting in the formation of ionic hydrophilic domains and hydrophobic perfluoroalkyl regions. The anion assumed the cisoid conformation in every salt except the rubidium salt. From a computational perspective, the transoid conformation is lower in energy than the cisoid and suggests that the metal cation’s affinity for oxygen and the formation of fluorous regions may be possible driving forces. The 1,3-dimethylimidazolium bis((trifluoromethyl)sulfonyl)imide “ionic liquid” salt crystallizes in a triclinic lattice and also forms fluorous regions from the –CF$_3$ groups.
Preparation of ionic liquids in general usually takes multiple steps with the final product containing trace protic or metal halide contamination. N-methyl bis(perfluoroalkylsulfonyl)imides can be used as a methylating agent to provide ionic liquids in a one step reaction, thus providing a pathway to halide-free ionic liquids. The perfluoroalkyl sulfanyl imide anion is an excellent leaving group by virtue of being the conjugate base of a strong acid and the delocalization of the negative charge.

Not only is the N-alkyl perfluoroalkylsulfonyl imide a good alkylating agent but it is also a powerful electrophilic fluorination reagent, particularly when in the form of \((\text{CF}_3\text{SO}_2)_2\text{NF}\). This was produced in high yield with excellent stability and desirable physical properties. These compounds are useful in a variety of fluorinations wherein electrophilic fluorine is needed, for example, fluorinating aromatic rings. Again, this is another example of what an excellent leaving group the perfluoroalkylsulfonyl imide anion is.

Another interesting application for the perfluoroalkyl sulfonimide anion is for lithium battery electrolytes. Ideally, to prevent concentration polarization problems in lithium batteries, lithium ions would be the only mobile ions in a single-ion conductor. And bis((perfluoroalkyl)sulfonyl) imide anions attached to a polyethylene glycol (PEG) chain such as \(\text{CH}_3(\text{OCH}_2)_n\text{OCF}_2\text{CFHO CF}_2\text{CF}_2\text{SO}_2\text{N}(\text{Li})\text{SO}_2\text{CF}_3\) were made by the
DesMarteau group and were attractive due to the possibility of limited anion motion, as pure cationic conduction is desired in a lithium battery, and also greater delocalization of negative charge in sulfonimide anions, which can reduce ion pairing and increase conductivity.\textsuperscript{21} The non-coordinating tendency of the bis((perfluoroalkyl)sulfonyl) imide anion is exploited here as well. The idea behind this is grounded in the Grotthuss hopping mechanism wherein the proton or lithium cation, in this case, can move or “hop” from one sulfonic acid group to another, providing the perfluorinated ionomer membrane is fully hydrated.\textsuperscript{22} Moreover, these salts can be dissolved in a polymer host or one can form a solid polymer electrolyte in which ionic charges are chemically bonded to the polymer host backbone.\textsuperscript{23,24}

The choice of the anion is of particular importance because, perhaps more than any other single factor, it appears that the anion of the ionic liquid controls the degree of solubility or insolubility the IL will have in molecular solvents such as water, chloroform, ether, etc…. In this research it was found that 1,3-dialkylimidazolium bromides and iodides were water-miscible while the bis((perfluoroalkyl)sulfonyl) imide ILs were not. The nature of the cation certainly plays some role when performing anion metathesis because the potassium, sodium, and lithium salts make the bis((perfluoroalkyl)sulfonyl) imide salts water soluble, and the cesium salts water insoluble.

**The 1,3-Dialkylimidazolium Cation and Ionic Liquids**

Imidazole is an aromatic heterocycle, classified as an alkaloid, and an important building block in biological systems. Imidazole is a 5-membered planar ring, which is soluble in water and other polar solvents. It exists in two equivalent tautomeric forms
because the hydrogen atom can be located on either of the two nitrogen atoms. The compound is classified as aromatic due to the presence of a sextet of $\pi$-electrons, consisting of a pair of electrons from the protonated nitrogen atom and one from each of the remaining four atoms of the ring. While five-membered ring heterocycles, like imidazole, don’t exhibit the resonance stabilization as benzene, they do offer versatility not offered by benzene. The conjugate acid of imidazole has a $pK_a$ 6.95 and imidazole has a $pK_a$ 14.5. This basicity of the sp$^2$ nitrogen atom allows for S$_N$2 reactions with alkyl halides to form 1,3-dialkylimidazolium halide salts. Salts of imidazole where the imidazole ring is in the cation form are known as imidazolium salts. These salts are formed from the protonation or substitution at the nitrogen atom of imidazole.

Melting points and boiling points of metals and compounds give a direct indication to the attractive forces between the particles. A high melting point indicates strong metallic bonding or the presence of a giant covalent structure. A lower melting point is associated with covalently bonded molecules held in a solid lattice by weak dispersion forces. An extremely low boiling point suggests a structure consisting of separate atoms held together by dispersion forces only.

Generally, melting points for the representative metals (Groups I and II) decrease as you go down a group and represent a periodic trend explained by increasing size as a result of new energy levels of electron clouds as you move from period to period, down a group. This makes each atom significantly more massive, in terms of mass and volume. Upon ionization, the ionic radius is smaller than the atomic radius of the same element, but the general trend of increasing size down a group continues. The positive charge
created is spread across a larger volume, thus making the charge more diffuse and weakening the attractive forces between neighboring particles.

These elementary ideas also apply to ionic liquids. The sizes and shapes of cations in ionic liquids are important in determining the melting points. Large ions tend to produce reductions in melting points of the salts. And 1,3-dialkylimidazolium ionic liquids are examples of salts containing large cations with a delocalized charge and an alkyl-shielded charge. The molecular interactions between ions result from their geometry and charge distribution. In simple salts the interactions are controlled by long-range Coulombic forces between the net charges of the ions. With molecular ions, such as the imidazolium cation and the bis((trifluoromethyl)sulfonyl) imide anion, the size and asymmetric charge distribution softens the Coulomb forces and generates directional interactions of shorter range. Ionic liquids are simply organic salts characterized by a low melting point.

A reduction in symmetry of the cations causes a distortion from ideal close packing of the ionic charges in a solid state lattice, a reduction in lattice energy, and depression of melting points. A change from the spherical (high symmetry) Na\(^+\) ion to the lower symmetry imidazolium cation distorts the Coulombic charge distribution. In addition, the imidazolium cation contains alkyl groups that do not participate in charge delocalization.

Imidazolium salts afford changes in ring substitution patterns, which can have significant effects on melting points. Substitution at C(2,4,5)-positions on the ring affect packing and space filling of the cation. Substitution at the C-2 position increases melting
points. This is not an obvious result but may be caused by changes in the cation structure that induce aromatic stacking or methyl-\(\pi\) interactions between cations.\(^{26}\)

Another factor to consider is substituent alkyl chain length. An increase in size and internal flexibility should lower melting points, whereas increasing dispersive interactions between alkyl chains should increase \(T_m\). Cations with short alkyl chains \((C_n \leq 3)\) form crystalline phases with comparatively high melting points. Salts with chains of intermediate lengths, \((4 \leq C_n \leq 12)\), exhibit a broad liquid range with low melting temperatures, and a tendency to supercool. Ions with long alkyl chains \((C \geq 12)\) result in complex phase diagrams involving liquid-crystalline phases.\(^{27}\)

The imidazolium cation was chosen for this research because of its versatility. N-methyl bis((perfluoroalkyl)sulfonyl)imides exhibit excellent alkylation activity (\(\text{CH}_3^+\) donor) and readily react with imidazoles and pyridine compounds to form ionic liquids. Pyridine offers the one nucleophilic nitrogen to which a methyl group can be attached, thus creating a symmetric cation. The commercial availability and the ease with which various \(n\)-alkylimidazoles can be acquired or synthesized simplify the ease with which an asymmetric imidazolium cation can be made. Lastly, with an eye towards lithium battery electrolytes and fuel cell membranes, the 1,3-dialkylimidazolium salts appear to be up to now the most stable and conductive ionic liquids.\(^{28}\)

**Perfluorocyclobutane Aromatic Ether Polymers**

The first report of the thermal dimerization of perfluoro olefins was of the cycloaddition of tetrafluoroethylene in 1947.\(^{29}\) It was subsequently discovered that substitution perfluoro olefins also undergo the same cyclodimerization reaction, with the
single requirement being the presence in the molecule of a terminal difluoromethylene group in the olefin.\textsuperscript{30}

Perfluorocyclobutane (PFCB) aromatic ether polymers possess many advantages such as ease of processing, and excellent thermal and mechanical properties. Monomers can be synthesized from mono-, di-, or tri-hydroxyl aromatic groups in two or three steps and can be polymerized neat or in solution without the need of catalyst or initiator by $2\pi + 2\pi$ cycloaddition for a step-growth polymerization. The thermal dimerization of tetrafluoroethylene (TFE) and substituted trifluorovinyl compounds to form perfluorinated cyclobutanes has been well documented.\textsuperscript{31} The ability of TFE and other perfluoro olefins to thermally cyclize with themselves has been attributed to the relief of steric strain between fluorine and the fluoro olefin $\pi$ orbitals in going from sp$^2$ to sp$^3$ hybridized carbon bond centers.\textsuperscript{32} This thermally accessible cyclization is not a pericyclic reaction, but proceeds through a radical mechanism, and considered to occur in a head-to-head fashion that produces a stable diradical intermediate.\textsuperscript{33}

![Figure 1.4: Polymerization of aryl trifluorovinyl ethers showing diradical intermediate](image)

Aryl trifluorovinyl ethers provide an excellent platform for integrating a fluorinated sulfonyl imide anion paired with a 1,3-dialkylimidazolium cation. From Figure 1.4 it is apparent that polymers are synthesized using a difunctional aryl trifluorovinyl ether. The synthetic versatility arises from the common linking group. Aromatic
trifluorovinyl ether monomers can be prepared in two steps: alkylation of a phenolic precursor with 1,2-dibromotetrafluoroethane, followed by zinc dehalogenation.\textsuperscript{34}

In 1996, Smith established the \textit{p}-bromo(trifluorovinyl oxy)benzene strategy that allows subsequent reaction with organolithium reagents or Grignard reagents without harming the fluorinated olefin.\textsuperscript{35} In this work, this \textit{p}-bromo(trifluorovinyl oxy)benzene intermediate strategy is used to incorporate a difunctional linker between two (trifluorovinyl oxy)benzene groups – a linker containing two fluorinated sulfonimidoyl imide anions, paired with two 1,3-dialkylimidazolium cations. The final goal is the synthesis of the polymeric ionic liquid shown in Figure 1.5.

\begin{figure}
\centering
\includegraphics[width=\textwidth]{pfcb_polymer.png}
\caption{PFCB Polymer containing 4-carbon ionic liquid linker}
\end{figure}

Since this cyclodimerization, or polymerization, is known to occur through a concerted radical mechanism, this chemistry was initially chosen as a model study to determine if the presence of the aromatic imidazolium cation, as an ionic liquid, would affect the reaction. If no detrimental effect is noticed, then incorporation of ionic liquid monomers into polymer systems could be possible with any polymerization proceeding through a radical mechanism.

\textbf{Nafion®}

For the past 30 years, DuPont™ Nafion® membranes and dispersions have been the product of choice for the fuel cell industry, providing unparalleled power output and
durability, basically the standard by which new membranes are measured. Polymer electrolyte membrane (PEM) fuel cells require many qualities to be successful, namely, high proton conductivity, good mechanical properties, and long term chemical stability. DuPont’s perfluorinated ionomer Nafion® along with several other closely related perfluorosulfonic acid (PFSA) ionomers possess these desirable properties but also possess limitations, most notably is a tendency toward diminished proton conductivity under conditions of low water availability.\(^{36}\)

Although the desired Nafion ionomer contains the \(-\text{SO}_3\text{H}^+\) functionality, Nafion ionomers are usually derived from the thermoplastic \(-\text{SO}_2\text{F}\) precursor form that can be extruded into sheets of required thickness. Strong interactions between the ionic groups form an obstacle to melt processing. This precursor does not possess the clustered morphology needed for proton transport but does possess Teflon-like crystallinity which persists when the sulfonyl fluoride form is hydrolyzed to the \(\text{K}^+\) form by reacting it with KOH in water and DMSO. Thereafter, the \(-\text{SO}_3\text{H}\) form is achieved by soaking the film in a sufficiently concentrated aqueous acid solution.

The PFSA precursor is prepared by copolymerization of its \(-\text{SO}_2\text{F}\) monomer with tetrafluoroethylene (TFE). The Nafion® monomer’s \(-\text{SO}_2\text{F}\) group makes it an excellent candidate for derivatization, particularly the bis((perfluoroalkyl)sulfonyl)imide acid group. Synthesis of bis((perfluoroalkyl)sulfonyl)imide imides has been an interest of the DesMarteau group for many years and, in 2002, the conventional sulfonic-acid-based Nafion ionomer was compared to a newly synthesized bis((perfluoroalkyl)sulfonyl)imide-based ionomer, and shown in Figure 1.6.\(^{37}\)
The –SO₂F monomer from DuPont is ideal for modifying to a bis((perfluoroalkyl)sulfonyl)imide, and the bis((perfluoroalkyl)sulfonyl)imide anion is ideal for pairing with a 1,3-dialkylimidazolium cation to form an ionic liquid monomer. Another goal of this research was to synthesize this IL monomer and copolymerize it with tetrafluoroethylene (TFE).

General Experimental Methods

NMR Spectroscopy

¹H and ¹⁹F NMR spectroscopic studies were carried on a JEOL ECX 300 (¹H—300.53 MHz and ¹⁹F—282.78 MHz), with earlier measurements in this research being done on a Bruker AC 200 (¹H—200.1 MHz and ¹⁹F—188.3 MHz). ¹H NMR spectra were referenced to external trimethyl silane(TMS), ¹⁹F chemical shifts were referenced to CFCl₃. The chemical shifts of residual H in CD₃CN, CDCl₃ and DMSO are 1.93 ppm, 7.24 ppm and 4.63 ppm, respectively, relative to TMS. Negative chemical shifts and positive chemical shifts indicate upfield and downfield from the reference.
correspondingly. The splitting patterns of resonance were described by the following: singlet (s), doublet (d), triplet (t), quartet, (q) and multiplet (m).

The NMR spectra were measured using solutions of 1–2 mmol/L concentrations (unless otherwise stated) and small amounts of CFCl₃ gas in an appropriate deuterated solvent. For moisture sensitive compounds, anhydrous deuterated solvents were used, which were prepared by drying them over appropriate drying reagents and then transferring into the one-piece-flask with molecular sieves for storage. Dry NMR samples were prepared in the 4 mm glass tubes fused to a joint. The sample tube containing the compound of interest was connected to a vacuum system for transferring the dry solvent and the internal reference into the sample tube at –196 °C. The 4 mm tube was sealed by a torch and inserted into a normal 5mm NMR tube for analysis.

**IR Spectroscopy**

Infrared spectra were recorded on a Perkin-Elmer 1600 and 2000 series FTIR spectrometer. Solid samples were prepared in one of the two ways: 1) 1-5mg of sample were dissolved in 2mL volatile solvent acetone and one drop of the solution was added on KCl or KBr plates; 2) a mixture of 5-10mg of sample and one drop of Nujol were added on KCl or KBr plates. After the solvent was evaporated, the sample film is formed between two plates and can be analyzed in the instrument. Gas samples were analyzed in cells of 10cm length, fitted with a glass Teflon valve. Windows of KCl or NaCl were attached using Halocarbon wax. Unless indicated otherwise, samples were a minimum of 99.5% pure by ¹⁹F NMR. IR spectra were scanned from 4000cm⁻¹ to 450 cm⁻¹ and
reported in wave numbers (cm⁻¹) with intensity abbreviations: vs (very strong), s (strong), m (medium), w (weak), and vw (very weak).

**Thermal Analysis**

Thermogravimetric Analysis (TGA) was performed on a Perkin-Elmer TGA7 with a data system using an IBM computer. TGA samples were typically around 5-10mg and were run in a nitrogen environment with a platinum sample pan, with heating rates of 10°C/min.

Differential Scanning Calorimetry (DSC) was performed on a Perkin-Elmer DSC7. The data were obtained in stainless steel pans for acidic and corrosive samples, or with aluminum pans, using around 5-10mg pure samples. The temperature change rate was around 10°C/min for heating and cooling.

Temperatures reported from TGA data are the onset $T_d$ as determined from the step tangent. Temperatures reported from DSC data are curve peaks, freezing points being exothermic upon cooling and melting points being endothermic upon heating.

**pH Value Measurement**

The pH values of aqueous solution were obtained on Fisher Accumet Model 925 pH meter, with the standard size glass body combination electrodes/calomel reference. At room temperature, the instrument was standardized at pH7.0 and pH4.0 using two Fisher certified buffers. The concentrations of solutions for measurement were in the range of 0.1M to 0.4M.

**Purification of Solvents and Experimental Practice**
All starting materials were obtained from commercial sources and used as received unless otherwise stated. Dry CH$_3$CN solvent was stored over CaH$_2$ and then distilled over P$_4$O$_{10}$ before using. Diethyl ether were stored overnight on KOH, refluxed over Na metal until a trace amount of benzophenone turned blue, and then distilled for use.

All the reactions were carried out in glass apparatus unless otherwise specified. Moisture or air sensitive compounds were handled in a dry box filled with nitrogen. Handling any kinds of highly toxic and corrosive gases such hydrogen chloride was done through vacuum system transfer.

**Glass Vacuum System**

The glass vacuum line shown in Figure 1.7 was used for reduced pressure distillation of high boiling point compounds, sublimation and trap-to-trap transfer of low boiling point compounds. The vacuum line was equipped with Kontes glass-Teflon valves and consisted of a single manifold with a built in trap-to-trap separation system, a liquid nitrogen trap, a diffusion pump and a mechanical Welch vacuum pump. An ultimate vacuum of 15-20 µmHg could be achieved in the system.
Figure 1.7: Vacuum Line System
CHAPTER II
DIFUNCTIONAL, MULTIFUNCTIONAL, AND NOVEL BIS((PERFLUOROALKYL)SULFONYL)IMIDE IONIC LIQUIDS

Introduction

A key feature of ionic liquids is the large number of possible ion combinations; this opens the possibility of altering the constituent ions to tailor for particular physical and chemical properties. At present there is no definitive way of determining which particular pairing will produce the desired properties. While general rules may apply a complete understanding is still under intense study.

The vast majority of IL studies involve modifications to the cation’s alkyl groups and studies of anionic influences simply compare one anion to another, for instance, the Cl$^-$ ion with the PF$_6^-$ ion. The typical approach to IL design is shown in Figure 2.1.

![Diagram of IL design](image)

**Figure 2.1:** Typical approach to IL design
The DesMarteau group has many years of experience in altering the fluorinated sulfonimide moiety. This has been particularly useful in the pursuit of lithium battery electrolytes and Proton Exchange Membrane Fuel Cells since these applications require mobility of lithium cations and protons, respectively, and desire an essentially non-coordinating, stationary anion.

**Difunctional and Multi-functional Perfluoroalkyl Sulfonimides**

The foundation for this chapter was laid by Dr. Axel Klauk and Dr. Jie Zhang of the DesMarteau group. Dr. Axel Klauk successfully synthesized 1,2-bis(chlorosulfonyl) tetrafluoroethylene and 1,2-bis(flurosulfonyl) tetrafluoroethylene.\(^{38}\) This clever synthesis allows two \(-\text{SO}_2\text{F}\) groups to be separated by only two \(\text{CF}_2\) groups. The difunctional \(-\text{SO}_2\text{F}\) precursor was used to make three ILs here. Dr. Jie Zhang synthesized difunctional \(N\)-fluoro perfluoroalkyl sulfonylimides with a variety of perfluorinated linkers, particularly \(-(\text{CF}_2)_n\)\(-,\ -(\text{CF}_2)_6\)\(-,\ -(\text{CF}_2)_2\text{O}(\text{CF}_2)_2\)\(-.\)\(^{39}\) These reagents exhibited excellent activity for electrophilic fluorination. Dr. Jie Zhang’s work also used the parent sulfonimide, \((\text{CF}_3\text{SO}_2)_2\text{N}\), to directly methylate and quaternate a variety of nitrogen compounds to make ionic liquids.\(^{40}\) The intent of this work was to combine all three accomplishments to make ILs with a difunctional anion.

The syntheses utilize one of the three basic ways in which the perfluorinated, and sometimes not completely fluorinated, sulfonimide is prepared. All three methods are shown in Scheme 2.1.
Scheme 2.1: Three synthetic paths to the sulfonimide moiety

Shown above are three most common ways in which the sulfonimide moiety is prepared in the DesMarteau group. Method 1 is a silyl derivatized sulfonyl amide reacting with a sulfonyl fluoride and there appears to be two driving forces at work here. Once the $S_N2$ transition state is established, there exists a good, stable leaving group, with low basicity, in the sulfonimide. Another prominent driving force is the fluorine atom’s affinity for the silicon atom. This affinity was exploited by DesMarteau in 1982 as an alternative approach in establishing a stable xenon-nitrogen bond. This reaction proceeds in high yield and is easy to purify under vacuum.
Method 2 is a base assisted condensation reaction with DIEA, followed with acidification of the sulfonimide, and then neutralized with cesium carbonate. The cesium salt’s poor solubility in water and dichloromethane make it unique and accords washing impurities away with water or dichloromethane with very little loss of product.

Method 3 is the same base assisted reaction as method 2 and can be used if both starting materials are very clean. As in both methods, the non-nucleophilic diisopropylethylamine (DIEA) and triethylamine (TEA) have been used with equal success. The only distinction is that acidification of the sulfonimide is omitted, and the subsequent neutralization with a metal carbonate is omitted. Neutralization can also be done with LiOH if a lithium counterion is necessary, for example, if a lithium battery electrolyte is to be explored. Neutralization of the DIEAH⁺ or TEAH⁺ salts is possible with either lithium or sodium hydroxide.

Essentially, two primary methods will be described to prepare perfluoroalkanesulfonimides: the reaction of a sulfonyl fluorides with sulfonamides in the presence of a base, or the sulfonyl fluoride with the sodium salt of N-(trimethylsilyl)trifluoromethylsulfonamide. It should also be noted that these methods are very moisture sensitive. CF₃SO₂NH₂ and CF₃SO₂N(Na)SiMe₃ are very poor nucleophiles as evidenced by the need for the sterically hindered base and 48 hour reaction time, respectively. The importance of maintaining dry conditions cannot be stressed enough as CF₃SO₂NH₂ and CF₃SO₂N(Na)SiMe₃ cannot kinetically compete with moisture. One of the above methods may be preferred over the other in certain situations and will be discussed as they arise in this work.
Research and Discussion

The first ILs prepared were an extension of Axel Klauk’s synthesis of the difunctional sulfonyl chloride separated by two CF$_2$ groups. This preparation also served as an introduction to some well established chemistry in the DesMarteau group. The scheme is shown below.
Scheme 2.3: Synthesis of difunctional IL with two carbon linker

The 1,2-bis(chlorosulfonyl) tetrafluoroethylene was from Dr. Klauck’s research and fluorinated with KF in dry acetonitrile. It was prepared years earlier and stored in slightly acidic water. No hydrolysis had occurred in spite of how easy fluorinated sulfonyl chlorides and sulfonyl fluorides hydrolyze. This only occurs in the presence of a base with significant nucleophilicity.

The sodium salt of N-(trimethylsilyl)trifluoromethylsulfonamide, CF$_3$SO$_2$N(Na)Si(CH$_3$)$_3$, is a very important compound in our group, as well as silyl compounds of the form R$_f$SO$_2$N(Na)Si(CH$_3$)$_3$. The silyl sodium salt is critical to the coupling reaction forming the sulfonimide moiety, particularly end-capping with a sulfonimide. And synthesis of this salt, CF$_3$SO$_2$N(Na)Si(CH$_3$)$_3$, begins with triflic acid or triflic anhydride. Basically though, any perfluorosulfonyl fluoride can be derivatized to a silyl compound and further coupled to another sulfonyl fluoride. With this in mind, the door is opened to difunctional and multi-functional sulfonimides.

Triflic anhydride is a versatile compound that has found many uses in synthetic chemistry. Brice and Trott first reported the isolation of trifluoromethanesulfonic acid anhydride as it was obtained as a by-product from the synthesis of trifluoromethanesulfonyl chloride.$^{42}$

\[
\begin{align*}
\text{CF}_3\text{SO}_3\text{H} & \xrightarrow{\text{PCl}_5} \text{CF}_3\text{SO}_2\text{Cl} + \text{(CF}_3\text{SO}_2\text{O})_2\text{O}
\end{align*}
\]

Scheme 2.4: First synthesis of triflic anhydride
Considerably better yields of the anhydride (65-83%) are realized by treatment of triflic acid with phosphorus pentoxide. This is how triflic anhydride is made in our group and is not a trivial procedure. Addition of P₄O₁₀ to triflic acid is exothermic and temperature is maintained at 0°C to minimize formation of the sulfonic ester side product. One reported synthesis performs the dehydration at room temperature with no mention of the sulfonic ester, methyl triflate, being formed. The procedure reported is interesting in that the P₄O₁₀ is mixed with an equal volume of Celite; we have not tried mixing the P₄O₁₀ with Celite and the mixture always turns from slurry to a solid mass before the phosphorus pentoxide is completely added. The Celite probably prevents clumping and accords a better flowing solid while remaining inert to the dehydration. Maintaining dry conditions is also important to minimize decomposition of the anhydride as it is very electrophilic. This is more apparent if one considers the likely mechanism for the dehydration. When proton acids catalyze dehydration (CF₃SO₃H here) the mechanism is typically E1. In alcohols, the principal process is conversion of the ROH to ROH₂⁺ and cleavage of the latter to R⁺ and H₂O, and some acids a secondary process probably involves conversion of the alcohol to an ester. However, with triflic acid there is no second proton available to facilitate elimination once (CF₃SO₂)⁺ is formed. A proposed mechanism from this point can be achieved with some electron pushing, bond formation with the conjugate base, or small molecule elimination (SO₂), and accounts for the formation of triflic anhydride and methyl triflate. One should keep in mind this is a proposed mechanism since, after elimination of the SO₂ molecule, a very unstable CF₃⁺ would result. See Scheme 2.4.
A trap-to-trap distillation is done to isolate the anhydride and the best results are achieved when a second atmospheric pressure distillation is performed under nitrogen. Purification of the anhydride is time consuming and it has become more cost effective to purchase triflic anhydride and use as purchased. It’s also critical to dispense and then store triflic acid or triflic anhydride in a dry atmosphere. For best results, tailor reaction scales to the available packaging because once a bottle has been exposed to air there will be severe hydrolysis to triflic acid.

Triflic anhydride is used to prepare trifluoromethylsulfonyl amide, \( \text{CF}_3\text{SO}_2\text{NH}_2 \). Care should be taken to slowly drop the triflic anhydride into the condensed ammonia (\(-80\ ^\circ\text{C}\)) because the reaction is very exothermic. The sulfonyl amide can be titrated with NaOH and stored as the sodium salt indefinitely. This justifies amidating excess triflic
anhydride according to quantity/size availability. During titration, excess hydroxide must be avoided because it hydrolyzes the SO₂Cl or SO₂F group in the coupling reaction. Moreover, the sylilation should not be performed with the expectations of storing the derivatized trimethylsilyl trimethylsulfonyl amide sodium salt indefinitely. Even when stored in a dry box some decomposition can occur. If possible, the sodium salt of the perfluorosulfonyl amide should be weighed according to the coupling reaction that follows the silylation, and the same vessel used for the coupling reaction.

Trifluoromethanesulfonyl fluoride has exclusively been made by electrochemical fluorination of methanesulfonyl fluoride (or chloride) in liquid hydrogen fluoride, which is obviously dangerous and why the amidation of triflic anhydride is the chosen path to trifluoromethanesulfonyl amide, CF₃SO₂NH₂. Moreover, CF₃SO₂F has a boiling point of -21°C and requires vacuum line techniques for handling. The other perfluorosulfonamide (C₄F₉SO₂NH₂), in this work, made into a silyl derivative starts with perfluorobutylsulfonyl fluoride. This sulfonyl fluoride is liquid at room temperature and is amidated by condensing NH₃ at -78°C. The same titration with NaOH and subsequent silylation apply and is shown in Scheme 2.6.

\[
\begin{align*}
R_fSO_3H & \xrightarrow{P_2O_{10}} (R_fSO_2)_{2}O \xrightarrow{NH_3} R_fSO_2NH_2 \xrightarrow{NaOH} R_fSO_2NH(Na) \xrightarrow{HMDS} R_fSO_2N(Na)SiMe_3 \\
R_fSO_2F & \xrightarrow{NH_3} R_fSO_2F \xrightarrow{NH_3} R_fSO_2NH(Na) \xrightarrow{HMDS} R_fSO_2N(Na)SiMe_3 \tag{2}
\end{align*}
\]

**Scheme 2.6:** Synthesis of Silyl Starting Materials

CF₃SO₂N(Na)SiMe₃ can be made once the sulfonamide is neutralized by aqueous NaOH. The CF₃SO₂NH(Na) can be almost quantitatively obtained but, as mentioned
earlier, a slight excess of the sulfonamide should be used to avoid hydroxide contamination. Due to the moisture sensitivity of the silyl derivative and hexamethyldisilazane, HMDS, the sodium salt has to be dried at 100°C under high vacuum before proceeding to 2. The excess CF₃SO₂NH₂ or RᵣSO₂NH₂ will sublime under these conditions and can be removed. HMDS can be used as solvent and reactant in the silylation reaction or an equal volume of dry acetonitrile can be added to save cost on HMDS. The silylated product, CF₃SO₂N(Na)SiMe₃, is very moisture sensitive and must be handled and stored in a dry box.

For monofunctional sulfonimides a slight excess of the –SO₂F compound can be used while difunctional or multifunctional syntheses should contain exact molar quantities. For the difunctional or multifunctional sulfonimides, purification is possible with a slight excess of the CF₃SO₂N(Na)SiMe₃. After synthesis of a difunctional, (CF₃SO₂N(Na)SO₂)₂Rᵣ, the excess CF₃SO₂N(Na)SiMe₃ can be hydrolyzed to (CH₃)₃Si-OH and CF₃SO₂NH(Na). Trimethylsilanol has a boiling point of 99°C and can be removed under high vacuum. The sodium salt, CF₃SO₂NH(Na), has to be acidified to the sulfonamide and sublimed.

While the first difunctional sulfonyl fluorides with the two-carbon linker were inherited from the laborious work of Dr. Axel Klauck, the other difunctional sulfonyl fluorides originate from some commercially available α,ω-diiodoperfluoroalkyl compounds, I(CF₂)ₙI. Difunctional sulfonyl halides are not available commercially so the I(CF₂)ₙI compounds are synthesized using a deiodosulfination procedure commonly used in the DesMarteau group and shown in Scheme 2.7.
Scheme 2.7: Synthesis of $\alpha,\omega$-diiodoperfluoroalkane sulfonyl fluorides

While the chemistry involved remains the same, techniques for these syntheses varies from DesMarteau group member to member and it was a combination of Dr. Zhou’s and Dr. Ford’s techniques that optimized results for this work. Only one study on deiodosulfination could be found and concluded basically that the mechanism was free radical in nature and electron transfer processes were involved. Some possible free radical chain mechanisms were later proposed in a review article written by the same author.

Deiodosulfinations can be performed in a variety of solvent mixtures; the mixture used in our group is acetonitrile and water. This reaction has also been performed with sodium sulfite instead of sodium hydrosulfite. Sodium bicarbonate is added to the mixture for basicity. The dithionite ion ($S_2O_4^{2-}$) undergoes both acid and alkaline hydrolysis and complicates knowing definitively if the reducing agent is the $SO_2$ radical or the $SO_3$ radical.
\[
2 S_2O_4^{2-} + H_2O \rightarrow S_2O_3^{2-} + 2 HSO_3^{-}
\]

\[
3 NaS_2O_4 + 6 NaOH \rightarrow 5 Na_2SO_3 + Na_2S + 3 H_2O
\]

**Scheme 2.8:** Acid and Alkaline Hydrolysis of Dithionate Ion

The basicity is also necessary to prevent formation of a sulfinic acid (RSO₂H), which, in the presence of air, is easily oxidized to a sulfonic acid (RSO₃H). This poor storage stability is the reason why the sulfinate (6) is not isolated and immediately oxidized with Cl₂. Some key points in the chlorination is rapid bubbling of the chlorine gas, effective cooling at 0°C, vigorous stirring, and maintaining a blanket of chlorine gas above the solution to ensure a saturated chlorine solution. These factors combine to prevent possible side reactions that re-oxidize the sulfinate back to the perfluorinated iodide compound. The sulfinate solution being dropped into the chlorine solution obviously contains iodide ions, I⁻, from the deiodosulfination and, upon dropping, the solution will turn from yellow to red-brown, back to yellow again.

The iodide ion present during chlorination reacts with Cl₂ to form ICl – a red-brown compound. The red-brown color should not remain for more than a few seconds and is controlled by the above-mentioned factors. ICl is an undesirable side product and because of the difference in electronegativity between I and Cl, iodine monochloride is highly polar and behaves as a source of electrophilic I⁺, which is responsible for converting the sulfinate back to RᵢI. A quick color change back to yellow indicates that excess chlorine has reacted with ICl to form ICl₃, a bright yellow, innocuous, desired side
ICl actually exists as $\text{I}_2\text{Cl}_6$ with two bridging Cl atoms. Scheme 2.8 illustrates these desired and undesired reactions.

\[
\text{desired main reaction: } \text{R}_f\text{SO}_2\text{Na} + \text{Cl}_2 \rightarrow \text{R}_f\text{SO}_2\text{Cl}
\]

\[
\text{side reactions: }
\begin{align*}
\text{NaI} + \text{Cl}_2 & \rightarrow \text{NaCl} + \text{ICl} \\
(\text{red-brown}) \\
\text{xs Cl}_2 & \rightarrow \text{I}_2\text{Cl}_6 (\text{yellow}) \\
\text{ICl} & \rightarrow \text{R}_f\text{SO}_2\text{Na} \\
\text{R}_f\text{SO}_2\text{I} & \rightarrow \text{R}_f\text{I}
\end{align*}
\]

**Scheme 2.9:** Reactions present during chlorination

Subsequent replacement of the chlorine atoms in 7 with fluorine is a nucleophilic displacement reaction performed with activated KF in dry acetonitrile. This reaction proceeded at room temperature in 24 hours as long as a molar excess of KF greater than 5:1 is used. Final bis-sulfonyl fluoride compounds were obtained by distillation.

The next reaction is a coupling reaction and basically end caps the difunctional $\text{FO}_2\text{S(CF}_2)_4\text{SO}_2\text{F}$ to form two sulfonyl imide groups. Since a CF$_3$ group was desired on each end of the molecule then CF$_3\text{SO}_2\text{N(Na)SiMe}_3$ was used. This is Method 1 from Scheme 2.1 and utilized because CF$_3\text{SO}_2\text{F}$ is a gas requiring vacuum line techniques to handle. Dry acetonitrile is the desired solvent for this reaction but normal refluxing requires several days to complete. Higher boiling solvents can be used, such as dioxane, but are difficult to remove. A closed system, heated to 110 °C, with acetonitrile was used and the reaction completes in 48 hours. A stainless steel bomb reactor at 120 °C has been
used earlier in our group but a one-piece reactor equipped with an Ace-thread sidearm became the preferred reaction vessel as it allows easier monitoring of the reaction, if necessary. Quantitative yields for this reaction are obtained.

\[
\begin{align*}
\text{FO}_2\text{CF}_2\text{CF}_2\text{CF}_2\text{CF}_2\text{SO}_2\text{F} & \quad + \quad 2 \ \text{CF}_3\text{SO}_2\text{N}^+\text{SiMe}_3 \\
\text{CF}_3\text{SO}_2\text{N}^+\text{SO}_2\text{CF}_2\text{CF}_2\text{CF}_2\text{CF}_2\text{SO}_2\text{N}^+\text{SiMe}_3 & \quad + \quad 2 \ \text{FSiMe}_3
\end{align*}
\]

(8) \quad \text{dry CH}_3\text{CN} \quad 48\text{h}, \quad 110^\circ\text{C}

\[
\begin{align*}
\text{CF}_3\text{SO}_2\text{N}^+\text{SO}_2\text{CF}_2\text{CF}_2\text{CF}_2\text{CF}_2\text{SO}_2\text{N}^+\text{SiMe}_3 & \quad + \quad 2 \ \text{FSiMe}_3
\end{align*}
\]

(9)

**Scheme 2.10:** Preparation of Difunctional Sulfonimide

There are several ways to acidify the sulfonimide moiety. Monofunctional sulfonimides can actually be acidified with concentrated HCl when stirred overnight and extracted with ether. The excess HCl and water can be removed on the vacuum line and the acid form of the sulfonimide is sublimed. For the difunctional sulfonimides concentrated sulfuric acid can be used but sublimation of the higher molecular weight compounds requires higher temperatures that cause the sulfuric acid to volatilize and collect on the cold finger along with the compound. Sometimes, a second sublimation will purify the compound. Another method for acidifying the difunctional sulfonimides is through ion exchange using Nafion-H beads. This is very tedious in that the Nafion has to be regenerated by heating in concentrated nitric acid, followed by washing with DI water until neutral. This has to be done two or three times for complete regeneration, then an aqueous solution of the sodium sulfonyl imide is passed through slowly and then dried on the vacuum line. Further purification was done by sublimation at 130 °C and high vacuum of 15 millitorr.
Methylation of these difunctional NH compounds was done with trimethyl orthoacetate (TMOA). The attraction for this method was its appeal for making imidazolium or pyridinium ionic liquids in a halide-free process. Trimethyl orthoacetate is also considerably safer to use than stronger alkylating agents, like dimethyl sulfate. Methylation of the sulfonimide with TMOA is an acid catalyzed process wherein a methoxy group on TMOA is protonated by the N-H compound, thus making it a good leaving group. After losing a methanol group, the carbocation undergoes a rearrangement to form a methyl cation and methyl acetate. The sulfonimide then reacts with the methyl cation to form the N-methyl sulfonimide.

Another method of methylating the sulfonimide is by foregoing the acidification step and directly methylating it with dimethyl sulfate. Dimethyl sulfate is a known carcinogen and therefore doesn’t have the industrial appeal the trimethyl orthoacetate method does. This methylation saves the time it takes to meticulously acidify the sulfonimide. The DMS reaction takes only 3 hours at 110 °C. Dimethyl sulfate is an inexpensive commercial compound, and reacts readily by the S_N2 mechanism. The leaving group is the methyl sulfate ion. In this research, DMS was often chosen as the methylating agent over the trimethyl orthoacetate simply because it avoided acidification of the sulfonimide with Nafion-H beads or lengthy sublimations.

Referring back to Scheme 2.2, the final reaction is the direct methylation of an alkylimidazole with the N-methyl bis(perfluoroalkylsulfonyl) imide. The aforementioned resonance stability and the strong electron withdrawing ability of two R_fSO_2 groups on the one nitrogen atom make the bis((trifluoromethyl)sulfonyl)imide an excellent
candidate for donating a CH$_3^+$ group to a Lewis base like a 1-alkylimidazole, or possibly a pyridine derivative. Chloroform was chosen as the solvent and typically heated to 70 °C overnight. A slight excess of the alkylimidazole accords removal of the alkylimidazole and the chloroform by vacuum. Very high yields of 98% were obtained.

Monitoring these reactions is equally straightforward and achieved with both $^{19}$F and $^1$H NMR. The fluorine atoms adjacent to the sulfonimide moiety exhibit the expected behavior of downfield chemical shifts in going from the sodium salt anion form to the methylated sulfonimide, and then exhibit upfield shifts upon donating the methyl group to the 1-alkylimidazole and returning to the anion. The protons on the 1-alkylimidazole ring, most notably the C-2 proton, exhibit a significant downfield shift in going from the 1-alkylimidazole to the 1,3-dialkylimidazolium cation. The typical shifts for all bis((perfluoroalkyl)sulfonyl)imides progressing through this synthesis is shown in Scheme 2.11.
Scheme 2.11: Typical $^{19}$F NMR for IL Synthesis

The chemical shifts are shown for the difunctional sulfonimide with the 2-carbon linker and any CF$_2$ groups beyond, or in between, the CF$_2$ adjacent to the SO$_2$ undergo much less drastic chemical shift changes during these reactions. These CF$_2$ chemical shifts tend to be in the region of -118 ppm to -120 ppm and do experience changes of 0.5 ppm or less, but nothing as drastic as the alpha CF$_2$ and CF$_3$ groups. These dramatic shifts of 6 ppm were very informative and educational. For example, when monitoring reaction progress, there is no overlap of peaks and integration of signals establishes
unequivocally where the reaction stands. However, a change in solvent from polar to non-polar can shift a $^{19}$F NMR chemical upfield as much as 2 ppm but the significant shifts seen here cause no ambiguity.

Both paths to the methylated sulfonimide are shown in Scheme 2.10 and some discussion about the acid form is warranted since $^{19}$F NMR is utilized to monitor reaction progress. When proceeding through the acid form, dry CD$_3$CN or dry CDCl$_3$ is imperative as the NMR solvent because the presence of water can produce large effects on the observed spectra. An insightful study of these effects was done by Dr. Ming-Hu Tu of the DesMarteau group in 2005.$^{50}$ To summarize the study, if water is present, the shifts of CF$_3$ and CF$_2$ adjacent to the SO$_2$ moved to higher fields by 2.9 and 3.8 ppm, respectively. While water has no influence on the $^{19}$F NMR chemical shift of a perfluorosulfonimide salt, the presence of water in the corresponding perfluorosulfonimide acid can cause the relevant chemical shifts to appear in the same position as the salt and cause confusion to the chemist. In the $^1$H NMR, the proton shift shifted from 12.1 ppm to 4.2 ppm – and can appear anywhere in between depending on the amount of water present.$^{47}$

Monitoring the final reaction of direct methylation of the imidazole is not limited to $^{19}$F NMR; significant chemical shift changes occur when the 1-alkylimidazole is transformed into the 1,3-dialkylimidazolium cation and easily observed with $^1$H NMR. One example of these changes is illustrated in Scheme 2.12.
Scheme 2.12: Observed $^1$H chemical shifts of methylimidazole to 1,3-dimethyl imidazolium cation

Here are the observed downfield shifts marking the transition from methylimidazole to the 1,3-dimethyl imidazolium cation. The alkyl imidazole goes from a neutral compound to a positively charged ring and should be expected to draw some electron density from groups on the ring, therefore deshielding the protons on the ring and alpha to the ring. The presence of the non-coordinating sulfonimide anion does not hydrogen bond with the C-2 proton, the most acidic proton of the imidazolium cation, and allows an unaltered look at these effects.

As mentioned in Chapter 1, the most popular path to ionic liquids is through anion metathesis. Direct methylation was shown as a viable path in this work yet anion metathesis was also utilized. Tracking progress through an anion exchange using $^{19}$F NMR is not a definitive tool since the poorly coordinating sulfonimide anion remains anionic with the interchange of cations. However, $^1$H NMR is indispensable in determining proper anion metathesis. The desired 1,3-dialkylimidazolium cation is first typically made by reacting a 1-alkylimidazole with an alkyl halide using classic SN$_2$ reaction conditions. This quaternization reaction forms a halide salt, which is then mixed
with the sulfonimide salt in a solvent system that exploits solubility differences. Imidazolium sulfonimide ILs are not soluble in water so lithium or sodium salts of the sulfonimide were used in this work to promote solubility in water and allow the IL to form a separate layer when mixed with a imidazolium halide water solution. Cesium sulfonimide salts are not very soluble in water and methylene chloride was used to mobilize the cesium sulfonimide ions. Once the water layer is removed and the IL thoroughly washed and dried on the vacuum line, $^1$H NMR is used to verify complete exchange.

While Scheme 2.12 above illustrates the proton chemical shifts of a methylation, Scheme 2.13 below shows the observed shifts in anion metathesis.

![Scheme 2.13: $^1$H NMR shifts observed with anion metathesis](image)

The protons on the 1,3-dialkylimidazolium ring, most notably the C-2 proton, exhibit a significant upfield shift during the metathesis of the bromine anion, capable of hydrogen bonding, to the non-coordinating sulfonimide anion. It is well known that the formation of a H-bond causes the proton chemical shift to move to lower field. This relationship is clearly observed, albeit in reverse, in the above scheme. At identical
concentrations, the chemical shifts of the ring protons will increase (downfield shift) with increasing basicity and thus H-bonding ability.

Another series of difunctional sulfonimide ionic liquids was synthesized with the only difference being that the sulfonimide groups were separated by four CF$_2$ groups instead of two CF$_2$ groups. Small scale reactions of these ILs were done via direct methylation for comparison to those made by the easier means of anion metathesis. One undesirable property of ionic liquids is discoloration and the difunctional sulfonimides, especially the heavier molecular weight di-anions, tend to discolor if acidified with H$_2$SO$_4$, sublimed, and then methylated with trimethyl orthoacetate. Purification of the methylated sulfonimide requires high vacuum sublimation in excess of 90 °C and gives a tan compound, even when methylation is done with dimethyl sulfate. Sometimes this discoloration will carry to the final ionic liquid.

The alkylation of a 1-alkylimidazole is carried out at 70 °C and anytime an imidazole is heated discoloration usually occurs. Reactions that minimize discoloration of the final IL are attractive and anion metathesis reactions done from the lithium, sodium or cesium sulfonimide salt can be done at room temperature. To further minimize discoloration, it was helpful to avoid using acetone to wash any glassware used in the preparation on the ILs. All glassware should be washed with soap and water, rinsed with DI water, and dried in the oven. The presence of acetone could not be detected in the NMR but is suspected that the discoloration stems from the stabilizers and additives in the acetone that leave behind a residue upon evaporation.
A tetra-functional lithium salt was prepared according to the scheme below. This scheme characterizes the events involved with this synthesis. Procedures are simply modifications of the methods previously discussed and presented in the experimental section. TGA analysis was done on the tetra-functional lithium salt (T_d 470 °C). The $^{19}$F NMR was fairly clean (maybe 3-5% contaminant at -78.1 ppm) and did give the appropriate peaks of -78.8 ppm for the CF$_3$ fluorine atoms, -112.2 ppm for the CF$_2$SO$_2$ fluorine atoms, and -119.3 ppm for the CF$_2$CF$_2$ atoms. The $^{19}$F NMR peaks are not as well resolved as in the difunctional anions because not all CF$_2$ groups are identical and there is obvious overlapping of signals.
Acidification of the salt was attempted with the Nafion-H ion exchange resin but protonation was never complete. Methylation was still attempted with trimethyl orthoacetate but, not surprisingly, it never completed methylation. During methylation with trimethyl orthoacetate an unexplained peak started appearing at -78.0 ppm. In short, a clean tetra-functional lithium salt was prepared but failed to drive the methylation to completion.
The previous approach using trimethyl orthoacetate was abandoned and dimethyl sulfate was used to methylate another portion of the clean lithium tetra-functional salt. Methylating the acid form with DMS was attempted and this obviously did not work. Once again, a byproduct appeared during the methylation reaction with an inexplicable peak at -78.0 ppm. With 100 mg of this “methylated” sulfonimide product, an attempt was made to prepare the RTIL by methylating methyl imidazole in CHCl₃. The ¹⁹F NMR was quite messy and showed the inexplicable peak at -78.0 ppm. The ¹H NMR was also troubling. There were two peaks and some smaller ones where the methyl protons of the dimethyl imidazolium cation appear.

The problem most likely occurred during purification of the methylated compound. This is not an easy process because the second methyl group of dimethyl sulfate is not removed and the methyl sulfate anion is the leaving group, not the sulfate anion. The problem with the ¹H NMR is most likely the presence of lithium methyl sulfate and even possibly some residual dimethyl sulfate that wasn’t removed by vacuum.

A new batch of sodium tetra salt was used as starting material. This was methylated with DMS and separated with an ethyl acetate/water solution. The methylation of methyl imidazole was done and the ¹⁹F NMR suggests that the reaction either did not complete or not enough methyl imidazole was used.

Because of the above difficulties, anion metathesis with [BMIM][Br] was performed with the tetra-functional lithium salt and a clean IL was obtained. This trying process illustrated the difficulties associated with purifying ILs due to their ability to solubilize salts and solvents. The heavier molecular weight associated with the tetra-
functional anion also makes purification more difficult. It prevents purification by sublimation of the acid form or the methyl form, as well as making the IL a solid at room temperature.

To verify that higher molecular weight anions impact the melting points of these difunctional and multi-functional ILs, some interesting and novel ionic liquids were prepared and the glass transitions and melting points were determined. Removal of any remaining solvent can be difficult and if the melting point is exceeded during removal of the solvent a melting point is not observed. This is common with amorphous solids like ionic liquids – only one melt is observed. The results are shown in the table below.

<table>
<thead>
<tr>
<th>Ionic Liquid</th>
<th>Tm</th>
<th>Tg</th>
<th>Td</th>
</tr>
</thead>
<tbody>
<tr>
<td>CF$_3$SO$_2$NSO$_2$CF$_2$CF$_2$CF$_2$SO$_2$NSO$_2$CF$_3$</td>
<td>75°</td>
<td>N/A</td>
<td>390°</td>
</tr>
<tr>
<td>CF$_3$SO$_2$NSO$_2$CF$_2$CF$_2$CF$_2$SO$_2$NSO$_2$CF$_3$</td>
<td>79°</td>
<td>N/A</td>
<td>400°</td>
</tr>
<tr>
<td>CF$_3$SO$_2$NSO$_2$CF$_2$CF$_2$CF$_2$SO$_2$NSO$_2$CF$_3$</td>
<td>105°</td>
<td>N/A</td>
<td>398°</td>
</tr>
<tr>
<td>CF$_3$SO$_2$NSO$_2$CF$_2$CF$_2$CF$_2$SO$_2$NSO$_2$CF$_3$</td>
<td>53°</td>
<td>N/A</td>
<td>395°</td>
</tr>
<tr>
<td>CF$_3$SO$_2$NSO$_2$CF$_2$CF$_2$CF$_2$SO$_2$NSO$_2$CF$_3$</td>
<td>N/A</td>
<td>-60°</td>
<td>398°</td>
</tr>
</tbody>
</table>
### Table 2.1: Melting Point Comparison of Select ILs

<table>
<thead>
<tr>
<th>Structure</th>
<th>Melting Point</th>
<th>Glass Transition</th>
</tr>
</thead>
<tbody>
<tr>
<td>CF₃SO₂NSO₂CF₂CF₂SO₂NSO₂CF₃</td>
<td>68°</td>
<td>450°</td>
</tr>
<tr>
<td>H₃C-N=CH₃</td>
<td>N/A</td>
<td>-68°</td>
</tr>
<tr>
<td>H₃C-N=CH₃</td>
<td>N/A</td>
<td>441°</td>
</tr>
<tr>
<td>CF₃SO₂NSO₂CF₃</td>
<td>25°</td>
<td>&gt;400</td>
</tr>
<tr>
<td>H₃C-N=CH₃</td>
<td>N/A</td>
<td>&gt;400</td>
</tr>
<tr>
<td>CF₃SO₂NSO₂CF₃</td>
<td>-2°</td>
<td>-86°</td>
</tr>
<tr>
<td>H₃C-N=CH₃</td>
<td>N/A</td>
<td>441°</td>
</tr>
</tbody>
</table>

The symmetric MMIM ionic liquids, as predicted, allow better packing and thus have higher melting points, stronger cohesion forces, when compared within their respective anions. The more flexible alkyl chains on the imidazolium cation obviously disrupt packing and manifest as lower melting points and glass transitions.

The difunctional cations were prepared using the sonochemical methodology discussed earlier in the chapter. In this case an excess of the alkylimidazole was used with a α,ω-alkyl halide instead of an excess of the alkyl halide with the alkylimidazole. The linking alkyl chain between the two imidazolium cations is apparently not as flexible as the independent alkyl chains on a 1,3-dialkylimidazolium cation and limits the freedom of movement for the tethered imidazolium cations. The intent of pairing the
difunctional cations with difunctional anions shown in the above table was to explore the idea that some interesting properties may result from random, disoriented ion pairing unlike the ordered dication-to-dianion the way they are drawn. Pronounced effects were not observed and, without the possibility of x-ray crystallography on amorphous ionic liquids such as these, it was difficult to say how exactly the dications and dianions were packing.
Experimental

Preparation of FSO$_2$CF$_2$CF$_2$SO$_2$F (1)

To the flask containing the sulfonyl chloride compound and a stir bar, 150mL of dry CH$_3$CN was added to the 28.5 g (95.3 mmol) of ClSO$_2$(CF$_2$)$_2$SO$_2$Cl. While inside the dry bag, 33.2g (572 mmol) of dry KF was placed in the same 250mL round bottom flask. The reaction mixture was allowed to stir at room temperature overnight while under a nitrogen atmosphere. Once the reaction was complete, the product and CH$_3$CN were distilled to another flask, away from the KF, with high vacuum and at room temperature. Water was then added to the CH$_3$CN mixture to separate the product into a separate layer. A yield of 24.1 g was obtained for a 95% yield.

$\text{F}^a\text{SO}_2\text{CF}_2^b\text{CF}_2\text{SO}_2\text{F}$ $^{19}\text{F NMR (CD}_3\text{CN, ppm)} \delta_a +47.7$ (2F, t) $\delta_b -107.6$ (4F, t); $^3J_{ab}= 7.5\text{Hz}$

Preparation of CF$_3$SO$_2$NH$_2$

Approximately 100 g (or 100 mL) were condensed into a 500 mL three-neck round bottom flask at -80 ºC, and under a nitrogen atmosphere. Then the triflic anhydride 50 g (177 mmol) was slowly dropped into the ammonia using a dropping funnel. After the addition the mixture was allowed to stir and slowly come to room temperature. The NH$_3$ was evaporated and the product was sublimed at 80 ºC under high vacuum. A 91% yield of 24.0 g was obtained.

CF$_3$SO$_2$NH$_2$. $^{19}\text{F NMR (CD}_3\text{CN)} \delta -79.4$ ppm (s); $^1\text{H NMR (CD}_3\text{CN)} \delta 7.4$ ppm (br).

Preparation of CF$_3$SO$_2$NH(Na)
In a typical procedure, 5.59 g (37.5 mmol) of CF$_3$SO$_2$NH$_2$ was put in an Erlenmeyer flask and 1.0 M NaOH was used to bring the solution to pH 8.4. The solution was stirred for three hours and then connected to a dynamic vacuum at 100 ºC and left overnight. This was to remove any unreacted CF$_3$SO$_2$NH$_2$ by sublimation. A 95.5% yield was obtained with 6.41 g of CF$_3$SO$_2$NH(Na).

CF$_3$SO$_2$NH(Na). $^{19}$F NMR (CD$_3$CN) δ -79.2 ppm (s); $^1$H NMR (CD$_3$CN) δ 2.6 ppm (br).

Preparation of CF$_3$SO$_2$N(Na)Si(CH$_3$)$_3$ (2)

In a one-piece reactor equipped with a reflux condenser and an Ace thread sidearm, 25 mL of dry CH$_3$CN, 25 mL of HMDS, and 10.4 g (60.7 mmol) of CF$_3$SO$_2$NH(Na) was added. This was refluxed at 110 ºC overnight. A $^{19}$F NMR suggested the reaction was complete. The solvent and excess HMDS was removed and the remaining salt was heated overnight on the vacuum line at 100 ºC.

CF$_3$SO$_2$N(Na)Si(CH$_3$)$_3$. $^{19}$F NMR (CD$_3$CN) δ -78.6 ppm (s); $^1$H NMR (CD$_3$CN) δ 0.01 ppm (br).

Preparation of CF$_3$SO$_2$N(Na)SO$_2$CF$_2$SO$_2$F (3)

Using the dry box, 3.70 g (15.2 mmol) of CF$_3$SO$_2$N(Na)SiMe$_3$ was placed in a 100 mL one-piece reactor equipped with an ace-thread side arm. Then, 50 mL of dry CH$_3$CN was vacuum transferred to the flask followed by the vacuum transfer of 2.00 g (7.5 mmol) of FSO$_2$(CF$_2$)$_2$SO$_2$F. The reaction was run for 48 hours at 110 ºC in a closed system.
\[ \text{CF}_3^a\text{SO}_2\text{N(Na)}\text{SO}_2\text{CF}_2 \text{b}\text{CF}_2\text{SO}_2\text{N(Na)}\text{SO}_2\text{CF}_3 \]

\( ^{19}\text{F} \text{ NMR (CD}_3\text{CN, ppm)} \) \( \delta_a -78.8 \)

(6F, s) \( \delta_b -110.5 \) (4F, s).

**Preparation of CF\(_3\)\text{SO}_2\text{N(CH}_3\text{)}\text{SO}_2\text{CF}_2 \text{b}\text{CF}_2\text{SO}_2\text{N(CH}_3\text{)}\text{SO}_2\text{CF}_3 (\text{4})**

The sodium sulfonimide salt (3) (1.0 g, 2.2 mmol) was placed in a 25 mL flask equipped with a stopcock adaptor and under a nitrogen atmosphere. Then 3 mL of dimethyl sulfate was added. The reaction was heated to 110\(^\circ\)C in an oil bath for 3 hours. Vacuum filtration along with washing with water was done to remove excess DMS and impurities. The remaining solid was brown in color and allowed to dry overnight under vacuum at room temperature. A sublimation of the solid was done at 50\(^\circ\)C.

The product contained moisture as evidenced by \(^1\text{H} \text{NMR} \) so it was separated with ethyl acetate and NaHCO\(_3\) solution. The ethyl acetate layer was dried over Na\(_2\)SO\(_4\), decanted, and the solvent removed.

\[ \text{CF}_3^a\text{SO}_2\text{N(CH}_3\text{)}\text{SO}_2\text{CF}_2 \text{b}\text{CF}_2\text{SO}_2\text{N(CH}_3\text{)}\text{SO}_2\text{CF}_3 (\text{4}) \]  

\( ^{19}\text{F} \text{ NMR (CD}_3\text{CN, ppm)} \) \( \delta_a -72.6 \) (6F, s) \( \delta_b -104.3 \) (4F, s); \(^1\text{H} \text{NMR (CD}_3\text{CN)} \) \( \delta 3.65 \) ppm (s).

**Preparation of RTILs: CF\(_3\)\text{SO}_2\text{N(C}_n\text{MIM)}\text{SO}_2\text{CF}_2 \text{b}\text{CF}_2\text{SO}_2\text{N(C}_n\text{MIM)}\text{SO}_2\text{CF}_3 (\text{5a, 5b, 5c})**

In a 50 mL rb flask with a stir bar, 30 mL of CHCl\(_3\) was placed with 0.75 g (1.36 mmol) of [CF\(_3\)SO\(_2\)N(CH\(_3\))SO\(_2\)CF\(_2\)]\(_2\) was added. Then 0.47 g (3.8 mmol) of n-butyl imidazole was added. The mixture was refluxed at 75\(^\circ\)C overnight. The CHCl\(_3\) was decanted and the IL was dried on the vacuum line overnight at 75\(^\circ\)C to remove excess n-butyl imidazole and moisture.
RTILs of form CF$_3$SO$_2$N(C$_n$MIM)SO$_2$CF$_2$CF$_2$SO$_2$N(C$_n$MIM)SO$_2$CF$_3$ (5a, 5b, 5c)

1-Methyl-3-methylimidazolium + (CF$_3$SO$_2$NSO$_2$CF$_2$)$_2$ (5a) $^1$H NMR (CD$_3$CN) $\delta$

8.35 ppm (1H, s), 7.30 (2H, s), 3.80 (6H, s); $^{19}$F NMR (CD$_3$CN, ppm) $\delta_a$ -78.8 (6F, s) $\delta_b$ -110.5 (4F, s); mp 68°C, T$_d$ 450°C.

1-Ethyl-3-methylimidazolium + (CF$_3$SO$_2$NSO$_2$CF$_2$)$_2$ (5b) $^1$H NMR (CD$_3$CN) $\delta$

8.39 ppm (1H, s), 7.37 (1H, s), 4.14 (2H, q, $^3J_{HH} = 7.3$Hz), 3.80 (3H, s), 1.44 (3H, t, $^3J_{HH}$ = 7.3Hz); $^{19}$F NMR (CD$_3$CN, ppm) $\delta_a$ -78.8 (6F, s) $\delta_b$ -110.5 (4F, s); T$_g$ -73°C, T$_d$ 456°C.

1-Butyl-3-methylimidazolium + (CF$_3$SO$_2$NSO$_2$CF$_2$)$_2$ (5c) $^1$H NMR (CD$_3$CN) $\delta$

8.38 ppm (1H, s), 7.34 (2H, m), 4.10 (2H, t, $^2J_{HH} = 7.4$Hz), 3.80 (3H, s), 1.77 (2H, p, $^2J_{HH}$ = 4.8Hz), 1.32 (2H, m, $^2J = 7.6$Hz), 0.92 (3H, t, $^2J = 7.3$Hz); $^{19}$F NMR (CD$_3$CN, ppm) $\delta_a$ -78.8 (6F, s) $\delta_b$ -110.5 (4F, s); T$_g$ -68°C, T$_d$ 441°C.

Preparation of NaO$_2$SCF$_2$CF$_2$CF$_2$CF$_2$SO$_2$Na (6)

Since the $\alpha,\omega$-diiodo compound is a liquid, the 40.54 g (89.3 mmol) of I(CF$_2$)$_4$I was dropped into a 500 mL round bottom flask containing a solution of 80 mL of acetonitrile and 120 mL water with 30 g NaHCO$_3$ and 39 g Na$_2$S$_2$O$_4$ dissolved in it. The diiodo compound was slowly added over the course of 45 minutes because the HCO$_3$/S$_2$O$_4$ solution is difficult to stir and an excess of the hydrosulfite is desired. Once added, the flask was put in a water bath, heated to 40 °C, and allowed to stir overnight. A $^{19}$F NMR was taken to ensure completion. This salt is not isolated and chlorination is immediately performed.
\[
\text{NaO}_2\text{SCF}^a\text{CF}_2^b\text{CF}_2^b\text{CF}_2^a\text{SO}_2\text{Na} (6) \quad ^{19}\text{F NMR (CD}_3\text{CN)} \delta_a -121.7 \text{ (4F, m), } \delta_b - 129.6 \text{ (4F, m).}
\]

**Preparation of ClO\textsubscript{2}SCF\textsubscript{2}CF\textsubscript{2}CF\textsubscript{2}CF\textsubscript{2}SO\textsubscript{2}Cl (7)**

For the chlorination, enough DI H\textsubscript{2}O was added to the NaSO\textsubscript{2}(CF\textsubscript{2})\textsubscript{4}SO\textsubscript{2}Na reaction mixture to dissolve the solids, which took the volume to approximately 500 mL. The chlorination was done in two batches – each was 250 mL of the above solution. Then a 1000 mL 3-neck round bottomed flask was equipped with a Cl\textsubscript{2} gas inlet, a separatory funnel for the NaSO\textsubscript{2}(CF\textsubscript{2})\textsubscript{4}SO\textsubscript{2}Na solution, and a Cl\textsubscript{2} gas outlet through a H\textsubscript{2}O bubbler. Approximately 100 mL of DI H\textsubscript{2}O was placed in the 3-neck flask, cooled in an ice bath at 0 °C, and chlorine gas was rapidly bubbled into the DI water until the solution was yellow and the flask contained a Cl\textsubscript{2} blanket of gas above the solution. With the blanket of Cl\textsubscript{2} gas, each drop turned reddish brown as it fell to the chlorine solution and immediately dissipated to the yellow color upon delivery. The first batch was slowly added over the course of 90 minutes. The second batch was also added in the same way. The –SO\textsubscript{2}Cl compound precipitated out and was vacuum filtered after completion of both batches.

The sulfonyl chloride compound was dissolved in CH\textsubscript{2}Cl\textsubscript{2}, washed with water several times, and then dried over anhydrous Na\textsubscript{2}SO\textsubscript{4}. Evaporation of the CH\textsubscript{2}Cl\textsubscript{2} was done on the vacuum line while keeping the flask containing the –SO\textsubscript{2}Cl compound and CH\textsubscript{2}Cl\textsubscript{2} at 0 °C. A total of 28.53 g was obtained for an 80% yield.

\[
\text{ClO}_2\text{SCF}_2^a\text{CF}_2^b\text{CF}_2^b\text{CF}_2^a\text{SO}_2\text{Cl} (7) \quad ^{19}\text{F NMR (CD}_3\text{Cl}_3) \delta_a -103.8 \text{ (4F, m), } \delta_b - 118.1 \text{ (4F, m).}
\]
Preparation of $\text{FO}_2\text{SCF}_2\text{CF}_2\text{CF}_2\text{SO}_2\text{F}$ (8)

To the flask containing the sulfonoyl chloride compound, 150 mL of dry $\text{CH}_3\text{CN}$ was added to the 28.53 g (71.5 mmol) of $\text{ClSO}_2(\text{CF}_2)_6\text{SO}_2\text{Cl}$. While inside the dry bag 25.9 g of dry KF was placed in the same 250 mL round bottom flask. The reaction mixture was allowed to stir at room temperature overnight while under a nitrogen atmosphere. Once the reaction was complete, the product and $\text{CH}_3\text{CN}$ were distilled to another flask, away from the KF, with high vacuum and at room temperature. Water was then added to the $\text{CH}_3\text{CN}$ mixture to separate the product into a separate layer. The organic layer was dried with $\text{P}_4\text{O}_{10}$ and distilled from the $\text{P}_4\text{O}_{10}$ using high vacuum. A total of 25.59 g was obtained for a 95% yield.

$\delta^\text{19F} \text{NMR (CD}_3\text{CN)} \delta_a-103.2 \text{ (4F, m), } \delta_b -120.2 \text{ (4F, m), } \delta_c +46.8 \text{ (2F, s).}$

Preparation of $\text{CF}_3\text{SO}_2\text{N(Na)SO}_2\text{CF}_2\text{CF}_2\text{CF}_2\text{SO}_2\text{N(Na)SO}_2\text{CF}_3$ (9)

The silyl compound (2) was synthesized according to the amount of difunctional – $\text{SO}_2\text{F}$ to be used and left in the reaction flask – a one-piece reactor with an Ace thread arm and reflux column with a Rotaflow valve. Assuming a quantitative yield on the 41.2 mmol of $\text{CF}_3\text{SO}_2\text{NH(Na)}$ accorded a 5% excess of $\text{CF}_3\text{SO}_2\text{NSiMe}_3$ when 7.16 g (19.6 mmol) of the difunctional (CF$_2$CF$_2$SO$_2$F)$_2$ was considered.

The 7.16 g (19.6 mmol) of (CF$_2$CF$_2$SO$_2$F)$_2$ was placed in a 25 mL round bottomed flask along with some $\text{P}_4\text{O}_{10}$ and stirred. Then 100 mL of dry $\text{CH}_3\text{CN}$ was collected in a separate flask on top of some $\text{P}_4\text{O}_{10}$. The acetonitrile was vacuum
transferred into the flask containing the silyl compound, and then the (CF$_2$CF$_2$SO$_2$F)$_2$ was vacuum transferred.

The mixture was heated to 110 ºC in a closed system for 72 hours and a $^{19}$F NMR showed that the reaction was complete.

The CH$_3$CN and FSiMe$_3$ were evaporated and the sodium salt dried on the vacuum line overnight at 90 ºC. A clean product of 12.70 g was obtained for a 97% yield.

$\text{CF}_3\text{SO}_2\text{N(Na)}\text{SO}_2\text{CF}_2\text{CF}_2\text{SO}_2\text{N(Na)}\text{SO}_2\text{CF}_3$ (9) $^{19}$F NMR (CD$_3$CN)

$\delta_a$ -78.9 (6F, s), $\delta_b$ -112.3 (4F, m), $\delta_c$ -119.3 (4F, m).

Preparation of $\text{CF}_3\text{SO}_2\text{N(CH}_3\text{)}\text{SO}_2\text{CF}_2\text{CF}_2\text{CF}_2\text{SO}_2\text{N(CH}_3\text{)}\text{SO}_2\text{CF}_3$ (10)

The sodium sulfonimide salt 6.00 g (9.0 mmol) was placed in a 25 mL flask equipped with a stopcock adaptor under a nitrogen atmosphere. Then 15 mL of freshly distilled dimethyl sulfate was syringed and injected into the flask. The reaction was heated to 105 ºC in an oil bath overnight and a $^{19}$F NMR spectrum was taken to determine completion of the reaction.

DI water was added and the mixture was allowed to stir overnight to decompose the DMS. In the morning a light brown solid was removed by filtration and then 10 mL of ethyl acetate and a NaHCO$_3$ solution was used to more thoroughly separate and dry the compound. After separation the ethyl acetate was removed by vacuum. This product was not sublimed as the others were in previous experiments because the $^1$H and $^{19}$F NMR’s looked very clean and the compound was a very light tan color. The yield was 75% for a total of 4.40 g.
CF$_3^a$SO$_2$N(CH$_3$)$_2$SO$_2$CF$_2^b$CF$_2^c$SO$_2$N(CH$_3$)$_2$SO$_2$CF$_3^a$ (10) \textsuperscript{19}F NMR (CD$_3$CN) $\delta$ $a$ -72.6 (6F, s), $\delta_b$ -105.8 (4F, m), $\delta_c$ -118.6 (4F, m); \textsuperscript{1}H NMR (CD$_3$CN) $\delta$ 3.64 (6H, s).

Preparation of RTILs: CF$_3$SO$_2$N(C$_n$MIM)SO$_2$CF$_2$CF$_2$CF$_2$SO$_2$N(C$_n$MIM)SO$_2$CF$_3$ (11a, b, c)

The direct methylation process was typified above in preparation of 5. The preparations of these RTILs typify the anion metathesis process.

The sodium salt of the difunctional sulfonimide (5.35 g, 8.00 mmol) was readily dissolved in 5 mL of H$_2$O. Then 3.68 g (16.8 mmol) of [BMIM][Br] was dissolved in a separate 5 mL of H$_2$O. Upon mixing a white precipitate formed immediately and then a thick tan liquid settled to the bottom to form a separate layer. This was allowed to stir overnight. The water was decanted and the IL washed several times with DI H$_2$O. The IL was dried at 100°C on the vacuum line overnight. The resulting product was a blonde, viscous, transparent liquid.

1-Methyl-3-methylimidazolium + (CF$_3^a$SO$_2$NSO$_2$CF$_2^b$CF$_2^c$)$_2$ (11a) \textsuperscript{1}H NMR (CD$_3$CN) $\delta$ 8.35 ppm (1H, s), 7.30 (2H, s), 3.80 (6H, s); \textsuperscript{19}F NMR (CD$_3$CN, ppm) $\delta$ $a$ -78.8 (6F, s) $\delta_b$ -110.5 (4F, s); mp 68°C, $T_d$ 450°C.

1-Ethyl-3-methylimidazolium + (CF$_3^a$SO$_2$NSO$_2$CF$_2^b$CF$_2^c$)$_2$ (11b) \textsuperscript{1}H NMR (CD$_3$CN) $\delta$ 8.39 ppm (1H, s), 7.37 (1H, s), 4.14 (2H, q, $^3$$J_{HH}$ = 7.3Hz), 3.80 (3H, s), 1.44 (3H, t, $^3$$J_{HH}$ = 7.3Hz); \textsuperscript{19}F NMR (CD$_3$CN, ppm) $\delta$ $a$ -78.8 (6F, s) $\delta_b$ -110.5 (4F, s); $T_g$ -73°C, $T_d$ 456°C.
1-Butyl-3-methylimidazolium + (CF$_3$$_a$SO$_2$NSO$_2$CF$_2$$_b$CF$_2$$_c$)$_2$ (11c) ¹H NMR

(CD$_3$CN) δ 8.38 ppm (1H, s), 7.34 (2H, m), 4.10 (2H, t, $^2$$J_{HH}$ = 7.4Hz), 3.80 (3H, s), 1.77 (2H, p, $^2$$J_{HH}$ = 4.8Hz), 1.32 (2H, m, $^2$$J$ = 7.6Hz), 0.92 (3H, t, $^2$$J$ = 7.3Hz) ; ¹⁹F NMR (CD$_3$CN, ppm) δ$_a$ -78.8 (6F, s) δ$_b$ -110.5 (4F, s); T$_g$ -68°C, T$_d$ 441°C.

Preparation of Tetra-functional RTIL: CF$_3$$_a$SO$_2$N(BMIM)SO$_2$(CF$_2$$_b$,$^c$)$_4$SO$_2$N(BMIM)SO$_2$(CF$_2$$_b$,$^c$)$_4$SO$_2$N(BMIM)SO$_2$CF$_3$ (14)

Both the lithium salt and the imidazolium salt are very soluble in water so 0.50 g (0.19 mmol) of the lithium tetra-functional salt and 0.41 g (0.205 mmol) of the [BMIM][Br] were dissolved separately and then mixed. A tan suspension formed immediately and this mixture was stirred vigorously. A small amount of CH$_2$Cl$_2$ had to be added because the ionic liquid stuck to the stir bar and halted stirring. This was allowed to stir overnight.

A CH$_2$Cl$_2$ extraction was done, washed with DI water several times, and the methylene chloride removed on the vacuum line at 85 °C. The ¹⁹F and ¹H NMR suggest a clean ionic liquid was synthesized. A TGA was performed and showed a T$_d$ around 390 °C.

CF$_3$$_a$SO$_2$N(BMIM)SO$_2$(CF$_2$$_b$,$^c$)$_4$SO$_2$N(BMIM)SO$_2$(CF$_2$$_b$,$^c$)$_4$SO$_2$N(BMIM)SO$_2$CF$_3$ (14) ¹H NMR (CD$_3$CN) δ 8.36 ppm (1H, s), 7.33 (2H, m), 4.10 (2H, t, $^2$$J_{HH}$ = 7.4Hz), 3.78 (3H, s), 1.77 (2H, p, $^2$$J_{HH}$ = 4.8Hz), 1.30 (2H, m, $^2$$J$ = 7.6Hz), 0.92 (3H, t, $^2$$J$ = 7.3Hz) ; ¹⁹F NMR (CD$_3$CN, ppm) δ$_a$ -78.9 (6F, s) δ$_b$ -112.2 (12F, m), δ$_c$ -112.2 (12F, m); T$_d$ 390°C.
CHAPTER III
SYNTHESIS OF AROMATIC TRIFLUOROVINYL ETHER MONOMERS CONTAINING SULFONIMIDE IONIC LIQUID FUNCTIONALITY

Introduction

The use of fluorine in high-performance polymers has become of greater significance in recent years, and the benefits of working with fluorinated polymers have become more widely known. Some benefits of incorporating fluorine into polymers include thermal/oxidative stability, optical transparency, greater solvent compatibility, and increased environmental stability.\(^{51}\) An interesting route to the incorporation of fluorine into high-performance polymers has involved an unlikely chemical reaction, the thermal \([2\pi + 2\pi]\) cyclodimerization of fluorinated olefins. This reaction proceeds at relatively mild temperatures and produces a covalent linkage that is chemically, thermally, and oxidatively stable.\(^{52}\) The first report of cyclodimerization of fluorinated olefins was provided by Lewis and Naylor of DuPont in 1947 while studying the pyrolysis of PTFE and the compound octafluorobutane, along with tetrafluoroethylene (TFE) and perfluoropropene (PFP), was isolated from the pyrolysis off-gas stream.\(^{53}\) In 1988, Heinze and Burton reported that \(\alpha,\beta\beta\)-trifluorostyrenes are unstable to cyclodimerization at room temperature.\(^{54}\) In particular, 1,4-bis(trifluorovinyl)benzene was observed to “gel” overnight at room temperature and this dimerization was later exploited for cross-linking.

Aryl trifluorovinyl ethers are more stable than the trifluorostyrenes at room temperature but do undergo cyclodimerization at elevated temperatures and provided an excellent platform to make a fluorinated ionic liquid polymer. A possible route was to
prepare a difunctional trifluorovinyl ether (TFVE) monomer that could undergo a thermal polymerization via the step reaction polymerization. The versatility of perfluorocyclobutane (PFCB) ring-containing polymers was chosen over other possible options for several reasons. First, it’s well established that the cyclodimerization proceeds through a free radical mechanism under mild conditions and without the aid of an initiator, therefore providing an excellent model for verifying if dimerization or polymerization occurs when fluorinated IL functionality is incorporated into a monomer. Moreover, the synthetic methods for aromatic trifluorovinyl ethers are very straightforward and provide useful monomers using a single synthetic scheme. Finally, it provides the opportunity to synthesize some unique polymeric ionic liquids. Consider Figure 3.1 below.

Figure 3.1: PFCB Polymer containing 4-carbon ionic liquid linker
Successfully synthesizing this polymeric IL is appealing because it would incorporate the sulfonimide anion, and the IL moiety, directly into the backbone of a polymer. Although this is not a perfluorinated polymer, the few examples of polymeric ILs have been in pure hydrocarbon polymers. The IL moiety in these few cases was a pendant and not directly part of the backbone.\textsuperscript{55,56} The focus of these two referenced cases of polymeric ILs was ionic conductivity, particularly how ionic conductivity correlates to the glass transition. In addition, the imidazolium cation, by virtue of its alkyl chain versatility, was the pendant, and not the anion. In our research, the interest was to take advantage of ionic liquids’ high conductivity and pursue possible electrochemical applications. The basic objective in synthesizing a polymeric IL was to see if a film could be made that retained its high conductivity. From here it would be a small step to make proton conductive IL polymers.

When considering this particular polymer in Figure 3.1 from the perspective of a polymer chemist, some distinct features are apparent. Imposing some polymer terms here helps to bring ILs and polymers together. In contrast to the cations being polymer pendants, as previously mentioned, here the ionic charge is actually part of the backbone. Plasticizers are added to polymers to create free space, allow mobility, and thus lower glass transitions. With a little imagination, one can envision these imidazolium cations as a plasticizer, of sort, with the added ability of being able to add different lengths of alkyl groups in the same way pendant groups are lengthened in polymers to lower glass transition temperatures. Pendant groups and plasticizers are two features used to change a polymer’s glass transition. There is also one more feature used to change a polymer’s
glass transition – backbone flexibility. And this potential polymer has some flexibility by virtue of the oxygen atoms between the PFCB group and the benzene ring.

Because ILs are known for their wide liquid range and non-volatility, they can be used in plastics at higher temperatures than traditional plasticizers. The low volatility and high temperature stability of many ILs make them useful for applications at elevated temperatures with minimal loss in flexibility and extended material lifetime. The cations and anions in ILs have a strong affinity for each other, making plasticizer loss by liquid leaching, solid-solid migration, or evaporation much less likely compared to molecular plasticizers.

The use of ILs in polymer systems have been explored on a number of fronts, but the majority of early papers in this field focused on polymerization using ILs as solvents, with emphasis on the environmental aspects and ability to form new structures. Attributes of these reactions, such as long free radical lifetimes, high molecular weight products, rapid polymerization schemes, have made a significant impact in the polymer field. The separation step after the reaction has proven difficult and uneconomical.

On the other hand, ILs can be formulated as plasticizers by at least three methods: direct compounding using a high shear mixer, solvent casting, and polymerization using the plasticizer as the reaction solvent. While the focus of this work concerns the synthesis of monomeric and polymeric ionic liquids, the potential applications are certainly the target.

**Results and Discussion**
The strategy for preparing the above polymeric IL begins with the $p$-bromo(trifluorovinylxyloxy)benzene strategy established in 1996 by Dow. This approach allows subsequent reaction with organolithium or Grignard reagents without attacking the fluorinated olefin.\textsuperscript{58} In this work, the $p$-bromo(trifluorovinylxyloxy)benzene intermediate strategy is used to incorporate a difunctional linker between two (trifluorovinylxyloxy)benzene groups – a linker containing two fluorinated sulfonyl imide anions, separated by four CF$_2$ groups, and paired with two 1,3-dialkylimidazolium cations. The final goal is the synthesis of the polymeric ionic liquid shown in Figure 3.1 above.

The strategy began with a model study of a monofunctional monomer capable only of dimerization. Troubleshooting problems associated with a basic methodology could most likely be diagnosed and solved more easily than beginning with the difunctional monomer. The synthesis of the monomer is summarized below in Scheme 3.1. Successful monofunctional monomer synthesis and dimerization has been performed by former group members.\textsuperscript{59,60} However, the dimerization was done with the acid form and the cesium salt, not an ionic liquid derivative.
Scheme 3.1: Proposed Synthesis of Monofunctional TFVE Monomer

The 4-bromo trifluorovinyloxy benzene compound was generously supplied by Tetramer Technologies, Inc. The first step is a metal-halogen exchange using \textit{t}-butyllithium at -78°C to convert the aromatic carbon into a nucleophile. The organolithium intermediate, once formed, is immediately transferred by cannula technique to the electrophilic sulfuryl chloride, SO$_2$Cl$_2$, also at -78°C. This allowed the addition of the highly electron withdrawing SO$_2$Cl group to the ring. While the yields were disappointing, the resulting sulfonyl chloride was often clean once distilled. Conversion to the sulfonyl fluoride is a nucleophilic displacement reaction that proceeds to completion with near quantitative yields.

The coupling reaction between the benzene sulfonyl fluoride with the silyl compound, CF$_3$SO$_2$N(Na)SiMe$_3$, was problematic. First, the trifluorovinyl group was attacked by the silyl derivative. Trifluorovinyl ether groups are always susceptible to
nucleophilic attack but when attached to the electron donating benzene ring it makes it less susceptible to a degree. This problem was solved by protecting the double bond with bromination. The addition of bromine to the vinyl group is not uncommon because there may be times when the trifluorovinyl ether group may be too electron withdrawing, therefore making the lithium intermediate a less effective nucleophile. To enhance this nucleophilicity, or just activate the ring, bromine can be added across the double bond to donate electron density to the ring and the nucleophilic carbon of the lithium intermediate. The need here is simply for protection though. However, this electron donating ability works against the reaction and the progress was very slow and never proceeds to completion. Over time hydrolysis occurs to give undesirable byproducts. Excess trimethylsilyl compound can be added to push the reaction more, but never to an acceptable level. Even the addition of a hindered base like triethylamine will aid, just not enough to push the reaction to completion. The coupling with the silyl derivative is typically done in our group with a perfluorinated sulfonyl fluoride and proceeds to completion with relative ease. The lack of reaction on the part of the aromatic sulfonyl fluoride suggests that the S-F bond is not polarized enough for displacement of the F atom, whereas the electron withdrawing perfluoro group of the RₙSO₂F is adequate.

Since this methodology was essentially to determine if dimerization would occur with the sulfonimide IL moiety, another approach was considered. A CF₃ group would certainly be less cluttered in terms of $^{19}\text{F}$ NMR spectra but not critical to the exercise. It was decided to use the base assisted condensation reaction method discussed in Chapter 2 (Scheme 2.1). This simply involved amidating the benzene sulfonyl fluoride (or benzene
sulfonyl chloride) and then coupling it with the commercially available nonafluorobutyl sulfonyl fluoride, C$_4$F$_9$SO$_2$F.

The base assisted reaction worked fine and acidification of the monofunctional sulfonimide was done with concentrated HCl, followed by an ether extraction. Sulfuric acid can be used and is often followed by sublimation but was not utilized for fear of possible damage to the trifluorovinyl group upon heating. Cesium carbonate was used to neutralize the acid form and allow washing of any impurities with water and CH$_2$Cl$_2$. For the perfluorinated difunctional sulfonimides presented in the preceding chapter, the preferred methylating agent was dimethyl sulfate because acidifying the difunctional sulfonimide was difficult. Methylation of the cesium salt with dimethyl sulfate was unsuccessful and resulted in the disappearance of all three vinyl fluorine atoms. Since the acid form was readily available the methylation was successfully prepared with trimethyl orthoacetate.

With the process to the TFVE benzene methylated sulfonimide finally established, the final step was equally elusive. Using the sulfonimide to methylate a 1-alkylimidazole was not as clean as with the perfluorinated form and created unaccountable side products. Since the benzene ring can donate electron density to the sulfonimide, it makes the CH$_3$ group on the sulfonimide less susceptible to nucleophilic attack; it makes the sulfonimide a slightly weaker leaving group; and higher temperatures had to be employed to methylate the alkyl imidazole. As a result of the higher temperatures, it is plausible that the nucleophilic nitrogen on the alkyl imidazole was
attacking the trifluorovinyl group. The problems associated with methylyating the imidazole using this compound are summarized in Figure 3.2.

1. Nucleophilic attack on perfluorinated double bond

2. Poor methylating agent

1. Rf inductively makes the N-CH$_3$ bond more polarized.
2. Resulting sulfonimide anion is stabilized with inductive and resonance effects.

1. R-group or Ar-group can donate electron density to N-CH$_3$ bond, making the CH$_3$ less electrophilic.
2. Less inductive or mesomeric stabilization.

**Figure 3.2: Problems Associated with Methylating Imidazole**

Once again the trifluorovinyl group was vulnerable to reaction conditions and the obvious solution would be to protect it with bromine. This was illogical since the gist of directly methylating the alkyl imidazole with the sulfonimide was to create a “halide-free” ionic liquid and deprotecting the brominated trifluorovinyl group requires the use of zinc. However, this was done to see if dehalogenating an ionic liquid and regaining the double bond was possible but the question of trace amounts of a transition metal still remained. With this in mind it was decided to save a few steps and utilize anion metathesis to make the monomeric ionic liquid. Once an alkylimidazole is quaternized into a halide salt and becomes imidazolium cation, there are no nucleophilic nitrogen
atoms on the ring and therefore no threat to the trifluorovinyl group. By removing the nucleophilicity of the imidazole by first converting it to the imidazolium cation and then introducing it to the trifluorovinyl group, the integrity of the trifluorovinyl monomer was preserved. Moreover, anion metathesis can be done at room temperature, giving more assurance that the trifluorovinyl group will not react.

Since, at the required temperatures to facilitate methylation, the 1-alkylimidazole is nucleophilic enough to attack the trifluorovinyl ether group, 1,3-imidazolium halide salts had to be synthesized for anion metathesis with the sodium, lithium, or cesium sulfonimide salts. Reaction of a 1-alkylimidazole with an alkyl halide is a typical $S_N2$ reaction and our synthesis was done with varying success using classic $S_N2$ conditions, often simply using an excess of the alkyl halide as the solvent and reactant. Since this reaction required elevated temperatures up to 100°C up to 12 hours, the resulting salt was often discolored and this discoloration was carried along to the final IL.

The use of solvent-free sonochemical preparation had significant appeal.\textsuperscript{61} This approach requires shorter reaction time and low reaction temperature in contrast to several hours needed under conventional heating conditions using an excess of reactants. Interestingly, during sonication, the formation of the imidazolium halide could be visibly monitored as the reaction contents turned from a clear solution to opaque (emulsion) and finally to a clear viscous phase or semi-solid. A laboratory ultrasonic cleaning bath was used and workup only involved the removal of residual alkyl halide, or alkylimidazolate, under vacuum. Washing with ethyl acetate/ether and then drying was also possible. This
method was extremely helpful in minimizing discoloration of the final IL and producing pure imidazolium halide salts for metathesis.

The subsequent dimerization of the monofunctional trifluorovinyloxy benzene sulfonimide was successful. The path was difficult, but the fact that a cyclodimerization was possible with a monomeric ionic liquid was established. In addition a workable scheme to use for preparing monomeric ionic liquids containing the trifluorvinyl ether benzene sulfonyl imide functionality was developed. The method is shown below in Scheme 3.2. This methodology lays the groundwork for the difunctional monomer containing the perfluorinated 4-carbon linker between the two sulfonimides and the trifluorovinyl ether benzene rings.

Scheme 3.2: Revised Path to Benzene TFVE Monomer

Extension of this methodology to a difunctional monomer for polymerization was relatively straightforward. Scheme 3.2 above can be utilized by replacing the C₄F₉SO₂F
with the difunctional sulfonyl fluoride, $\text{FO}_2\text{S(CF}_2)_4\text{SO}_2\text{F(8)}$. With Scheme 3.2 a small excess of the more volatile $\text{C}_4\text{F}_9\text{SO}_2\text{F}$ is used to allow easier purification by removing the excess by vacuum distillation. In making the difunctional monomer a slight excess of the sulfonyl amide was used and the excess removed by sublimation. The subsequent acidification, neutralization with cesium carbonate, and anion metathesis worked well. Anion metathesis was performed with butyl methyl imidazolium bromide because the consequent ionic liquid typically has the lower viscosity for sulfonimide ILs. Lower viscosity could potentially improve its cycloaddition polymerization.

While the monomer is a thick, high viscosity liquid at room temperature, it does become more free-flowing upon heating to 130 °C but the rate of polymerization drops considerably as the concentration of vinyl groups decrease. To push the cyclopolymerization to completion, temperatures in excess of 180°C had to be employed. No solvents were used as it is known that neat polymerizations result in higher molecular weight polymers for typical PFCB aryl ether polymers.\textsuperscript{62} It is also well known that the TFVE group is susceptible to attack at higher temperatures by nucleophiles or protons so care was taken to clean glassware and create an inert atmosphere in the polymerization process. In spite of taking the necessary precautions the resulting ionic liquid polymer darkens to a glassy substance at room temperature.

Molecular weight determination was elusive on two fronts as there is little precedent for polymeric ionic liquids. GPC molecular weight determination was deceiving and suggested a polymeric weight far less than the weight of the starting
monomer. This was probably due to the PILs limited solubility in chloroform and increased interaction with column media.

Electrospray ionization (ESI) is a technique used in mass spectrometry to produce ions. It is especially useful in producing ions from macromolecules because it overcomes the propensity of these molecules to fragment when ionized. The development of electrospray ionization for the analysis of biological macromolecules was rewarded with the Nobel Prize in Chemistry to John Bennett Fenn in 2002. This technique had obvious appeal to our higher molecular weight ionic liquids and was contracted to the Clemson University Genetics and Biochemistry Department. The results were also ambiguous, at best. While the $^{19}$F and $^1$H NMR were very clean, the ESI/MS results suggested that only dimers and trimers were present, which seemed very unlikely given that TFVE monomers often polymerize to molecular weights in excess of 18,000 g/mole.

With a purified monomer sample, it was decided to investigate a copolymerization with the biphenyl trifluorovinyl ether (BPVE) monomer to increase molecular weight of the polymer. The behavior of the BPVE polymerization is well established and it was hoped that the monomeric ionic liquid would not adversely affect the cycopolymerization.

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

\[\text{O} + \text{SO}_2\text{NSO}_2(\text{CF}_2)_4\text{SO}_2\text{NSO}_2 \rightarrow 175^\circ C \rightarrow 21\]

\[
\begin{align*}
\text{F} & \quad \text{F} \\
\text{F} & \quad \text{F} \\
\text{F} & \quad \text{SO}_2\text{NSO}_2(\text{CF}_2)_4\text{SO}_2\text{NSO}_2 \\
\text{F} & \quad \text{O} \\
\text{BMIM}^+ & \quad \text{BMIM}^+ \\
\end{align*}
\]
Figure 3.3: Copolymerization of RTIL Monomer and BPVE

In the first attempt the biphenyl TFVE and the monomeric ionic liquid did not mix, even at the elevated temperature of 175°C, and the two monomers basically polymerized separately. It was decided a solvent may need to be employed in spite of knowing that these cyclopolymerizations form higher molecular weights neat and tend to form cyclic oligomers and lower molecular weight polymers when dissolved in solvents. Acetonitrile was considered but would require a high pressure setup for the cyclopolymerization. The biphenyl TFVE monomer was very soluble in acetonitrile but the polymer was not soluble in acetonitrile. Benzonitrile was a good candidate but the solubility of the polymer was suspect. A variety of solvents were considered – including DMF and biphenyl ether. The biphenyl polymer is soluble in both solvents. Mixtures of 50% RTIL/50% BPVE and 5% RTIL/95% BPVE were attempted using benzonitrile as a solvent and thin films were made. After processing and making a film, thermogravimetric analysis on the 5% RTIL/95% BPVE polymer showed a 5-8% drop in weight at 400°C (typical for these RTILs) and then a catastrophic drop at 500°C, which is typical of BPVE polymers. The DSC spectrum indicated a glass transition at 120°C, which is about 40°C lower than the glass transition temperatures of the BPVE polymers reported by Dr. Jin. Two interesting aspects of incorporating only 4-5% of the RTIL monomer into the BPVE matrix was that it allowed complete dissolution of the polymer in acetonitrile (ACN) and that it lowered the $T_g$ by 40°C.

An interesting observation was made concerning the chemical shifts of the trifluorovinyl ether fluorine atoms as the substituent para to the trifluorovinyl ether group
was transformed. As substituents with increasing electron withdrawing character were added \textit{para} to the TFVE group, the fluorine atoms geminal to each other (\textit{cis} and \textit{trans} to \textit{O}) would predictably experience downfield shifts – a result of deshielding. However, the fluorine atom geminal to the oxygen atom would behave contradictory to this, which seemed counterintuitive given that this particular fluorine atom was closest to the ring and should have more strongly felt the electron withdrawing effect of the ring’s \textit{para} substituents.

A kinetic study on TFVE cyclodimerization had been reported to determine if the electronic effect seen by $^{19}$F NMR was transferred to the reactivity of the trifluorovinyl ether. The lack of copolymerization between the two monomers was probably due to a solubility difference. However, in order to ascertain if it could be due to different monomer reaction rates, a monofunctional monomer was studied according to the literature. This monomer was heated neat in an NMR tube to 130 °C and the conversion of the TFVE group was measured at 10 hour intervals.
Figure 3.4: Dimer conversion of monomeric IL versus time at 130 °C and compared to selected monomers from Dr. Spraul’s study. ■ R = NHCOOEt, ◆ R = Br, ▲ R = COOEt, ● R = SO₂N(BMIM)⁺SO₂C₄F₉.

It’s obvious from the comparative data above that the monomeric IL dimerizes slower than the analogous TFVE compounds with different substituents. Cycloaddition of TFVE’s is considered to be a second order reaction.⁶⁷ Therefore a plot of $x/(1-x)$ versus time ($t$) should give a linear plot where slope $k$ is the rate constant. The rate constant and linear fit $R^2$ values are reported in Table 3.1 along with the reported values.⁶⁸ The author also noted that with every 1 ppm upfield shift of the fluorine atom trans to the oxygen atom the rate of cycloaddition was increased by $3.1 \times 10^{-2} \text{ h}^{-1}$ at 130 °C.
<table>
<thead>
<tr>
<th>Functional group</th>
<th>Rate Constant $^a$ k (h$^{-1}$)</th>
<th>$^b$ R$^2$</th>
<th>Half-life (h)</th>
</tr>
</thead>
<tbody>
<tr>
<td>NHCOOEt</td>
<td>5.2 x 10$^{-2}$</td>
<td>0.932</td>
<td>19.9</td>
</tr>
<tr>
<td>H</td>
<td>4.1 x 10$^{-2}$</td>
<td>0.976</td>
<td>24.4</td>
</tr>
<tr>
<td>Br</td>
<td>3.9 x 10$^{-2}$</td>
<td>0.920</td>
<td>25.9</td>
</tr>
<tr>
<td>COOEt</td>
<td>2.4 x 10$^{-2}$</td>
<td>0.961</td>
<td>42.0</td>
</tr>
<tr>
<td>SO$_2$N(BMIM)SO$_2$C$_4$F$_9$</td>
<td>2.5 x 10$^{-2}$</td>
<td>0.978</td>
<td>40.3</td>
</tr>
</tbody>
</table>

**Table 3.1:**Kinetic data for selected dimerization reactions

$^a$ Conversion calculated using $^{19}$F NMR and linear fit of data. $^b$ R$^2$ values from linear fit of data.

**Figure 3.5:** Second order plot of monomeric IL conversion

This study originated from unexpected $^{19}$F NMR chemical shifts of the trifluorovinyl ether group as it relates to the substituent *para* to the TFVE group. Once
again the presence of an ionic liquid moiety complicates the study even more. The chemical shift of the fluorine atom chosen for the comparative study was supposed to provide insight into the reactivity of the TFVE monomer. The monomeric IL differs from the monomers previously studied in that they have ionic charges which, even if they are hindered, are attracted to each other more strongly than the van der Waals of the monomers previously studied. The reported study allowed predictability in the dimerization of a TFVE benzene but the chemical shift of the F atom \( \text{trans} \) to the oxygen atom (-125.8 ppm) would suggest that the kinetics of the monomeric IL would be similar to that if the \( \text{para} \) substituent was a proton. However, the kinetic rate constant puts it closer to that of the COOEt substituent. This may be due to the higher viscosity of the ionic liquid monomer.
Experimental

Preparation of p-trifluorovinyloxy benzene sulfonyl chloride, \( \text{CF}_2\text{CFO}(\text{C}_6\text{H}_4)\text{SO}_2\text{Cl} \) (13)

After flushing a one-neck 250 mL flask with a side arm stopcock with nitrogen thoroughly, two 12-inch non-coring needles were inserted backwards through the septum and a stopper was placed on the needlepoints to prevent moisture from entering the vessel. 10 mL of dry ether was injected into the flask. 7.85 g (31.53 mmol) of the 4-bromo compound was then injected, vigorous stirring initiated, and the flask was cooled to -80°C.

After cooling, a total of 20.40 mL of 1.7M t-butyllithium (34.68 mmol) was injected dropwise over the course of 30 minutes. This was then allowed to stir for 45 minutes while maintaining -80°C. During this time, in a 2-neck flask adjacent to the t-BuLi reaction and equipped with a stir bar, 3.06 mL of freshly distilled \( \text{SO}_2\text{Cl}_2 \) and 10 mL of dry ether was added. One neck equipped with a septum for the cannula transfer of the lithium intermediate, and the other neck was equipped with a stopcock connected to the house vacuum line to assist in pulling the lithium intermediate solution to the second flask. This was cooled to -80°C and the cannula transfer was made.

This was allowed to stir for 15 minutes and the flask was flash warmed with air, allowed to come to room temperature, and 40 mL of DI water was added and stirred.

Using a separatory funnel, the bottom water layer was removed and the top ether/pentane layer was poured into a 50 mL round bottom flask. The ether and pentane was removed on the rotary evaporator and then further dried on the vacuum line overnight, leaving a dark red liquid. A short-path distillation was run at 110 °C and 20
torr. The distillate was much more clear, a transparent tan liquid. A 50% yield of 4.23 g was obtained.

\[
\begin{align*}
F_A & F_x \\
F_M & -O- \quad \text{SO}_2 \text{Cl} \\
& H_a \quad H_b
\end{align*}
\]

\(1^1\text{H NMR (CD}_3\text{CN)} \delta_b 8.11 \text{ ppm (2H, m)}, \delta_a 7.4 \text{ ppm (2H, m)}; ^{19}\text{F NMR (CD}_3\text{CN, ppm)} \delta_A -117.6 \text{ (1F, dd)}, \delta_M -123.9 \text{ (1F, dd)}, \delta_X -136.2 \text{ (1F, dd), } ^2J_{AM}=96\text{Hz}, ^2J_{AX}=59\text{Hz,} ^3J_{MX}=110\text{Hz; bp 225}^\circ\text{C.}
\]

Preparation of \( p\)-trifluorovinyloxy benzene sulfonyl amide, \( \text{CF}_2\text{CFO(C}_6\text{H}_4\text{)}\text{SO}_2\text{NH}_2 \) (14)

In a 2-neck 100 mL round bottomed flask equipped with a stir bar, The distilled \( \text{CF}_2\text{CFO(C}_6\text{H}_4\text{)}\text{SO}_2\text{Cl} \) (4.23 g, 15.7 mmol) from the previous experiment was dissolved in 10 mL of dry ether. While under a nitrogen atmosphere, approximately 50 mL of ammonia was condensed at \(-80\) °C. This was allowed to stir overnight and slowly come to room temperature. The next day the remaining \( \text{NH}_3\) and ether were removed on the vacuum line. Acetone was then used to dissolve the compound and the solid \( \text{NH}_4\text{Cl} \) was removed by filtration. The acetone was removed on the vacuum line. Sublimation at 105 °C and 20 millitorr was done. A white solid of 80% yield was obtained for 3.2 g.
$^1$H NMR (CD$_3$CN) $\delta_b$ 7.91 ppm (2H, m), $\delta_a$ 7.34 ppm (2H, m); $^{19}$F NMR (CD$_3$CN, ppm) $\delta_A$ -118.1 (1F, dd) $\delta_M$ -125.3 (1F, dd) $\delta_X$ -135.4 (1F, dd), $^2J_{AM}$=96Hz, $^2J_{AX}$=59Hz, $^3J_{MX}$=110Hz.

Preparation of cesium salt of [$p$-trifluorovinyloxy benzene sulfonyl]perfluorobutyl sulfonoyl imide, CF$_2$CFO(C$_6$H$_4$)SO$_2$N(Cs)SO$_2$C$_4$F$_9$ (15)

The sulfonamid (2.0 g, 7.8 mmol) was placed in a 50 mL round bottom flask with a stir bar. Approximately 20 mL of dry CH$_3$CN was added and capped. This was taken into the glove bag and 4.1 mL (23.4 mmol) of dry DIEA was injected. This flask was connected to a pressure-equalizing funnel with 3.2 g (10.2 mmol) of C$_4$F$_9$SO$_2$F and a positive nitrogen flow passing through it at all times and allowed to stir for 10 minutes. The C$_4$F$_9$SO$_2$F was dropped in slowly to the sulfonamide solution. This was allowed to stir overnight and the CH$_3$CN and excess C$_4$F$_9$SO$_2$F were removed on the vacuum line. A thick, light tan liquid remained, indicating a clean product.

Instead of using 35% HCl, 10 mL of concentrated H$_2$SO$_4$ was used to acidify the sulfonimide. Under nitrogen, using a dropping funnel and with the flask in an ice bath, the sulfuric acid was dropped in and, once all the acid was added, the ice bath was removed and allowed to come to room temperature on its own. This was stirred for one and a half hour. Then 10 mL of diethyl ether was added and stirred vigorously. Water was added until two layers formed. The ether layer was separated and evaporated on the vacuum line. Then a clear aqueous solution containing 2.6 g Cs$_2$CO$_3$ (7.8 mmol) was
added and a tan precipitate formed. The ppt was filtered with a Buchner funnel, washed several times with DI water, and twice with CH₂Cl₂. A 81% yield of 4.8 g was obtained.

The acid form is a light tan solid and the cesium salt form is a very light tan solid, almost white.

\[ \begin{align*}
1^\text{H} \text{ NMR} \ (\text{CD}_3\text{CN}) \ & \delta_a \ 7.25 \text{ ppm} \ (2\text{H, m}), \ \delta_b \ 7.91 \text{ ppm} \ (2\text{H, m}); \\
19^\text{F} \text{ NMR} \ (\text{CD}_3\text{CN}, \text{ppm}) \ & \delta_A \ -118.6 \ (1\text{F, dd}) \ \delta_M \ -125.8 \ (1\text{F, dd}) \ \delta_X \ -135.0 \ (1\text{F, dd}), \ \delta_M = 96\text{Hz}, \ \delta_X = 59\text{Hz},
\end{align*} \]

\[ \begin{align*}
J_M = 96\text{Hz}, \ J_X = 59\text{Hz},
\end{align*} \]

\[ \begin{align*}
J_M = 110\text{Hz}, \ \delta_b \ -112.5 \ (2\text{F, t}), \ \delta_c \ -120.4 \ (2\text{F, s}), \ \delta_d \ -125.2 \ (2\text{F, t}), \ \delta_e \ -80.3 \ (3\text{F, t}).
\end{align*} \]

Preparation of RTIL: CF₂CFO(C₆H₄)SO₂(C₄F₉)(16)

The cesium salt, 1.0 g (1.5 mmol), was placed in a round bottomed flask and 0.35 g (1.6 mmol) of the butyl methyl imidazolium bromide was added. About 10mL of DI water was added and the solution was stirred overnight. The next morning a very thick tan liquid was at the bottom of the flask. The water was decanted, washed with DI water several times, and the thick liquid dried on the vacuum line overnight at 70°C. A 95% yield was obtained.
Preparation of Dimer of RTIL: \( \text{CF}_2\text{CFO(C}_6\text{H}_4\text{)SO}_2\text{N(BMIM)}\text{SO}_2\text{C}_4\text{F}_9 \) (17)

The thermal cyclodimerization of 16 was preceded by drying the RTIL on the vacuum line overnight at 90°C to remove any traces of solvent or moisture. The dimer is then placed in a closed vacuum system and heated overnight at 185°C.

\[ \text{1H NMR (CD}_3\text{CN)} \delta_a 8.41 \text{ ppm (1H, s), } \delta_b 7.32 \text{ ppm (1H, s), } \delta_c 7.35 \text{ ppm (1H, s), } \delta_d 3.80 \text{ ppm (2H, s), } \delta_e 4.11 \text{ ppm (2H, t), } \delta_f 1.79 \text{ ppm (2H, m), } \delta_g 1.30 \text{ ppm (2H, m), } \delta_h 0.93 \text{ ppm (3H, t), } \delta_i 7.25 \text{ ppm (2H, m), } \delta_j 7.92 \text{ ppm (2H, m); } \text{19F NMR (CD}_3\text{CN, ppm)} \delta_a -126.7, -125.8, -130.9 \text{ ppm (2F, m), } \delta_b -125.2 \text{ ppm (2F, t), } \delta_c -80.3 \text{ ppm (3F, t).} \]
127.5, -128.0, -128.8, -129.4, -130.2, -130.5, -131.0, δ_b-112.5 (2F, t), δ_c-120.5 (2F, s), δ_d-125.2 (2F, t), δ_e-112.6 ppm (2F, t), δ_f-120.5 ppm (2F, s), δ_g-125.2 ppm (2F, m), δ_h-80.3 ppm (3F, t).

Preparation of 1,1’-Bis[4-(trifluorovinyl)oxyphenylsulfonyl]-1,4-(disulfonyloctafluorobutyl)diimide Cesium salt, [CF₂CFO(C₆H₄)SO₂N(Cs)SO₂CF₂CF₂]₂ (18)

In a 2-neck 100mL round-bottomed flask, 3.18 g (12.56 mmol) of the CF₂CFO(C₆H₄)SO₂NH₂ was dried on the vacuum line, and then dissolved in 30 mL of dry acetonitrile and allowed to stir under a nitrogen atmosphere. Then 28.25 mmol or 4.9 mL of dry DIEA was added through the septum and allowed to stir for 10 minutes. Then 1.86 g (5.09 mmol) of FSO₂(CF₂)₄SO₂F was added to the flask. This was allowed to stir overnight at room temperature.

The CH₃CN and excess DIEA were evaporated on the vacuum line at 40 °C overnight to remove the excess DIEA because of its high boiling point and the viscosity of the DIEAH⁺ ionic liquid. Also, to remove any undetectable sulfonamide starting material, sublimation conditions of 100 °C and high vacuum were used.

Approximately 10 mL of ether was used to solubilize the ionic liquid, and then approximately 50 mL of concentrated HCl solution added and allowed to stir for 2 hours. An ether extraction was then done and the solvent removed on the rotary evaporator.

This isolated the acid form of the disulfonimide. An aqueous solution of 2.05 g (6.28
mmol) Cs₂CO₃ was added to precipitate the Cs salt compound. A yield of 4.73 g was obtained for an 85% yield.

![Chemical Structure](image1)

**18**

1H NMR (CD₃CN) δₐ 7.25 ppm (2H, m), δ₇ 7.91 ppm (2H, m); 19F NMR (CD₃CN, ppm) δₐ -118.6 (1F, dd) δₐ -125.8 (1F, dd) δₐ -135.0 (1F, dd), ²Jₐₐ = 96Hz, ²Jₐₙ = 59Hz, ³Jₐₙ = 110Hz, δₐ -112.2 (4F, t), δₐ -119.3 (4F, t).

**Preparation of RTIL: [CF₂CFO(C₆H₄)SO₂N(BMIM)SO₂CF₂CF₂]²⁻ (19)**

The cesium disulfonimide salt, 0.50 g (0.46 mmol), was weighed and set aside. Then 0.200 g (0.92 mmol) of the [BMIM][Br] were dissolved separately in DI H₂O and stirred. The cesium salt was sprinkled in and allowed to stir overnight. A small amount of CH₂Cl₂ was added to aid in the dissolution of the cesium salt. When the CH₂Cl₂ was added the bottom layer turned cloudy but became clear with overnight stirring. Then a CH₂Cl₂ extraction was done and the methylene chloride was evaporated. The methylene chloride layer was washed two times with DI water to ensure all the cesium bromide had been removed. The methylene chloride was evaporated and the rtol was dried overnight on the vacuum line at 70 ºC. A 95% yield was obtained.

![Chemical Structure](image2)

**19**
$^1$H NMR (CD$_3$CN) $\delta_a$ 8.39 ppm (2H, s), $\delta_b$ 7.32 ppm (2H, s), $\delta_c$ 7.35 ppm (2H, s), $\delta_d$ 3.78 ppm (6H, s), $\delta_e$ 4.09 ppm (4H, t), $\delta_f$ 1.79 ppm (4H, m), $\delta_g$ 1.30 ppm (4H, m), $\delta_h$ 0.93 ppm (6H, t), $\delta_i$ 7.21 ppm (4H, m), $\delta_j$ 7.89 ppm (4H, m); $^{19}$F NMR (CD$_3$CN, ppm) $\delta_A$ -118.6 (2F, dd), $\delta_M$ -125.8 (2F, dd), $\delta_X$ -135.0 (2F, dd), $^2J_{AM} = 96$Hz, $^2J_{AX} = 59$Hz, $^3J_{MX} = 110$Hz, $\delta_b$-112.2 (4F, t), $\delta_c$-119.4 (4F, t); $T_d$=367°C, $T_g$= -16°C.

Preparation of Polymeric RTIL:

$[\text{O(C}_4\text{F}_6\text{O(C}_6\text{H}_4\text{SO}_3\text{N(BMIM)SO}_2\text{CF}_2)}_n\text{SO}_2\text{N(BMIM)SO}_2\text{C}_6\text{H}_4]_n$ (20)

After drying 19 on the vacuum line at 70°C overnight, the temperature is taken up to 190°C for 8 hours.

$^1$H NMR (CD$_3$CN) $\delta_a$ 8.41 ppm (2H, s), $\delta_b$ 7.32 ppm (2H, s), $\delta_c$ 7.35 ppm (2H, s), $\delta_d$ 3.80 ppm (6H, s), $\delta_e$ 4.11 ppm (4H, t), $\delta_f$ 1.79 ppm (4H, m), $\delta_g$ 1.30 ppm (4H, m), $\delta_h$ 0.93 ppm (6H, t), $\delta_i$ 7.25 ppm (4H, m), $\delta_j$ 7.92 ppm (4H, m); $^{19}$F NMR (CD$_3$CN, ppm) $\delta_a$ -126.4, -127.1, -127.2, -127.9, -128.6, -129.3, -129.4, -130.1, -130.6, -131.1, $\delta_b$-112.1 (4F, m), $\delta_c$-119.4 (4F, s); $T_d$=390°C, $T_g$= 16°C.

Preparation of Random Block Co-polymer with 5% RTIL/95% BPVE (21)

In a 25mL glass reactor equipped with a stir bar, 0.30 g (0.27 mmol) of the BMIM monomer was placed and flushed with nitrogen. Then 1.80 g (5.13 mmol) of the biphenyl TFVE was then added to the BMIM monomer. The IL would not dissolve in
the BPVE even with vigorous stirring. Two additions of 0.3 mL of benzonitrile were added and the IL solubilized after the second 0.3 mL addition, nothing after the first 0.1 mL addition. This was heated to 175 ºC for 72 hours and a $^{19}$F NMR spectrum was taken. Alongside this reaction was placed a control reaction consisting of only 0.60 g (1.71 mL) BPVE and 0.2 mL benzonitrile. This reaction was also complete after 72 h.

Both reactions had the benzonitrile removed on the vacuum line at 100 ºC for 48 h. Two portions of both reactions were taken and processed differently. One was dissolved in THF and placed on a glass slide and allowed to evaporate. The other portion was dissolved in THF and methanol added to precipitate the higher molecular weight polymer. The precipitate was filtered and dried on the vacuum line. This solid (supposed higher molecular weight portion) was then dissolved in THF and placed on a glass slide and allowed to evaporate.

$^1$H NMR (CD$_3$CN) $\delta_a$ 8.41 ppm (2H, s), $\delta_b$ 7.32 ppm (2H, s), $\delta_c$ 7.35 ppm (2H, s), $\delta_d$ 3.80 ppm (6H, s), $\delta_e$ 4.11 ppm (4H, t), $\delta_f$ 1.79 ppm (4H, m), $\delta_g$ 1.30 ppm (4H, m), $\delta_h$ 0.93 ppm (6H, t), $\delta_i$ 7.25 ppm (4H, m), $\delta_j$ 7.92 ppm (4H, m); $^{19}$F NMR (CD$_3$CN, ppm) $\delta_a$ -128.3, -128.5, -129.1, -129.3, -130.0, -130.7, -130.8, -131.4, -131.5, -131.8, $\delta_b$-113.2 (4F, m), $\delta_c$-120.6 (4F, s); $T_d$=390ºC, $T_g$= 120ºC
Typical Procedure for 1,3-Dialkylimidazolium Halide Salts

Preparation of n-Butyl Methylimidazolium Bromide (22)

Approximately 1.8 g of 1-methylimidazole was placed on some KOH pellets and allowed to stand overnight. The 1-methylimidazole was distilled under vacuum from the KOH, yielding 1.74 g (12.7 mmol) of clean starting material. The 4.0 g of n-butyl bromide was washed with concentrated H$_2$SO$_4$ and then stirred overnight with P$_4$O$_{10}$. The n-butyl bromide was distilled from the P$_4$O$_{10}$ using the vacuum line at room temperature.

The 1.74 g (21.2 mmol) of 1-MIM was placed in a 25 mL flask and capped with a septum. Then 3.48 g (25.4 mmol) of n-butyl bromide was syringed into the flask and placed on the sonicator. The water bath was heated to 50 ºC and sonicated overnight. The flask was placed on the vacuum line and heated to 70 ºC overnight for drying.

$^1$H NMR (CD$_3$CN) $\delta_a$ 9.28 ppm (1H, s), $\delta_b$ 7.44 ppm (1H, t), $\delta_c$ 7.48 ppm (1H, t), $\delta_d$ 3.86 ppm (3H, s), $\delta_e$ 4.18 ppm (2H, t), $\delta_f$ 1.79 ppm (2H, m), $\delta_g$ 1.30 ppm (2H, m), $\delta_h$ 0.93 ppm (3H, t); T$_m$ 83ºC.
CHAPTER IV
SYNTHESIS OF NAFION BASED IONIC LIQUID MONOMERS CONTAINING
SULFONIMIDE IONIC LIQUID FUNCTIONALITY

Introduction

Since the accidental discovery of Teflon® by Roy Plunkett in 1937 a number of fluorinated plastics have reached commercial status. These plastics, exemplified by polytetrafluoroethylene (PTFE), have outstanding electrical, chemical, and thermal properties. Pipes, valves, optical fibers, surgical implants, and the well-known nonstick coatings for cookware are some typical examples for the application of PTFE. A variety of comonomers have since been introduced in the PTFE chains to obtain copolymers of lower molar mass and reduced melt-viscosity, while maintaining adequate mechanical and physical properties. Two common examples of such copolymers are hexafluoropropylene (FEP) and perfluoroalkyl-vinyl-ethers (PFAs).

Research efforts directed towards energy conversion technology and the widespread commercialization of fuel cells has been under intense investigation. Polymeric materials, typically functionalized by acid groups, have dominated as the ion-exchange component for membranes in proton exchange membrane fuel cells (PEMFC). The current state of the art proton exchange membrane is Nafion®, a DuPont product that was developed in the late 1960s. As most fluoropolymers, Nafion® is quite resistant to chemical attack and Nafion’s poly(perfluorosulfonic acid) structure imparts exceptional oxidative and chemical stability, which is important in fuel cell applications.
Nearly all existing membrane materials for PEM fuel cells rely on absorbed water and its interaction with acid groups to produce proton conductivity. Water uptake is also important in determining the ultimate performance of these materials. Water is needed as the mobile phase to facilitate proton conductivity. However, absorbed water also affects the mechanical properties of the membrane by acting as a plasticizer, lowering the $T_g$ and modulus of the membrane. Devising systems that can conduct protons with little or no water is perhaps the greatest challenge for new membrane materials.\(^{71}\)

Ionic liquids are excellent candidates for improving a variety of properties in membranes. From the perspective of electrochemistry, RTILs themselves are ionic conductors and in some aspects exceed typical ionic conductors for which the use of a solvent is a prerequisite for ionic conductivity in electrochemical devices.\(^{72}\) Consideration of durability and nonvolatility has also brought RTILs to the forefront for wet devices. Numerous efforts have also been made to use polymers with RTILs as ion-conducting polymer electrolytes. These include incorporation of RTILs in a polymer matrix such as a thermoplastic polymer\(^{73}\) or a perfluorinated ion exchange membrane,\(^{74}\) polymerization of a vinyl monomer in RTILs,\(^{75}\) and fixing of the cation structure in the polymer segments.\(^{76}\)

Like many other fluoropolymers, Nafion is quite resistant to chemical attack and 1,3-dialkylimidazolium sulfonimide ILs are currently the most conductive and thermally stable ILs. It is the combination of the two properties into one polymeric ionic liquid that is explored in this work. Perhaps the most glaring hurdle in this work is the effect the presence of an ionic liquid moiety will have on the mechanical properties on a membrane
since room temperature ionic liquids exist because of their low glass transition temperatures. The synthesis of such a material needs to be explored and should not be simply dismissed because the presence of IL moieties will predictably lower the Nafion T_g. The possibility always exists that IL presence in a polymer, especially when directly incorporated as a pendant in this case, may increase long term performance in high temperature environments, improve electrode processing and attachment, or even enhance a fuel cell’s ability to endure startup and shutdown of the fuel cell with the repeated swelling/drying/heating/cooling of the membrane.

**Results and Discussion**

Considering that DuPont introduced Nafion® in 1962 and is still the gold standard for membranes is impressive. Briefly, polymers for PEMFCs are either non-fluorinated or fluorinated, both functionalized by acid groups. Proton exchange membranes for fuel cells and ion exchange are commercially available under the Nafion®, Flemion®, Hyflon®, and Aciplex® trade names. The prime differences lie in the side-chain length and have been studied extensively. Structural features such as water clustering, water-channel dimensions and topology, and the dynamics of the hydronium ions and water molecules have all been analyzed in relation to the dynamical properties of the polymer backbone and side-chains. It is generally found that mobility is promoted by high water content, with the side-chains participating actively in the H_3O^+/H_2O transport mechanism. Nafion, whose side-chain length is intermediate of the three sulfonic acid polymers shown below, is found to have the most mobile polymer side-chains at the higher level of hydration, suggesting that there could be an optimal side-chain length in these systems.
There are also some indications that the water-channel network connectivity is optimal for a high water-content Nafion system, and that this could explain why Nafion appears to exhibit the most favorable overall hydronium/water mobility.

Modification of Nafion’s structure and comparative studies of these ionomers with Nafion have been done in the DesMarteau group for over 20 years. In 2002, an experimental bis[(perfluoroalkyl)sulfonyl]imide-based ionomer performed better in a membrane-electrode assembly (MEA) than that of one based on the commercially available Nafion 1135 membrane. The primary structures of the perfluorinated ionomers studied are shown below.

![Figure 4.1: General Structures of Three Perfluorinated Sulfonic Acid Polymers](image)
**Figure 4.2:** Primary Structures of DuPont Nafion and Bis[(perfluoroalkyl)sulfonyl]imide Ionomers

With the synthesis of the above ionomer well established in our group it would appear this bis[(perfluoroalkyl)sulfonyl]imide ionomer is merely one step from being a polymeric ionic liquid (PIL). The focus in this work is two fold. The first is to establish a synthetic path to the monomeric ionic liquid utilizing the halide-free methodology. Second is to co-polymerize the monomer with tetrafluoroethylene (TFE) and observe any property changes.

Ionomers containing the bis[(perfluoroalkyl)sulfonyl]imide acid group have been synthesized by the DesMarteau group since 1995, so modifying the Nafion sulfonyl fluoride monomer to the sulfonimide acid was straightforward. The trifluorovinyl ether group is protected by bromination because direct reaction with the sodium N-silyl form, CF$_3$SO$_2$N(Na)SiMe$_3$ (2), results in vinyl attack. Once the bromine protected sulfonyl fluoride is coupled with the silylated sulfonamide, it is then dehalogenated with activated zinc and acidified with HCl solution. Methylating a monofunctional sulfonimide with trimethyl orthoacetate with the acid form worked well under mild conditions for the ILs prepared in Chapter Two but here, even at 70 °C, the vinyl group was attacked. The vinyl had to remain protected during methylation. To expedite the process dimethyl sulfate was used to methylated the sodium salt of the sulfonimide. It was also discovered later that the unprotected vinyl group was not attacked by dimethyl sulfate as long as extremely dry conditions were maintained.
Once again, synthesizing a “halide-free” monomer proved more difficult than expected. Just as in the previous chapter where the methylation of 1-alkylimidazole resulted in vinyl attack, the same results were observed here. We knew vinyl attack was a possibility but in this case both sides of the sulfonimide had perfluorinated alkyl groups which improve leaving group ability and inductively remove electron density from the CH$_3$ group, making it more susceptible to nucleophilic attack. The reaction does occur at milder conditions initially but requires heating to 70 ºC for completion; this is where vinyl attack occurs. To preserve the vinyl group, debromination was reserved for the final step. The path used is depicted below.
Scheme 4.1: Methodology 1 to Nafion IL Monomer

However, when considering that one of the purposes of synthesizing this monomer for polymerization is to prepare a halide-free ionic liquid, this route may lead to traces of zinc bromide in the IL. Fuel cell contamination is one of the most important
issues in fuel cell performance and applications. Contamination is closely associated with proton exchange membrane fuel cell (PEMFC) durability and stability, both of which are important factors in the development and commercialization of PEMFC technology. Studies have identified that the membrane electrode assembly (MEA), the heart of the PEMFC, is the fuel cell component most affected by contamination. Another methodology was considered – anion metathesis. This path also permits possible metal contaminants. The first methodology would allow trace amounts of zinc bromide and the anion exchange path concedes sodium bromide as a possible trace metal. The advantage depicted in Scheme 4.2 trades three steps and workups for one simple anion metathesis wherein the IL drops out of water.

![Scheme 4.2: Methodology 2 to Nafion IL Monomer](image)

The sodium salt of the perfluorosulfonimide monomer 24 copolymerizes well with tetrafluoroethylene in an aqueous emulsion system. However, the copolymerization of 24 and TFE does not behave as a typical emulsion polymerization wherein some of the hydrophobic monomer is solubilized in the interior of a micelle. The emulsifying agent disperses and stabilizes the monomer. For the sodium salt monomer 24, the monomer has a hydrophobic region and a hydrophilic region; therefore, the monomer dissolves in
an aqueous medium, behaving as an emulsifying agent itself. To account for this behavior and through years of experience, polymerization of the perfluorosulfonimide sodium salt employs a continuous-feed semi-batch reactor. The system uses a high-pressure metering syringe pump for the continuous addition of aqueous monomer 24 to the autoclave at a rate close to the uptake rate of 24.

TFE is added incrementally and the consumption is monitored by drops in pressure.

With the ionic liquid monomer 27, we weren’t sure how it may behave, but it is certain that 1,3-dialkylimidazolium bis[(perfluoroalkyl)sulfonyl]imide ionic liquids are not water soluble, therefore eliminating the benefit of having both hydrophobic and hydrophilic regions in the monomer. It was decided to try a solution polymerization in a bomb reactor for initial studies. A solution and appropriate initiator had to be decided.

In a free radical addition polymerization, the choice of polymerization initiator depends mainly on two factors: a) its solubility and b) its decomposition temperature. If the polymerization is performed in an organic solvent, then the initiator should be soluble in that solvent and the decomposition temperature of the initiator must be at or below the boiling point of the solvent. Commonly, 2,2'-azo-bis-isobutyrylnitrile (AIBN) and benzoyl peroxide suit these requirements. For emulsion polymerization or polymerization in an aqueous system, a water soluble initiator like potassium persulfate would be suitable. Determination of monomer reactivity is not always obvious or straightforward. Researchers generally rely on their experience and published data on individual monomers. This monomeric IL was a Nafion derivative and suspected to behave similarly.
As for the initiator, a perfluoro diacyl peroxide was chosen. These are an interesting and useful source of perfluoroalkyl radicals and made in our group. This choice was made due to the mild thermal conditions required and the clean reaction which generates the perfluoroalkyl radical.

![2,2'-azo-bis-isobutyrylnitrile (AIBN), benzoyl peroxide, perfluoroisobutyrylperoxide](image)

**Figure 4.3: Common Free Radical Initiators**

The perfluoroisobutyrylperoxide initiator is shown above. The obvious advantage of using this initiator is that when considering a free radical polymerization, the polymer chain initiates and terminates with the initiator, and this perfluorinated initiator would terminate the polymer chain with a perfluoroalkyl group. Termination with the \((\text{CF}_3)_2\text{FC} \cdot \text{radical may be ideal but the more likely termination would that of an acid fluoride. The solvent chosen for polymerization was trichlorotrifluoroethane, } \text{CF}_2\text{ClCFCI}_2. \) From the literature,\textsuperscript{84} thermolysis and hydrolysis data for the peroxide was collected using CF\textsubscript{2}ClCFCI\textsubscript{2}. Thermolysis rates were determined at 60 °C, 70 °C, and 80 °C and followed first order kinetics.\textsuperscript{85} However, the ionic liquid monomer was not soluble in R-113 but did form a suspension when shaken.

Initiator concentrations of 0.2 mole percent were used along with temperatures ranging from 58 °C to 74 °C. Reaction times of 12 hours and 48 hours were used also. After reaction, warm acetonitrile was used to wash unreacted monomer and possible
oligimers containing high concentrations of the IL functionality. Confirmation of unreacted IL monomer was determined using $^{19}$F NMR by removing the acetonitrile from the washing and then using an internal standard (CFCI$_3$) delivered using the vacuum line. The extent of copolymerization was determined using TGA. The decomposition temperature for the IL monomer is 400 °C with the $T_d$ of PTFE typically around 600 °C. This difference of 200 °C allows an integral procedure to estimate the weight percentage of the polymer chain pendant. DSC was performed to determine if the IL presence resulted in a noticeable glass transition. Based on the decomposition of the pendants at 400 °C the temperature scan chosen was from room temperature to 350 °C. Even with 30% by weight of IL monomer incorporated no detectable glass transition was observed. PTFE typically shows a primary melt at 327 °C, which did occur with the IL pendant, and sometimes a secondary melt or smaller melts of crystalline regions around 340 °C.

There are many areas still to be investigated regarding the presence of an IL pendant in PTFE – mechanical strength, film processing, water uptake, conductivity, and plasticizer effect. A Nafion® based IL monomer is certainly not the only choice available. Hyflon® and Aciplex® based ILs would certainly be interesting to explore. In the previous chapter the presence of a fixed IL moiety even at 1% to 3% had an effect on the glass transition as much as 40 °C. Examining the effect in PTFE was not determined but incorporating lower scan temperatures and/or forming a film initially may be more revealing. In the event films were made it would be very interesting to use microscopic methods to see what effects, if any, occur as a result of an IL pendant.
These types of perfluorinated IL monomers are still basically unexplored in the way of conductivity and morphology effects but obviously have potential as non-volatile and non-leachable plasticizers.
Experimental

Preparation of Brominated Nafion Monomer, CF₂BrCFBrOCF₂CF(CF₃)OCF₂CF₂SO₂F

(23)

The DuPont sulfonyl fluoride monomer (20.0 g, 45.3 mmol) was put in a round bottomed flask equipped with a stir bar and placed in an ice bath at 0 ºC. Then 7.96 g (49.8 mmol) of Br₂ was added very slowly with a pressure-equalizing funnel over the course of 2 hours. Excess Br₂ was determined once the reddish color persisted for 30 minutes. Some Br₂ remained in the funnel and as the reaction continued overnight the Br₂ vaporized and was thus available for reaction as Br₂. The light in the hood was left on overnight as well so as to encourage a free radical reaction. Having Br₂ vapor is favorable for the free radical reaction to occur.

The excess bromine was reduced by slowly adding 5% NaHSO₃ solution until the reddish color disappeared. The organic layer (bottom) was removed using a separatory funnel and washed three times with DI water, and then it was dried over Na₂SO₄. This flask was attached to a distillation set-up and the product was distilled under dynamic high vacuum. A percent yield of 88% was obtained.

\[ \text{Br} \quad \text{Br} \]
\[ \text{F}_2^a \text{C} \quad \text{-CF}^b \]
\[ \text{O} \quad \text{-CF}_2^c \text{CF}_2^d \text{-O} \quad \text{-CF}_2^e \text{CF}_2^f \text{SO}_2^f \]
\[ \text{F}^h \]

\[ \text{23} \]

\(^{19}\text{F NMR (CDCl}_3\text{, ppm) } \delta_a -63.6 (2\text{F, s}), \delta_b -71.8 (1\text{F, m)}, \delta_c -84.1 (2\text{F, AB pattern multiplet}), \delta_d -145.4 (1\text{F, t-m)}, \delta_e -80.2 (3\text{F, qm)}, \delta_f -79.4 (2\text{F, m)}, \delta_g -112.3 (2\text{F, m)} \delta_h +45.2 (1\text{F, s}). \]
Preparation of Brominated Nafion® Monomer with Trifluoromethyl Sulfonimide Anion, CF$_2$BrCFBrOCF$_2$CF(CF$_3$)OCF$_2$CF$_2$SO$_2$N(Na)SO$_2$CF$_3$ (24)

In a 250 mL one piece reactor with an Ace thread sidearm, 7.30 g (30.0 mmol) of CF$_3$SO$_2$N(Na)-SiMe$_3$ was added. Then 80 mL of dry CH$_3$CN and 20.0 g (33.0 mmol) of the brominated monomer was condensed into the reactor using the vacuum line. Once at room temperature, the mixture was placed in an oil bath for 48 hours at 110 ºC, in a closed system. The solvent and excess brominated monomer was removed on the vacuum line by heating for 2 nights at 80 ºC.

$^{19}$F NMR (CDCN, ppm) $\delta_a$ -63.6 (2F, s), $\delta_b$ -71.8 (1F, m), $\delta_c$ -83.1 (2F, AB pattern multiplet), $\delta_d$ -144.6 (1F, m), $\delta_e$ -77.8 (3F, qm), $\delta_f$ -78.8 (2F, m), $\delta_g$ -115.8 (2F, m) $\delta_h$ -78.9 (3F, s).

Preparation of Methylated, Brominated Sulfonimide Sodium Salt Monomer, CF$_2$BrCFBrOCF$_2$CF(CF$_3$)OCF$_2$CF$_2$SO$_2$N(CH$_3$)SO$_2$CF$_3$ (25)

The bromine protected sodium sulfonimide salt remained in the one-piece reactor because of its glass-like nature and difficulty to remove. Approximately 10 mL of dimethyl sulfate was syringed into the one-piece reactor after flushing with N$_2$ for 15 minutes. The sulfonimide salt was adequately dissolved and then the reaction vessel was immersed in an oil bath at 110 ºC for 3 hours. Ice was added and allowed to stir for 24
hours and the solution was neutralized with NaOH pellets and NaOH solution to pH7.
On this occasion there was significant enough product to separate using a separatory funnel. The organic/product layer was light brown. It was washed three times with DI water. A yield of 6.85 g was obtained for a 65% yield over the course of two experiments.

![Chemical structure](image)

\[ \text{H} \text{NMR (CDCN, ppm)} \delta 3.91 \text{ (s)}; \text{} ^{19} \text{F NMR (CDCN, ppm)} \delta_a -63.6 \text{ (2F, s), } \delta_b -71.8 \text{ (1F, m), } \delta_c -83.1 \text{ (2F, m), } \delta_d -144.6 \text{ (1F, m), } \delta_e -77.8 \text{ (3F, qm), } \delta_f -78.8 \text{ (2F, m), } \delta_g -109.5 \text{ (2F, m), } \delta_h -72.8 \text{ (3F, s).}

**Preparation of RTIL: Brominated Nafion® Monomer with Trifluoromethyl Sulfonimide Anion and 1,3-Butylmethylimidazolium Cation (26)**

The sodium salt of the brominated sulfonimide Nafion monomer (5.08 g, 6.92 mmol) was readily dissolved in 8 mL of H$_2$O. Then 1.60 g (7.30 mmol) of [BMIM][Br] was dissolved in a separate 5 mL of H$_2$O. Upon mixing a white precipitate formed immediately and then a thick tan liquid settled to the bottom to form a separate layer. This was stirred overnight. Some CH$_2$Cl$_2$ was added to aid in the stirring.

The next day the water was decanted and the IL/CH$_2$Cl$_2$ layer was washed several times with water and dried on the vacuum line overnight at 100 ºC.
\begin{align*}
^1\text{H NMR} \ (\text{CD}_3\text{CN}) & \delta_a \ 8.36 \text{ ppm} \ (1\text{H, s}), \ \delta_b \ 7.30 \text{ ppm} \ (1\text{H, m}), \ \delta_c \ 7.33 \text{ ppm} \ (1\text{H, m}), \ \delta_d \ 3.78 \text{ ppm} \ (3\text{H, s}), \ \delta_e \ 4.09 \text{ ppm} \ (2\text{H, t}), \ \delta_f \ 1.77 \text{ ppm} \ (2\text{H, m}), \ \delta_g \ 1.28 \text{ ppm} \ (2\text{H, m}), \ \delta_h \ 0.91 \text{ ppm} \ (3\text{H, t}); \ ^{19}\text{F NMR} \ (\text{CDCN}, \ \text{ppm}) \ & \delta_a \ -63.6 \ (2\text{F, s}), \ \delta_b \ -71.9 \ (1\text{F, m}), \ \delta_c \ -83.1 \ (2\text{F, m}), \ \delta_d \ -144.7 \ (1\text{F, m}), \ \delta_e \ -77.8 \ (3\text{F, qm}), \ \delta_f \ -78.8 \ (2\text{F, m}), \ \delta_g \ -115.7 \ (2\text{F, m}), \ \delta_h \ -78.9 \ (3\text{F, s}).
\end{align*}

Preparation of RTIL: Debromination of Brominated Nafion® Monomer RTIL with Zinc metal (27)

The RTIL, 4.81 g (5.5 mmol), was put in a round-bottom flask and taken into the dry box along with the activated zinc. Then 1.08 g of activated zinc was added to the round bottomed flask, the reflux condenser attached, and removed from the dry box. Then 15 mL of dry CH$_3$CN was added and the reaction flask was connected to a reflux condenser that had a positive flow of nitrogen gas. This was refluxed overnight at 80 ºC and a progress NMR revealed the reaction was complete. The CH$_3$CN was removed by vacuum and a viscous brown liquid remained.

ZnBr is very soluble in water so Vertrel XF was used to isolate the product. This was washed twice with DI water. A separatory funnel was used to remove the bottom layer of Vertrel/product, placed in a 25 mL conical flask and connected to the vacuum line. This was vacuumed overnight at room temperature and only a tan, viscous liquid remained.
\[ H \text{ NMR (CD}_3\text{CN)} \delta_a 8.36 \text{ ppm (1H, s)}, \delta_b 7.30 \text{ ppm (1H, m)}, \delta_c 7.33 \text{ ppm (1H, m)}, \delta_d 3.78 \text{ ppm (3H, s)}, \delta_e 4.09 \text{ ppm (2H, t)}, \delta_f 1.77 \text{ ppm (2H, m)}, \delta_g 1.28 \text{ ppm (2H, m)}, \delta_h 0.91 \text{ ppm (3H, t); } \]
\[ ^{19}\text{F NMR (CDCN, ppm)} \delta_A -112.4 \text{ (1F, dd), } \delta_M -120.8 \text{ (1F, dd), } \delta_X -135.5 \text{ (1F, dd), } \delta_b -78.0 \text{ (2F, m), } \delta_c -144.3 \text{ (1F, m), } \delta_d -79.0 \text{ (3F, m), } \delta_e -78.9 \text{ (3F, m), } \delta_f -83.7 \text{ (2F, s), } \delta_g -79.1 \text{ (3F, m).}
\]

Copolymerization of TFE with Nafion IL derivative (28)

\[ \text{In a 10mL SS bomb reactor with 5 glass beads, 0.50 g (0.7 mmol) of the RTIL that had been dissolved/emulsified in about 8-10 mL of CF}_2\text{ClCFCl}_2 \text{ was added. Then 0.10 mL of the bis[2,3,3,3-tetrafluoro-1-oxo-2-( trifluoromethyl)propyl] peroxide initiator was added by syringe for a 0.2 molar percentage of initiator.}
\]

\[ \text{The reactor was closed, immersed in liquid nitrogen, and evacuated on the vacuum line to 20 mtorr. After evacuation, 495 torr (5 mmol, 0.50 g) of TFE was condensed into the reactor using the vacuum line. The reactor was closed and wrapped in heating tape. This was attached to a variac and the shaker and brought to 74 }^\circ\text{C. The} \]
reactor at 74 °C was shaken overnight. The resulting mixture was removed from the reactor and the solvent was removed on the vacuum line overnight at 85 °C.

In a small vial, 0.10 g of the polymer “blend” was added and approximately 1 mL of CH₃CN was added. This was warmed and stirred vigorously for two hours. If 100% of the monomer had not polymerized, then 0.050 g (0.070 mmol) would be present in the solution. Using the vacuum line, 7 torr (0.070 mmol) of CFCl₃ was added to the NMR tube. A ¹⁹F NMR was run and the integration suggested that approximately 75% of the IL monomer had not polymerized, and therefore the washed polymerized product should have 25% by weight IL monomer. This was not in exact agreement with the TGA because the TGA suggested that only 15% remained in the polymer, and not 25%.
CHAPTER V
SYNTHESIS OF LOW VISCOSITY IONIC LIQUIDS

Introduction

When considering ionic liquids as alternatives for organic solvents, the properties that concerned researchers most were their physicochemical and thermodynamic properties. Ionic liquids are generally more viscous than traditional organic solvents as shown in Table 5.1. One obvious limiting factor with using ILs as alternative reaction media is the operational costs associated with pumping, mixing, and filtering ionic liquids with reactants and products. However, the addition of cosolvents to an IL can lower the viscosity to an acceptable level. Another way to avoid this problem is to design and synthesize ionic liquids with low viscosity. Two of the most fluid ionic liquid families are from the dicyanamide anion, DCA or N(CN)$_2^-$, and the bis(trifluoromethylsulfonyl)amide anion, TFSI, Tf$_2$N, or (CF$_3$SO$_2$)$_2$N$^-$, with the bis((trifluoromethyl)sulfonyl)amide anion typically being the more thermally stable by approximately 150°C when paired with the same cation as the dicyanamide anion (DCA). The melting point and viscosity of ionic liquids with the dicyanamide anion, (CN)$_2$N$^-$, have reported values as low as -21 °C and 21 cP, respectively.
<table>
<thead>
<tr>
<th>Ionic liquids</th>
<th>Temperature (K)</th>
<th>Viscosity (η), cP</th>
</tr>
</thead>
<tbody>
<tr>
<td>[MMIM] [(CF₃SO₂)₂N]</td>
<td>293</td>
<td>44</td>
</tr>
<tr>
<td>[EMIM] [(CF₃SO₂)₂N]</td>
<td>293</td>
<td>34</td>
</tr>
<tr>
<td>[BMIM] [(CF₃SO₂)₂N]</td>
<td>293</td>
<td>52</td>
</tr>
<tr>
<td>[i-BMIM] [(CF₃SO₂)₂N]</td>
<td>293</td>
<td>83</td>
</tr>
<tr>
<td>[EMIM][BF₄]</td>
<td>295</td>
<td>34</td>
</tr>
<tr>
<td>[BMIM] [PF₆]</td>
<td>298</td>
<td>207</td>
</tr>
<tr>
<td>[EMIM][(CN)₂N]</td>
<td>298</td>
<td>21</td>
</tr>
<tr>
<td>[MMIM][NTFSI]</td>
<td>298</td>
<td>34</td>
</tr>
<tr>
<td>[MMIM][NTFSI]</td>
<td>298</td>
<td>34</td>
</tr>
<tr>
<td><strong>Aqueous</strong></td>
<td><strong>H₂O</strong></td>
<td><strong>1.002</strong></td>
</tr>
</tbody>
</table>

**Table 5.1**: Typical Viscosities of ILs and H₂O

<table>
<thead>
<tr>
<th>Conductivity (mS/cm)</th>
<th>Viscosity (cP)</th>
</tr>
</thead>
<tbody>
<tr>
<td>25.0</td>
<td>600</td>
</tr>
<tr>
<td>20.0</td>
<td>400</td>
</tr>
<tr>
<td>15.0</td>
<td>200</td>
</tr>
<tr>
<td>10.0</td>
<td>100</td>
</tr>
<tr>
<td>5.0</td>
<td>50</td>
</tr>
<tr>
<td>0.0</td>
<td>0</td>
</tr>
</tbody>
</table>

**Figure 5.1**: Plot of Conductivity versus Viscosity for Ionic Liquids

Low viscosity is a major requirement for electrochemical applications and the loose correlation between conductivity and viscosity is shown in Figure 5.1. Some of the obvious problems associated with RTILs as reaction media are thermal conductivity,
filtration, and distillation – all likely related to viscosity. Despite an obvious advantage given by decreasing viscosity, to the best of our knowledge, there have been only a few reports on low-viscosity ILs, with those focusing on phosphonium ILs, particularly for several trimethylphosphine-based RTILs.\textsuperscript{86}

There are some contradictions between the fact that ionic liquids have low vapor pressure and the aim to achieve low viscosity with ILs – a tradeoff between cohesion and viscosity, if you will. Low vapor pressure is one of the main attractions of these liquids and the high cohesion of molten salts associated with electrostatic forces also makes them more viscous than other liquids. The smaller the ions, the higher the cohesion is an accepted rule of thumb. It would seem that increasing the size of the ions, by increasingly lowering the Coulombic attractions, would be the way to achieve high fluidities. Unfortunately another effect comes into play as the ions are increased in size. This is the van der Waals interaction. It is important to keep this as low as possible by maintaining an unpolarizable outer surface on the anions. This is the reason for the prevalence of perfluorinated species among the ionic liquids used in practice as their surface consists of tightly bound lone pairs of electrons on the fluorine atom. And even perfluorinated species, begin to cause fluidity decreases when their size becomes large enough as we have seen with the difunctional and multi-functional perflouroalkyl sulfonimide ionic liquids synthesized in this work.

We decided to evaluate an interesting sulfonimide anion (CF\textsubscript{3}SO\textsubscript{2}N’SO\textsubscript{2}C\textsubscript{4}F\textsubscript{9}) previously prepared at Clemson.\textsuperscript{87}

\textbf{Results and Discussion}
Structural effects of anions and cations on ionic liquid properties, such as viscosity, are well known but unpredictable. Herein we compared two imidazolium ionic liquids containing the nonafluorobutylsulfonyl (trifluoromethylsulfonyl) imide (NTFSI) anion. In studies of anion structure on properties of 1,3-dialkylimidazolium ILs, we unexpectedly found that the unsymmetrical anion, C\textsubscript{4}F\textsubscript{9}SO\textsubscript{2}N(-)SO\textsubscript{2}CF\textsubscript{3} (NTFSI),\textsuperscript{88} gave low viscosities. The straightforward synthesis is given in Schemes 5.1 and 5.2.

\[
\begin{align*}
(CF_3SO_2)_2O & \xrightarrow{1. NH_3, 2. NaOH} CF_3SO_2NH(Na) \\
& \xrightarrow{HMDS, dry CH_3CN, 80^\circ C, 24h} CF_3SO_2N(Na)SiMe_3 \\
CF_3SO_2N(Na)SiMe_3 + C_4F_9SO_2F & \xrightarrow{dry CH_3CN, 80^\circ C, 48h} NaCF_3SO_2NSO_2C_4F_9 \\
& \xrightarrow{NTFSI(Na), 95\%} \text{NTFSI(Na)}
\end{align*}
\]

**Scheme 5.1:** Preparation of NTFSI(Na) (29)

These synthetic reactions are easily monitored by both \(^{19}\text{F}\) and \(^1\text{H}\) NMR. The fluorine atoms adjacent to the sulfonimide moiety exhibit the expected behavior in going from the sodium salt silyl derivative form and the sulfonyl fluoride to the sulfonimide.

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The protons on the 1-alkylimidazole ring, most notably the C-2 proton, exhibit a significant upfield shift during the metathesis of the bromine anion.

Alternatively, the same ionic liquids were synthesized by direct methylation of methylimidazole and butylimidazole using the methylated nonafluorobutylsulfonyl trifluoromethylsulfonyl imide. This synthetic route eliminates any risk of halide contamination when the RTIL application may involve the use of transition metals.

These two ILs showed excellent thermal stability with TGA decomposition onset temperatures above 400 ºC. DSC data were taken with a heating speed of 10 ºC min\(^{-1}\) and a cooling rate of 20 ºC min\(^{-1}\). The symmetric cation 1-methyl,3-methylimidazolium salt had a glass transition of -86 ºC and the asymmetric cation 1-butyl-3-methylimidazolium salt had a Tg of -90 ºC. If one considers the glass transition as a cohesion indicator, it appeared promising that a low viscosity IL had been prepared.

The dimethyl imidazolium bis(trifluoromethylsulfonyl) imide IL, [MMIM][TFSI], is reported in the literature by various sources to have a viscosity between 44 cP at 20 ºC, and up to 100 cP at 25 ºC. The analogous [MMIM][NTFSI] ionic liquid reported here had a viscosity measurement of 92 cP at 25 ºC. The [BMIM][TFSI] IL has been reported by different sources to have viscosities ranging from 34 cP to 69 cP, while the analogous [BMIM][NTSI] again gave an inexplicable viscosity of 125 cP. Viscosity measurements were made on a TA Instruments AR 2000ex rheometer, using the steel 40mm cone and plate geometry. These results clearly show that there are many as yet unexplored routes to useful ILs with low viscosity and other useful properties.
Along the way to this asymmetric NTFSI anion we discussed the possibility of preparing this using the base-assisted coupling reaction. The corresponding NMR spectra of the products are identical but two distinct differences surface. The sodium or lithium salt using the base-assisted path is very white but the salt from the silyl path had a slight tan color. The most revealing difference is the fact that the base assisted path requires half the time and effort as the silyl methodology. These two methodologies are juxtaposed below. This coupling, solvent free base-assisted reaction would be an excellent candidate to try using sonication. The sonication in the preparation of the imidazolium halide allowed lower temperatures to be utilized, therefore minimizing discoloration of the halide salt and subsequent ionic liquid. A similar advantage may be possible with the base assisted coupling reaction.
**Scheme 5.3**: Comparison of Two Paths to Asymmetric NTFSI Anion
Experimental

Typical procedure for CF$_3$SO$_2$N(Na)Si(CH$_3$)$_3$ (2)

Approximately 50 mL of HMDS and 50 mL of dry CH$_3$CN was added to a 250 mL round bottomed flask and 19.2 g (112 mmol) of CF$_3$SO$_2$N(Na)Si(CH$_3$)$_3$ was added. The reaction mixture was refluxed for 24 h at 80 ºC. The solvent and excess HMDS are removed via high vacuum and the remaining solid dried overnight at 100 ºC under high vacuum, and then stored in a dry box.

(2) CF$_3$SO$_2$N(Na)Si(CH$_3$)$_3$: δH 0.02(s); δF -78.6(s).

Typical procedure for CF$_3$SO$_2$N(Na)SO$_2$C$_4$F$_9$ using silyl derivative method (29a).

In a 250 mL flask, 3.17 g (13 mmol) of CF$_3$SO$_2$N(Na)Si(CH$_3$)$_3$, 50 mL of dry CH$_3$CN, and 5.90 g (19.5 mmol) of C$_4$F$_9$SO$_2$F were added. In a closed system, the mixture was heated for 48 h at 110 ºC. The solvent and excess SO$_2$F compound were removed on the vacuum line and dried at 80 ºC overnight. A total of 5.17 g was obtained for 87% yield.

(29a)CF$_3$A$^\text{a}$SO$_2$N(Na)SO$_2$CF$_2$B$^\text{b}$CF$_2$C$^\text{c}$CF$_2$D$^\text{d}$CF$_3$E$^\text{e}$

$^{19}$F NMR (CD$_3$CN, ppm) δF -78.9(s, 3F$_A$), δF -80.3 (m, 3F$_E$), δF -112.7 (m, 2F$_B$), δF -120.4 (m, 2F$_C$), δF -125.2 (m, 2F$_D$).

Typical procedure for CF$_3$SO$_2$N(Na)SO$_2$C$_4$F$_9$ using base-assisted method (29b).

Trifluoromethylsulfonamide, CF$_3$SO$_2$NH$_2$ (4.10 g, 27.5 mmol), was weighed into a 25 mL round bottomed flask containing a stir bar. The flask was closed with a septum and purged with nitrogen gas. Dry distilled triethylamine (13.9 g, 137 mmol) was added with the help of a syringe. To the clear stirred solution, dry distilled
perfluorobutylsulfonyl fluoride (10.8 g, 35.7 mmol) was injected and the mixture was heated at 60 °C overnight. Excess triethylamine and perfluorosulphonylfluoride was evaporated under dynamic vacuum. To the viscous brown liquid, conc. sulfuric acid was added and the clear solution was sublimed under dynamic vacuum at 80 °C. White solid was collected on the cold finger and scraped off.

The white solid was neutralized with NaOH solution in D.I water to pH 7.2. The water was evaporated and the white solid was dried under dynamic vacuum at 80 °C overnight to furnish the sodium salt of the sulphonimide.

\[(29b) \text{CF}_3^\text{A} \text{SO}_2\text{N}(\text{Na})\text{SO}_2\text{CF}_2^\text{B}\text{CF}_2^\text{C}\text{CF}_2^\text{D}\text{CF}_3^\text{E}\]

\(^{19}\text{F NMR (CD}_3\text{CN, ppm)}: \delta_\text{F} -78.9 (s, 3\text{F}_\text{A}), \delta_\text{F} -80.3 (\text{m}, 3\text{F}_\text{E}), \delta_\text{F} -112.7 (\text{m}, 2\text{F}_\text{B}), \delta_\text{F} -120.4 (\text{m}, 2\text{F}_\text{C}), \delta_\text{F} -125.2 (\text{m}, 2\text{F}_\text{D}).\]

**Typical procedure for CF\(_3\)SO\(_2\)N(MMIM)SO\(_2\)C\(_4\)F\(_9\) (30a).**

Approximately 10 mL of H\(_2\)O were used to dissolve 3.6 g (16 mmol) of [MMIM][I] and another 10 mL of H\(_2\)O were used to dissolve 6.1 g (13.5 mmol) of the CF\(_3\)SO\(_2\)N(Na)SO\(_2\)C\(_4\)F\(_9\). The two solutions were mixed and became cloudy. This was allowed to stir overnight at which time an oily substance formed on the bottom of the vial. A CH\(_2\)Cl\(_2\) extraction was done, washed twice with DI H\(_2\)O, and the methylene chloride was removed on the vacuum line by heating for 5 hours at 60 °C.

\[(30a) \text{CF}_3^\text{A} \text{SO}_2\text{N}(\text{MMIM})\text{SO}_2\text{CF}_2^\text{B}\text{CF}_2^\text{C}\text{CF}_2^\text{D}\text{CF}_3^\text{E}\]

\(^{19}\text{F NMR (CD}_3\text{CN, ppm)}: \delta_\text{F} -78.9 (s, 3\text{F}_\text{A}), \delta_\text{F} -80.3 (\text{t}, 3\text{F}_\text{E}), \delta_\text{F} -112.7 (\text{m}, 2\text{F}_\text{B}), \delta_\text{F} -120.4 (\text{m}, 2\text{F}_\text{C}), \delta_\text{F} -125.2 (\text{m}, 2\text{F}_\text{D}); \ ^1\text{H NMR (CD}_3\text{CN, ppm)}: \delta_\text{H} 8.31 (s, 1\text{H}), \delta_\text{H} 7.29 (\text{m}, 2\text{H}), \delta_\text{H} 3.78 (s, 6\text{H}).\]
Typical procedure for CF$_3$SO$_2$N(BMIM)SO$_2$C$_4$F$_9$ (30b).

Approximately 20 mL of H$_2$O were used to dissolve 3.6 g (16 mmol) of [BMIM][Br] and another 20 mL of H$_2$O were used to dissolve 6.3 g (13 mmol) of the CF$_3$SO$_2$N(Na)SO$_2$C$_4$F$_9$. The two solutions were mixed and stirred overnight. The RTIL is separated and washed several times with DI H$_2$O. Any remaining H$_2$O is removed over two nights on the vacuum line at a reduced pressure of 20 torr, 70 ºC, and with stirring.

$^{19}$F NMR (CD$_3$CN, ppm) $\delta$F -78.9 (s, 3F$_A$), $\delta$F -80.3 (t, 3F$_E$), $\delta$F -112.7 (m, 2F$_B$), $\delta$F -120.4 (m, 2F$_D$), $\delta$F -125.2 (m, 2F$_C$); $^1$H NMR (CD$_3$CN, ppm) $\delta$H 8.35 (s, 1H), $\delta$H 7.33 (m, 1H), $\delta$H 7.30 (m, 1H), $\delta$H 4.09 (t, 2H), $\delta$H 3.78 (s, 3H), $\delta$H 1.77 (m, 2H), $\delta$H 1.30 (m, 2H), $\delta$H 0.91 (t, 3H).
APPENDICES
$\text{FSO}_2\text{CF}_2\text{CF}_2\text{SO}_2\text{F}$

**Compound 1**

$\text{CF}_3\text{SO}_2\text{NSO}_2\text{CF}_2\text{CF}_2\text{SO}_2\text{NSO}_2\text{CF}_3$

**Compound 3**

$^{19}\text{F NMR (CD}_3\text{CN)}, \text{ Compound 1}$

$^{19}\text{F NMR (CD}_3\text{CN)}, \text{ Compound 3}$

114
$^{19}$F NMR (CD$_3$CN), Compound 3

$^{19}$F NMR (CD$_3$CN), Compound 4
$^{19}$F NMR (CD$_3$CN), Compound 5a
DSC Compound 5a

\[
\begin{align*}
\text{BMIM}^\oplus & \quad \text{BMIM}^\oplus \\
\text{CF}_3\text{SO}_2\text{NSO}_2\text{CF}_2\text{SO}_2\text{NSO}_2\text{CF}_3
\end{align*}
\]

5a

DSC Compound 5b

\[
\begin{align*}
\text{EMIM}^\oplus & \quad \text{EMIM}^\oplus \\
\text{CF}_3\text{SO}_2\text{NSO}_2\text{CF}_2\text{SO}_2\text{NSO}_2\text{CF}_3
\end{align*}
\]

5b

$^{19}$F NMR (CD$_3$CN), Compound 5b
^{1}H NMR (CD$_3$CN), Compound 5b
\[ \text{ClSO}_2\text{CF}_2\text{CF}_2\text{CF}_2\text{SO}_2\text{Cl} \]

\(^{19}\text{F NMR (CD}_3\text{CN), Compound 7}\)
$^{19}$F NMR (CD$_3$CN), Compound 8

$^{19}$F NMR (CD$_3$CN), Compound 9
$^{19}$F NMR (CD$_3$CN), Compound 10

$^1$H NMR (CD$_3$CN), Compound 10
$^1$H NMR (CD$_3$CN), Compound 11a

$^{19}$F NMR (CD$_3$CN), Compound 11a
TGA Compound 11a
DSC Compound 11a

\[
\text{Onset Y} = 18.6848 \text{ mW}
\]
\[
\text{Onset X} = 105.498 \degree \text{C}
\]

\[\text{EMIM}^\text{\(\oplus\)} \quad \text{EMIM}^\text{\(\oplus\)}
\]
\[
\text{CF}_3\text{SO}_2\text{NSO}_2\text{CF}_2\text{CF}_2\text{SO}_2\text{NSO}_2\text{CF}_3
\]

\[\text{11b}\]

\[\text{\(^{19}\text{F NMR (CD}_3\text{CN), Compound 11b}}\]

125
$^1$H NMR (CD$_3$CN), Compound 11b

TGA Compound 11b
DSC Compound 11b

$^{1}H$ NMR (CD$_3$CN), Compound 11c
$^1$H NMR (CD$_3$CN), Compound 11c

TGA Compound 11c
$^{19}$F NMR (CD$_3$CN), Compound 12

$^1$H NMR (CD$_3$CN), Compound 12
$^{19}\text{F NMR (CD}_3\text{CN)}, \text{Compound 13}$

$^{1}\text{H NMR (CD}_3\text{CN)}, \text{Compound 13}$
$^{19}$F NMR (CD$_3$CN), Compound 13

$^{19}$F NMR (CD$_3$CN), Compound 14
$^{19}$F NMR (CD$_3$CN), Compound 14

$^1$H NMR (CD$_3$CN), Compound 14
$^{19}\text{F NMR } (\text{CD}_3\text{CN}), \text{ Compound 16}$

$^1\text{H NMR } (\text{CD}_3\text{CN}), \text{ Compound 16}$
TGA Compound 16
135

$^{19}$F NMR (CD$_3$CN) 17
$^{19}\text{F NMR (CD$_3$CN) 17}$
$^{19}\text{F NMR (CD}_2\text{CN)}$ 18
$^1H$ NMR (CD$_3$CN 18)
$^{19}$F NMR (CD$_3$CN) 19
TGA Compound 19

Onset Y = 97.5319 %
Onset X = 367.422 °C

\[ \text{[F}_2\text{C=CFO(C}_6\text{H}_4\text{)SO}_2\text{N(BMIM)SO}_2\text{CF}_2\text{]}_2 \]
Expt 99 IL PFCB dried at 150°C 1 day

TGA Compound 20
$^{19}$F NMR Compound 21
DSC Compound 21
$^1$H NMR Compound 22
$^{19}$F NMR of Nafion® Sulfonyl Fluoride Monomer
$\text{CBrF}_2\text{CBrF}$

$\text{OCF}_2\text{CFOCF}_2\text{CF}_2\text{SO}_2\text{F}$

$\text{CF}_3$

$\text{ Compound 23}$
$\text{CBF}_2\text{CBF}^+\text{Na}^-$

$\text{OCF}_2\text{CFOCF}_2\text{CF}_2\text{SO}_2\text{NSO}_2\text{CF}_3$

$\text{CF}_3 \quad 24$

$^{19}\text{F NMR Compound 24}$
$^{19}$F NMR Compound 26

$^{19}$F NMR Compound 27
**1H NMR Compound 27**

**19F NMR of Washing from 28 Polymerization**
TGA Comparison of 28 before and after washing
DSC of IL Polymer 28

¹⁹F NMR Low Viscosity IL 29
TGA of Low Viscosity IL 29

19F NMR Compound 30a
$^1$H NMR Compound 30a

TGA Compound 30a
[MMIM$^+$][CF$_3$SO$_2$N·SO$_2$C$_4$F$_9$]

30a

DSC Compound 30a

$^1$H NMR Compound 30b
$\text{H}_2\text{C} \rightleftharpoons \text{C}_2\text{H}_3$

$\text{CF}_3\text{SO}_2\text{NSO}_2\text{CF}_2\text{CF}_2\text{CF}_3$

$30b$
TGA Compound 30b

DSC Compound 30b
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